

Perfluoroalkyl Derivatives of Sulphur. Part XV.¹ Preparation and Certain Reactions of Methyl Polyfluoroalkyl Sulphoxides and Sulphones and their Conversion into Polyfluoroalkanesulphonic Acids

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Oxidation of various methyl polyfluoroalkyl sulphides and of ethyl trifluoromethyl sulphide gives either the corresponding sulphoxides or the sulphones depending on the oxidising agent or the conditions used. Carbanion formation with both the sulphoxides and the sulphones has been demonstrated by deuterium exchange and by reaction with sodium hypochlorite, and with methyl heptafluoro-*n*-propyl sulphone by reaction with benzaldehyde and with iodine in the presence of base to give heptafluoro-*n*-propyl *trans*-styryl sulphone and tri-iodomethyl heptafluoro-*n*-propyl sulphone, respectively, in high yield. Oxidation of methyl heptafluoro-*n*-propyl sulphone with neutral permanganate or basic hydrolysis of trichloromethyl heptafluoro-*n*-propyl sulphone gives heptafluoro-*n*-propane-1-sulphonic acid as its potassium salt in good yield.

THE preparations of methyl and ethyl polyfluoroalkyl sulphides by photochemical reaction of polyfluoroiodoalkanes, R_FI, with dimethyl sulphide,² dimethyl disulphide,³ and diethyl disulphide⁴ have been reported previously. Methyl polyfluoroalkyl sulphides were formed in high yield (>80%) when dimethyl disulphide was used, but the yields were lower when the mono-sulphide was employed because of the side reaction:



The preparation of the methyl polyfluoroalkyl sulphides was the first stage in an investigation to determine whether polyfluoroalkanesulphonic acids could be synthesised in reasonable yield from the readily available polyfluoroiodoalkanes. The most general method used for the preparation of perfluoroalkanesulphonic acids involves the electrochemical fluorination of alkanesulphonyl chlorides or fluorides,⁵⁻⁷ but this method suffers from the disadvantage that the yields of perfluoroalkanesulphonyl fluorides fall off markedly with increasing alkyl chain length.⁷ Also polyfluoroalkanesulphonic acids cannot be prepared by this method.

In the present work the oxidations of certain methyl polyfluoroalkyl sulphides, R_FSMe {R_F = n-C₃F₇, (CF₃)₂CF, or (CF₃)₂CF·[CF₂]₄}, to the corresponding sulphoxides and sulphones have been studied. The oxidation of ethyl trifluoromethyl sulphide to the corresponding sulphone has also been investigated. The preparation of heptafluoropropanesulphonic acid (as its potassium salt) from methyl heptafluoro-*n*-propyl sulphone by two methods is described and various reactions of the sulphones and sulphoxides are reported.

Oxidation of Alkyl Polyfluoroalkyl Sulphides.—The conditions used and the products obtained from the oxidations of the alkyl polyfluoroalkyl sulphides are shown in Table I.

¹ Part XIV, R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 2438.

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

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

⁴ R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 2180.

⁵ T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 1956, 173.

⁶ J. Burdon, I. Farazmand, M. J. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1957, 2574.

The oxidations with hydrogen peroxide were carried out in glacial acetic acid and, depending on the ratio of peroxide to sulphide, either the corresponding sulphoxide or the sulphone was obtained in high yield.

TABLE I

Oxidation of alkyl polyfluoroalkyl sulphides

Sulphide	Oxidising agent	Conditions	Product	Yield (%)
n-C ₃ F ₇ ·SMe	H ₂ O ₂ , 1 : 1 ratio	100°, 24 h	n-C ₃ F ₇ ·S(O)Me	71
n-C ₃ F ₇ ·SMe	H ₂ O ₂ , 9 : 1 ratio	100°, 216 h	n-C ₃ F ₇ ·SO ₂ Me	86
C ₇ F ₁₅ ·SMe	H ₂ O ₂ , 10 : 1 ratio	Reflux, 20 h	C ₇ F ₁₅ ·SO ₂ Me	83
n-C ₃ F ₇ ·SMe	Fuming HNO ₃	100°, 14 h	n-C ₃ F ₇ ·S(O)Me	70
(CF ₃) ₂ CF·SMe	Fuming HNO ₃	100°, 14 h	(CF ₃) ₂ CF·S(O)Me	72
n-C ₃ F ₇ ·SMe	KMnO ₄ - AcOH	0—20°, 5 h	n-C ₃ F ₇ ·SO ₂ Me	85
(CF ₃) ₂ CF·SMe	KMnO ₄ - AcOH	0—20°, 5 h	(CF ₃) ₂ CF·SO ₂ Me	59
CF ₃ ·SEt	KMnO ₄ - AcOH	0—20°, 5 h	CF ₃ ·SO ₂ Et	78
n-C ₃ F ₇ ·SMe	NaIO ₄ -H ₂ O	100°, 168 h	C ₃ F ₇ ·SO ₂ Me	60
n-C ₃ F ₇ ·SMe	NaIO ₄ - H ₂ O-MeOH	100°, 24 h	C ₃ F ₇ ·S(O)Me	60

The reactions did not give side-products but they suffered from the disadvantage that prolonged heating was required, which necessitated the use of sealed tubes for low-boiling sulphides. It has been reported that oxidation of a polyfluoroalkyl sulphide with hydrogen peroxide in acetic acid can give either the corresponding sulphoxide⁸⁻¹¹ or the sulphone,^{9,10,12-14} depending on the conditions.

The first preparation⁸ of a polyfluoroalkyl sulphoxide

⁷ T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 1957, 2640.

⁸ L. M. Yagupol'skii and A. G. Panteleimonov, *J. Gen. Chem. (U.S.S.R.)*, 1965, **35**, 1123.

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

¹⁰ K. Inukai, T. Ueda, and H. Murmatsu, *Bull. Chem. Soc. Japan*, 1966, **39**, 2191.

¹¹ I. L. Knunyants, I. N. Rozhkov, A. M. Alexandrov, and L. M. Yagupol'skii, *J. Gen. Chem. (U.S.S.R.)*, 1967, **37**, 1210.

¹² R. B. Ward, *J. Org. Chem.*, 1965, **30**, 3009; U.S.P. 3,346,606/1967.

¹³ B.P. 896,373/1962.

¹⁴ C. S. Scanley, U.S.P. 3,333,007/1967.

involved the oxidation of methyl trifluoromethyl sulphide with concentrated nitric acid to give methyl trifluoromethyl sulphoxide (30%). In the present work the use of fuming nitric acid and a longer reaction time has given much higher yields (*ca.* 70%) of sulphoxides, but the method suffers from the same disadvantage as the hydrogen peroxide oxidations.

The oxidations with potassium permanganate were carried out in glacial acetic acid and gave exclusively the sulphone. This reagent gave high yields of sulphones with the sulphides $n\text{-C}_3\text{F}_7\text{SMe}$ and CF_3SEt , but a lower yield with the sulphide $(\text{CF}_3)_2\text{CF}\cdot\text{SMe}$, attributed to handling losses on work-up of the small scale reaction. Potassium permanganate was favoured for the oxidation of low-boiling sulphides since reaction occurred in the range 0–20° and so obviated the use of sealed tubes for the reactions. Similar oxidations of polyfluoroalkyl sulphides with potassium permanganate have been reported.^{11,15,16}

The attempted oxidation of methyl heptafluoro-*n*-propyl sulphide with aqueous sodium periodate in the range 5–20° gave only unchanged reactants. However, a reaction carried out at 100° (7 days) gave unchanged sulphide (80%) and methyl heptafluoropropyl sulphone (60%). This was unexpected since the oxidation of sulphoxides to sulphones is generally more difficult than the oxidation of sulphides to sulphoxides. Although exceptions are known,¹⁷ sodium periodate is regarded as a mild oxidising agent and has been used to oxidise a large number of sulphides to sulphoxides.¹⁸ Certain sulphoxides have been reported¹⁹ to disproportionate into the corresponding sulphides and sulphones on heating. That a similar disproportionation was not occurring in the present case was shown by heating the sulphoxide at 100° (7 days); only unchanged sulphoxide (95%) was recovered.

The presence of the oxygen atom in methyl heptafluoro-*n*-propyl sulphoxide should make it more susceptible to hydrogen bonding than the parent sulphide, and hence more soluble in water. This greater solubility of the sulphoxide in water could account for its faster oxidation than that of the parent sulphide. To test this hypothesis the reaction was repeated in the presence of methanol, a solvent for both aqueous sodium periodate and the sulphoxide, which it was hoped would nullify the effect of the greater solubility of the sulphoxide in water and thus permit its isolation. This reaction gave the sulphoxide (60%) contaminated with only a trace of the sulphone.

Carbanion Reactions of Alkyl Polyfluoroalkyl Sulphoxides and Sulphones.— α -Carbanions derived from polyfluoroalkyl sulphones are stabilised by the combined inductive effect of the sulphonyl group and the polyfluoroalkyl group. This stabilisation will be aided by a

mesomeric effect which probably involves some sharing of the carbon *2p* electrons with the *3d* orbitals of sulphur.²⁰ The same factors also apply to the stabilisation of the sulphoxides, but the stabilisation will be reduced.

The formation of α -carbanions from polyfluoroalkyl sulphoxides and sulphones was demonstrated by the observation that the compounds $n\text{-C}_3\text{F}_7\text{SOME}$ and $n\text{-C}_3\text{F}_7\text{SO}_2\text{Me}$ exchanged their hydrogen atoms for deuterium in the presence of deuterium oxide and sodium deuterioxide. The exchange in both cases was shown qualitatively by i.r. spectroscopy, the intensities of the bands between 3.30 and 3.40 μm (C–H str.) decreased and new bands between 4.35 and 4.70 μm (C–D str.) appeared.

In the case of the sulphone the extent of exchange was measured by n.m.r. and mass spectroscopy. The ratio of hydrogen to fluorine in the non-deuteriated sulphone, as given by the n.m.r. integration curves, was compared with that for an internal standard, 2-bromo-2-chloro-1,1,1-trifluoroethane. This was repeated for the deuteriated mixture. The two results permitted the ratio of hydrogen present in the non-deuteriated sulphone to that present in the deuteriated mixture to be determined as 100 : 12, which represented an 88% replacement of H by D. The extent of replacement was confirmed by mass spectrometry. Neither the non-deuteriated sulphone nor the deuteriated sulphone mixture gave parent ion peaks, so the peaks at *m/e* 79, 80, 81, and 82, assigned to the ions $\text{CH}_3\cdot\text{SO}_2^+$, $\text{CH}_2\text{D}\cdot\text{SO}_2^+$, $\text{CHD}_2\cdot\text{SO}_2^+$, and $\text{CD}_3\cdot\text{SO}_2^+$, respectively, were used in the assessment. The following assumptions were made: (i) The breakdown patterns of the deuteriated and non-deuteriated sulphones were the same; (ii) ions corresponding to $\text{CHD}\cdot\text{SO}_2^+$ (*m/e* 79) and $\text{CD}_2\cdot\text{SO}_2^+$ (*m/e* 80) were not formed [a peak was not observed in the spectrum of the non-deuteriated sulphone at *m/e* 79 ($\text{CH}_2\cdot\text{SO}_2^+$)]; and (iii) the contributions of the ³⁴S, ¹³C, and ¹⁸O isotopes were negligible. On the basis of these assumptions the ratio of the species $\text{CH}_3\cdot\text{SO}_2^+$, $\text{CH}_2\text{D}\cdot\text{SO}_2^+$, $\text{CHD}_2\cdot\text{SO}_2^+$, and $\text{CD}_3\cdot\text{SO}_2^+$ was found to be 1.1 : 4.8 : 38 : 86, which represents an overall exchange of H by D of 87%, in agreement with the n.m.r. result.

In the case of the sulphoxide, n.m.r. spectroscopy indicated a 90% exchange of H by D. The mass spectrum of the deuteriated sulphoxide mixture showed parent-ion peaks at *m/e* 232, 233, 234, and 235, corresponding to the ions $\text{C}_3\text{F}_7\text{SOME}^+$, $\text{C}_3\text{F}_7\text{SO}\cdot\text{CH}_2\text{D}^+$, $\text{C}_3\text{F}_7\text{SO}\cdot\text{CHD}_2^+$, and $\text{C}_3\text{F}_7\text{SO}\cdot\text{CD}_3^+$, respectively, and in the ratio 1.2 : 1.7 : 14 : 37, which represents an 87% replacement of H by D.

Methyl heptafluoropropyl sulphide did not react under comparable conditions or in the presence of ethanol as solvent. This result indicates the importance of the inductive effect of the oxygen atoms on sulphur in stabilising the carbanion.

¹⁵ K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Amer. Chem. Soc.*, 1950, **72**, 3642.

¹⁶ L. M. Yagupol'skii, A. G. Panteleimonov, and V. U. Orda, *J. Gen. Chem. (U.S.S.R.)*, 1964, **34**, 3498.

¹⁷ S. A. Kahn, *Chem. Comm.*, 1968, 1036, and references quoted therein.

¹⁸ N. Leonard and C. R. Johnson, *J. Org. Chem.*, 1961, **27**, 282.

¹⁹ F. Ostermeyer and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1960, **82**, 3752.

²⁰ S. Oae and C. C. Price, 'Sulphur Bonding,' Ronald Press Co., New York, 1962.

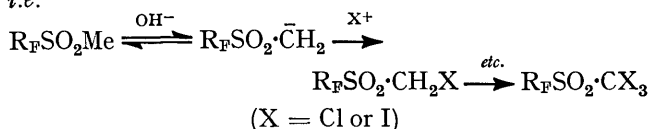
A series of polyfluoroalkyl sulphones which contained α -hydrogen atoms and methyl heptafluoro-n-propyl sulphoxide were shown to react with sodium hypochlorite to give chlorinated products. Similarly methyl heptafluoro-n-propyl sulphone reacted with iodine in the presence of base. The results of these halogenations are shown in Table 2. The reactions proceeded smoothly

TABLE 2
Halogenations of alkyl polyfluoroalkyl sulphones and sulphoxides

Reactants	Product	Yield (%)
$n\text{-C}_3\text{F}_7\cdot\text{SO}_2\text{Me}-\text{NaOCl}$	$n\text{-C}_3\text{F}_7\cdot\text{SO}_2\cdot\text{CCl}_3$	98
$n\text{-C}_3\text{F}_7\cdot\text{SO}_2\text{Me}-\text{NaOI}$	$n\text{-C}_3\text{F}_7\cdot\text{SO}_2\cdot\text{Cl}_3$	84
$(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{Me}-\text{NaOCl}$	$(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\cdot\text{CCl}_3$	75
$(\text{CF}_3)_2\text{CF}\cdot[\text{CF}_2]_4\cdot\text{SO}_2\text{Me}-\text{NaOCl}$	$(\text{CF}_3)_2\text{CF}\cdot[\text{CF}_2]_4\cdot\text{SO}_2\cdot\text{CCl}_3$	81
$\text{CF}_3\cdot\text{SO}_2\text{Et}-\text{NaOCl}$	$\text{CF}_3\cdot\text{SO}_2\cdot\text{CCl}_2\text{Me}$	90
$n\text{-C}_3\text{F}_7\cdot\text{S(O)Me}-\text{NaOCl}$	$n\text{-C}_3\text{F}_7\cdot\text{SO}_2\cdot\text{CCl}_3$	82

at room temperature, high yields of products were obtained, and solvents were unnecessary although aqueous methanol was used in the iodination reaction.

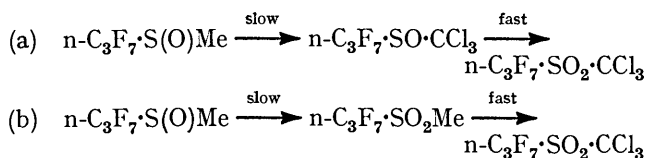
The mechanism of the reaction with the sulphones is believed to be similar to that of the haloform reaction, *i.e.*



The reaction of the sulphone $n\text{-C}_3\text{F}_7\cdot\text{SO}_2\text{Me}$ with sodium hypochlorite was terminated before reaction was complete and the organic layer was shown to consist only of the trichloromethyl sulphone and unchanged methyl sulphone. The absence of the monochloro- and dichloro-methyl sulphones is consistent with the foregoing mechanism, since the substitution of a chlorine atom for a hydrogen atom will further activate the remaining hydrogens towards base. The reactivities of the sulphones will thus lie in the order $\text{CHCl}_2\cdot\text{SO}_2\text{R}_F > \text{CH}_2\text{Cl}\cdot\text{SO}_2\text{R}_F > \text{CH}_3\cdot\text{SO}_2\text{R}_F$.

The α -hydrogen atoms of unsubstituted dialkyl sulphones are not sufficiently acidic to react under the conditions used in the present experiments, but the hydrogen atoms in chloromethyl trichloromethyl sulphone have been reported to react.²¹

The reaction of the sulphoxide $n\text{-C}_3\text{F}_7\cdot\text{S(O)Me}$ with sodium hypochlorite gave only the corresponding trichloromethyl sulphone. This indicates that oxidation and chlorination occurred either by a synchronous process or by a two-stage reaction in which the second step was the faster, *i.e.* (a) or (b). Of the two possibilities



²¹ R. J. Herschler and W. L. Schilling, *Fr.P.* 1,406,124/1965 (*Chem. Abs.*, 1965, **63**, 11,363).

²² A. E. Wood and E. G. Travis, *J. Amer. Chem. Soc.*, 1928, **50**, 1226.

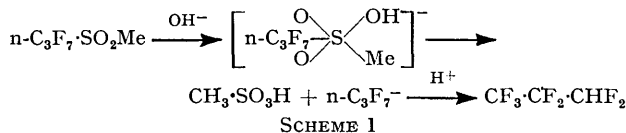
(a) and (b) the latter is considered more likely because (i) the $-I$ effect of the chlorine atoms will make the oxidation of the sulphoxide $n\text{-C}_3\text{F}_7\cdot\text{SO}\cdot\text{CCl}_3$ more difficult than the oxidation of the sulphoxide $n\text{-C}_3\text{F}_7\cdot\text{S(O)Me}$ and (ii) a carbanion in which the charge is α to a sulphonyl group is more readily formed than one in which the charge is α to a sulphinyl group.

Although no direct evidence is available in support of the foregoing postulate, it is perhaps significant that alkyl sulphides have been oxidised to the corresponding sulphones (presumably *via* the sulphoxide), without chlorination, by sodium hypochlorite at room temperature.²²

An attempt to prepare tri-iodomethyl heptafluoro-n-propyl sulphoxide or sulphone by the reaction of the corresponding methyl sulphoxide with sodium hypoiodite in the presence of base gave only unchanged reactant sulphoxide.

It has been reported²³ that methyl trifluoromethyl sulphone condenses with aromatic aldehydes, in the presence of base, to give compounds of the type $\text{CF}_3\cdot\text{SO}_2\cdot\text{CH}\cdot\text{CHAr}$. We have now shown that methyl heptafluoro-n-propyl sulphone undergoes a similar condensation with benzaldehyde to give heptafluoro-n-propyl *trans*-styryl sulphone (85%). The *trans*-configuration was assigned on the basis of the large coupling constant (15.5 Hz) observed between the olefinic protons.

Other Reactions.—In contrast to alkyl sulphones, which are resistant to nucleophilic attack on the sulphur atom,²⁴ methyl heptafluoro-n-propyl sulphone is readily cleaved by dilute aqueous sodium hydroxide at 100°. The ease of this reaction may be attributed to withdrawal of electron density from the sulphur atom by the perfluoroalkyl group. The reaction may be represented as shown in Scheme 1. Similarly methyl heptafluoro-n-



propyl sulphoxide reacted with dilute aqueous sodium hydroxide at 100° to give 1*H*-heptafluoropropane (92%). The alkaline hydrolysis of methyl trifluoromethyl sulphoxide has been reported⁸ to give trifluoromethane and sodium ethanesulphinate by an analogous reaction.

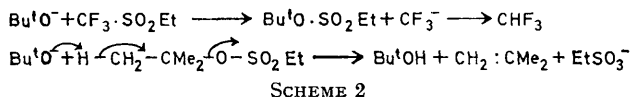
Diethyl sulphone has been reported²⁵ to react with potassium hydroxide by a β -elimination mechanism to give ethylene and potassium ethanesulphinate. However, ethyl trifluoromethyl sulphone when treated with sodium hydroxide afforded trifluoromethane (92%) and sodium ethanesulphonate *via* attack on the sulphur atom by hydroxide ion. In an attempt to prevent attack on the sulphur atom the reaction was repeated with *t*-butoxide ion as the base and *t*-butyl alcohol as the solvent. The volatile products formed were trifluoromethane

²³ L. M. Yagupol'skii and A. G. Panteleimonov, *J. Gen. Chem. (U.S.S.R.)*, 1966, **36**, 433; *Russ. P.* 167,867/1965.

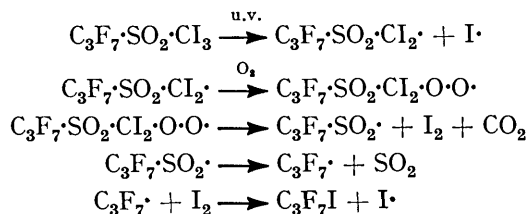
²⁴ L. A. Paquette, *J. Amer. Chem. Soc.*, 1964, **86**, 4085.

²⁵ G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 1928, 3127.

(85%) and isobutene. The presence of trifluoromethane suggests that, despite steric inhibition, attack has again taken place on the sulphur atom. A mechanism which explains the observed products is that of Scheme 2.



Attempts to convert trichloromethyl heptafluoro-*n*-propyl sulphone into the corresponding trifluoromethyl



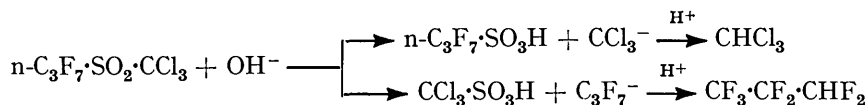
compound by reaction with antimony trifluoride were unsuccessful. At temperatures below 100° the sulphone was largely (*ca.* 90%) recovered unchanged. When the

The subsequent failure of the trichloromethyl sulphone to react with aqueous potassium hydroxide is ascribed to the low solubility of the sulphone in water. When the reaction was repeated in aqueous dioxan as solvent potassium heptafluoropropanesulphonate (72%), 1*H*-heptafluoropropane (13%), carbon monoxide, and chloroform were formed. The carbon monoxide was presumably formed by hydrolysis of the chloroform.

The products indicate that the trichloromethyl anion is displaced in preference to the heptafluoropropyl anion.

Attempts to oxidise methyl heptafluoro-*n*-propyl sulphone to heptafluoropropanesulphonic acid with fuming nitric acid were unsuccessful. At 100° (24 h) no significant reaction occurred; after prolonged reflux (9 days) carbon dioxide was evolved, the reaction vessel was badly etched, and no unchanged sulphone was recovered. Attempts to oxidise bis(trifluoromethyl) disulphide to trifluoromethanesulphonic acid with concentrated nitric acid have been reported to result in decomposition.²⁶

Thus a useful new route for the conversion of poly-



reactants were heated at 140° (7 days) breakdown of the sulphone occurred to give sulphur dioxide, 1-chloroheptafluoropropane, pentafluoropropionyl chloride, silicon tetrafluoride, and unidentified material.

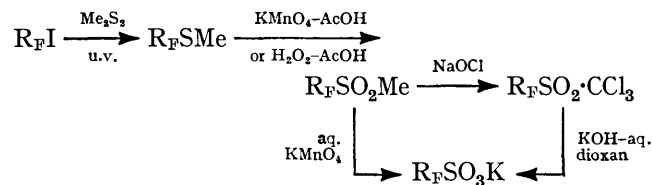
During the isolation of tri-iodomethyl heptafluoro-*n*-propyl sulphone it was observed that the compound decomposed rapidly on exposure to light and air, whereas it was stable in the dark. The major products from the decomposition of the sulphone in sunlight in the presence of oxygen were heptafluoro-1-iodopropane, sulphur dioxide, carbon dioxide, and iodine. In addition small quantities of carbonyl fluoride and silicon tetrafluoride were detected. These are probably formed by the reaction of perfluoroalkyl radicals with oxygen and the glass walls of the vessel.

Preparation of Potassium Heptafluoropropane-1-sulphonate.—This compound was prepared by two methods: (a) the oxidation of methyl heptafluoro-*n*-propyl sulphone and (b) the basic hydrolysis of trichloromethyl heptafluoro-*n*-propyl sulphone.

The oxidation of the sulphone with potassium permanganate in water at reflux temperature gave the sulphonate in 85% yield. This method has been reported previously¹² for the oxidation of a mixture of $\alpha\omega$ -bis(methylsulphonyl)polyfluoroalkanes to the corresponding $\alpha\omega$ -disulphonates.

Substitution of a trichloromethyl group for the methyl group in the sulphone $\text{n-C}_3\text{F}_7 \cdot \text{SO}_2\text{Me}$ should render the sulphur atom more susceptible to nucleophilic attack.

fluoroiodoalkanes into the corresponding polyfluoroalkanesulphonic acids has now been developed.



EXPERIMENTAL

Volatile materials were handled in a conventional high-vacuum apparatus to avoid contact with air or moisture. Pure products were separated by repeated fractional condensation, by distillation, by methods described in the text, or by g.l.c. [Perkin-Elmer 451 or 452 instrument; columns packed with Silicone M.S.550 oil (30%) on Celite] and were examined by i.r. (Perkin-Elmer 257 instrument with sodium chloride optics) and n.m.r. spectroscopy (Perkin-Elmer R10 machine operating at 60.00 MHz for ¹H and 56.46 MHz for ¹⁹F; internal tetramethylsilane and external trifluoroacetic acid as the respective references), and mass spectrometry (A.E.I. MS/2H or MS/9 instrument).

The alkyl polyfluoroalkyl sulphides were prepared as reported previously.^{3,4}

Oxidation of Alkyl Polyfluoroalkyl Sulphides.—(A) *With potassium permanganate.* (a) *Heptafluoro-*n*-propyl methyl sulphide.* The sulphide (3.82 g, 17.7 mmol) was dissolved in glacial acetic acid (60 ml) contained in a flask fitted with a stirrer and a total reflux head maintained at -78°. The flask was cooled (0°), stirring was commenced, and potassium permanganate (4.18 g, 25.8 mmol), dissolved in the minimum quantity of hot water, was slowly added (1 h). Stirring was continued for 4 h, during which time the flask attained room

²⁶ R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 1954, 4228.

temperature. An aqueous solution of sodium disulphite was then added, to destroy the manganese dioxide formed. The product, which separated as the lower liquid, was removed, washed with aqueous sodium hydrogen carbonate, and dried over molecular sieve (type 4A). The flask residue was partially neutralised with aqueous sodium hydrogen carbonate and extracted with ether (3×100 ml). The extract was neutralised (aq. NaHCO_3), dried (MgSO_4), and distilled. The residue was combined with that separated previously and the combined material was distilled from a micro-distillation unit (5 ml) to give *heptafluoro-n-propyl methyl sulphone* (3.73 g, 15.0 mmol, 85%) (Found: C, 19.5; H, 1.2. $\text{C}_4\text{H}_3\text{F}_7\text{O}_2\text{S}$ requires C, 19.4; H, 1.2%), b.p. 154° ; ^1H n.m.r. for $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-SO}_2\text{Me}$ τ 6.81 (s), ^{19}F n.m.r. δ 5.0 (3F, t, $J_{1,3}$ 9.4 Hz, CF_3), 38.1 (2F, complex, $\text{CF}_2\text{-S}$), and 47.8 (2F, t, $J_{2,3}$ 2.8 Hz, $\text{CF}_2\text{-CF}_3$) p.p.m.

(b) *Heptafluoroisopropyl methyl sulphide*. The sulphide (1.83 g, 8.5 mmol) and potassium permanganate (1.83 g, 11.5 mmol), treated under the conditions described in (a), gave *heptafluoroisopropyl methyl sulphone* (1.24 g, 5.0 mmol, 59%) (Found: C, 19.6; H, 1.3; F, 53.2. $\text{C}_4\text{H}_3\text{F}_7\text{O}_2\text{S}$ requires C, 19.4; H, 1.2; F, 53.6%), b.p. (Siwoloboff) 152° ; ^1H n.m.r. for $(\text{CF}_3)_2\text{CF}\text{-SO}_2\text{Me}$ τ 6.69 (dsept, $J_{3,2}$ 3.6, $J_{3,1}$ 0.7 Hz, Me), ^{19}F n.m.r. δ -5.9 (6F, d, $J_{1,2}$ 7.2 Hz, $2 \times \text{CF}_3$), and 95.8 (1F, septq, $\geq\text{CF}$) p.p.m.

(c) *Ethyl trifluoromethyl sulphide*. The sulphide (4.20 g, 32.3 mmol) and potassium permanganate (8.00 g, 50.3 mmol), treated under the conditions described in (a), gave *ethyl trifluoromethyl sulphone* (4.06 g, 25.2 mmol, 78%) (Found: C, 22.2; H, 3.1; S, 19.7. $\text{C}_5\text{H}_5\text{F}_3\text{O}_2\text{S}$ requires C, 22.2; H, 3.1; S, 19.6%), b.p. 142° ; ^1H n.m.r. for $\text{CF}_3\text{-SO}_2\text{-CH}_2\text{Me}$ τ 8.55 (3H, t, J 7.2 Hz, Me) and 6.65 (2H, q, CH_2), ^{19}F n.m.r. δ 1.5 (s) p.p.m.

(B) *With fuming nitric acid*. (a) *Heptafluoro-n-propyl methyl sulphide*. The sulphide (3.04 g, 14.2 mmol) and fuming nitric acid (d 1.51; 12 ml) were sealed in a Pyrex tube (250 ml) and heated at 100° (14 h). The tube was then cooled (-78°) and the contents neutralised carefully with aqueous sodium hydrogen carbonate, which caused the product to separate as the lower layer. Isolation and purification were carried out as in experiment (A) (a), and gave *heptafluoro-n-propyl methyl sulphoxide* (2.30 g, 9.9 mmol, 70%) (Found: C, 20.8; H, 1.6. $\text{C}_4\text{H}_3\text{F}_7\text{OS}$ requires C, 20.8; H, 1.3%), b.p. $141\text{--}142^\circ$; ^1H n.m.r. for $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-SOMe}$ at τ 7.13 (ddt, $J_{5,3}$ 2.6, $J_{5,4}$ 1.3, $J_{5,2}$ 0.7 Hz, Me), ^{19}F n.m.r. δ 4.9 (3F, s, CF_3), 41.3 (1F, ABq, $J_{3,4}$ 270 Hz, CF), 49.1 (2F, s, CF_2), and 49.5 (1F, ABq, CF) p.p.m.

(b) *Heptafluoroisopropyl methyl sulphide*. The sulphide (5.24 g, 24.2 mmol) and fuming nitric acid (d 1.51; 20 ml) treated as in (B) (a), gave *heptafluoroisopropyl methyl sulphoxide* (4.08 g, 17.6 mmol, 72%) (Found: C, 20.6; H, 1.3%), b.p. 141° ; ^1H n.m.r. for $\text{CF}_3\text{-CF}(\text{CF}_3)\text{-S(O)Me}$ at τ 7.05 (dsept, $J_{4,3}$ 3.1, $J_{4,1} \approx J_{4,2}$ 0.7 Hz), ^{19}F n.m.r. δ -6.2 (3F, quinq, $J_{1,2} \approx J_{1,3}$ 8.3 Hz, CF_3), -4.6 (3F, quinq, CF_3), and 106.2 (1F, qq, $\geq\text{CF}$) p.p.m.

(C) *With hydrogen peroxide*. (a) *Heptafluoro-n-propyl methyl sulphide*. *Experiment 1*. The sulphide (6.00 g, 27.8 mmol), hydrogen peroxide (100 vol.; 3.6 ml, 28.1 mmol), and glacial acetic acid (10 ml) were sealed in a Pyrex tube (300 ml) and heated at 100° (24 h). The resultant material was neutralised with aqueous sodium hydrogen carbonate and extracted with ether (3×20 ml). The

extract was dried (MgSO_4) and distilled, and the residue was distilled from a micro-distillation unit (10 ml) to afford *heptafluoro-n-propyl methyl sulphoxide* (4.60 g, 19.8 mmol, 71%).

Experiment 2. The sulphide (2.92 g, 13.5 mmol), hydrogen peroxide (100 vol.; 15 ml, 117 mmol), and glacial acetic acid (20 ml) were sealed in a Pyrex tube (300 ml) and heated at 100° (9 days), and the product was worked up as in the preceding experiment to give *heptafluoro-n-propyl methyl sulphone* (2.89 g, 11.7 mmol, 86%).

(b) *Dodecafluoro-5-trifluoromethylhexyl methyl sulphide*. The sulphide (2.04 g, 4.90 mmol), hydrogen peroxide (100 vol.; 10 ml), and glacial acetic acid (10 ml) were heated under reflux until evolution of oxygen ceased. More hydrogen peroxide (2×10 ml) was added and the reflux was continued (total 16 h). The resultant solution was cooled, neutralised with aqueous sodium hydrogen carbonate, and then extracted with ether (2×20 ml). The extract was dried (MgSO_4) and distilled to afford a white solid, which on sublimation *in vacuo* (60°), gave *dodecafluoro-5-trifluoromethylhexyl methyl sulphone* (1.82 g, 4.06 mmol, 83%) (Found: C, 21.2; H, 0.7; F, 63.6; S, 7.4. $\text{C}_8\text{H}_3\text{F}_{15}\text{O}_2\text{S}$ requires C, 21.4; H, 0.7; F, 63.6; S, 7.2%), m.p. 48° ;

^1H n.m.r. for $(\text{CF}_3)_2\text{CF}\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-SO}_2\text{Me}$ τ 6.75 (s), ^{19}F n.m.r. δ -6.6 (6F, ttd, $J_{1,3}$ 14.5, $J_{1,4}$ 8.9, $J_{1,2}$ 6.1 Hz, $2 \times \text{CF}_3$), ca. 37 (4F, complex, $2 \times \text{CF}_2$), ca. 43 (4F, complex, $2 \times \text{CF}_2$), and 110.4 (1F, complex, $\geq\text{CF}$) p.p.m.

(D) *With sodium periodate*. *Heptafluoro-n-propyl methyl sulphide*. *Experiment 1*. The sulphide (2.16 g, 10.0 mmol) and aqueous sodium periodate (0.5M; 20.0 ml, 10.0 mmol), sealed in a Pyrex tube (300 ml) and heated at 100° (7 days), gave unchanged sulphide (1.74 g, 8.0 mmol, 80% recovered) and a higher-boiling fraction which consisted of two layers. The upper, aqueous layer was discarded and the lower layer was dried over molecular sieve (type 4A) to give *heptafluoro-n-propyl methyl sulphone* (0.30 g, 1.2 mmol, 60%).

A reaction carried out at room temperature gave unchanged sulphide (87%).

Experiment 2. The sulphide (2.41 g, 11.2 mmol), aqueous sodium periodate (0.5M; 20.0 ml, 10.0 mmol), and methanol (15 ml) were sealed in a Pyrex tube (300 ml) and heated at 100° (24 h); the products, worked up as in the preceding experiment, gave unchanged sulphide (1.83 g, 8.5 mmol, 76% recovered) and *heptafluoro-n-propyl methyl sulphoxide* (0.38 g, 1.6 mmol, 60%), shown by i.r. spectroscopy to be contaminated with a trace of the corresponding sulphone.

Reactions of Alkyl Polyfluoroalkyl Sulphones.—(A) *With sodium hydroxide*. (a) *Heptafluoro-n-propyl methyl sulphone*. The sulphone (0.960 g, 3.87 mmol) and aqueous sodium hydroxide (2M; 2.0 ml, 4.0 mmol), sealed in a Pyrex tube (60 ml) and heated at 100° (44 h), gave unchanged sulphone (0.211 g, 0.85 mmol, 22% recovered) and *1H-heptafluoropropane* (0.491 g, 2.88 mmol, 96%) (Found: M , 170. Calc. for C_3HF_7 : M , 170).

(b) *Ethyl trifluoromethyl sulphone*. The sulphone (0.851 g, 5.25 mmol) and aqueous sodium hydroxide (5M; 5.0 ml, 25.0 mmol), sealed in a Pyrex tube (80 ml) and heated at 100° (36 h), gave trifluoromethane (0.337 g, 4.85 mmol, 92%) (Found: M , 70. Calc. for CHF_3 : M , 70) and an aqueous residue which when neutralised with hydrochloric acid and then evaporated to dryness was shown by i.r. spectroscopy to contain sodium ethanesulphonate.

(B) *With sodium hypochlorite*. (a) *Heptafluoro-n-propyl*

methyl sulphone. A mixture of the sulphone (3.04 g, 12.2 mmol) and aqueous sodium hypochlorite (ca. 80 ml; 14% w/v available chlorine) was stirred vigorously at room temperature (72 h). The resultant lower layer was separated, washed with water (2 × 5 ml), dried over molecular sieve (type 4A), and identified as *heptafluoro-n-propyl trichloromethyl sulphone* (4.20 g, 12.0 mmol, 98%) (Found: C, 13.6; Cl, 30.1. $C_4Cl_3F_7O_2S$ requires C, 13.6; Cl, 30.2%), b.p. 172°; ^{19}F n.m.r. for $CF_3^1\cdot CF_2^2\cdot CF_2^3\cdot SO_2\cdot CCl_3$ δ 2.9 (3F, t, $J_{1,3}$ 9.2 Hz, CF_3), 20.5 (2F, qt, $J_{3,2}$ 2.4 Hz, CF_2^2S), and 46.6 (2F, t, $CF_2^2\cdot CF_3$) p.p.m.

In a separate experiment the reaction was stopped after 12 h and the organic layer was shown by g.l.c. (2 m column at 120°) to consist of two components only; the trichloromethyl sulphone and unchanged methyl sulphone.

(b) *Ethyl trifluoromethyl sulphone*. The sulphone (2.43 g, 15.0 mmol) and aqueous sodium hypochlorite (ca. 80 ml) were stirred vigorously at room temperature (36 h); the product, worked up as in experiment (a), gave 1,1-dichloroethyl trifluoromethyl sulphone (3.14 g, 13.6 mmol, 90%) (Found: C, 15.9; H, 1.3; Cl, 30.5; S, 14.0. $C_3H_3F_3Cl_2O_2S$ requires C, 15.6; H, 1.3; Cl, 30.7; S, 13.8%), b.p. (Siwoloboff) 146°.

(c) *Heptafluoroisopropyl methyl sulphone*. A mixture of the sulphone (1.92 g, 7.74 mmol) and aqueous sodium hypochlorite (50 ml) was treated for 36 h and worked up as in experiment (a), to give *heptafluoroisopropyl trichloromethyl sulphone* (2.06 g, 5.85 mmol, 75%) (Found: C, 14.1; Cl, 29.9; F, 37.5. $C_4Cl_3F_7O_2S$ requires C, 13.6; Cl, 30.2; F, 37.9%), b.p. (Siwoloboff) 173°; ^{19}F n.m.r. for $(CF_3)_2CF\cdot SO_2\cdot CCl_3$ δ -7.1 (6F, d, J 9.3 Hz, 2 × CF_3) and 85.0 (1F, sept, $\geq CF$) p.p.m.

(d) *Dodecafluoro-5-trifluoromethylhexyl methyl sulphone*. A mixture of the sulphone (0.981 g, 2.19 mmol) and aqueous sodium hypochlorite (50 ml) was stirred for 36 h and the resultant mixture was extracted with ether (3 × 20 ml). The extracts were washed with water (2 × 10 ml), dried over molecular sieve (type 4A), and distilled to leave a white solid which was sublimed *in vacuo* (30°) to give *dodecafluoro-5-trifluoromethylhexyl trichloromethyl sulphone* (0.976 g, 1.77 mmol, 81%) (Found: C, 17.4; Cl, 19.3. $C_8Cl_3F_{15}O_2S$ requires C, 17.7; Cl, 19.4%), m.p. 31–32°; ^{19}F n.m.r. for $(CF_3)_2CF\cdot CF_2^d\cdot CF_2^e\cdot CF_2^f\cdot SO_2\cdot CCl_3$ δ -6.3 (6F, ttd, $J_{a,c}$ ca. 14.5, $J_{a,d}$ ca. 9, $J_{a,b}$ ca. 6 Hz, 2 × CF_3), 19.5 [2F, complex, $CF_2(f)$], 37.5 [2F, complex, $CF_2(c)$], 41.8 [2F, complex, $CF_2(e)$], 43.0 [2F, complex, $CF_2(d)$], and 110.2 (1F, complex, $\geq CF$) p.p.m.

(C) *Reaction of Ethyl Trifluoromethyl Sulphone with Sodium t-Butoxide*.—The sulphone (0.802 g, 4.94 mmol) and a solution of sodium t-butoxide (0.79 g, 8.2 mmol) in t-butyl alcohol (15 ml), sealed in a Pyrex tube (80 ml) and heated at 100° (36 h), gave, as volatile products, trifluoromethane (0.295 g, 4.22 mmol, 85%) and isobutene (0.190 g, 3.40 mmol) (Found: M , 58. Calc. for C_4H_8 : M , 56).

(D) *Reactions of Heptafluoro-n-propyl Methyl Sulphone*.—(a) *With benzaldehyde*. A mixture of the sulphone (1.25 g, 5.01 mmol), benzaldehyde (0.53 g, 5.00 mmol), and ethanol (0.5 ml) was treated with aqueous sodium hydroxide (5M; ca. 1 ml, 5 mmol). The resultant material was stirred (10 min) and then diluted with water (ca. 10 ml) and the stirring was continued (1 h). The precipitate was washed with water and recrystallised from ethanol, and dried (P_2O_5 ; 48 h) *in vacuo* to afford white crystals of *heptafluoro-n-propyl trans-styryl sulphone* (1.47 g, 4.25 mmol,

85%) (Found: C, 39.0; H, 2.2; F, 39.6. $C_{11}H_7F_7O_2S$ requires C, 39.3; H, 2.1; F, 39.7%), m.p. 37–39°; 1H n.m.r. for $CF_3\cdot CF_2\cdot CF_2\cdot SO_2\cdot CH\cdot CHPh$ τ ca. 2.46 (5H, complex, Ph), ca. 2.10 (1H, AB, $J_{H,H}$ 15.5 Hz, $CHSO_2$), and ca. 3.10 (1H, AB, $CHPh$), ^{19}F n.m.r. δ 2.7 (3F, t, J 9.6 Hz, CF_3), 36.1 (2F, q, CF_2), and 46.6br (2F, s, CF_2) p.p.m.

(b) *With potassium permanganate*. The sulphone (2.32 g, 9.35 mmol), potassium permanganate (4.08 g, 27.0 mmol), and water (5 ml), were refluxed (24 h). Excess of permanganate was destroyed with hydrogen peroxide (100 vol.) and the resultant suspension was filtered through glass wool. The filtrate was neutralised with hydrochloric acid and evaporated to dryness. The solid residue was extracted with ethanol; the extract was filtered, and evaporated to leave a solid which was dried (H_3PO_4) to give *potassium heptafluoropropanesulphonate* (2.29 g, 7.93 mmol, 85%) (Found: C, 12.3; S, 11.0. $C_3F_7KO_3S$ requires C, 12.5; S, 11.1%), m.p. 278°; ^{19}F n.m.r. for $CF_3\cdot CF_2\cdot CF_2\cdot SO_3K$ (20% in H_2O) δ 2.4 (3F, t, $J_{1,3}$ 9.0 Hz, CF_3), 37.5 (2F, qt, $J_{3,2}$ 1.0 Hz, CF_2^2S), and 47.6 (2F, t, $CF_2^2\cdot CF_3$) p.p.m.

(c) *With iodine in the presence of base*. A solution of iodine (3.56 g, 14.0 mmol) and potassium iodide (ca. 5 g) in water (20 ml) was added dropwise to a stirred solution of the sulphone (0.904 g, 3.64 mmol) in methanol (2 ml), followed, dropwise, by aqueous sodium hydroxide (2M; ca. 10 ml). The yellow precipitate was filtered off under nitrogen, washed with water until free from iodide ion, and dried *in vacuo* (P_2O_5) to give *heptafluoro-n-propyl tri-iodomethyl sulphone* (1.92 g, 3.06 mmol, 84%) (Found: C, 8.0; I, 60.9. $C_4F_7I_3O_2S$ requires C, 7.7; I, 61.0%), m.p. 100–110° (decomp.); ^{19}F n.m.r. for $CF_3\cdot CF_2\cdot CF_2\cdot SO_2\cdot CI_3$ δ 4.2 (3F, t, $J_{1,3}$ 9.5 Hz, CF_3), 15.4 (2F, qt, $J_{3,2}$ 1.8 Hz, CF_2^2S), and 48.8 (2F, t, $CF_2^2\cdot CF_3$) p.p.m.

The tri-iodomethyl sulphone was unstable in solution in hexane or ethanol.

(d) *With fuming nitric acid*. The sulphone (2.44 g, 9.8 mmol) and fuming nitric acid (d 1.51; 12 ml), sealed in a Pyrex tube (300 ml) and heated at 100° (14 h), gave, as the only identified material, unchanged sulphone (2.18 g, 8.8 mmol, 90% recovered). In a second experiment carried out at 150° (72 h) the sulphone (74%) was recovered unchanged. In a third experiment the sulphone (2.53 g, 10.2 mmol) and fuming nitric acid (d 1.51; 20 ml) were refluxed for 9 days, during which time a gas was evolved which gave a precipitate with aqueous barium hydroxide. All the sulphone reacted; no solid or liquid products were isolated but the flask was severely etched.

Photolytic Decomposition of Heptafluoropropyl Tri-iodomethyl Sulphone.—A Pyrex flask containing the sulphone (ca. 0.5 g) and oxygen (0.5 atm) was placed in direct sunlight (2 h). The sulphone darkened rapidly and iodine was deposited on the sides of the flask. An examination of the volatile products by i.r. spectroscopy showed the presence of heptafluoro-1-iodopropane, sulphur dioxide, carbonyl fluoride, and silicon tetrafluoride.

In a control experiment a sample of the sulphone kept in the dark *in vacuo* (24 h) showed no decomposition.

Reactions of Heptafluoropropyl Trichloromethyl Sulphone.—(a) *With potassium hydroxide*. The sulphone (1.97 g, 5.60 mmol), aqueous potassium hydroxide (2M; 8.0 ml, 16.0 mmol), and dioxan (10 ml), sealed in a Pyrex tube (80 ml) and heated at 100° (7 days), gave (i) carbon monoxide (0.063 g, 2.3 mmol) (Found: M , 28. Calc. for CO: M , 28), (ii) 1H-heptafluoropropane (0.119 g, 0.70 mmol,

13%) (Found: M , 170. Calc. for C_3HF_7 : M , 170), (iii) chloroform (0.06 g, 0.51 mmol, 9%), (iv) a higher-boiling liquid fraction which contained water and dioxan, and (v) a solid residue.

The solid residue was extracted with water, the extract was neutralised with hydrochloric acid, and the solution was evaporated to dryness. The solid obtained was extracted with acetone to leave a residue which gave a negative result when tested for fluoride ion. The acetone extract was evaporated to dryness to yield an off-white solid (1.25 g), which when redissolved in acetone and then precipitated with chloroform gave potassium heptafluoropropane-1-sulphonate (1.16 g, 4.02 mmol, 72%).

In a separate experiment the sulphone and aqueous potassium hydroxide (2M) were heated at 100° (14 days) in the absence of a solvent; the sulphone (92%) was recovered unchanged.

(b) *With antimony trifluoride.* The sulphone (2.18 g, 6.21 mmol), antimony trifluoride (4.46 g, 24.9 mmol), and antimony pentachloride (ca. 0.2 g), sealed in a Pyrex tube (80 ml) and heated at 140° (7 days), gave as volatile products a mixture (as shown by i.r. spectroscopy) of silicon tetrafluoride, sulphur dioxide, 1-chloroheptafluoropropane,²⁷ and pentafluoropropionyl chloride,²⁸ and unidentified material.

In a second experiment carried out at 100° (48 h) the sulphone (94%) was recovered unchanged.

Reactions of Heptafluoro-n-propyl Methyl Sulphoxide.—(a) *With sodium hydroxide.* The sulphoxide (1.73 g, 7.45 mmol) and aqueous sodium hydroxide (2M; 3.8 ml, 7.6 mmol), sealed in a Pyrex tube (80 ml) and heated at 100° (44 h), gave 1H-heptafluoropropane (1.16 g, 6.85 mmol, 92%).

(b) *With sodium hypochlorite.* The sulphoxide (2.10 g, 9.05 mmol) and aqueous sodium hypochlorite (75 ml; 14% w/v available chlorine) were vigorously stirred at room temperature (6 days). The lower liquid layer was separated, dried over molecular sieve (type 4A), and examined by i.r. spectroscopy and g.l.c. (8 m column at 160°), which showed the presence of unchanged sulphoxide (0.45 g, 1.94 mmol, 21% recovered) and heptafluoro-n-propyl trichloromethyl sulphone (2.04 g, 5.80 mmol, 82%).

(c) *With iodine and base.* The sulphoxide (0.93 g, 4.00 mmol) was treated with an aqueous solution of iodine and potassium iodide. The mixture was warmed to 50° and aqueous sodium hydroxide (2M) was added until the yellow colour disappeared. The lower liquid layer was separated and was identified as unchanged sulphoxide (0.86 g, 3.81 mmol, 92% recovered).

(d) *Thermal stability at 100°.* A sample of the sulphoxide, heated *in vacuo* in a sealed tube at 100° (7 days), gave only unchanged sulphoxide (95%).

Reactions with Deuterium Oxide.—(a) *Heptafluoro-n-propyl methyl sulphide.* The sulphide (2.00 g, 9.3 mmol), deuterium oxide (3.00 g, 0.150 mol), and a catalytic quantity of sodium deuterioxide (ca. 0.001 g) were sealed in a Pyrex ampoule (30 ml); the tube was shaken at room temperature for 36 h to give unchanged sulphide (1.95 g, 9.1 mmol, 95%), identified by i.r. spectroscopy and mass spectroscopy, and unchanged deuterium oxide. In a second experiment carried out in the presence of ethanol the sulphide (98%) was recovered unchanged.

(b) *Methyl heptafluoro-n-propyl sulphone.* The sulphone

(2.01 g, 8.1 mmol), deuterium oxide (3.00 g, 0.150 mol), and a catalytic quantity of sodium deuterioxide (ca. 0.001 g) were stirred vigorously at room temperature (72 h). The lower layer was separated, dried over molecular sieve (type 4A), and shown to be a mixture of deuteriomethyl heptafluoropropyl sulphones (1.69 g, ca. 6.6 mmol, 82%); m/e 169 (28%, $C_3F_7^+$), 82 (86, $CD_3O_2S^+$), 81 (38, $CHD_2O_2S^+$), 80 (4.8, $CH_2DO_2S^+$), 79 (1.1, $CH_3O_2S^+$), and 69 (100, CF_3^+).

(c) *Heptafluoro-n-propyl methyl sulphoxide.* The sulphoxide (1.68 g, 7.25 mmol), treated with deuterium oxide in the presence of a trace of sodium deuterioxide as in the previous experiment, gave a mixture of deuteriomethyl heptafluoro-n-propyl sulphoxides (1.29 g, ca. 5.5 mmol, 76%); m/e 235 (37%, $C_4D_3F_7OS^+$), 234 (14, $C_4HD_2F_7OS^+$), 233 (1.7, $C_4H_2DF_7OS^+$), 232 (1.2, $C_4H_3F_7OS^+$), 169 (17, $C_3F_7^+$), 69 (62, CF_3^+), 66 (100, CD_3OS^+), 65 (37, CHD_2OS^+), 64 (5.5, CH_2DOS^+ , CD_2OS^+), 63 (4.9, CH_3OS^+ , CFS^+), and 50 (23, CD_3S^+ , CF_2^+).

Mass Spectra.—(a) *Alkyl polyfluoroalkyl sulphones.* These compounds did not show a parent-ion peak in their spectra, in contrast to the corresponding sulphides.² In the methyl sulphones, cleavage of the CH_3-S bond gave a weak peak corresponding to CH_3^+ (m/e 15) and cleavage of the R_F-S bond gave the base peak at m/e 79 ($MeSO_2^+$) and peaks due to R_F^+ . The spectrum of ethyl trifluoromethyl sulphone showed a similar pattern, with cleavage of the R_F-S bond giving strong peaks at m/e 93 (78%, $C_2H_5SO_2^+$) and 69 (34, CF_3^+), but cleavage of the C_2H_5-S bond gave the base peak at m/e 29 ($C_2H_5^+$). The spectrum of heptafluoro-n-propyl *trans*-styryl sulphone again showed a similar pattern, with strong peaks at m/e 167 (88%, $PhCH:CHSO_2^+$) and 103 (base peak, $PhCH:CH^+$).

(b) *Halogenoalkyl polyfluoroalkyl sulphones.* Again no parent-ion peak was observed for these sulphones. With the trichloromethyl sulphones cleavage of the CCl_3-S bond gave rise to the base peak at m/e 123, 121, 119, and 117 (CCl_3^+). Cleavage of the R_F-S bond gave rise to a peak corresponding to R_F^+ and the compounds $n-C_3F_7SO_2CCl_3$ and $C_7F_{15}SO_2CCl_3$ each showed a weak peak due to R_FSO^+ . 1,1-Dichloroethyl trifluoromethyl sulphone showed a base peak at m/e 101, 99, and 97 ($CH_3CCl_2^+$) and strong peaks due to CF_3^+ (m/e 69), CH_2CCl^+ (63 and 61), and SO_2^+ (64).

(c) *Methyl polyfluoroalkyl sulphoxides.* These compounds showed a parent-ion peak of medium intensity in their spectra. Cleavage of the CH_3-S bond gave a weak peak corresponding to CH_3^+ (m/e 15) and cleavage of the R_F-S bond gave rise to the base peak at m/e 63 (CH_3SO^+) and a peak corresponding to R_F^+ . Some evidence was obtained for the loss of an oxygen atom from the sulphoxides, since weak peaks associated with the breakdown of the corresponding sulphides $n-C_3F_7SMe^2$ and $(CF_3)_2CF-SMe^2$ were observed.

We thank Pennwalt Corporation for financial support and Dr. M. G. Barlow for help with the interpretation of the n.m.r. spectra.

[2/1726 Received, 24th July, 1972]

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