

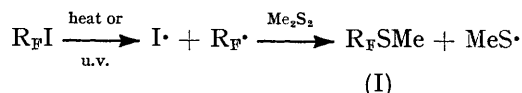
## Perfluoroalkyl Derivatives of Sulphur. Part XVIII.<sup>1</sup> Reactions of Polyfluoroiodoalkanes with Sodium Methanethiolate in the Presence of Dimethyl Disulphide, and Related Reactions <sup>2</sup>

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Reaction of sodium methanethiolate with polyfluoroiodoalkanes in the presence of dimethyl disulphide in dimethyl sulphoxide as solvent gives the corresponding methyl polyfluoroalkyl sulphides in high yield (*ca.* 80%); optimum conditions for the reaction involving heptafluoro-1-iodopropane have been determined. The reaction also works in the absence of the disulphide (yields *ca.* 70%) and on replacement of the disulphide by dimethyl sulphide. The reactions of heptafluoro-1-iodopropane with sodium ethanethiolate in the presence of and in the absence of diethyl disulphide and the preparation of some alkyl perfluoroalkyl sulphoxides are also described.

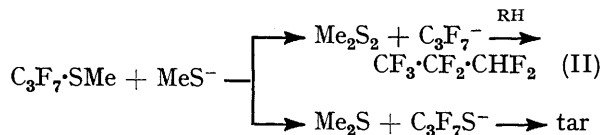
METHYL POLYFLUOROALKYL SULPHIDES (I), precursors to of the corresponding polyfluoroiodoalkanes in the the industrially important polyfluoroalkanesulphonic presence of dimethyl sulphide<sup>3</sup> or better dimethyl

convenient on a large scale and the corresponding thermal reactions with dimethyl disulphide give lower yields.<sup>4</sup>



In the present work the reaction of sodium methanethiolate with polyfluoroiodoalkanes in the presence of dimethyl disulphide and solvent dimethyl sulphoxide ( $\text{Me}_2\text{SO}$ ) has been found to give the corresponding sulphides (I) in good yield, thus obviating the use of photochemical reactions. The best conditions for the preparation of methyl heptafluoro-*n*-propyl sulphide (I;  $\text{R}_\text{F} = n\text{-C}_3\text{F}_7$ ) by this method have been determined

sulphide, and an involatile black oil. These products indicate that methanethiolate ion attack takes place at both the sulphur atom and the methyl carbon atom in the sulphide (I), *i.e.*



Similar conditions were used in the reactions of a range of polyfluoroiodoalkanes and the results obtained are shown in Table 2. The longer chain compounds ( $\text{C}_6$  to  $\text{C}_9$ ) required longer reaction times (*ca.* 40 h) in order to give reasonable conversions of the reactant iodoalkanes.

TABLE 1

Reaction of heptafluoro-1-iodopropane with sodium methanethiolate in the presence of dimethyl disulphide

Expt.	Molar ratio of reactants			Reactant $\text{R}_\text{F}\text{I}$ (mmol)	Solvent (cm <sup>3</sup> )	Time (h)	Temp. (°C)	$\text{R}_\text{F}\text{I}$ consumed (%)	Product (%) <sup>*</sup>		
	$\text{R}_\text{F}\text{I}$	$\text{MeSNa}$	$\text{Me}_2\text{S}_2$						$\text{R}_\text{F}\text{SMe(I)}$	$\text{R}_\text{F}\text{H}$	
1	1	1.1	4	4.8	Me <sub>2</sub> SO	(20)	168	25	41	29 †	46
2	1	1.5	4	10.9		(40)	44	100	89	42	26
3	1	0.2	10	9.0		(10)	20	110	61	57	Trace
4	1	4.5	2	6.3		(10)	4	110	100	15	30
5	1	0.75	5	12.0		(4)	20	110	72	55	17
6	1	0.75	2	16.0		(5)	20	110	62	59	8
7	1	0.9	5	9.5		(10)	15	110	65	56	9
8	1	0.8	5	16.0		(5)	40	110	76	40	6
9	1	1.7	5	8.4		(6)	20	110	64	61	11
10	1	1.5	5	8.6 †		(6)	20	105	93	80	8
11	1	1.6	10	10.0 †		(6)	20	108	92	76	15
12	1	1.2	5	14.2 †		(10)	20	105	87	75	7
13	1	1.1	5	15.0 †		(10)	67	105	90	60	8

\* Yields based on iodoalkane consumed. † Reaction mixture was shaken vigorously. ‡ Low yield probably caused by poor mixing of reactants. Optimum conditions: ratio  $\text{Me}_2\text{S}_2 : \text{C}_3\text{F}_7\text{I}$  between 2 : 1 and 5 : 1; temp. 105–110 °C; reaction time *ca.* 20 h; vol.  $\text{Me}_2\text{SO}$  approx. equal to sum of volumes of reactants; vigorous shaking.

TABLE 2

Reactions of polyfluoromonoiodoalkanes with sodium methanethiolate in the presence of dimethyl disulphide

$\text{R}_\text{F}\text{I}$	Reactant $\text{R}_\text{F}\text{I}$ (mmol)	Molar ratio of reactants			Solvent $\text{Me}_2\text{SO}$ (cm <sup>3</sup> )	Temp. (°C)	Time (h)	Recovered $\text{R}_\text{F}\text{I}$ (%)	Products (%) <sup>*</sup>	
		$\text{R}_\text{F}\text{I}$	$\text{MeSNa}$	$\text{Me}_2\text{S}_2$					$\text{R}_\text{F}\text{SMe}$	$\text{R}_\text{F}\text{H}$
$\text{CF}_3\text{I}$	20.8	1	1.2	5	10	90	22	7	86	10
$\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$	8.6	1	1.5	5	6	105	20	7	80	8
$(\text{CF}_3)_2\text{CFI}$	7.4	1	1.9	4	5	110	20	20	39	5
$\text{CF}_3[\text{CF}_2]_5\text{I}$	20.0	1	1.1	5	20	105	43	31	88	5
$(\text{CF}_3)_2\text{CF}[\text{CF}_2]_4\text{I}$	16.0	1	1.25	6	15	110	41	34	88	7
$\text{CF}_3[\text{CF}_2]_7\text{I}$	20.0	1	1.2	5	20	110	44	22	87	2
$(\text{CF}_3)_2\text{CF}[\text{CF}_2]_6\text{I}$	20.0	1	1.1	5	25	100	42	26	75	4

\* Yields based on  $\text{R}_\text{F}\text{I}$  consumed.

and these conditions have been used for the preparation of a variety of sulphides (I).

The conditions employed and the results obtained during the optimisation study of the reaction involving heptafluoro-1-iodopropane are shown in Table 1. Experiment 10 represents the best conditions found for the preparation of sulphide (I;  $\text{R}_\text{F} = n\text{-C}_3\text{F}_7$ ) on this particular scale.

At higher ratios of thiolate to iodoalkane the conversion of iodoalkane was high, but the yield of sulphide (I) was relatively low, the major product being 1*H*-heptafluoropropane (II). A separate experiment showed that the sulphide (I;  $\text{R}_\text{F} = n\text{-C}_3\text{F}_7$ ) reacts with methanethiolate ion to give a mixture of compound (II), dimethyl

This is attributed to the lower miscibility of these iodoalkanes with the solvent system; all the iodoalkanes formed separate layers during reaction and, thus, vigorous shaking and longer reaction times were required. The secondary iodoalkane, heptafluoro-2-iodopropane, gave a relatively low yield of the sulphide (I;  $\text{R}_\text{F} = \text{iso-C}_3\text{F}_7$ ), although the iodoalkane conversion was high. A similar, but less marked effect, was observed<sup>5</sup> in the photochemical reaction of this iodoalkane with dimethyl disulphide. The low yield from this iodoalkane, in which chain branching occurs on the  $\alpha$ -carbon atom, is probably associated with steric effects and with the difference in reactivity of, and ease of olefin formation from, the carbanion  $(\text{CF}_3)_2\text{CF}^-$  as compared with

carbanions of type  $R_FCF_2^-$ . Chain branching remote from the reaction site, *e.g.* in nonadecafluoro-1-iodo-7-methyloctane,  $(CF_3)_2CF\cdot[CF_2]_6I$ , had little effect either on the yield of sulphide (I) or on the iodoalkane conversion. Attempts to improve the yield of sulphide (I;  $R_F = iso-C_3F_7$ ) by use of other solvents were unsuccessful; the solvents used and the results are shown in Table 3. The use of trifluoroiodoethylene under the optimised conditions gave trifluoroethylene (5%) as the only isolable product. Thus direct nucleophilic displacement of iodide ion from the olefin did occur to some extent but the major mode of reaction probably involves nucleophilic attack on the  $CF_2$  group.

did not take place in the absence of sodium methanethiolate. The postulated direction of polarisation of the carbon-iodine bond in heptafluoro-1-iodopropane, brought about by the strong electron-withdrawing inductive effect of the perfluoroalkyl residue and the ready polarisability of iodine, is consistent with the results obtained from the reactions of other nucleophiles with polyfluoroiodoalkanes.<sup>6,7</sup> It is, however, possible that the high nucleophilicity of  $MeS^-$  and the use of a polar solvent makes  $S_N2$  displacement of  $I^-$  from  $R-I$  an important contributing reaction.

Hexafluoropropene (3%) and methyl pentafluoroprop-1-enyl sulphide (VII) (22%), by-products in the reaction

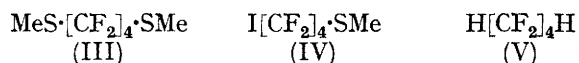
TABLE 3

Reactions of heptafluoro-2-iodopropane with sodium methanethiolate in the presence of dimethyl disulphide

Expt.	Solvent (cm <sup>3</sup> )	Time (h)	Temp. (°C)	Products (%) *				
				$R_F SMe$	$R_F H$	$C_3F_6$	$CF_3\cdot CF\cdot CF\cdot SMe$	
1	$(MeO\cdot[CH_2]_2)_2O$	(10)	20	17	13	4	9	
2		(10)	20	34	15	12	9	
3		(10)	70	110	35	12	9	7
4	$(MeO\cdot[CH_2]_2\cdot O\cdot[CH_2]_2)_2O$	(10)	67	110	28	21	5	6

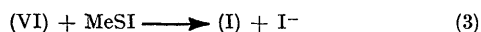
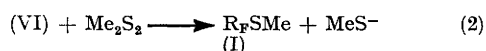
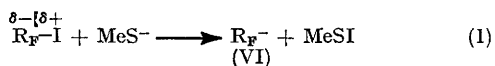
\* Yields based on iodoalkane consumed.

The reaction of octafluoro-1,4-di-iodobutane with sodium methanethiolate and dimethyl disulphide under the optimised conditions (16 h) gave unchanged diiodide (27%), octafluoro-1,4-bis(methylthio)butane (III) (31%), 4-iodo-octafluorobutyl methyl sulphide (IV) (50%), and 1*H,4H*-octafluorobutane (V) (2%); a longer reaction time (46 h) gave unchanged di-iodide (9%) and the products (III) (34%), (IV) (25%), and (V) (1%), *i.e.*

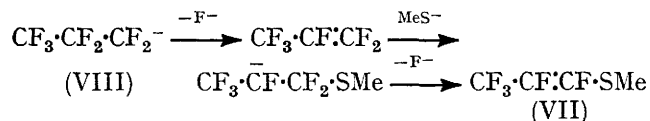


a decrease in yield of (III) + (IV).

The proposed mechanism for the reaction of polyfluoroiodoalkanes with methanethiolate ion in the presence of dimethyl disulphide is shown in Scheme 1 (where RH is any hydrogen-containing compound present).



of heptafluoro-1-iodopropane with sodium methanethiolate and dimethyl disulphide in the absence of solvent ( $Me_2SO$ ), are considered to be formed from the intermediate carbanion (VIII) by loss of fluoride ion followed by attack of methanethiolate ion on the resultant olefin, *i.e.*



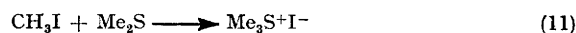
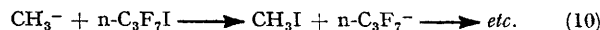
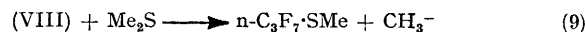
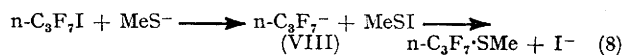
The observed *cis* : *trans* isomer ratio in the sulphide (VII) obtained was identical with that found for the sulphide (VII) formed by reaction of sodium methanethiolate with hexafluoropropene.<sup>8</sup> Similar by-products were observed in the reactions of sodium methanethiolate with heptafluoro-2-iodopropane in 2,5,8-trioxanonane or 2,5,8,11,14-pentaioxapentadecane as solvent (Table 3). In solvent  $Me_2SO$  loss of fluoride ion from the carbanion does not successfully compete with the reactions (2)–(4) (Scheme 1). 2*H*-Heptafluoropropane was not a reaction product, although a control experiment showed that it was formed in good yield when hexafluoropropene was heated alone in  $Me_2SO$ ; hexafluoropropene is thus captured almost

Heptafluoro-1-iodo-octane reacted with sodium methanethiolate in Me<sub>2</sub>SO as solvent at room temperature (40 h) to give the corresponding sulphide (I; R<sub>F</sub> = n-C<sub>8</sub>F<sub>17</sub>) in reasonable yield (69%).

The successful reaction of sodium methoxide in moist Me<sub>2</sub>SO with polyfluoroiodoalkanes, used to prepare pure samples of 1*H*-tridecafluoro-*n*-hexane (81%) and 1*H*-nonadecafluoro-7-methyloctane (73%), was consistent with methoxide attack on iodine to generate R<sub>F</sub><sup>-</sup> which then abstracted a proton.

The use of sodium methoxide instead of sodium methanethiolate to initiate the reaction of heptafluoro-1-iodopropane with dimethyl disulphide in Me<sub>2</sub>SO as solvent was therefore investigated, but gave 1*H*-heptafluoropropane (68%) and only a low yield of the required sulphide (I; R<sub>F</sub> = n-C<sub>3</sub>F<sub>7</sub>) (16%). The isolation of methanol as a product, and the dramatic increase in p*K*<sub>a</sub>

carried out in which the iodopropane : thiolate ion ratio was varied in order to determine if the sulphide was involved in the reaction; the results are in Table 5. Experiments 2 and 3, in which significantly higher molar amounts of the sulphide n-C<sub>3</sub>F<sub>7</sub>·SMe were produced than reactant thiolate used, show clearly that dimethyl sulphide is involved, possibly as in Scheme 2.



SCHEME 2

The reaction of heptafluoro-1-iodopropane with sodium ethanethiolate in the presence of diethyl disulphide in

TABLE 4

Reactions of polyfluoroiodoalkanes with sodium methanethiolate in the presence of dimethyl sulphide

R <sub>F</sub> I	R <sub>F</sub> I recovered (%)	Products (%) *			
		R <sub>F</sub> SMe	R <sub>F</sub> H	CF <sub>3</sub> ·CF <sub>2</sub> ·CF <sub>2</sub> ·SMe	C <sub>3</sub> F <sub>6</sub>
n-C <sub>3</sub> F <sub>7</sub> I	28	76	22	Trace	
(CF <sub>3</sub> ) <sub>2</sub> CFI	62	15	23	9	5
n-C <sub>6</sub> F <sub>13</sub> I	38	93	5		

\* Yields based on iodoalkane consumed.

TABLE 5

Reactions of heptafluoro-1-iodopropane with sodium methanethiolate in the presence of dimethyl sulphide

Expt.	Reactant MeSNa (mmol)	Ratio of reactants			Solvent Me <sub>2</sub> SO (cm <sup>3</sup> )	Temp. (°C)	Time (h)	Recovered reactants (%)		Products (%)	
		C <sub>3</sub> F <sub>7</sub> I	MeSNa	Me <sub>2</sub> S				C <sub>3</sub> F <sub>7</sub> I	Me <sub>2</sub> S	R <sub>F</sub> SMe	R <sub>F</sub> H
1	7.7	1	1.1	6.5	6	90	19	28	90	76 (3.80 *)	22
2	1.1	1	0.11	5	6	90	24	77	96	92 (2.10 *)	8
3	2.6	1	0.28	5	6	90	24	61	92	90 (3.35 *)	10
4	7.0	1	0.73	5	6	90	24	25	84	90 (6.50 *)	10

\* Mmol.

for alcohols (*ca.* 17 to *ca.* 30 when dissolved in Me<sub>2</sub>SO)<sup>9</sup> suggests that the carbanion (VIII) has reacted mainly by abstraction of proton from methanol generated *via* methoxide attack on Me<sub>2</sub>SO.

The reactions of three polyfluoroiodoalkanes with sodium methanethiolate in the presence of dimethyl sulphide in Me<sub>2</sub>SO as solvent were investigated, using a molar ratio R<sub>F</sub>I : MeS<sup>-</sup> : Me<sub>2</sub>S of 1 : 1.3 : 5 with vigorous shaking at 100 °C; the results are shown in Table 4. In these reactions sufficient thiolate ion was present for the product sulphides, R<sub>F</sub>SMe, to be formed *via* a reaction path which did not involve the dimethyl sulphide, *i.e.*



Heptafluoro-2-iodopropane reacts significantly more slowly than the -1-iodopropane.

Me<sub>2</sub>SO as solvent gave 1*H*-heptafluoropropane (12%) and ethyl heptafluoro-*n*-propyl sulphide (42%); the low yield of the latter was possibly due to its decomposition *via* further attack by the excess of thiolate present (C<sub>3</sub>F<sub>7</sub>I : EtS<sup>-</sup> 1 : 1.7). However, a corresponding reaction, carried out in the absence of the disulphide, gave ethyl heptafluoro-*n*-propyl sulphide in high yield (82%).

The yields of methyl polyfluoroalkyl sulphides obtained from the methanethiolate reactions (route A) are compared in Table 6 with the yields of the same compounds prepared by the photochemical reactions of dimethyl disulphide with the polyfluoroiodoalkanes (route B). It can be seen that the ionic route (A) compares favourably with the radical route (B), especially for the longer chain compounds, and this, coupled with the shorter reaction time (*ca.* 20 h as compared to 21 days) and the easier practical techniques involved, makes

bromosuccinimide (NBS) and *t*-butyl hypochlorite, oxidise <sup>10</sup> dialkyl sulphides exclusively to the corresponding sulphoxides under mild conditions. In view of the relatively severe conditions previously used <sup>11</sup> for the oxidation of methyl polyfluoroalkyl sulphides to the corresponding sulphoxides, *e.g.* fuming nitric acid at 100 °C, the oxidation of methyl polyfluoroalkyl sulphides with these reagents was investigated.

The reaction of methyl trifluoromethyl sulphide with *t*-butyl hypochlorite in methanol at room temperature gave the corresponding sulphoxide in excellent yield

(Regnault's method), i.r. spectroscopy (Perkin-Elmer 257 instrument 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 902 instrument). Spectroscopic data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 21626 (13 pp., 1 microfiche).†

Commercial samples of the dialkyl disulphides and dimethyl sulphide were carefully purified before use. The polyfluoroiodoalkanes and trifluoroiodoethylene <sup>14</sup> were

TABLE 6  
Comparison of synthetic routes to methyl polyfluoroalkyl sulphides

R <sub>F</sub> I	Route A (ionic)			Route B (photochemical)	
	R <sub>F</sub> I recovered (%)	Products (%)		Products (%)	
		R <sub>F</sub> SMe *	R <sub>F</sub> H *	R <sub>F</sub> SMe *	R <sub>F</sub> H *
CF <sub>3</sub> I	7	86	10	92	5
<i>n</i> -C <sub>3</sub> F <sub>7</sub> I	7	80	8	93	6
(CF <sub>3</sub> ) <sub>2</sub> CFI	20	39	5	83	12
CF <sub>3</sub> [CF <sub>2</sub> ] <sub>5</sub> I	31	88	5	76	15
(CF <sub>3</sub> ) <sub>2</sub> CF[CF <sub>2</sub> ] <sub>4</sub> I	34	88	7	80	17
CF <sub>3</sub> [CF <sub>2</sub> ] <sub>7</sub> I	22	87	2	73	10
(CF <sub>3</sub> ) <sub>2</sub> CF[CF <sub>2</sub> ] <sub>6</sub> I	26	75	4	74	15

\* Yields based on R<sub>F</sub>I consumed.

(81%). Although NBS was a less effective reagent under the normal conditions of its use, *i.e.* in methanol at -78 °C or even at 20 °C, with the sulphide recovered unchanged, in aqueous dioxan (80% v/v) a 93% yield of sulphoxide was obtained at room temperature. Methyl polyfluoroalkyl sulphides are less reactive than dialkyl sulphides towards positive halogen compounds, as expected from the proposed <sup>12</sup> mechanism *via* a chloro-sulphonium ion:



The sulphoxides CF<sub>3</sub>·<sup>+</sup>S(O)·CH<sub>3</sub> and CF<sub>3</sub>·<sup>+</sup>S(O)·C<sub>6</sub>H<sub>13</sub>-*n* were also prepared from the corresponding sulphides by oxidation with hydrogen peroxide.<sup>11</sup> *n*-Hexyl trifluoromethyl sulphide was prepared (60%) by the standard reaction <sup>13</sup> of 1-iodohexane with bis(trifluoromethylthio)-mercury.

#### EXPERIMENTAL

Volatile materials were handled in a conventional vacuum system to avoid contact with air and moisture. Pure products were separated either by preparative-scale g.l.c. [Perkin-Elmer F21 or Pye 105 instrument; columns packed with organic compounds (20 or 30%), as indicated in the text, on Celite] or by fractional condensation *in vacuo*, and were examined by molecular weight determination

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

<sup>10</sup> R. Harville and S. F. Reed, jun., *J. Org. Chem.*, 1968, **33**, 3976.

<sup>11</sup> R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1973, 676.

<sup>12</sup> C. R. Johnson and J. J. Rigau, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 5398.

prepared by literature methods or were gifts from the Pennwalt Corporation. *t*-Butyl hypochlorite <sup>15</sup> was prepared (56%) by bubbling chlorine gas into an aqueous solution of sodium hydroxide and *t*-butyl alcohol. Bis-(trifluoromethylthio)mercury <sup>16</sup> was prepared (46%) by the reaction of carbon disulphide with freshly prepared mercury(II) fluoride.

*Reactions of Polyfluoroiodoalkanes with Sodium Methanethiolate and Dimethyl Disulphide.*—(a) *Heptafluoro-1-iodopropane*. The reaction, carried out under the determined optimum conditions, is described in detail, and the results obtained and the conditions used during the optimisation study are given in Table 1.

A mixture of the iodopropane (2.55 g, 8.61 mmol), sodium methanethiolate (0.90 g, 12.90 mmol), dimethyl disulphide (4.05 g, 43.09 mmol), and solvent Me<sub>2</sub>SO (6 ml), sealed in a Pyrex tube (*ca.* 100 ml) and shaken at 105 °C (20 h), gave (i) 1*H*-heptafluoropropane (0.11 g, 0.67 mmol, 8%) (Found: *M*, 169. Calc. for C<sub>3</sub>HF<sub>7</sub>: *M*, 170), (ii) a liquid mixture (1.84 g), (iii) unchanged dimethyl disulphide (2.49 g, 26.49 mmol, 61% recovered), and (iv) a black oil, which on saturation with water (*ca.* 60 ml), gave, as an immiscible layer, a small quantity of unchanged dimethyl disulphide contaminated with unchanged heptafluoro-1-iodopropane; the aqueous phase gave positive tests for fluoride and iodide ions. The liquid mixture was separated by g.l.c. (8 m silicone MS 550 oil at 100 °C) into its components: unchanged heptafluoro-1-iodopropane (0.19 g, 0.65 mmol, 7.5% recovered), unchanged dimethyl disulphide (0.16 g, 1.70 mmol, 4% recovered), dimethyl sulphide (0.12 g, 1.93 mmol), and methyl heptafluoro-*n*-propyl sulphide

<sup>13</sup> J. F. Harris, jun., *J. Org. Chem.*, 1967, **32**, 2063.

<sup>14</sup> J. D. Park, R. H. Seffl, and J. R. Lacher, *J. Amer. Chem. Soc.*, 1956, **78**, 59 and references therein.

<sup>15</sup> H. M. Teeter and E. W. Bell, *Org. Synth.*, 1963, Coll. Vol. IV, p. 125.

<sup>16</sup> E. H. Mann, D. D. Coffman, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.

(1.37 g, 6.34 mmol, 80%) (Found: C, 22.2; H, 1.5%; *M*, 214. Calc. for  $C_8H_3F_7S$ : C, 22.2; H, 1.4%; *M*, 214).

(b) *Heptafluoro-1-iodopropane in the absence of solvent.* A mixture of the iodopropane (1.42 g, 4.80 mmol), dimethyl disulphide (2.82 g, 30.00 mmol), and sodium methanethiolate (0.58 g, 8.26 mmol), sealed in a Pyrex tube (*ca.* 300 ml) and shaken at 95 °C (43 h), gave (i) a mixture (0.12 g, 0.72 mmol), separated by g.l.c. (4 m silicone MS 550 oil at 20 °C) into its components, 1*H*-heptafluoropropane (0.10 g, 0.60 mmol, 15%), and hexafluoropropene (0.02 g, 0.12 mmol, 3%); (ii) a liquid mixture (1.12 g), separated by g.l.c. (2 m silicone SE 30 oil at 50–150 °C) into its components: unchanged heptafluoro-1-iodopropane (0.24 g, 0.81 mmol, 17% recovered), unchanged dimethyl disulphide (0.30 g, 3.19 mmol, 11% recovered), methyl heptafluoro-*n*-propyl sulphide (0.42 g, 1.94 mmol, 49%), and methyl pentafluoroprop-1-enyl sulphide (0.16 g, 0.88 mmol, 22%); and (iii) a black tar.

(c) *Other polyfluoromonoiodoalkanes.* The results obtained from comparable reactions of other polyfluoromonoiodoalkanes with dimethyl disulphide and sodium methanethiolate in solvent  $Me_2SO$  are given in Table 2.

(d) *Trifluoroiodoethylene.* The reaction of trifluoroiodoethylene with sodium methanethiolate and dimethyl disulphide under the conditions described in experiment (a) gave unchanged trifluoroiodoethylene (8% recovered) and trifluoroethylene (5%) as the only isolated fluorinated products.

(e) *Octafluoro-1,4-di-iodobutane.* A mixture of the di-iodobutane (4.54 g, 10.00 mmol), dimethyl disulphide (4.70 g, 50.0 mmol), and sodium methanethiolate (1.28 g, 18.28 mmol) in solvent  $Me_2SO$  (6 ml), sealed in a Pyrex tube (*ca.* 100 ml) and shaken at 90 °C (16 h), gave (i) dimethyl sulphide (0.008 g, 0.13 mmol), (ii) 1,1,2,2,3,3,4,4-octafluorobutane (0.03 g, 0.14 mmol, 2%), (iii) unchanged dimethyl disulphide (2.31 g, 24.58 mmol, 49% recovered) contaminated with traces of 1*H*-octafluoro-4-iodobutane and methyl 4*H*-octafluorobutyl sulphide (on the basis of their g.l.c. retention times), and (iv) higher-boiling material which was saturated with water (*ca.* 40 ml); the resultant brown oil (5.48 g) was separated by g.l.c. (4 m silicone MS 550 oil at 160 °C) into its components: unchanged di-iodobutane (1.21 g, 2.67 mmol, 27% recovered), methyl octafluoro-4-iodobutyl sulphide (1.38 g, 3.69 mmol, 50%), dimethyl sulphide (0.10 g, 1.6 mmol), unchanged dimethyl disulphide (2.12 g, 22.6 mmol, 45% recovered), and octafluoro-1,4-bis(methylthio)butane\* (0.67 g, 2.28 mmol, 31%) (Found: C, 24.2; H, 2.1; F, 51.5.  $C_8H_8F_8S_2$  requires C, 24.5; H, 2.0; F, 51.7%), b.p. (Siwoloboff) 182.5–183.5 °C.

A second reaction carried out at 90 °C (46 h) gave unchanged octafluoro-1,4-di-iodobutane (9% recovered), octafluoro-1,4-bis(methylthio)butane (34%), methyl octafluoro-4-iodobutyl sulphide (25%), and 1,1,2,2,3,3,4,4-octafluorobutane (1%).

*Reactions of Polyfluoroiodoalkanes with Sodium Methanethiolate.*—(a) *Heptafluoro-1-iodopropane.* A mixture of the iodopropane (1.48 g, 5.00 mmol), and sodium methanethiolate (0.44 g, 6.28 mmol) in solvent  $Me_2SO$  (5 ml), sealed in a Pyrex tube (*ca.* 100 ml) and shaken at 100 °C (18 h), gave 1*H*-heptafluoropropane (0.13 g, 0.79 mmol, 17%) and a mixture (0.88 g) which was separated by g.l.c. (7 m silicone SE 30 oil at 120 °C) into its components: unchanged heptafluoro-1-iodopropane (0.09 g, 0.31 mmol, 6% recovered), methyl heptafluoro-*n*-propyl sulphide (0.73 g,

3.38 mmol, 73%), and methyl heptafluoroprop-1-enyl sulphide (0.04 g, 0.22 mmol, 5%).

(b) *Heptadecafluoro-1-iodooctane.* A mixture of the iodo-octane (2.73 g, 5.00 mmol) and sodium methanethiolate (0.46 g, 6.72 mmol) in solvent  $Me_2SO$  (10 ml) was stirred at room temperature (40 h) and the resultant material was saturated with water (40 ml) and then extracted with ether (2 × 10 ml). The extract was dried ( $Na_2SO_4$ ), the ether was removed *in vacuo*, and the resultant liquid was shown by g.l.c. (2 m silicone SE 30 oil at 60 °C) to consist of unchanged heptadecafluoro-1-iodooctane (0.46 g, 0.67 mmol, 13% recovered), methyl heptadecafluoro-*n*-octyl sulphide (1.37 g, 2.94 mmol, 69%), and 1*H*-heptadecafluoro-*n*-octane (trace).

*Reaction of Heptafluoro-1-iodopropane with Sodium Methoxide and Dimethyl Disulphide.*—A mixture of the iodopropane (2.98 g, 10.07 mmol), sodium methoxide (0.72 g, 13.26 mmol), and dimethyl disulphide (5.30 g, 56.39 mmol) in solvent  $Me_2SO$  (15 ml), sealed in a Pyrex tube (*ca.* 300 ml) and heated to 105 °C (38 h), gave (i) 1*H*-heptafluoropropane (1.10 g, 6.47 mmol, 68%); (ii) a liquid mixture (0.52 g) which was separated by g.l.c. (4 m silicone MS 550 oil at 50–120 °C) into its components: unchanged heptafluoro-1-iodopropane (0.08 g, 0.27 mmol, 3% recovered), methyl heptafluoro-*n*-propyl sulphide (0.34 g, 1.57 mmol, 16%), methanol (0.10 g, 3.13 mmol), and dimethyl disulphide (trace); and (iii) an involatile black oil which was not investigated.

*Attempted Reaction of Heptafluoro-1-iodopropane with Dimethyl Disulphide.*—A mixture of the iodopropane (2.96 g, 10.00 mmol) and dimethyl disulphide (10.60 g, 0.11 mol) in solvent  $Me_2SO$  (10 ml), sealed in a Pyrex tube (*ca.* 100 ml) and heated at 100 °C (20 h), gave unchanged heptafluoro-1-iodopropane (2.63 g, 8.89 mmol, 89% recovered) as the only observed fluorine-containing product.

*Reactions of Polyfluoromonoiodoalkanes with Sodium Methanethiolate and Dimethyl Sulphide.*—(a) *Heptafluoro-1-iodopropane.* A series of reactions were carried out at 90 °C in sealed tubes which were shaken; these reactions employed varying ratios of iodopropane, methanethiolate, and dimethyl sulphide and the results are shown in Table 5. It was demonstrated in a separate experiment that the iodopropane did not react with the dimethyl sulphide in solvent  $Me_2SO$  under the same conditions; heptafluoro-1-iodopropane (97%) was recovered.

(b) *Heptafluoro-2-iodopropane.* A mixture of the 2-iodopropane (2.96 g, 10.00 mmol), sodium methanethiolate (0.74 g, 10.60 mmol), and dimethyl sulphide (3.10 g, 50.0 mmol) in solvent  $Me_2SO$  (10 ml), sealed in a Pyrex tube (*ca.* 300 ml) and shaken at 90 °C (20 h), gave (Table 4) (i) a mixture of 2*H*-heptafluoropropane (0.15 g, 0.89 mmol, 23%) and hexafluoropropene (0.03 g, 0.20 mmol, 5%) as shown by g.l.c. (4 m DNP at 80 °C); (ii) unchanged dimethyl sulphide (0.90 g, 14.5 mmol, 29% recovered); (iii) a mixture (4.01 g) separated by g.l.c. (8 m silicone MS 550 oil at 100 °C) into its components: unchanged heptafluoro-2-iodopropane (1.84 g, 6.21 mmol, 62% recovered), methyl heptafluoroisopropyl sulphide (0.12 g, 0.56 mmol, 15%), methyl pentafluoroprop-1-enyl sulphide (0.06 g, 0.34 mmol, 9%), and unchanged dimethyl sulphide (1.99 g, 32.1 mmol, 64% recovered); and (iv) a black oil which was not investigated further.

(c) *Tridecafluoro-1-iodohexane.* A mixture of the iodo-hexane (8.92 g, 20.00 mmol), sodium methanethiolate (1.48 g, 21.1 mmol), and dimethyl sulphide (6.20 g, 0.10 mol) in solvent  $Me_2SO$  (20 ml), sealed in a Pyrex tube (*ca.* 300 ml

and shaken at 100 °C (43 h), gave (Table 4) (i) a mixture (10.02 g) which was separated by g.l.c. (8 m silicone MS 550 oil at 100 °C) into its components: unchanged tridecafluoro-1-iodohexane (1.36 g, 3.05 mmol, 15% recovered), methyl tridecafluoro-*n*-hexyl sulphide (3.89 g, 10.63 mmol, 87%), 1*H*-tridecafluorohexane (0.18 g, 0.45 mmol, 5%), and unchanged dimethyl sulphide (4.59 g, 74.04 mmol, 74% recovered); and (ii) an involatile brown oil which was saturated with water (*ca.* 100 ml); the resultant immiscible organic phase was distilled to give a mixture (2.67 g), b.p. 23 °C at 0.1 mmHg, which was separated by g.l.c. (as above) into its components: unchanged tridecafluoro-1-iodohexane (2.05 g, 4.61 mmol, 23% recovered), methyl tridecafluoro-*n*-hexyl sulphide (0.28 g, 0.77 mmol, 6%), and unchanged dimethyl sulphide (0.34 g, 5.48 mmol, 5% recovered).

*Reaction of Methyl Heptafluoro-*n*-hexyl Sulphide with*

requires C, 23.0; H, 0.2%), b.p. (Siwoloboff) 135—136 °C at 730 mmHg.

*Reaction of 1-Iodohexane with Bis(trifluoromethylthio)-mercury.*—A mixture of the iodohexane (8.48 g, 40.0 mmol) and the mercurial (17.78 g, 44.1 mmol) was stirred at 180 °C (5 h) and the volatile products were treated with hydrogen chloride to remove unchanged mercurial as mercury(II) chloride. The reaction gave (i) a mixture (0.25 g, 2.89 mmol; *M*, 88) of trifluoromethanethiol and an unknown compound and (ii) *n*-hexyl trifluoromethyl sulphide\* (4.47 g, 24.0 mmol, 60%) (Found: C, 45.1; H, 6.9; F, 30.5.  $C_7H_{13}F_3S$  requires C, 45.2; H, 7.0; F, 30.6%), b.p. (Siwoloboff) 141—142 °C.

*Oxidation of *n*-Hexyl Trifluoromethyl Sulphide.*—A mixture of the sulphide (3.12 g, 20.0 mmol), hydrogen peroxide (92.0 mmol, 2.5 ml of 27.5% solution) and glacial acetic

*Reaction of Hexafluoropropene with Dimethyl Sulphoxide.*— A mixture of hexafluoropropene (0.60 g, 4.0 mmol) and Me<sub>2</sub>SO (5 ml), sealed in a Pyrex tube (ca. 100 ml) and shaken at 100 °C (20 h), gave (i) a mixture (0.53 g, 3.35 mmol; *M*, 158) of 2*H*-heptafluoropropane (0.51 g, 2.98 mmol, 74%) and dimethyl sulphide (0.02 g, 0.37 mmol), (ii) a mixture (0.10 g) shown by g.l.c. (2 m APL at 30 °C) to

consist of dimers of hexafluoropropene and two unknown components, and (iii) a residual black oil soluble in water.

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