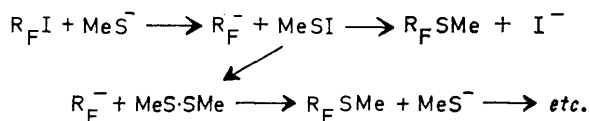


## Perfluoroalkyl Derivatives of Sulphur. Part XIX.<sup>1</sup> Reaction of Fluoroolefins with Fluoride Ion in the Presence of Dimethyl Disulphide, and Related Reactions

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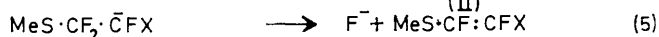
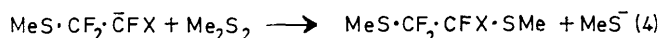
Tetrafluoroethylene and chlorotrifluoroethylene react with caesium fluoride in the presence of dimethyl disulphide to give 1,2-bis(methylthio)-adducts and methyl pentafluoroethyl sulphide or 1-chlorotetrafluoroethyl methyl sulphide. Hexafluoropropene gives methyl tetrafluoro-1-trifluoromethylethyl sulphide and olefin telomers under comparable conditions. Pentafluoroethane is the only isolated product of the reaction of tetrafluoroethylene with caesium fluoride in the presence of dimethyl sulphide. The reactions of sodium methanethiolate with chlorotetrafluoroethylene and hexafluoropropene are also described.

THE synthesis of methyl polyfluoroalkyl sulphides by the reaction of polyfluoroiodoalkanes with sodium methanethiolate in the presence or in the absence of dimethyl disulphide has been reported:<sup>1</sup>



This mechanism has now been tested by an investigation of the reaction of dimethyl disulphide with a polyfluoroalkyl carbanion formed by nucleophilic attack of fluoride ion on a fluoro-olefin.<sup>2</sup> Use of tetramethylene sulphone as solvent, caesium fluoride as fluoride ion source, and tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoropropene as olefins gave the expected methyl polyfluoroalkyl sulphides (I).

*Tetrafluoroethylene and Chlorotrifluoroethylene.*—Tetrafluoroethylene gave the sulphide (Ia) (15%), tetrafluoro-1,2-bis(methylthio)ethane (IIa) (77%), and pentafluoroethane (2%); chlorotrifluoroethylene afforded the sulphide (Ib) (15%), 1-chlorotrifluoro-1,2-bis(methylthio)ethane (IIb) (56%), and a mixture of *cis*- and *trans*-2-chlorodifluorovinyl methyl sulphide (IIIb) (13%), probably formed as in the Scheme. The greater nucleophilicity of methanethiolate ion makes equation (3) more



a; X=F b; X=Cl c; X=CF RH=C-H containing species

### SCHEME

favoured than equation (1) and explains the relatively low yield of (Ia) and (Ib) and the predominance of (IIa) and (IIb). In accord with the Scheme, equations (3) and

(4), the reaction of sodium methanethiolate with the olefins in the presence of dimethyl disulphide gave, in both cases, molar yields of the bis(methylthio)-adducts in excess of those stoichiometrically possible if only the methanethiolate added initially as sodium salt has attacked the olefins; further methanethiolate had thus been generated by equation (4). A control experiment showed that the possibility that free-radical addition of the disulphide to the olefin was taking place could be discounted.

The olefin conversions, as distinct from yields based on the olefin converted, in the reactions initiated by sodium methanethiolate were low (C<sub>2</sub>F<sub>4</sub>, 55%; C<sub>2</sub>F<sub>3</sub>Cl, 19%) compared with the quantitative conversions in the reactions initiated with caesium fluoride, possible since caesium salts are more soluble than sodium salts in tetramethylene sulphone; that the nucleophilic reactivity of sodium and lithium salts in dimethyl sulphoxide is lower than the reactivities of the same salts of other alkali metals, has been ascribed to ion-pair formation.<sup>3</sup>

The slow reaction of tetrafluoroethylene with caesium fluoride in the presence of dimethyl disulphide at room temperature (94% olefin recovered after 20 h) is consistent with the slow room temperature oligomerisation of tetrafluoroethylene by caesium fluoride.<sup>4</sup> The reaction of tetrafluoroethylene with caesium fluoride in the presence of dimethyl sulphide gave pentafluoroethane (70%) *via* proton abstraction as the only isolated product, thus showing that carbanionic attack on sulphur or carbon of a monosulphide is not possible.

Hydrolysis of 1-chlorotrifluoro-1,2-bis(methylthio)ethane (IIb) with water at 80 °C resulted in complete decomposition to give carbon dioxide, methanethiol, fluoride ion, and chloride ion.

*Hexafluoropropene.*—Reactions of hexafluoropropene with caesium fluoride in the presence of dimethyl disulphide to give (Ic) in up to 38% yield are shown in the Table. The dimethyl disulphide adduct (IIc), expected by analogy with (IIa and b), was not detected in the products from any of the reactions, although the isolation of methyl pentafluoroprop-1-enyl sulphide (IIIc) in reasonable yield (12–21%) indicates that the carbanion

<sup>1</sup> Part XVIII, B. Haley, R. N. Haszeldine, B. Hewitson, and A. E. Tipping, *J.C.S. Perkin I*, 1976, 525.

<sup>2</sup> J. A. Young, *Fluorine Chem. Rev.*, 1967, 1, 359.

<sup>3</sup> D. Martin, A. Weise, and H-J. Niclas, *Angew. Chem. Internat. Edn.*, 1967, 6, 318.

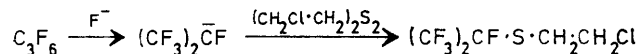
<sup>4</sup> W. T. Flowers, R. N. Haszeldine, and C. Vallance, unpublished results.

precursor to (IIc) or (IIIc),  $\text{MeS}\cdot\text{CF}_2\cdot\bar{\text{C}}\text{F}\cdot\text{CF}_3$ , is formed. That loss of fluoride ion from the carbanion predominates over attack on dimethyl disulphide is also shown by the reaction of sodium methanethiolate with hexafluoropropene in the presence of dimethyl disulphide; the unsaturated sulphide (IIIc) (95%) was the only product isolated.

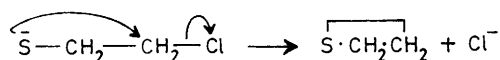
The high yield of olefin oligomers (54%) formed in the low-temperature reaction in tetramethylene sulphone as solvent suggests that attack of  $(\text{CF}_3)_2\text{CF}^-$  on dimethyl disulphide is more favoured at higher temperature, although the higher concentration of dissolved olefin in the liquid phase at lower temperatures also favours oligomer formation. Bis-(2-methoxyethyl) ether, a preferred solvent for fluoro-olefin oligomerisation,<sup>5</sup> offers no advantage in the preparation of the sulphur compounds.

The stabilities of the intermediate carbanions in the above reactions are  $\text{MeS}\cdot\text{CF}_2\cdot\bar{\text{C}}\text{F}\cdot\text{CF}_3 > \text{MeS}\cdot\text{CF}_2\cdot\bar{\text{C}}\text{FCl} > \text{MeS}\cdot\text{CF}_2\cdot\bar{\text{C}}\text{F}_2^-$ , and in general the more reactive the anion the more readily does it carry out nucleophilic attack on the dimethyl disulphide to give (II). There is a marked difference between the secondary carbanion  $(\text{CF}_3)_2\text{CF}^-$ , which readily attacks dimethyl disulphide, and  $\text{MeS}\cdot\text{CF}_2\cdot\bar{\text{C}}\text{F}\cdot\text{CF}_3$ , which does not, presumably since the MeS group facilitates fluoride loss from the adjacent  $\text{CF}_2$  group in the anion.

Attempts to prepare substituted-alkyl polyfluoroalkyl sulphides by the photochemical reactions of polyfluoroiodoalkanes with substituted dialkyl disulphides or sulphides<sup>6</sup> were unsuccessful. The carbanionic route provided an alternative. Thus the reaction of hexafluoropropene with caesium fluoride in the presence of bis-(2-chloroethyl) disulphide gave 2-chloroethyl tetrafluoro-1-trifluoromethylethyl sulphide in reasonable yield (50%).



The other major product, ethylene sulphide, arises by rapid internal nucleophilic displacement of chloride ion from the 2-chloroethanethiolate ion liberated following a mechanism of the type shown in the Scheme; the thiolate ion does not attack hexafluoropropene:

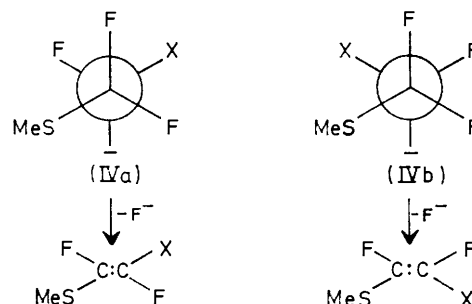


The dehydrochlorination of the chloroethyl sulphide required relatively vigorous conditions (90 °C for 16 h with a ten molar excess of powdered KOH) and gave tetrafluoro-1-trifluoromethylethyl vinyl sulphide (53%).

*Reactions of Methanethiolate with Hexafluoropropene and with Chlorotrifluoroethylene.*—These reactions, in diethyl ether, give a different range of products from those obtained with tetramethylene sulphone as solvent. When the reaction mixtures were warmed from -196 °C to room temperature the unsaturated sulphides were

<sup>5</sup> W. Brunskill, W. T. Flowers, R. Gregory, and R. N. Haszeldine, *Chem. Comm.*, 1970, 1444; W. Brunskill, W. T. Flowers, and R. N. Haszeldine, unpublished results.

obtained in good yield: (IIIb) (77%) and (IIIc) (90%) when an excess of olefin was used to minimise possible polysubstitution reactions. The unsaturated sulphides (IIIb and c) were obtained as mixtures of *cis*- and *trans*-isomers in the ratios 55 : 45 and 9 : 91, respectively, and identified *via* the vicinal olefinic F-F coupling constants: *trans* (ca. 140 Hz)  $\gg$  *cis* (20 and 40 Hz). The *cis* : *trans* isomer ratios of the olefins (IIIb and c) were the same as found for the olefins obtained from the caesium fluoride or sodium methanethiolate reactions in tetramethylene sulphone in the presence of dimethyl disulphide, indicating a similar reaction path. Thus, provided that the carbanion centre is tetrahedral with the lone pair occupying an  $sp^3$  orbital<sup>7</sup> and *trans*-elimination of fluoride ion from the carbanion is preferred, the carbanion conformer (IVa; X =  $\text{CF}_3$ ) is preferred over (IVb; X =  $\text{CF}_3$ ), whereas with the carbanion conformers (IVa; X = Cl) and (IVb; X = Cl) there is apparently no such preference.



Use of tetramethylene sulphone as solvent instead of ether gave high recoveries of unchanged olefin ( $\text{C}_3\text{F}_6$ , 81%;  $\text{C}_2\text{F}_3\text{Cl}$ , 72%), and in the latter reaction the sulphide (IIIb) (14% based on olefin consumed) and a higher boiling oil were also formed. The oil showed six fluorine absorptions in its  $^{19}\text{F}$  n.m.r. spectrum (between -6 and +43 p.p.m.) which were assigned to vinylic fluorine atoms, the  $^1\text{H}$  n.m.r. spectrum showed one broad absorption at 4.37 p.p.m. to high field of benzene (SMe), and the mass spectrum contained strong peaks at  $m/e$  212 ( $\text{C}_6\text{H}_{12}\text{S}_4^+$ ), 202 and 200 ( $\text{C}_4\text{H}_9\text{ClFS}_3^+$ ), and 174 and 172 ( $\text{C}_4\text{H}_6\text{ClFS}_2^+$ ), assigned to the parent ions shown. This suggests that polysubstitution of the olefin by methanethiolate ion occurs and that polymeric products of the olefin are also formed as indicated by the number of fluorine absorptions in the  $^{19}\text{F}$  n.m.r. spectrum. The mass spectral parent peaks are tentatively assigned to the compounds  $(\text{Me}_2\text{S})_2\text{C}:\text{C}(\text{SMe})_2$ ,  $(\text{MeS})_2\text{C}:\text{CCl}\cdot\text{SMe}$ , and  $(\text{MeS})_2\text{C}:\text{CFCl}$  or  $\text{MeS}\cdot\text{CF}:\text{CCl}\cdot\text{SMe}$ , respectively. The absence of the di- and tri-substitution products  $\text{MeS}\cdot\text{CF}:\text{CF}\cdot\text{SMe}$  and  $(\text{MeS})_2\text{C}:\text{CF}\cdot\text{SMe}$  (parent ion peaks at  $m/e$  156 and 184, respectively) shows that loss of fluoride ion is favoured over loss of chloride ion.

The difference in results obtained from the reactions

<sup>6</sup> R. N. Haszeldine, B. Higginbottom, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 155; R. N. Haszeldine, B. Hewitson, and A. E. Tipping, *ibid.*, 1974, 1706.

<sup>7</sup> J. D. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 48.

carried out in ether and in tetramethylene sulphone is attributed to the major difference in m.p.s of the solvents. Diethyl ether melts at *ca.*  $-120^{\circ}\text{C}$  and so the reactants were intimately mixed above this temperature when warming from  $-196^{\circ}\text{C}$  to room temperature, by which time the reaction was complete. In contrast appreciable mixing of the reactants in tetramethylene sulphone (m.p.  $25^{\circ}\text{C}$ ) will only occur at much higher temperature, when an appreciable amount of the volatile olefin will be in the vapour phase.

In an attempt to prepare pure samples of the poly-substitution products the reaction of chlorotrifluoroethylene with an excess of sodium methanethiolate (1 : 2.5 molar ratio) in diethyl ether at room temperature was investigated. This gave the monosubstituted olefin (IIIb) (21%) and an involatile oil containing three components (ratio *ca.* 1 : 1 : 2) which could not be separated by g.l.c. since they decomposed on the column. The mass spectrum of the oil showed peaks at *m/e* 202 and 200 and 174 and 172 corresponding to the trisubstituted and disubstituted products, respectively, observed in the reaction in tetramethylene sulphone.

The synthesis of unsaturated sulphides by the reactions of anhydrous sodium alkanethiolates with fluoro-olefins in aprotic solvents has not been widely investigated.<sup>8</sup> The major route to such compounds has been the dehydrohalogenation or dehalogenation of the adducts of the corresponding thiols with fluoro-olefins.<sup>9</sup>

#### EXPERIMENTAL

Techniques used were as described in Part XVIII,<sup>1</sup> except that for g.l.c. a Griffin and George D6 gas density balance or a Perkin-Elmer F21, Pye 104, or Pye 105 instrument was used, with columns packed with Silicone SE30 oil (20%) on Celite unless stated to the contrary.  $^1\text{H}$  and  $^{19}\text{F}$  N.m.r. spectra were run with internal tetramethylsilane and external trifluoroacetic acid as the respective references. All reactions were carried out *in vacuo* in sealed Pyrex tubes (*ca.* 300 cm<sup>3</sup>) unless stated to the contrary. Bis-(2-chloroethyl) disulphide (67%) was prepared by the reaction of ethylene sulphide with sulphuryl chloride.<sup>10</sup> Spectroscopic data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 21681 (12 pp., 1 microfiche).†

*Reactions of Fluoro-olefins with Caesium Fluoride in the Presence of Dimethyl Disulphide.*—(a) *Tetrafluoroethylene.* A mixture of the olefin (1.50 g, 15.00 mmol), caesium fluoride (3.32 g, 21.80 mmol), dimethyl disulphide (7.52 g, 80.0 mmol), and tetramethylene sulphone (8 cm<sup>3</sup>), shaken at  $80^{\circ}\text{C}$  (20 h), gave (i) pentafluoroethane (0.04 g, 0.36 mmol, 2%); (ii) methyl pentafluoroethyl sulphide\* (0.21 g, 1.27 mmol, 8%) (Found: *M*, 167. Calc. for  $\text{C}_3\text{H}_5\text{F}_5\text{S}$ : *M*, 166); (iii) a mixture (6.16 g) shown by i.r. spectroscopy and g.l.c. (2 m column at  $50\text{--}150^{\circ}\text{C}$ ) to consist of unchanged dimethyl disulphide (4.64 g, 49.37 mmol, 62% recovered), methyl

pentafluoroethyl sulphide (0.17 g, 1.02 mmol, 7%), and tetrafluoro-1,2-bis(methylthio)ethane<sup>11</sup> (1.30 g, 6.70 mmol, 45%); and (iv) a mixture (1.19 g) obtained by distillation under reduced pressure of an oil which separated on saturation of the involatile residue with water. This mixture was shown by i.r. spectroscopy and g.l.c. (as above) to consist of dimethyl disulphide (0.26 g, 2.77 mmol, 3% recovered) and tetrafluoro-1,2-bis(methylthio)ethane (0.93 g, 4.79 mmol, 32%); the latter was identified by comparison of the n.m.r. spectra of a pure sample separated by g.l.c. (4 m column at  $120^{\circ}\text{C}$ ) with those reported.<sup>11</sup>

A similar reaction mixture, shaken at room temperature (20 h), gave unchanged tetrafluoroethylene (94% recovered) and a trace of methyl pentafluoroethyl sulphide as the only isolated products.

(b) *Chlorotrifluoroethylene.* A mixture of the olefin (4.66 g, 40.0 mmol), caesium fluoride (6.10 g, 40.14 mmol), dimethyl disulphide (18.80 g, 0.20 mol), and tetramethylene sulphone (30 cm<sup>3</sup>), shaken at  $94^{\circ}\text{C}$  (50 h), gave a volatile fraction (5.42 g) which was separated by g.l.c. (2 m column at  $50\text{--}130^{\circ}\text{C}$ ) into its three components: (i) unchanged dimethyl disulphide (4.03 g, 42.88 mmol, 21% recovered); (ii) a mixture of *cis*- and *trans*-2-chlorodifluorovinyl methyl sulphide (0.38 g, 5.53 mmol, 14%); and (iii) 1-chlorotetrafluoroethyl methyl sulphide\* (1.01 g, 5.53 mmol, 14%) (Found: C, 19.9; H, 1.7; F, 41.5%; *M*<sup>+</sup>, 184 and 182. Calc. for  $\text{C}_3\text{H}_3\text{ClF}_4\text{S}$ : C, 19.7; H, 1.6; F, 41.6%, *M*, 182.5), b.p.  $75.3 \pm 0.5^{\circ}\text{C}$ . Saturation with water (*ca.* 150 cm<sup>3</sup>) of the non-volatile oil obtained from the reaction gave an immiscible organic phase (18.55 g) which was distilled to afford (i) a mixture (11.79 g), which was separated by g.l.c. (as above) into its components, unchanged dimethyl disulphide (11.32 g, 117.7 mmol, 59% recovered), a mixture (0.35 g, 2.42 mmol, 6%) of *cis*- and *trans*-2-chlorodifluorovinyl methyl sulphide, and 1-chlorotetrafluoroethyl methyl sulphide (0.12 g, 0.65 mmol, 1%); (ii) 1-chlorotrifluoro-1,2-bis(methylthio)ethane\* (4.02 g, 19.14 mmol, 48%) (Found: C, 23.1; H, 3.0; F, 27.5%; *M*<sup>+</sup>, 212 and 210. Calc. for  $\text{C}_4\text{H}_6\text{ClF}_3\text{S}_2$ : C, 22.8; H, 2.9; F, 27.1%; *M*, 210.5), b.p. (Siwoloboff)  $189\text{--}190^{\circ}\text{C}$ ; and (iii) a residue (1.87 g), shown by g.l.c. (2 m column at  $180^{\circ}\text{C}$ ) to consist of 1-chlorotrifluoro-1,2-bis(methylthio)ethane (0.69 g, 3.24 mmol, 8%) and tetramethylene sulphone (1.18 g).

(c) *Hexafluoropropene.* The reaction conditions were varied in order to improve the yield of methyl tetrafluoro-1-trifluoromethylethyl sulphide. Experiment 1 is described in full and the conditions and results for all the experiments are shown in the Table.

A mixture of the olefin (3.00 g, 20.0 mmol), caesium fluoride (3.34 g, 22.0 mmol), dimethyl disulphide (9.40 g, 0.10 mol), and tetramethylene sulphone (10 cm<sup>3</sup>), shaken at  $90^{\circ}\text{C}$  (20 h), gave (i) 2*H*-heptafluoropropane (0.07 g, 0.4 mmol, 2%); (ii) a mixture (2.50 g) separated by g.l.c. (8 m Silicone MS550 oil at  $100^{\circ}\text{C}$ ) into its components, dodecafluoro-2-methylpent-2-ene<sup>5</sup> (0.22 g, 0.7 mmol, 7%),

<sup>8</sup> L. M. Yagupol'skii, and A. M. Aleksandrov, *J. Gen. Chem. (U.S.S.R.)*, 1969, **39**, 726; W. R. Cullen, D. S. Dawson, and P. S. Dahliwal, *Canad. J. Chem.*, 1967, **45**, 783; K. Inukai, T. Ueda, and H. Muramatsu, *Bull. Chem. Soc. Japan*, 1966, **39**, 2191; J. F. Harris, jun., *J. Org. Chem.*, 1967, **32**, 2063; K. Inukai, T. Ueda, and H. Muramatsu, *Bull. Chem. Soc. Japan*, 1967, **40**, 1288.

<sup>10</sup> G. Yu Epshtein, I. A. Usov, and S. Z. Ivin, *J. Gen. Chem. (U.S.S.R.)*, 1964, **34**, 1961.

<sup>11</sup> R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 2438.

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

<sup>8</sup> Y. Ya Yakubovich, I. N. Belaeva, P. O. Gitel, V. V. Smolanit-skaya, and L. V. Sankina, *J. Gen. Chem. (U.S.S.R.)*, 1967, **37**, 787; R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, *J.C.S. Perkin I*, 1975, 2015.

methyl tetrafluoro-1-trifluoromethylethyl sulphide <sup>6</sup> (1.30 g, 6.0 mmol, 30%) (Found: C, 22.4; H, 1.6. Calc. for C<sub>4</sub>H<sub>3</sub>F<sub>7</sub>S: C, 22.2; H, 1.4%), methyl pentafluoroprop-1-enyl sulphide (0.33 g, 1.9 mmol, 9%), perfluoro-(2,4-dimethyl-3-ethylpent-2-ene) <sup>5</sup> (0.05 g, 0.1 mmol, 2%), and unchanged dimethyl disulphide (0.60 g, 6.4 mmol, 6% recovered); (iii) a mixture (5.28 g) shown by g.l.c. (as above) to consist of methyl tetrafluoro-1-trifluoromethylethyl sulphide (0.13 g, 0.6 mmol, 3%), methyl pentafluoroprop-1-enyl sulphide (0.42 g, 2.4 mmol, 12%), perfluoro-(2,4-dimethyl-3-ethylpent-2-ene) (0.18 g, 0.4 mmol, 6%), and unchanged dimethyl disulphide (4.55 g, 48.4 mmol, 48% recovered); and (iv) an involatile oil which was saturated

positive test for fluoride ion. The liquid fraction (9.55 g) was separated by repeated condensation *in vacuo* into a lower boiling fraction (5.49 g), which was shown by g.l.c. (2 m column at 50 °C) to consist of diethyl ether (5.18 g) and methyl pentafluoroprop-1-enyl sulphide (0.31 g, 1.75 mmol, 19%), and a higher boiling fraction (4.06 g), which was shown by g.l.c. (as above) to consist of diethyl ether (0.27 g), methyl pentafluoroprop-1-enyl sulphide (1.24 g, 6.96 mmol, 76%), and unchanged dimethyl disulphide (2.55 g, 27.1 mmol, 36% recovered).

*Reaction of Tetrafluoroethylene with Caesium Fluoride and Dimethyl Sulphide.*—A mixture of the olefin (0.71 g, 7.1 mmol), caesium fluoride (1.61 g, 10.6 mmol), dimethyl

#### Reactions of hexafluoropropene with caesium fluoride and dimethyl disulphide

Expt.	Time (h)	Temp. (°C)	C <sub>3</sub> F <sub>6</sub> (mmol)	Solvent (cm <sup>3</sup> )	Product yield (%)				
					(CF <sub>3</sub> ) <sub>2</sub> CF·SMe <sup>a</sup> (Ic)	(CF <sub>3</sub> ) <sub>2</sub> CHF	C <sub>3</sub> F <sub>6</sub> <sup>b</sup> Dimer	C <sub>3</sub> F <sub>6</sub> <sup>b</sup> Trimer	CF <sub>3</sub> ·CF·CF·SMe (IIIc)
1	20	90	20	[CH <sub>2</sub> ] <sub>4</sub> SO <sub>2</sub> (10)	33	2	7	8	21
2	15	42	12	[CH <sub>2</sub> ] <sub>4</sub> SO <sub>2</sub> (6)	38	4	4	11	19
3	46	15	20	[CH <sub>2</sub> ] <sub>4</sub> SO <sub>2</sub> (10)	21	2	44	10	15
4	19	90	20	(MeO·[CH <sub>2</sub> ] <sub>2</sub> ) <sub>2</sub> O (10)	15	5	30	20	12

<sup>a</sup> Ref. 6. <sup>b</sup> Ref. 5.

with water (60 cm<sup>3</sup>) and the immiscible organic phase was separated and distilled to give unchanged dimethyl disulphide (1.54 g, 16.4 mmol, 16% recovered) and a tarry residue (2.24 g).

*Reactions of Fluoro-olefins with Sodium Methanethiolate in the Presence of Dimethyl Disulphide.*—(a) *Tetrafluoroethylene.* A mixture of the olefin (0.29 g, 2.90 mmol), sodium methanethiolate (0.07 g, 0.92 mmol), dimethyl disulphide (1.88 g, 20.0 mmol), and tetramethylene sulphone (6 cm<sup>3</sup>), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm<sup>3</sup>) and shaken at 85 °C (20 h), gave (i) unchanged tetrafluoroethylene (0.13 g, 1.30 mmol, 45% recovered), (ii) a mixture (1.39 g) which was separated by g.l.c. (2 m column at 105 °C) into its components, unchanged dimethyl disulphide (1.18 g, 12.56 mmol, 63% recovered) and tetrafluoro-1,2-bis-(methylthio)ethane (0.21 g, 1.08 mmol, 68%), and (iii) an involatile mixture of solid and oil which was not investigated further.

(b) *Chlorotrifluoroethylene.* A mixture of the olefin (1.75 g, 15.0 mmol), sodium methanethiolate (0.12 g, 1.71 mmol), dimethyl disulphide (7.05 g, 75.0 mmol), and tetramethylene sulphone (10 cm<sup>3</sup>), shaken at 90 °C (69 h), gave (i) unchanged chlorotrifluoroethylene (1.41 g, 12.10 mmol, 81% recovered), (ii) unchanged dimethyl disulphide (1.22 g, 13.0 mmol, 17% recovered), and (iii) an oil (4.68 g) which was obtained by saturation of the involatile material with water (*ca.* 60 cm<sup>3</sup>) and which on distillation at reduced pressure afforded a residual tar (0.08 g) and a mixture (4.60 g) shown by g.l.c. (2 m column at 110 °C) to consist of unchanged dimethyl disulphide (4.10 g, 43.62 mmol, 58% recovered) and 1-chlorotrifluoro-1,2-bis(methylthio)ethane (0.50 g, 2.38 mmol, 82%).

(c) *Hexafluoropropene.* A mixture of the olefin (2.25 g, 15.0 mmol), sodium methanethiolate (0.67 g, 9.6 mmol), dimethyl disulphide (7.05 g, 75.0 mmol), and diethyl ether (10 cm<sup>3</sup>), shaken (2 h) while the tube warmed from -196 °C to room temperature, gave (i) unchanged hexafluoropropene (0.87 g, 5.8 mmol, 39% recovered), (ii) a liquid fraction (9.55 g), (iii) unchanged dimethyl disulphide (3.46 g, 36.8 mmol, 49% recovered), and (iv) a yellow solid which was partially soluble in water; the aqueous solution gave a

positive test for fluoride ion. The liquid fraction (9.55 g) was separated by repeated condensation *in vacuo* into a lower boiling fraction (5.49 g), which was shown by g.l.c. (2 m column at 50 °C) to consist of diethyl ether (5.18 g) and methyl pentafluoroprop-1-enyl sulphide (0.31 g, 1.75 mmol, 19%), and a higher boiling fraction (4.06 g), which was shown by g.l.c. (as above) to consist of diethyl ether (0.27 g), methyl pentafluoroprop-1-enyl sulphide (1.24 g, 6.96 mmol, 76%), and unchanged dimethyl disulphide (2.55 g, 27.1 mmol, 36% recovered).

*Attempted Reaction of Tetrafluoroethylene with Dimethyl Disulphide.*—A mixture of the olefin (0.30 g, 3.0 mmol), dimethyl disulphide (1.41 g, 15.0 mmol), and tetramethylene sulphone (6 cm<sup>3</sup>), sealed *in vacuo* in a Pyrex tube (*ca.* 75 cm<sup>3</sup>) and shaken at 85 °C (20 h), gave unchanged tetrafluoroethylene (0.30 g, 3.0 mmol, 100% recovered).

*Reactions of Sodium Methanethiolate with Fluoro-olefins.*—(a) *Hexafluoropropene.* A mixture of the olefin (1.65 g, 11.0 mmol), sodium methanethiolate (0.38 g, 5.4 mmol), and diethyl ether (20 cm<sup>3</sup>), shaken (2 h) while the mixture warmed from -196 °C to room temperature, gave (i) a mixture (0.85 g, 5.45 mmol; *M*, 145) of unchanged hexafluoropropene (0.82 g, 5.46 mmol, 49% recovered) and diethyl ether (0.03 g); (ii) diethyl ether (*ca.* 19 cm<sup>3</sup>); (iii) a mixture (0.98 g) which was separated by g.l.c. (4 m column at 90 °C) into its components, diethyl ether (0.09 g), *trans-methyl pentafluoroprop-1-enyl sulphide* \* (0.81 g, 4.55 mmol, 82%) (Found: C, 27.3; H, 1.9%; *M*, 179. Calc. for C<sub>4</sub>H<sub>3</sub>F<sub>5</sub>S: C, 27.0; H, 1.7%; *M*, 178), b.p. (isoteniscope) 79.7 ± 0.5 °C, and *cis-methyl pentafluoroprop-1-enyl sulphide* \* (0.08 g, 0.45 mmol, 8%; *M*, 178); and (iv) a white solid residue which was totally soluble in water and gave a positive test for fluoride ion.

In a second experiment a mixture of the olefin (2.10 g, 14.0 mmol), sodium methanethiolate (0.90 g, 12.9 mmol), and tetramethylene sulphone (10 cm<sup>3</sup>), shaken at 50 °C (15 h), gave unchanged hexafluoropropene (1.70 g, 11.3 mmol, 81% recovered) as the only volatile product.

(b) *Chlorotrifluoroethylene in diethyl ether.* A mixture of the olefin (5.30 g, 45.5 mmol), sodium methanethiolate (2.75 g, 39.3 mmol), and diethyl ether (17 cm<sup>3</sup>), shaken (3 h) while the mixture warmed from -196 °C to room temperature, gave (i) a mixture (1.15 g, 10.6 mmol; *M*, 109) of unchanged chlorotrifluoroethylene (1.01 g, 8.7 mmol, 19% recovered) and diethyl ether (0.14 g), (ii) diethyl ether (13.25 g), (iii) 2-chlorodifluorovinyl methyl sulphide (4.11 g, 28.4 mmol, 77%) (Found: C, 25.3; H, 2.3; F, 26.3. Calc.

for  $C_3H_3ClF_2S$ : C, 24.9; H, 2.1; F, 26.3%), b.p. (Siwoloboff) 97—98 °C (lit.,<sup>9</sup> 96 °C); *m/e* 146 and 144 (100%,  $M^+$ ), and (iv) a mixture (2.9 g) of a yellow oil and solid which was not examined further.

The olefinic product was shown by n.m.r. spectroscopy to be a mixture of the *cis*- and *trans*-isomers\* in the ratio 55 : 45 but they could not be separated by g.l.c.

In a second experiment a mixture of the olefin (1.87 g, 16.0 mmol), sodium methanethiolate (2.78 g, 39.7 mmol), and diethyl ether (20 cm<sup>3</sup>), shaken at room temperature (72 h), gave a mixture (0.48 g, 3.3 mmol, 21%) of *cis*- and *trans*-2-chlorodifluorovinyl methyl sulphide and a yellow oil which was extracted with ether (2 × 20 cm<sup>3</sup>) to leave a white residue which gave a positive test for fluoride ion. The ether was removed from the extract to afford a yellow oil (*ca.* 2 g) which was shown by g.l.c. (2 m column at 180 °C) to consist of three components: <sup>1</sup>H n.m.r. 3.99 p.p.m. (SMe) to high field of external benzene, <sup>19</sup>F δ 6.3 and 42.2 p.p.m.; *m/e* 202 and 200 ( $C_5H_9ClS_3^+$ ) and 174 and 172 ( $C_4H_6ClFS_2^+$ ).

(c) *Chlorotrifluoroethylene in tetramethylene sulphone.* A mixture of the olefin (1.63 g, 14.0 mmol), the thiolate (0.83 g, 11.8 mmol), and tetramethylene sulphone (6 cm<sup>3</sup>), sealed in a Pyrex tube (*ca.* 100 cm<sup>3</sup>) and shaken at 50 °C (20 h), gave (i) unchanged chlorotrifluoroethylene (1.17 g, 10.1 mmol, 72% recovered), (ii) 2-chlorodifluorovinyl methyl sulphide (0.08 g, 0.6 mmol, 14%), and (iii) an oil (0.48 g), which was obtained by saturation of the residue with water (*ca.* 50 cm<sup>3</sup>). G.l.c. examination (2 m column at 180 °C) of the oil showed a number of overlapping peaks caused by decomposition of the oil on the column: <sup>1</sup>H n.m.r. band at 4.36 p.p.m. to high field of external benzene; <sup>19</sup>F δ -6.2, 6.4, 8.8, 22.2, and 42.6 p.p.m.; *m/e* 212 ( $C_6H_{12}S_4^+$ ), 202 and 200 ( $C_5H_9ClS_3^+$ ), and 174 and 172 ( $C_4H_6ClFS_2^+$ ).

*Hydrolysis of 1-Chlorotrifluoro-1,2-bis(methylthio)ethane.*—A mixture of the alkane derivative (0.42 g, 2.00 mmol) and water (1.0 g, 55.6 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 10 cm<sup>3</sup>) and heated at 80 °C until the immiscible organic phase disappeared (168 h), gave (i) a mixture (0.16 g, 3.48

mmol; *M*, 47) of methanethiol (0.12 g, 2.61 mmol, 65%) and carbon dioxide (0.04 g, 0.87 mmol); (ii) unchanged water (0.81 g, 45.0 mmol, 81% recovered); and (iii) a white solid which gave positive tests for fluoride and chloride ion.

*Reaction of Hexafluoropropene with Caesium Fluoride and Bis-(2-chloroethyl) Disulphide.*—A mixture of the olefin (3.00 g, 20.0 mmol), caesium fluoride (3.34 g, 22.0 mmol), the disulphide (9.40 g, 49.2 mmol), and tetramethylene sulphone (10 cm<sup>3</sup>), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm<sup>3</sup>) and shaken at room temperature (21 h), gave (i) a mixture (1.14 g, 7.64 mmol; *M*, 149) shown by i.r. spectroscopy and g.l.c. (4 m MS 550 oil at 20 °C) to consist of unchanged hexafluoropropene (1.07 g, 7.13 mmol, 36% recovered), 2*H*-heptafluoropropane (0.06 g, 0.35 mmol, 2%), and carbon dioxide (0.01 g); (ii) a mixture (0.33 g, 1.10 mmol, 17%) of perfluoro-(2-methylpent-2-ene) and perfluoro-(4-methylpent-2-ene); (iii) ethylene sulphide (0.48 g, 8.00 mmol); (iv) 2-chloroethyl tetrafluoro-1-trifluoromethylethyl sulphide\* (1.66 g, 6.28 mmol, 50%) (Found: C, 22.8; H, 1.6; F, 50.1. Calc. for  $C_5H_4ClF_7S$ : C, 22.7; H, 1.5; F, 50.3%), b.p. (Siwoloboff) 126—127 °C; and (v) an involatile yellow oil which was saturated with water (*ca.* 60 cm<sup>3</sup>) and the immiscible organic phase which separated was distilled to give only unchanged bis-(2-chloroethyl) disulphide (7.27 g, 38.1 mmol, 79% recovered), b.p. 88—90 °C at 1.0 mmHg.

*Dehydrochlorination of 2-Chloroethyl Tetrafluoro-1-trifluoromethylethyl Sulphide.*—A mixture of the sulphide (0.38 g, 1.42 mmol) and powdered potassium hydroxide (0.95 g, 17.0 mmol), sealed in a Pyrex tube (*ca.* 15 cm<sup>3</sup>) and heated at 90 °C (16 h), gave, as the only volatile product, tetrafluoro-1-trifluoromethylethyl vinyl sulphide\* (0.17 g, 0.75 mmol, 53%) (Found: C, 26.6; H, 1.1; F, 58.5. Calc. for  $C_5H_3F_7S$ : C, 26.3; H, 1.3; F, 58.3%), b.p. (isoteniscope) 68.8 ± 0.5 °C.

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