

P O L Y F L U O R O A L K Y L   S U L P H I D E S

b y

Rhymer B. Rigby, B.Tech.

ProQuest Number: 10996922

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



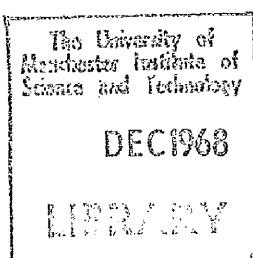
ProQuest 10996922

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code  
Microform Edition © ProQuest LLC.

ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 – 1346



This dissertation is submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy of the Victoria University of Manchester.

Unless otherwise stated the work described in this thesis is that of the author and has not been submitted, in whole or in part, at this or any other university.

UNIVERSITY OF MANCHESTER  
INSTITUTE OF SCIENCE AND TECHNOLOGY

OCTOBER 1968



The author obtained a Diploma of Technology (1st Class Honours) from Brunel College in 1963. This was converted to a Bachelor of Technology degree in 1966 after Brunel College was awarded university status. Since October 1964 the author has been engaged in research in the Department of Chemistry of the University of Manchester Institute of Science and Technology under the supervision of Professor R. N. Haszeldine and Dr. A. E. Tipping.

The author wishes to express his gratitude to Professor R. N. Haszeldine and Dr. A. E. Tipping for their continual advice and encouragement throughout this research. Thanks are also due to Dr. M. G. Barlow for the measurement and interpretation of Nuclear Magnetic Resonance Spectra and to members of the Department for useful discussions and generous gifts of chemicals. Finally the author wishes to thank the technical staff who operate the departmental services and the medical staff for their efficiency.

## SUMMARY

The work described in this dissertation concerns the preparation of polyfluoroalkyl sulphides from polyfluoromonoiodoalkanes and the subsequent oxidation of these sulphides to the corresponding sulfoxides, sulphones, and sulphonic acids.

Polyfluoromonoiodoalkanes were shown to react with dimethyl sulphide, under photochemical conditions, to give methyl polyfluoroalkyl sulphides (ca. 40-50%), trimethylsulphonium iodide and side-products arising from hydrogen abstraction. Free-radical mechanisms have been proposed and discussed.

Several related reactions were investigated; these included:

- (i) the photochemical reactions of two polyfluorodiiodoalkanes with dimethyl sulphide,
- (ii) the photochemical reactions of heptafluoro-1-iodopropane with methyl ethyl sulphide and with methyl trifluoromethyl sulphide, and
- (iii) the thermal reaction of heptafluoro-1-iodopropane with dimethyl sulphide.

The results obtained from these reactions have been compared with those obtained from the general reaction of polyfluoromonoiodoalkanes with dimethyl sulphide under photochemical conditions.

Polyfluoromonoiodoalkanes were also shown to react with dimethyl disulphide, under photochemical conditions, to give high yields of methyl polyfluoroalkyl sulphides (>80%). Moderate yields of ethyl polyfluoroalkyl sulphides (ca. 50%) were obtained from the photochemical reactions of trifluoriodomethane and heptafluoro-1-iodopropane with diethyl disulphide.

The reactions of fluorine-containing iodo-compounds with disulphides, under free-radical conditions, occurred readily and the following reactions were investigated:

- (i) the photochemical reaction of tetrafluoro-1,2-diiodoethane with dimethyl disulphide,
- (ii) the photochemical reaction of pentafluoriodobenzene with bis(trifluoromethyl) disulphide, and
- (iii) the thermal reaction of heptafluoro-1-iodopropane with dimethyl disulphide.

Heptafluoro-1-iodopropane was shown to react with sodium methanethiolate, in the presence of an excess of dimethyl disulphide, to give methyl heptafluoropropyl sulphide. A mechanism involving the  $\text{C}_3\text{F}_7^-$  carbanion has been proposed.

The polyfluoroalkyl sulphides prepared failed to react with iodomethane or with mercuric chloride. This lack of reactivity is in contrast to non-fluorinated alkyl sulphides and has been explained in terms of the strong electron-withdrawing effect of the polyfluoroalkyl group.

Certain of the polyfluoroalkyl sulphides were oxidised to the corresponding sulfoxides and sulphones. Fuming nitric acid or an equimolar quantity of hydrogen peroxide in acetic acid gave the sulfoxides in good yield (>70%). Potassium permanganate or an excess of hydrogen peroxide in acetic acid gave good yields of the sulphones (>70%). Sodium metaperiodate reacted very slowly with methyl heptafluoropropyl sulphide and was considered unsuitable as an oxidising agent for polyfluoroalkyl sulphides.

Methyl heptafluoropropyl sulphone was selected as being representative of methyl polyfluoroalkyl sulphones and the reactions

of this compound were investigated. Other sulphones were shown to undergo similar reactions but these were not investigated in the same detail.

Evidence for the formation of the carbanion,  $C_3F_7SO_2CH_2^-$ , from methyl heptafluoropropyl sulphone was obtained. The sulphone underwent deuterium-exchange with deuterium oxide in the presence of sodium deuterioxide, and gave compounds of the type  $C_3F_7SO_2CX_3$  (where  $X = Cl$  or  $I$ ) under 'haloform type' reaction conditions. Furthermore the sulphone condensed with benzaldehyde in the presence of sodium hydroxide to give trans-heptafluoropropyl styryl sulphone.

Methyl heptafluoropropyl sulphone reacted readily with aqueous sodium hydroxide at  $100^\circ$  and gave 1H-heptafluoropropane as the only fluorine-containing product. In contrast trichloromethyl heptafluoropropyl sulphone reacted with potassium hydroxide in aqueous dioxan at  $100^\circ$  and gave a mixture of 1H-heptafluoropropane (13%) and potassium heptafluoropropanesulphonate (72%). A possible explanation for the different results has been proposed. Potassium heptafluoropropanesulphonate was also prepared by the oxidation of methyl heptafluoropropyl sulphone with potassium permanganate. Attempts to oxidise methyl heptafluoropropyl sulphone with fuming nitric acid were unsuccessful.

Methyl heptafluoropropyl sulphoxide, in common with the corresponding sulphone, reacted with aqueous sodium hydroxide at  $100^\circ$  to give 1H-heptafluoropropane and underwent deuterium-exchange with deuterium oxide in the presence of sodium deuterioxide. However, the sulphoxide gave trichloromethyl heptafluoropropyl sulphone when allowed to react with sodium hypochlorite and failed to react with

iodine in the presence of sodium hydroxide. An explanation for this apparently anomalous behaviour has been proposed.

## CONTENTS

NOMENCLATURE	(i)
INTRODUCTION	1
Preparation of polyfluoroalkyl sulphides	1
Reactivity of polyfluoroalkyl sulphides	16
Polyfluoroalkyl sulfoxides	20
Polyfluoroalkyl sulphones	21
Polyfluoroalkanesulphonic acids	22
DISCUSSION	24
<u>Polyfluoroalkyl Sulphides</u>	24
Photochemical reactions of dimethyl sulphide with polyfluoroiodoalkanes	24
1. Polyfluoromonoiodoalkanes	24
2. Polyfluorodiiodoalkanes	33
Reactions related to the photochemical reaction of dimethyl sulphide with polyfluoromonoiodoalkanes	36
1. General	36
2. Photochemical reaction of methyl ethyl sulphide with heptafluoro-1-iodopropane	39
3. Photochemical reaction of methyl trifluoromethyl sulphide with heptafluoro-1-iodopropane	45
4. Photochemical reaction of bis(chloromethyl) sulphide with heptafluoro-1-iodopropane	50
5. Thermal reaction of dimethyl sulphide with heptafluoro-1-iodopropane	50
Photochemical reactions of polyfluoroiodoalkanes with alkyl disulphides	53
1. Polyfluoromonoiodoalkanes with dimethyl disulphide	53
2. Polyfluoromonoiodoalkanes with diethyl disulphide	56
3. Tetrafluoro-1,2-diiodoethane with dimethyl disulphide	58

Photochemical reaction of bis(trifluoromethyl) disulphide with pentafluoriodobenzene	60
Comparison of the photochemical and thermal reactions of dimethyl disulphide with heptafluoro-1-iodopropane	61
Reactions of heptafluoro-1-iodopropane with sodium alkanethiolates	62
Some effects of the polyfluoroalkyl group on the reactivity of alkyl sulphides	65
Oxidation of polyfluoroalkyl sulphides	65
1. With hydrogen peroxide	65
2. With fuming nitric acid	66
3. With potassium permanganate	67
4. With sodium metaperiodate	67
<u>Polyfluoroalkyl Sulphones</u>	70
Carbanion reactions of polyfluoroalkyl sulphones	71
1. Deuterium-exchange	71
2. Under 'haloform conditions'	72
3. With benzaldehyde	74
Nucleophilic displacements on the sulphur atom of polyfluoroalkyl sulphones	75
1. Methyl heptafluoropropyl sulphone	75
2. Trifluoromethyl ethyl sulphone	76
3. Trichloromethyl heptafluoropropyl sulphone	77
Miscellaneous reactions of polyfluoroalkyl sulphones	78
1. Photolytic decomposition of triiodomethyl heptafluoropropyl sulphone	78
2. Oxidation of methyl heptafluoropropyl sulphone	78
3. Attempted fluorination of trichloromethyl heptafluoropropyl sulphone	80



<u>Polyfluoroalkyl Sulphoxides</u>	81
Carbanion reactions of methyl heptafluoropropyl sulphoxide	81
1. Deuterium-exchange	81
2. Under 'haloform' conditions	82
Nucleophilic displacement on the sulphur atom of methyl heptafluoropropyl sulphoxide	84
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK	85
EXPERIMENTAL	87
General techniques	87
Preparation of reactants	91
Photochemical reactions of dimethyl sulphide with polyfluoroiodoalkanes	
1. With trifluoro <sup>iodo</sup> methane	96
2. With heptafluoro-1-iodopropane	97
3. With heptafluoro-2-iodopropane	98
4. With 1-chlorotetrafluoro-2-iodoethane	99
5. With pentadecafluoro-1-iodo-5-methylhexane	101
6. With tetrafluoro-1,2-diiodoethane	102
7. With octafluoro-1,4-diiodobutane	103
Thermal reaction of dimethyl sulphide with heptafluoro-1-iodopropane	104
Photochemical reaction of methyl ethyl sulphide with heptafluoro-1-iodopropane	105
Photochemical reaction of methyl trifluoromethyl sulphide with heptafluoro-1-iodopropane	107
Photochemical reaction of methanethiol with heptafluoro-1-iodopropane	108
Photochemical reactions of dimethyl disulphide with polyfluoroiodoalkanes	
1. With heptafluoro-1-iodopropane	109

2. With trifluoroiodomethane	111
3. With heptafluoro-2-iodopropane	111
4. With 1-chlorotetrafluoro-2-iodoethane	111
5. With pentadecafluoro-5-methylhexane	111
6. With tetrafluoro-1,2-diiodoethane	112
Attempted ionic reaction of dimethyl disulphide with tetrafluoroethylene	113
Thermal reaction of dimethyl disulphide with heptafluoro-1-iodopropane	114
Reactions of sodium alkanethiolates with heptafluoro-1-iodopropane	117
1. With sodium ethanethiolate	117
2. With sodium methanethiolate in the presence of dimethyl disulphide	118
Comparison of certain reactions of alkyl and polyfluoroalkyl sulphides	
1. With mercuric chloride	119
2. With iodomethane	120
Oxidation of polyfluoroalkyl sulphides	
1. Methyl heptafluoropropyl sulphide	121
a) With potassium permanganate	121
b) With fuming nitric acid	121
c) With hydrogen peroxide (1 : 1 molar ratio)	122
d) With an excess of hydrogen peroxide	122
e) With sodium metaperiodate at 5°	123
f) With sodium metaperiodate at 100°	123
g) With sodium metaperiodate in methanol	124
2. Methyl heptafluoroisopropyl sulphide	124
a) With potassium permanganate	124
b) With fuming nitric acid	124

3. Trifluoromethyl ethyl sulphide with potassium permanganate	124
4. Methyl pentadecafluoro-5-methylhexyl sulphide with hydrogen peroxide	125
Reactions of polyfluoroalkyl sulphones	
1. Methyl heptafluoropropyl sulphone	126
a) With sodium hydroxide	126
b) With deuterium oxide	
c) With sodium hypochlorite	127
d) With benzaldehyde	127
e) With iodine in the presence of base	128
f) With potassium permanganate	129
g) With fuming nitric acid	129
2. Trifluoromethyl ethyl sulphone	130
a) With sodium hydroxide	130
b) With sodium t-butoxide	130
3. Methyl heptafluoroisopropyl sulphone with sodium hypochlorite	131
4. Methyl pentadecafluoro-5-methylhexyl sulphone with sodium hypochlorite	132
5. Photolytic decomposition of triiodomethyl heptafluoropropyl sulphone	132
6. Trichloromethyl heptafluoropropyl sulphone	133
a) With potassium hydroxide	133
b) Attempted fluorination at 100°	134
c) Attempted fluorination at 140°	134
Reactions of methyl heptafluoropropyl sulphoxide	
1. With sodium hydroxide	135
2. With deuterium oxide	135
3. With sodium hypochlorite	135

3a. Attempted reaction with iodine in the presence of base	136
4. Thermal stability at 100°	136
Attempted reaction of methyl heptafluoropropyl sulphide with deuterium oxide	136
Photochemical reaction of bis(trifluoromethyl) disulphide with pentafluoriodobenzene	137
APPENDIX 1	
Mass spectra	139
APPENDIX 2	
Infrared spectra	162
APPENDIX 3	
N.m.r. spectra	171

## NOMENCLATURE

### Sulphides

Alkyl sulphides can be named in a number of ways, e.g., the compound  $\text{CF}_3\text{S}\cdot\text{CH}_3$  may be named:

- (i) methyl trifluoromethyl sulphide,
- (ii) trifluoromethylthiomethane,
- (iii) 1,1,1-trifluoro-2-thiapropane,
- (iv) 1,1,1-trifluorodimethyl sulphide.

The author has attempted, where possible, to conform with the nomenclature commonly used in the chemical literature, i.e., using the generic name sulphide. Thus  $\text{CF}_3\text{S}\cdot\text{CH}_3$  is called methyl trifluoromethyl sulphide. Where two or more sulphur-alkyl or sulphur-polyfluoroalkyl groups are contained in the molecule it is customary to refer to them as alkylthio- derivatives of the corresponding paraffin, e.g., 1,2-bis(methylthio)ethane,  $\text{CH}_3\text{S}\cdot\text{CH}_2\text{CH}_2\text{S}\cdot\text{CH}_3$ .

Unless otherwise stated, terms such as heptafluoropropyl refer to the straight-chain derivatives. Thus  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  is named methyl heptafluoropropyl sulphide, whereas  $(\text{CF}_3)_2\text{CF}\cdot\text{S}\cdot\text{CH}_3$  is named methyl heptafluoroisopropyl sulphide.

The order of writing the two alkyl groups attached to the sulphur atom is determined by the complexity of the group. The least complex group is written first, therefore the majority of the compounds described in this dissertation are referred to as methyl polyfluoroalkyl sulphides and not as polyfluoroalkyl methyl sulphides.

### Sulphoxides and Sulphones

The rules which determine the nomenclature of sulphides are also applicable to sulphoxides and sulphones.

### Thiols

Compounds of the type RSH, (R = alkyl), are called alkanethiols rather than mercaptans or alkyl hydrogen sulphides.

Although the corresponding anion  $\text{RS}^-$  is still referred to extensively as the mercaptide ion, the less popular term of thiolate ion has been used to be consistent with the term thiol.

## I N T R O D U C T I O N

## INTRODUCTION

The term polyfluoroalkyl sulphide is used to describe any dialkyl sulphide with at least one of the alkyl chains containing a high proportion of fluorine (e.g.,  $\text{CHF}_2$ ,  $\text{CF}_3\text{CH}_2$ ). The term perfluoroalkyl refers, specifically, to completely fluorinated alkyl groups (e.g.,  $\text{CF}_3$ ,  $\text{CF}_3\text{CF}_2$ ).

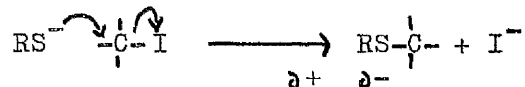
The chemistry of the trifluoromethylthio group has been the subject of a number of reviews<sup>1-3</sup> and the general field of polyfluoroalkyl derivatives of sulphur has been recently reviewed.<sup>4,5</sup> To minimise repetition the author has laid greatest emphasis upon more recent work, especially where this involves new synthetic routes.

### Preparation of Polyfluoroalkyl Sulphides

1. Comparison with Alkyl Sulphide Preparations. One of the most important methods for the preparation of alkyl sulphides is the reaction of an iodoalkane with an alkali metal alkanethiolate.



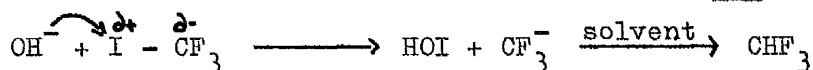
The reaction occurs by a nucleophilic substitution mechanism; the strong nucleophile,  $\text{RS}^-$ , attacks the  $\alpha$ -carbon atom of the iodoalkane and displaces the iodide ion, i.e.,



The polarisation of iodoalkanes,  $\text{R}-\text{I}$ , facilitates this reaction. However, with polyfluoroiodoalkanes the inductive effect of the fluorine atoms opposes the inductive effect of the iodine atom and results in a reversal of polarisation, i.e.,  $\text{R}_f-\text{I}$ . Although the anticipated inertness to nucleophilic attack on the carbon atom has not been demonstrated experimentally with thiolate ion, an analogy may be drawn from the reaction between trifluoriodomethane and alcoholic potassium hydroxide. This reaction appears to involve nucleophilic displacement on the positively polarised iodine atom to form the trifluoromethyl anion, which abstracts



a proton from the solvent to yield trifluoromethane, i.e.,

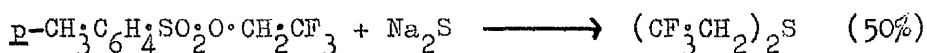


If the inductive effect of the polyfluoroalkyl chain could be 'buffered', by the interposition of a methylene group between the iodine atom and the polyfluoroalkyl group, it is possible that nucleophilic attack on the  $\alpha$ -carbon, by the thiolate ion, would occur.

Compounds of the type  $\text{R}_f\text{CH}_2\text{O}(\text{CH}_2)_n\text{X}$ , where the halogen atom, X, is separated from the polyfluoroalkyl chain by several carbon atoms, have been shown to react with thiols,

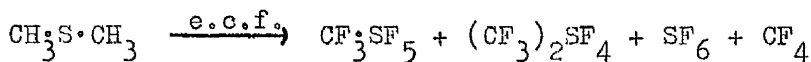


A better example of this buffer-action is afforded by 2,2,2-trifluoroethyl-p-toluenesulphonate, where the leaving group,  $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ , is separated from the polyfluoroalkyl group by a single methylene unit. This toluenesulphonate has been shown to react with sodium sulphide or sodium alkanethiolates to yield the corresponding sulphides, e.g.,

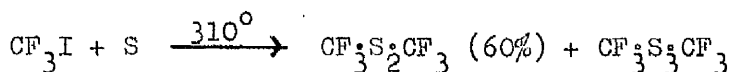


Polyfluoroalkyl sulphides have also been prepared by the reaction of fluorine-containing alkanethiols or their salts, with substituted halogenoalkanes.

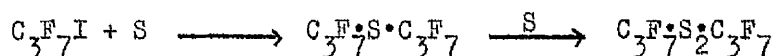
2. Electrochemical Fluorination. The direct fluorination of alkyl sulphides by electrochemical fluorination (e.c.f.) results in the oxidation of sulphur to the hexavalent state, e.g.,



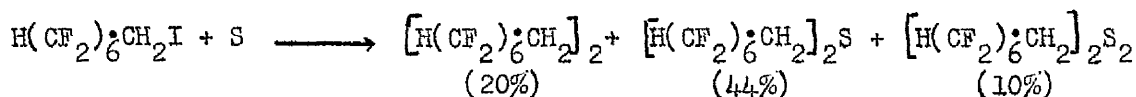
3. Reaction of Polyfluoroiodoalkanes with Sulphur. The thermal reaction of polyfluoroiodoalkanes with sulphur affords a good general route to polyfluoroalkyl disulphides, e.g.,



To explain the absence of significant quantities of monosulphide (<5%) in the thermal reaction of heptafluoro-1-iodopropane with sulphur, Hauptschein and Grosse proposed that the monosulphide was initially formed, but this reacted with sulphur faster than the iodo-compound and hence the disulphide was the major product.<sup>13</sup>

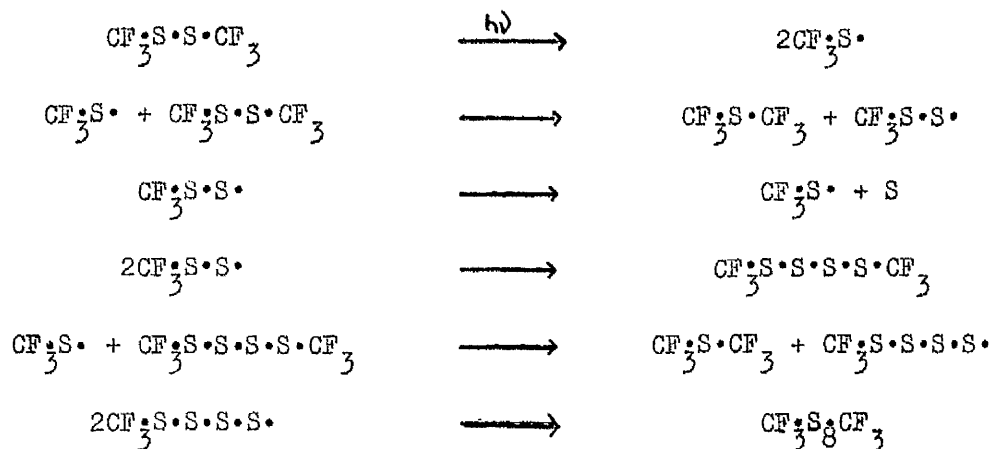


Other workers have subsequently obtained higher yields of the monosulphide (ca. 11%)<sup>14,15</sup> from this reaction, and in the reaction of 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1-iodoheptane with a slight deficit of sulphur the monosulphide was formed as the major product.<sup>16</sup>



However, monosulphides are not usually the major products.

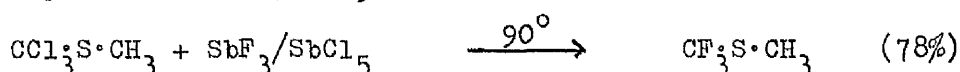
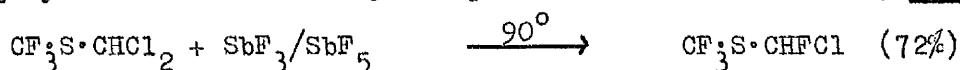
Irradiation of bis(trifluoromethyl)disulphide gives the monosulphide<sup>12</sup> and the following mechanism has been proposed:



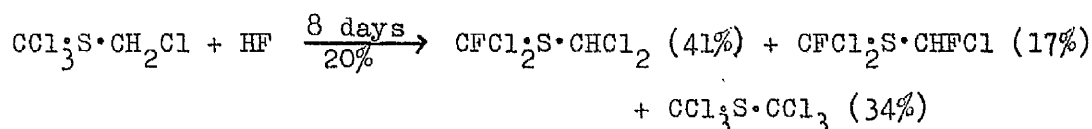
4. Halogen Exchange. Many of the earlier preparations of polyfluoroalkyl sulphides involved replacement of chlorine by fluorine in polychloroalkyl sulphides. A variety of fluorinating agents have been used, including anhydrous hydrofluoric acid,<sup>17,18</sup> mercuric fluoride,<sup>19</sup> antimony trifluoride, and antimony trifluoride with catalytic quantities of antimony pentafluoride<sup>17</sup> or pentachloride.<sup>20</sup>

The latter reagents appear to have been the most successful and

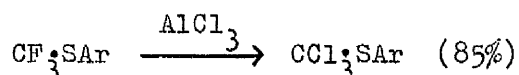
high yields of fluoromethyl sulphides have been reported, e.g.,<sup>17,20</sup>



These comparatively 'clean' reactions may be contrasted with the mixtures sometimes obtained with other reagents, e.g.,<sup>17</sup>

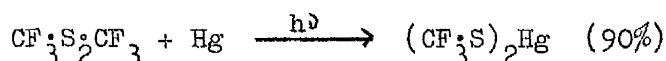


Trifluoromethyl aryl sulphides have been prepared by fluorination of the corresponding trichloromethyl sulphides. It has recently been shown that the reverse reaction may be effected using aluminium trichloride or phosphorus trichloride.<sup>21, 22</sup>

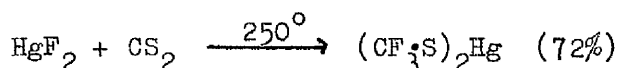


Attempts to chlorinate the corresponding sulfoxides and sulphones by this method were unsuccessful.

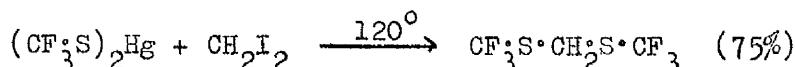
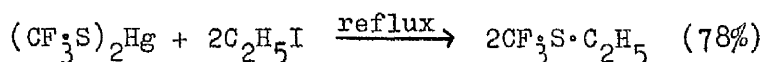
5. Reaction of Perfluoroalkylthiomethyls with Halogenoalkanes. Photolysis of bis(trifluoromethyl) disulphide in the presence of mercury gives bis-(trifluoromethylthio)mercury in high yield.<sup>12</sup>



A more direct synthesis from carbon disulphide and mercuric fluoride has been described.<sup>23</sup>



The mercurial reacts with halogenoalkanes to form alkyl trifluoromethyl sulphides.<sup>4, 24</sup> The reactions of bis(trifluoromethylthio)mercury have been reviewed;<sup>4</sup> however, a recent exhaustive study of the reactions of the mercurial with mono- and polyhalogenoalkanes has resulted in the preparation of a large number of polyfluoroalkyl sulphides, e.g.,<sup>23</sup>



The results indicate that the mercurial reacts fastest with those compounds which contain the greatest number of halogen atoms and also that bromo- and iodoalkanes react faster with the mercurial than chloroalkanes. The latter point is illustrated by the fact that, whereas carbon tetrachloride<sup>25</sup> can be used as an inert solvent for the mercurial at room temperature, tetrabromomethane reacts explosively with the mercurial under these<sup>24</sup> conditions.

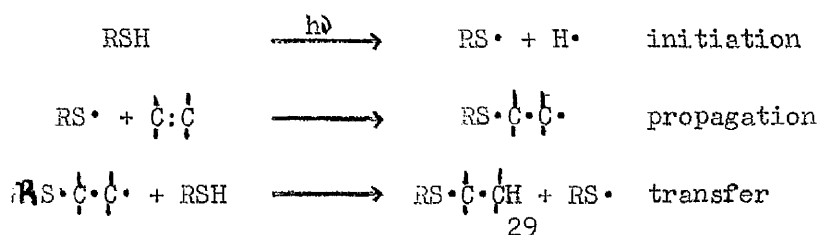
Trifluoromethylthiosilver<sup>23,26</sup> and trifluoromethylthiocopper<sup>23</sup> have also been prepared. The former has been shown to react with halogeno-<sup>26,27</sup>alkanes to give alkyl trifluoromethyl sulphides.

The facile preparation of alkyl trifluoromethyl sulphides from bis-(trifluoromethylthio)mercury suggests that, if higher homologues of the mercurial could be prepared, this would afford an excellent general method of preparation of polyfluoroalkyl sulphides. Regrettably attempts to prepare bis(heptafluoropropylthio)mercury, by irradiation of the correspond-<sup>28</sup>ing disulphide in the presence of mercury, resulted in very poor yields.

6. Free-radical Additions to Olefins. Addition of sulphur-containing compounds to olefins is probably the most general method of preparation of polyfluoroalkyl sulphides. The fluorine may be contained either in the attacking species, or the olefin, or both. However, with the exception of the readily prepared trifluoromethylthio-derivatives, very little information is available concerning the addition reactions of polyfluoroalkane thiols and polyfluoroalkanesulphenyl chlorides. Thus, generally, the preparation of polyfluoroalkyl sulphides by this method involves either attack by trifluoromethylthio- compounds on hydrocarbon-olefins or fluoro-olefins, or attack by alkylthio- compounds on fluoroolefins.

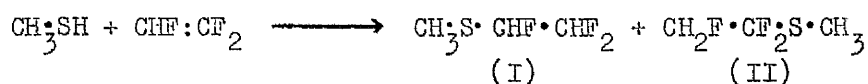
a) Thiols. Thiol radicals,  $RS^\cdot$ , may be generated from thiols by initiators, such as benzoyl peroxide, or by ultraviolet, X-, or  $\gamma$ - radiation. The radicals produced add to the olefins by a chain mechanism to form

sulphides.<sup>29-34</sup> The reaction scheme is outlined below:

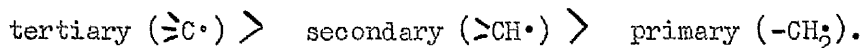


This mechanism has been reviewed in detail.<sup>29</sup>

Unsymmetrical olefins may undergo 'two-way addition' which results in the formation of two isomeric sulphides, e.g.,<sup>30</sup>



Examination of the results of a large number of free-radical additions to olefins has led to the conclusion that the orientation of addition, though influenced by steric and inductive effects, is primarily determined by the stability of the intermediate radical produced by the initial addition process. Usually, the order of radical stability is:



Thus with reference to the example cited above, it is predicted, and experimentally confirmed, that isomer (I) is the major product.<sup>30</sup>

If the two possible intermediate radicals are of comparable stability then secondary factors, such as the electrophilicity of the attacking radical, play an important role.

Free radicals are electron-deficient compounds and therefore electron seeking; electron-withdrawing groups on the radical will increase the electrophilic nature and consequently increase the tendency for the radical to attack the olefin at the point of highest electron density.

This polar effect is exhibited in the additions of thiyl radicals to trifluoroethylene. This olefin is polarised in the following way:  $\text{CHF} = \overset{\delta-}{\text{CF}_2}$  and the extent of addition to the negatively polarised =CHF group was found to rise from 74% to 96% as the electrophilicity of the radical increased from  $(\text{CH}_3)_3\text{C}\cdot\text{S}\cdot$  to  $\text{CF}_3\text{S}\cdot$  (Table I).<sup>30</sup>

TABLE 1.Isomer ratios in additions to trifluoroethylene.

Attacking Radical	% attack on starred carbon	
	$\text{CHF}^* = \text{CF}_2$	$\text{CHF} = \text{CF}_2^*$
$(\text{CH}_3)_3\text{C}\cdot\text{S}\cdot$	74	26
$(\text{CH}_3)_2\text{CH}\cdot\text{S}\cdot$	75	25
$\text{CH}_3\text{CH}_2\cdot\text{S}\cdot$	75	25
$\text{CH}_3\cdot\text{S}\cdot$	78	22
$\text{CH}_3\text{CO}\cdot\text{S}\cdot$	95	5
$\text{CF}_3\cdot\text{S}\cdot$	96	4

The polar effect is even more pronounced in the additions of thiyl radicals to hexafluoropropene which is polarised in the following way

$$\text{CF}_3^{\delta-}\text{CF}^{\delta+} = \text{CF}_2, \text{ (Table 2).}^{32}$$
TABLE 2.Isomer ratios in additions to hexafluoropropene.

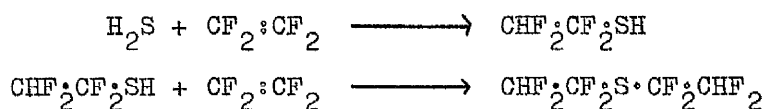
Attacking Radical	% attack on starred carbon	
	$\text{CF}_3^*\text{CF} = \text{CF}_2$	$\text{CF}_3\text{CF} = \text{CF}_2^*$
$\text{CH}_3\cdot\text{S}\cdot$	8	92
$\text{CF}_3\text{CH}_2\cdot\text{S}\cdot$	30	70
$\text{CF}_3\cdot\text{S}\cdot$	55	45

b) Hydrogen sulphide. Hydrogen sulphide behaves in a similar manner to thiols when subjected to irradiation or free-radical initiators.

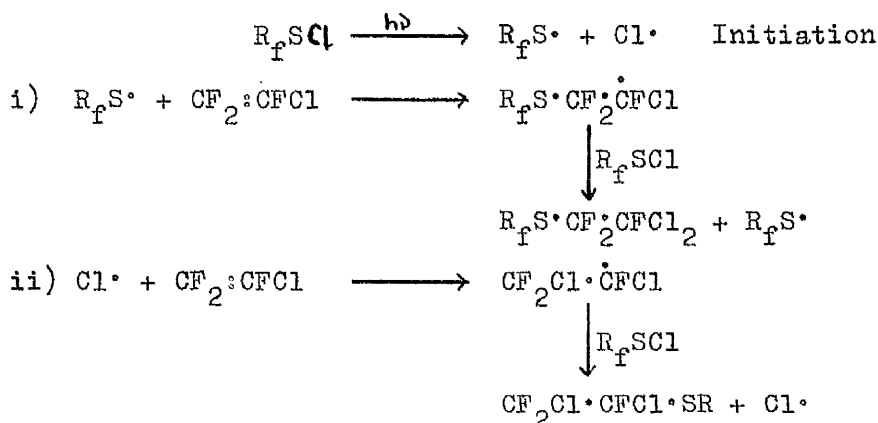


The  $\text{HS}\cdot$  radical adds to fluoroolefins to give, after chain transfer, a thiol. The thiol, in the presence of excess olefin, reacts further to give a sulphide, e.g.,

35,36



c) Sulphenyl chlorides. The free-radical additions of fluoroalkane-sulphenyl chlorides to olefins afford an excellent route to polyfluoroalkyl sulphides.<sup>37,38</sup> It has been proposed that either of the radicals produced by the decomposition of the sulphenyl chloride may act as the chain-propagating entity, i.e.,



Harris has compared the additions of trifluoromethanethiol and trifluoromethanesulphenyl chloride to a number of fluoroolefins. The results obtained suggest that the major chain-propagating unit is the chlorine atom (Table 3).

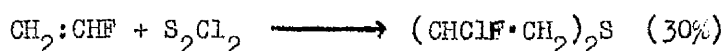
TABLE 3

Isomer ratios in the additions of trifluoromethanesulphenyl chloride and trifluoromethanethiol to fluoroolefins

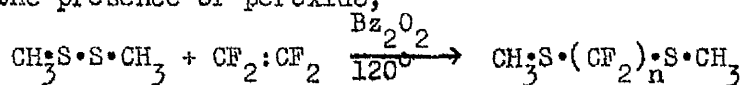
Source of $\text{CF}_3\text{S}\cdot$	OLEFINS				
	The figures in parentheses represent the % composition of the 1:1 adduct with respect to the orientation of the $\text{CF}_3\text{S}\cdot$ group				
	$\text{CHCl:CH}_2$	$\text{CF}_2\text{:CHF}$	$\text{CF}_2\text{:CFC1}$	$\text{CF}_2\text{:CH}_2$	$\text{CH}_3\text{O}\cdot\text{CF:CF}_2$
$\text{CF}_3\text{SCl}$	(95) (5)	(82) (18)	(22) (78)	(78) (22)	(38) (62)
$\text{CF}_3\text{SH}$	(0) (100)	(2) (98)	(100) (0)	(0) (100)	(43) (55)

The anomalous case of the reaction of trifluoromethanesulphenyl chloride with methyl trifluorovinyl ether,  $\text{CH}_3\text{O}\cdot\text{CF}:\text{CF}_2$ , in which it appears that the major chain-propagating unit is the thiyl group, may be explained by steric factors (see p.14 ).

d) Sulphur monochloride. Addition of sulphur monochloride to fluoro-olefins has not proved to be a useful route to polyfluoroalkyl sulphides. However, sulphur monochloride has been added to vinyl fluoride in the presence of peroxide, to give the corresponding sulphide in fair yield. <sup>39</sup>



e) Disulphides. Dimethyl disulphide has been added to tetrafluoroethylene in the presence of peroxide, <sup>40</sup>

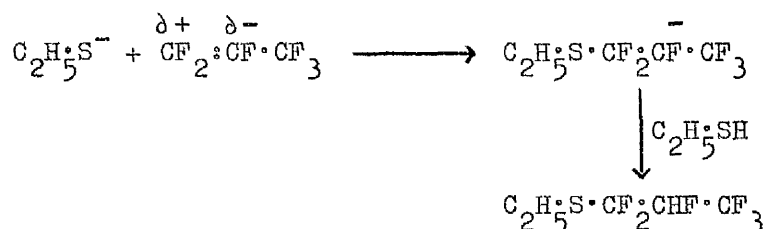


where  $n = 2-10$ .

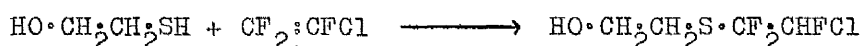
An early patent on polyfluoroalkyl sulphides describes a similar reaction between dimethyl disulphide and tetrafluoroethylene in the presence of iodine, at  $175^\circ$ . <sup>34</sup> Methyl ethyl disulphide has been shown to decompose to give free radicals below this temperature, <sup>41</sup> indicating that the reaction between dimethyl disulphide and tetrafluoroethylene is probably free radical in nature.

7. Ionic Reactions. a) Thiols. In contrast to hydrocarbon-olefins, fluoro-olefins undergo reactions with nucleophiles and resist electrophilic attack. This is a consequence of electron withdrawal by the strongly electronegative fluorine atoms which causes depletion of the electron density at the olefinic bond. Alkanethiols in the presence of a base add to fluoroolefins to give polyfluoroalkyl sulphides. <sup>9,30,42-46</sup> The base-catalysed addition of alkanethiols to fluoroolefins has not been subjected to the same rigorous examination as free-radical additions. However, the results indicate that attack by the thiolate ion occurs exclusively at the positively polarised carbon atom, <sup>30,42,43</sup> e.g.,



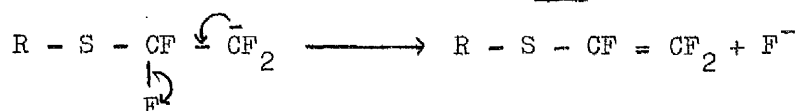


Under ionic conditions, 2-mercaptoethanol adds to fluoroolefins  
42,44  
by attack of the sulphur and not the oxygen.



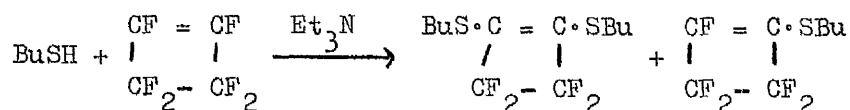
This has been attributed to the fact that thiols are stronger acids  
42  
than alcohols.

In aprotic solvents, using the sodium salt of the alkanethiol,  
attack on fluoroolefins results in the formation of unsaturated poly-  
46  
fluoroalkyl sulphides. This can be explained by the ejection of a  
fluoride ion from the intermediate carbanion, i.e.,

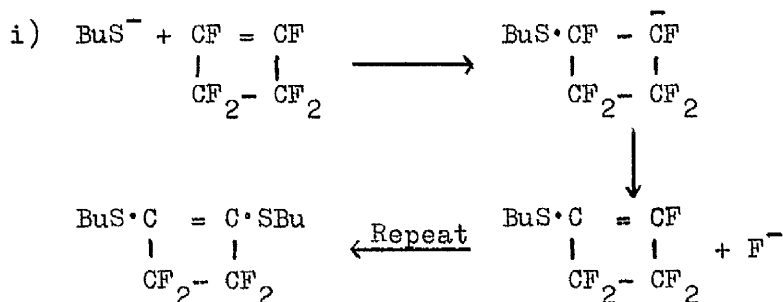


Unsaturated polyfluoroalkyl sulphides are sometimes formed in the  
presence of free thiol or proton-donating solvents, when a strong base  
42,44,47-50  
is present. This may be caused by the intermediate carbanion  
ejecting a fluoride ion, as shown above, rather than abstracting a  
proton, or by elimination of hydrogen fluoride after addition is  
complete.

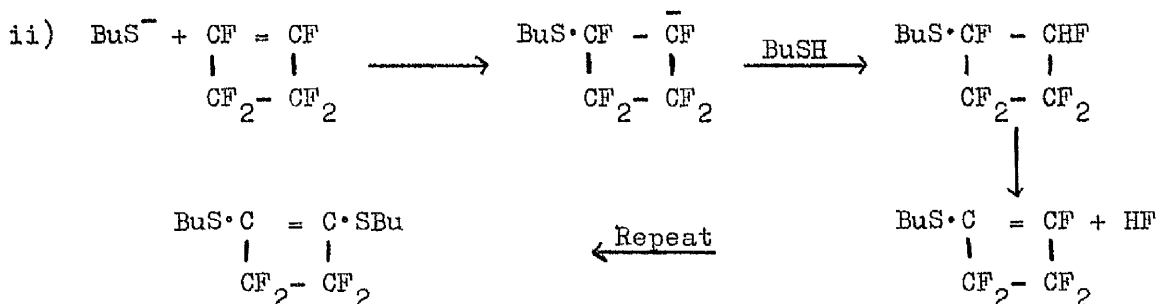
The two possibilities are illustrated by the attack of n-butane-  
42  
thiol on perfluorocyclobutene in the presence of triethylamine.



This reaction may occur by direct substitution,

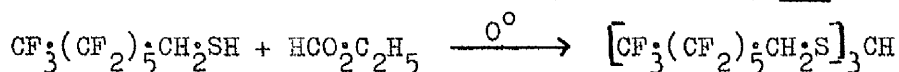


or by addition/elimination;

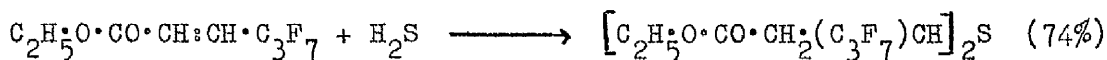


The authors concluded that, in this case, mechanism (ii) was correct since the intermediate saturated sulphides were isolated and shown to eliminate hydrogen fluoride.

A recent patent describes the formation of polyfluoroalkyl sulphides by the condensation of polyfluoroalkanethiols with ethyl formate in the presence of anhydrous hydrogen chloride, *e.g.*,



b) Hydrogen sulphide. Hydrogen sulphide has been added to fluoroolefins, in the presence of a base, to give polyfluoroalkyl sulphides as the major products, and only small quantities of the thiols, *e.g.*,



c) Polyfluoroalkanesulphenyl chlorides. Polyfluoroalkanesulphenyl chlorides have been added to symmetrical olefins under ionic conditions to give the 1 : 1 adduct. The only recorded addition to an unsymmetrical olefin gave a low yield of product but the orientation of the addition was consistent with the polarisation of the olefin, *i.e.*,



Alkanesulphenyl chlorides have been added to fluoroolefins to give the expected polyfluoroalkyl sulphide, <sup>55</sup> e.g.,

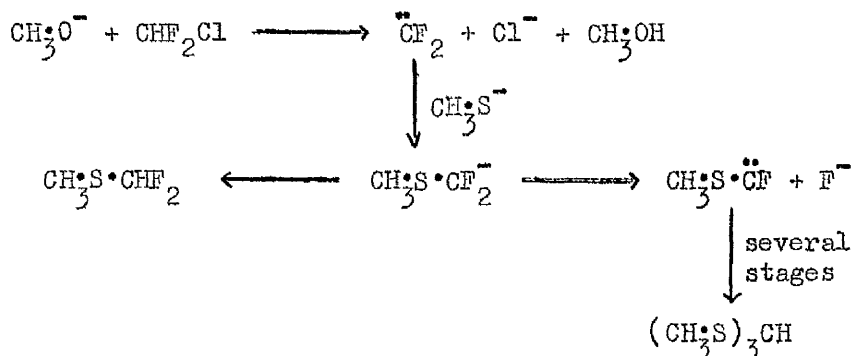


Trifluoromethanesulphenyl chloride reacts with aromatic hydrocarbons, <sup>56</sup> under Friedel-Crafts conditions, to give trifluoromethyl aryl sulphides.



Similar products are obtained from the reaction of trifluoromethanesulphenyl chloride with aryl magnesium halides. <sup>57</sup>

8. Via Carbenes. Polyfluoroalkyl sulphides have been prepared from reactions which involve carbene intermediates. <sup>55,58,59</sup> The reaction between sodium methanethiolate and chlorodifluoromethane, in the presence of sodium methoxide, has been intensively investigated and a carbene mechanism has <sup>58</sup> been proposed.



9. Free-radical Attack on Saturated Hydrocarbons. Trifluoromethanesulphenyl chloride reacts with saturated hydrocarbons under free-radical conditions, to give polyfluoroalkyl sulphides. <sup>60</sup> These reactions are interesting mechanistically and will be discussed in detail.

The results obtained from the free-radical reactions of trifluoromethanesulphenyl chloride with n-butane and with isobutane are given in Tables 4a and 4b respectively.

TABLE 4a

Products from n-butane

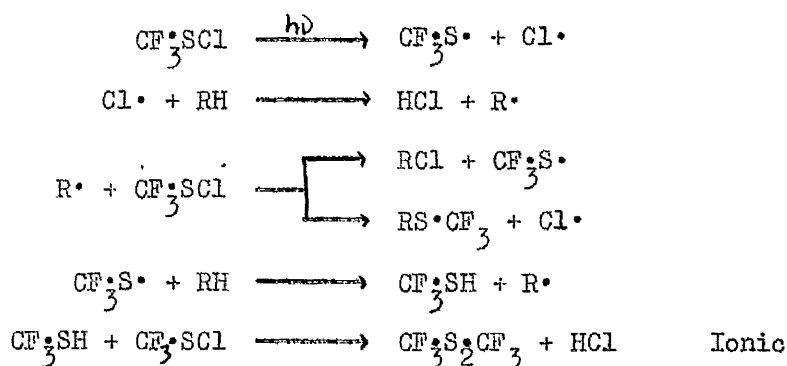
Product	Yield %
$\text{CF}_3\text{S}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	13
$\text{CF}_3\text{S}\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\text{CH}_3$	46
$\text{CH}_3\text{CHCl}\cdot\text{CH}_2\text{CH}_3$	12
$\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{CH}_2\text{CH}_3$	1
$\text{CF}_3\text{S}_2\text{CF}_3$	28
HCl	Not Recorded

TABLE 4b

Products from isobutane

Product	Yield %
$\text{CF}_3\text{S}\cdot\text{C}(\text{CH}_3)_3$	24
$\text{CF}_3\text{S}\cdot\text{CH}_2\text{CH}(\text{CH}_3)_2$	12
$(\text{CH}_3)_3\text{CCl}$	33
$(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\text{Cl}$	1
$\text{CF}_3\text{S}_2\text{CF}_3$	47
HCl	Not Recorded

To explain the products and isomer ratios, Harris proposed the following mechanism:



The products from the n-butane reaction show that the ratio of primary to secondary hydrogen abstraction is ca. 1:4; this selectivity is approximately double that obtained in other free-radical chlorinations, and Harris suggests that this is due to a species which is less reactive than the free chlorine atom, possibly the  $\text{CF}_3\text{S}\cdot$  radical. The selectivity of abstraction is supported by the products obtained from the isobutane reaction.

The results also indicate the operation of a steric effect. The high ratio of primary trifluoromethylthio- products to primary chloro-

products show that preferential attack of the hydrocarbon radical is on the sulphur atom. The relative ratios of the secondary products indicate that radical attack occurs both on the sulphur atom and the chlorine atom, but that attack on the former predominates. However, the tertiary products show that attack on the less sterically hindered, terminal, chlorine atom is preferred by the bulky t-butyl radical. Support for this postulate is obtained from the free-radical reaction between trichloromethanesulphenyl Chloride and cyclohexane, where the products, chlorocyclohexane and bis(trichloromethyl) disulphide, show that attack on the sterically hindered sulphur atom does not take place, and abstraction of the chlorine atom by the cyclohexyl radical occurs exclusively.<sup>62</sup>

The results of the reactions of trifluoromethanesulphenyl chloride with saturated hydrocarbons are in agreement with the results obtained from the free-radical additions of trifluoromethanesulphenyl to fluoro-olefins (p. 7), where it is proposed that both the chlorine atom and the trifluoromethylthio group are chain-propagating entities.

#### Unsaturated Polyfluoroalkyl Sulphides

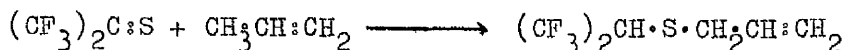
The preparation of unsaturated polyfluoroalkyl sulphides by nucleophilic attack of alkanethiols on fluoroolefins has been described (p. 10).

Free-radical additions of hydrogen sulphide and thiols to fluoro-olefins<sup>31,36</sup> and fluoroacetylenes<sup>63</sup> sometimes result in low yields of unsaturated polyfluoroalkyl sulphides.

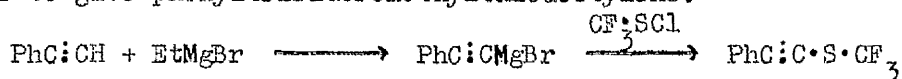
Propargylthiol reacts with chlorotrifluoroethylene under ionic conditions to yield the corresponding unsaturated sulphide.<sup>43</sup>



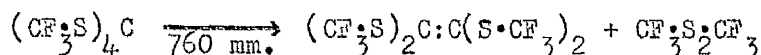
Hexafluorothioacetone has been condensed with compounds which contain allylic hydrogen atoms to give fluorine-containing allyl sulphides, e.g.,<sup>64</sup>



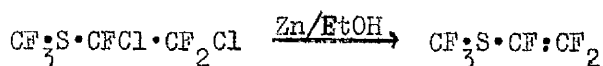
Treatment of phenylacetylene with ethyl magnesium bromide yields the acetylenic Grignard reagent which reacts with trifluoromethanesulphenyl chloride to give phenyltrifluoromethylthioacetylene.<sup>23</sup>



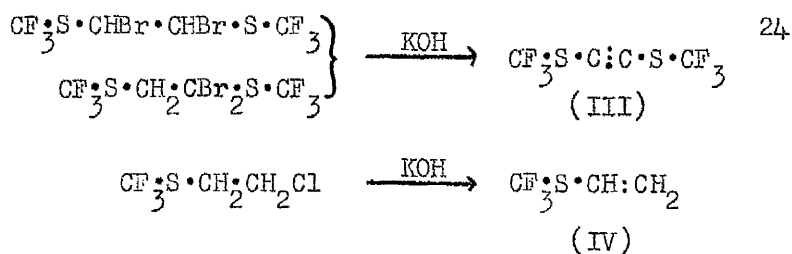
The reaction of tetrabromomethane with bis(trifluoromethylthio)-mercury, unless carefully controlled, can give unsaturated products. It is believed the expected tetra~~kis~~(trifluoromethylthio)methane is initially formed but that this breaks down under the heat generated during the reaction. This has been proved by the pyrolysis of tetra~~kis~~(trifluoromethylthio)methane at atmospheric pressure.<sup>23</sup>



Dehalogenation of polyfluoroalkyl sulphides, using zinc dust in ethanol, has also been used to prepare unsaturated polyfluoroalkyl sulphides, e.g.,<sup>37,65</sup>

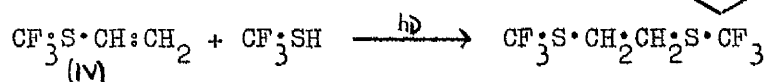
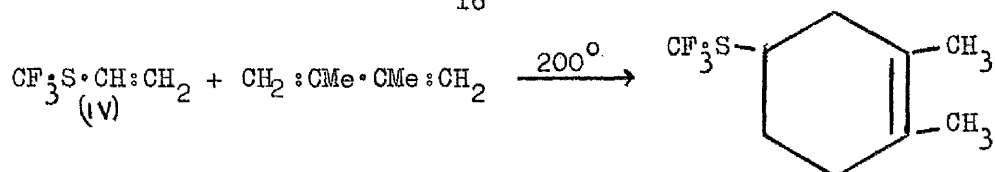


Dehydrohalogenation, with potassium hydroxide, has been used extensively to prepare unsaturated polyfluoroalkyl sulphides.<sup>9,24,31,33,35</sup>

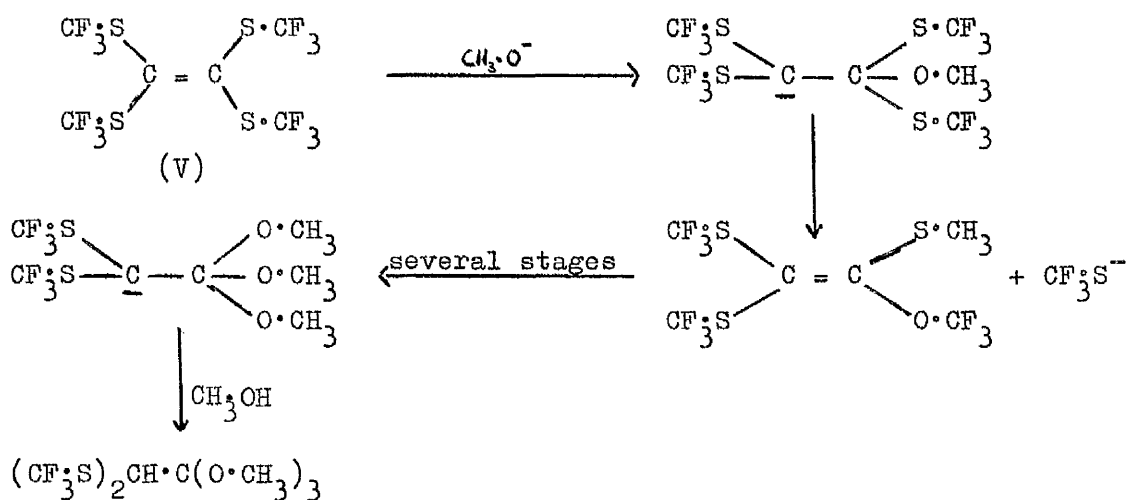


Bis(trifluoromethylthio)acetylene (III) undergoes free-radical and nucleophilic additions, and condenses with 2,3-dimethylbutadiene to give a Diels-Alder adduct.

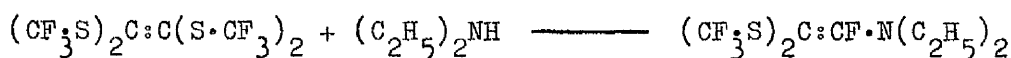
Trifluoromethyl vinyl sulphide (IV) has also been shown to be a dienophile, and to undergo free-radical addition reactions.



The reaction of tetrakis(trifluoromethylthio)ethylene (V) with methanol, in the presence of sodium methoxide, is believed to occur by the following mechanism:



Treatment of the olefin (V) with diethylamine results in a novel reaction.

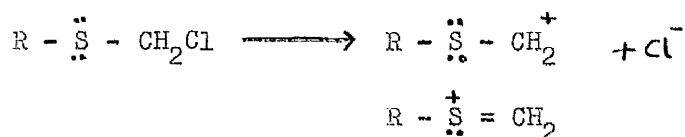


A mechanism which involves expulsion, and subsequent decomposition,<sup>23</sup> of the trifluoromethylthio group has been proposed.

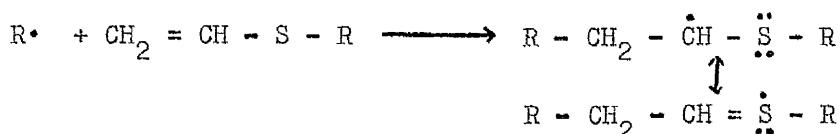
#### Reactivity of Polyfluoroalkyl Sulphides

The divalent sulphur atom, in alkyl sulphides, has two unshared pairs of electrons. Many of the reactions of alkyl sulphides, such as complex formation with mercuric chloride and the reactions with iodoalkanes to give trialkylsulphonium iodides, involve the use of these unshared electrons. It is believed that the rapid  $\text{S}_{\text{N}}1$  hydrolysis of  $\alpha$ -chloroalkyl sulphides is due to stabilisation of the intermediate carbonium ion by

the sulphur atom which donates an unshared electron pair to form a 3p - 2p $\pi$ -bond, i.e.,



Free-radical co-polymerisation studies indicate that methyl vinyl sulphide is a very reactive monomer.<sup>67</sup> This is attributed to the stabilisation of the intermediate radical by promotion of the lone electron to the d orbitals of sulphur, and 2p - 3p orbital overlap between the  $\alpha$ -carbon and the sulphur atom, again by utilisation of the unshared 3p electrons on the sulphur atom, i.e.,



The evidence for the ability of the sulphur atom to expand its valency shell has been reviewed.<sup>66,68</sup>

The strong electron-withdrawing effect of a polyfluoroalkyl chain tends to withdraw electron density from the sulphur atom which causes a reduction in the reactivity of the sulphur atom. Thus it has been shown that polyfluoroalkyl sulphides do not form complexes with mercuric chloride,<sup>20,24</sup> neither do they react with iodomethane,<sup>20</sup> under conditions where reaction with alkyl sulphides takes place.

The suppression of 'lone pair activity', however, is not complete and although calculations indicate that the trifluoromethylthio group, in trifluoromethyl phenyl sulphide, should be meta-directing, Yagupol'skii found that in the presence of strong electrophiles (e.g., NO<sub>2</sub><sup>+</sup>) ortho- and para-substitution occurs.<sup>69</sup>

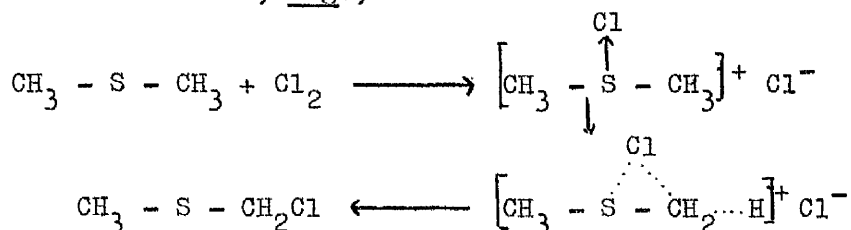
It has been shown also that free-radical chlorination of saturated polyfluoroalkyl sulphides containing  $\alpha$ -hydrogen atoms occurs adjacent to



the sulphur atom. <sup>9,33</sup> This presumably involves the type of radical stabilisation described previously in the polymerisation of vinyl sulphide.

The degree of fluorination affects the ease of polymerisation of vinyl sulphides. Trifluoromethyl vinyl sulphide polymerises fairly readily,<sup>24,33,54</sup> whereas initial attempts to form homo- and co-polymers of hexafluoro(methyl vinyl) sulphide were unsuccessful.<sup>37</sup> However, a recent patent describes the formation of low molecular weight polymers from hexafluoro(methyl vinyl) sulphide on irradiation.<sup>33</sup> It is difficult to draw any definite conclusions from these results, with regard to the deactivation of the sulphur atom, since it was found that the presence of hexafluoro(methyl vinyl) sulphide could inhibit the polymerisation of other monomers, and it has been suggested that the lack of reactivity of hexafluoro(methyl vinyl)sulphide is due to the formation of a very stable radical where the lone electron is delocalised by the d orbitals of the sulphur atom.<sup>37</sup>

The chlorination of alkyl sulphides, under ionic conditions, is considered to occur via an intermediate in which the sulphur atom donates a pair of electrons, e.g.,



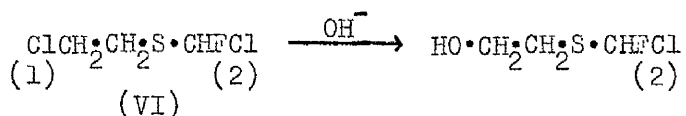
Polyfluoroalkyl sulphides have been chlorinated under vigorous conditions, using sulphuryl chloride,<sup>9</sup> and possibly an "ylide" intermediate is involved in these reactions.

### Stability of Polyfluoroalkyl Sulphides

The stability of polyfluoroalkyl sulphides is very much affected by the degree of fluorine substitution, for although bis(trifluoromethyl)

12  
sulphide is hydrolysed by base, only at elevated temperatures; it is found that as hydrogen replaces fluorine, the stability of the chain decreases. This instability is particularly manifest with monofluoro-18,19 methyl sulphides, which are very readily hydrolysed and spontaneously liberate hydrogen fluoride. Evidence for this was obtained from ethyl fluoromethyl sulphide which, on standing, attacked glass and significant 18 quantities of methylthiirane were detected.

Nucleophilic displacement of chlorine, in alkyl sulphides, is inhibited by the replacement of hydrogen atoms by fluorine atoms. However, this is probably an effect of electron withdrawal from the carbon atom rather than deactivation of the sulphur atom since, in the unsymmetrical alkyl sulphide (VI) only chlorine atom (1) is easily displaced 39 by base,



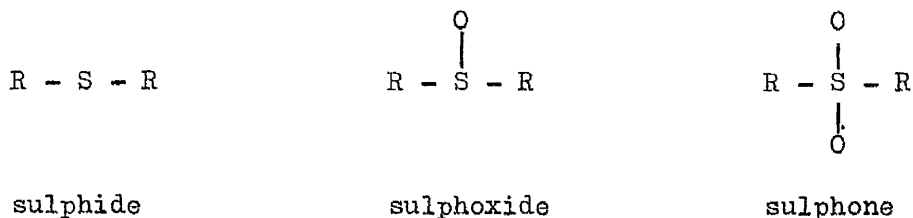
It is believed that dialkyl and alkyl aryl sulphides can form stable carbanions in the  $\alpha$ -position to the sulphur atom by delocalisation 66,68 of the extra electrons through 3d - 2p orbital overlap, i.e.,



It might be predicted that polyfluoroalkyl sulphides would be better able to stabilise such carbanions by reason of the greater inductive effect of the polyfluoroalkyl group. No direct comparison of the relative effectiveness of alkyl and fluoroalkyl sulphides has been made in this connection, but Yagupol'skii and co-workers conclude from their experiments that methyl trifluoromethyl sulphone undergoes carbanion reactions more 70 readily than alkyl aryl or dialkyl sulphones.

### Oxidation of Sulphides

The oxidation products of alkyl sulphides are given below:



The exact nature of the sulphur-oxygen link is the subject of some controversy. The most recent appraisal of the available evidence suggests the bond is a resonance hybrid of a semi-polar bond and a covalent double bond, viz:



but that the hybrid lies closer to the semi-polar bond than to the covalent double bond. Thus again sulphur is required to donate unshared electrons, and the fact that polyfluoroalkyl sulphoxides and sulphones have been prepared indicates that the presence of a polyfluoroalkyl chain does not completely suppress the availability of the unshared electrons on the sulphur atom.

### Polyfluoroalkyl Sulphoxides

Heating polyfluoroalkyl sulphides with hydrogen peroxide<sup>27,31,53,71</sup> in acetic acid, or with nitric acid<sup>71</sup> gives polyfluoroalkyl sulphoxides. Methyl trifluoromethyl sulphoxide readily undergoes attack by sodium<sup>71</sup> hydroxide to give fluoroform and sodium methanesulphonate.

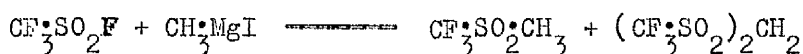


Very little information is available regarding other reactions of polyfluoroalkyl sulphoxides, though investigations of the relative inductive effects of the trifluoromethylthio, trifluoromethylsulphonyl,

and trifluoromethylsulphonyl groups have been made.<sup>27</sup>

### Polyfluoroalkyl Sulphones.

Polyfluoroalkyl sulphides have been oxidised to sulphones by hydrogen peroxide in acetic acid,<sup>27,31,40,48,51</sup> and by potassium permanganate<sup>42,53,70</sup> and chromic oxide<sup>20,24,53,70</sup> in acidic media. The degree of fluorination has an effect upon the ease of oxidation. Thus although ethyl trifluoromethyl sulphide may be oxidised by chromic acid, attempts<sup>20</sup> to oxidise pentafluoro(dimethyl) sulphide and bis(trifluoromethylthio) methane<sup>24</sup> with this reagent were unsuccessful. Bis(trifluoromethanesulphonyl)methane has been prepared by reaction of trifluoromethanesulphonyl fluoride with methyl magnesium iodide, showing that the<sup>72</sup> disulphone is not unstable.



Until recently bis(trifluoromethyl) sulphone, prepared in low<sup>73</sup> yield by the electrochemical fluorination of dimethyl sulphone, was the only completely fluorinated sulphone known. However, a recent paper<sup>74</sup> describes the preparation of bis(perfluoroalkyl) sulphones from fluoro-olefins and sulphonyl fluorides in the presence of caesium fluoride, e.g.,



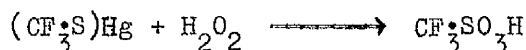
Hexafluoropropene gives only the sulphonyl fluoride and telomers of hexafluoropropene under these conditions.

By virtue of the electron-withdrawing polyfluoroalkanesulphonyl group the hydrogen atoms on the  $\alpha$ -carbon atom of polyfluoroalkyl sulphones are extremely acidic; bis(trifluoromethanesulphonyl)methane is comparable<sup>72</sup> in acid strength to hydrochloric acid. Methyl trifluoromethyl sulphone<sup>70,75</sup> has been shown to readily undergo carbanion reactions.

### Polyfluoroalkanesulphonic Acids.

A number of methods of preparation of polyfluoroalkanesulphonic acids have been described.<sup>4</sup> The most general method involves electrochemical fluorination of an alkanesulphonyl chloride to the corresponding perfluoroalkanesulphonyl fluoride, followed by hydrolysis with base.<sup>76-78</sup>

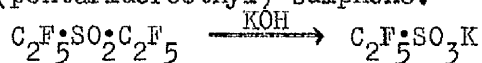
There is no recorded evidence of direct oxidation of a polyfluoroalkyl sulphide to the corresponding sulphonic acid. An attempt to oxidise bis(trifluoromethyl) disulphide by prolonged heating with nitric acid was unsuccessful. However, bis(trifluoromethylthio)mercury has been oxidised to trifluoromethanesulphonic acid with hydrogen peroxide.<sup>79</sup>



$\omega$ -Bis(methanesulphonyl)polyfluoroalkanes have been oxidised to the corresponding polyfluoroalkanesulphonic acids with alkaline potassium permanganate.<sup>40</sup>



Potassium pentafluoroethanesulphonate has been prepared by the basic hydrolysis of bis(pentafluoroethyl) sulphone.<sup>74</sup>



### DISCUSSION

The ultimate aim of the work subsequently described was to investigate new routes for the preparation of polyfluoroalkyl sulphides and to convert these sulphides into the corresponding sulphonic acids.

The most general method for the preparation of perfluoroalkane-sulphonic acids utilises electrochemical fluorination of alkanesulphonyl chlorides (see p. 22 ). This method suffers from the disadvantage that during the electrochemical fluorination (e.c.f.) of the longer-chain alkanesulphonyl chlorides, alkyl-chain fission occurs with an attendant reduction in the yields of perfluoroalkanesulphonyl fluorides (Table 5).

TABLE 5

Yields of perfluoroalkanesulphonyl fluorides from e.c.f.

78

*Sulphonyl fluoride	Yield %	*Sulphonyl fluoride	Yield %
$\text{CF}_3\text{SO}_2\text{F}$	87	$\text{C}_5\text{F}_{11}\text{SO}_2\text{F}$	48
$\text{C}_2\text{F}_5\text{SO}_2\text{F}$	79	$\text{C}_6\text{F}_{13}\text{SO}_2\text{F}$	36
$\text{C}_3\text{F}_7\text{SO}_2\text{F}$	68	$\text{C}_7\text{F}_{15}\text{SO}_2\text{F}$	31
$\text{C}_4\text{F}_9\text{SO}_2\text{F}$	58	$\text{C}_8\text{F}_{17}\text{SO}_2\text{F}$	25

\*Straight-chain derivatives.

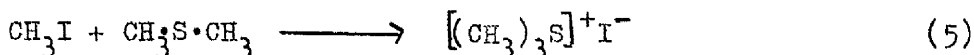
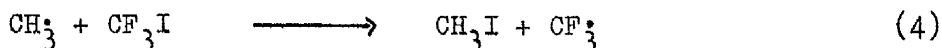
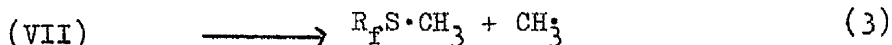
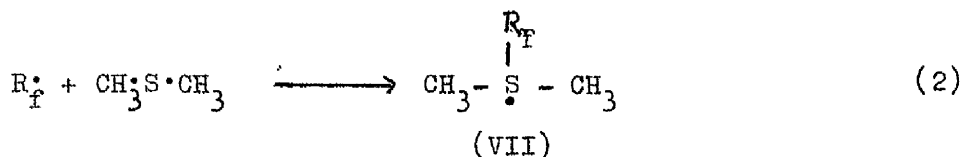
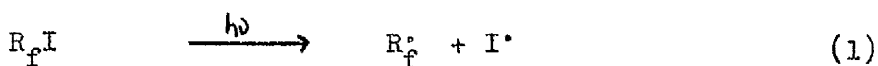
It was therefore hoped to devise a method of preparation of polyfluoroalkyl sulphides in which the yield was independent of the size of the polyfluoroalkyl group. Polyfluoroiodoalkanes were selected as starting materials because of their ready availability.

POLYFLUOROALKYL SULPHIDES

Photochemical Reactions of Dimethyl Sulphide with Polyfluoroiodoalkanes

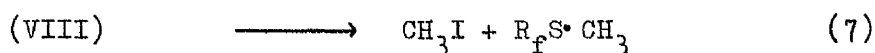
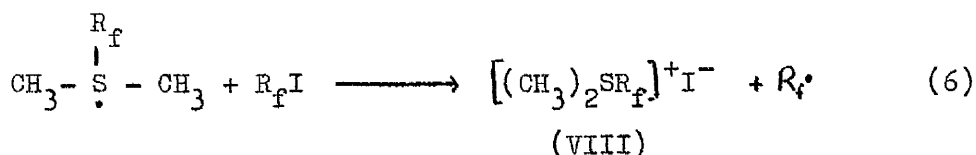
1. Polyfluoromonoiodoalkanes. In the course of an investigation into the effect of solvents on the free-radical addition of trifluoroiodomethane to trifluoroethylene Higginbottom observed<sup>30</sup> that in the reaction which employed dimethyl sulphide as solvent, the olefin was recovered unchanged, whereas all the trifluoroiodomethane was consumed. It was further shown that the trifluoroiodomethane had reacted with the solvent to form trifluoromethane, methyl trifluoromethyl sulphide, and trimethylsulphonium iodide. A similar result was obtained with pentafluoroiodoethane. Although no attempt was made to explain the formation of the H-polyfluoroalkanes, Higginbottom proposed two free-radical mechanisms to explain the formation of the methyl polyfluoroalkyl sulphides and trimethylsulphonium iodide (schemes A and B).

Scheme A



Scheme B

The first two steps of this mechanism are the same as those in scheme A, and these are followed by:



Both of these mechanisms require attack of a polyfluoroalkyl radical on dimethyl sulphide to form an intermediate sulphur radical (VII) in which the sulphur valence shell has expanded to accommodate nine electrons. In the first scheme (A), the intermediate radical (VII) decomposes to give a methyl polyfluoroalkyl sulphide and a methyl radical. The latter may then abstract an iodine atom from the polyfluoromonoiodoalkane to give iodomethane, and generate another polyfluoroalkyl radical which may continue the chain reaction. The ionic reaction of iodomethane and dimethyl sulphide at room temperature, to give trimethylsulphonium iodide (equation 5), is well known.<sup>80</sup>

Scheme B requires that the expanded sulphur radical (VII) abstracts an iodine atom from the polyfluoromonoiodoalkane to form a dimethylpolyfluoroalkylsulphonium iodide (VIII). This then dissociates into a methyl polyfluoroalkyl sulphide and iodomethane without the intermediate formation of a methyl radical.

The evidence for the ability of the sulphur atom to expand its valence octet has been reviewed<sup>66,68</sup> and the work of Price<sup>67,81</sup> is of particular significance.

The results of the present work (Table 6) largely support the two mechanisms postulated by Higginbottom, but it has been necessary to extend these mechanisms because:

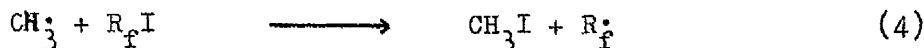
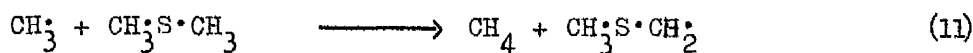
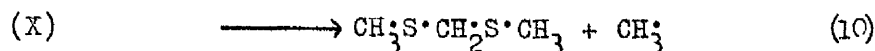
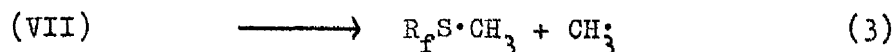
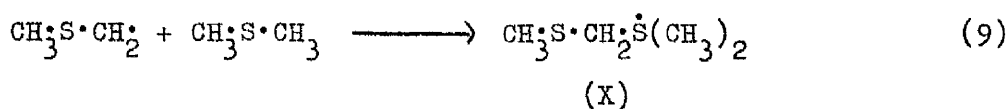
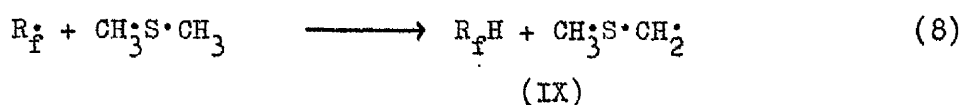
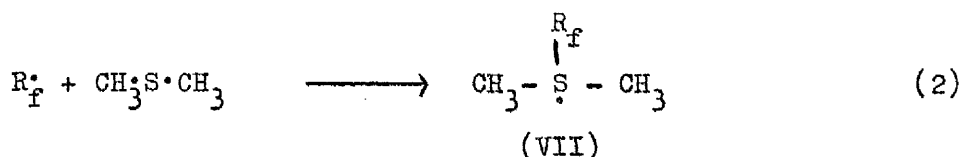
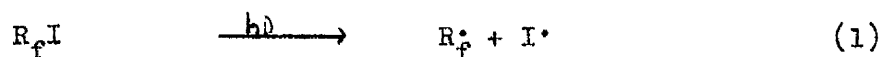


(i) in addition to the products isolated in the original work, bis(methylthio)methane and methane have now been identified, and

(ii) the present work shows that the yield of trimethylsulphonium iodide is almost quantitative with respect to the polyfluoromonoiodoalkane consumed, whereas originally it was found that the yield of trimethylsulphonium iodide was only equivalent to the yield of methyl polyfluoroalkyl sulphide.

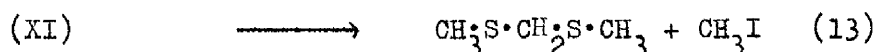
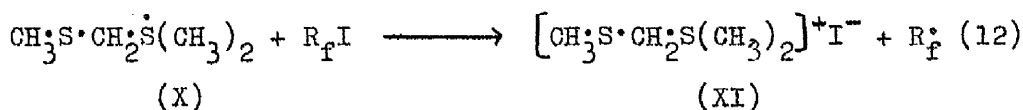
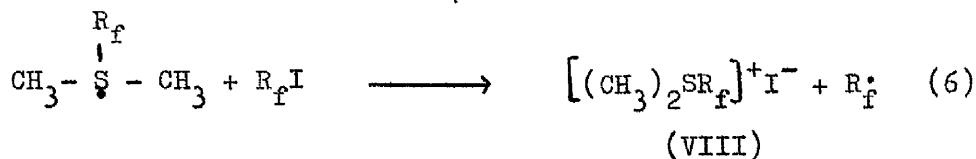
The modified reaction schemes (A' and B') are given below.

Scheme A'



Scheme B'

The steps up to the formation of the expanded radical (X) are the same as those for scheme A', and these are followed by:



Both schemes (A' and B') require that hydrogen abstraction by the polyfluoroalkyl radical (equation 8) competes with attack on the sulphur atom (equation 2). The methylthiomethyl radical (IX) formed by hydrogen abstraction may then attack another molecule of dimethyl sulphide to produce a radical (X) with an expanded valence shell. In scheme A', radical (X) dissociates to give a methyl radical and bis(methylthio)methane. The methyl radical may then either abstract a hydrogen atom to give methane, or an iodine atom to give iodomethane. The high yields of trimethylsulphonium iodide show the latter process is much preferred. In scheme B', radical (X) abstracts an iodine atom from the polyfluoromonoiodoalkane to give the complex sulphonium iodide (XI), which then dissociates into bis(methylthio)methane and iodomethane.

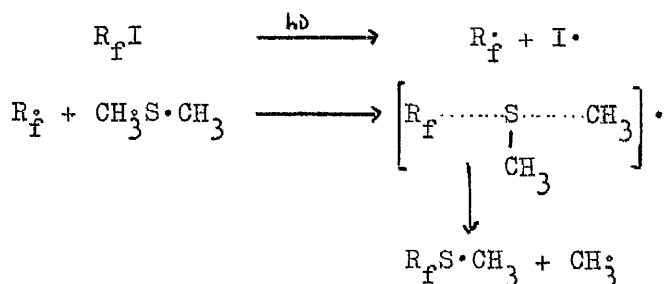
The formation of the methyl polyfluoroalkyl sulphides is believed to occur as originally proposed (schemes A and B).

It is proposed (equations 8 and 11) that hydrogen abstraction occurs from the dimethyl sulphide rather than from the methyl groups of the polyfluoroalkyl sulphide. Attack on the polyfluoroalkyl sulphide is not favoured because:

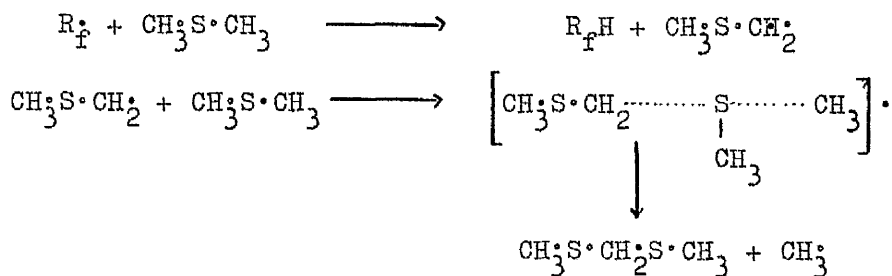
- (i) the dimethyl sulphide is present in excess, and  
 (ii) stabilisation of the resultant radical,  $R_fS\cdot CH_2$ , by  $\pi$ -bond formation between the sulphur and carbon atoms would be less than for the radical  $CH_3S\cdot CH_2$ , due to deactivation of the sulphur atom, in the former case, by the inductive effect of the polyfluoroalkyl group.

A third reaction scheme, C, which would explain the observed products involves an SH2 attack by the polyfluoroalkyl radical on the sulphur atom. This terminology was suggested by Eliel<sup>82</sup> to represent the homolytic equivalent of a bimolecular nucleophilic substitution reaction (SN2). Bimolecular homolytic substitution is believed to be the mechanism by which radical attack on disulphides occurs<sup>83</sup> (see p.56).

Scheme C

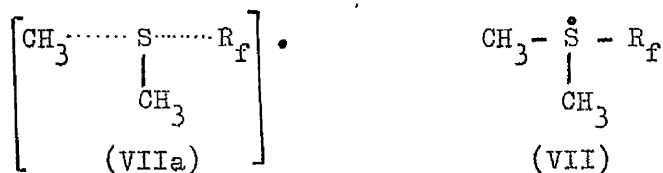


The formation of bis(methylthio)methane may be explained by a similar process,

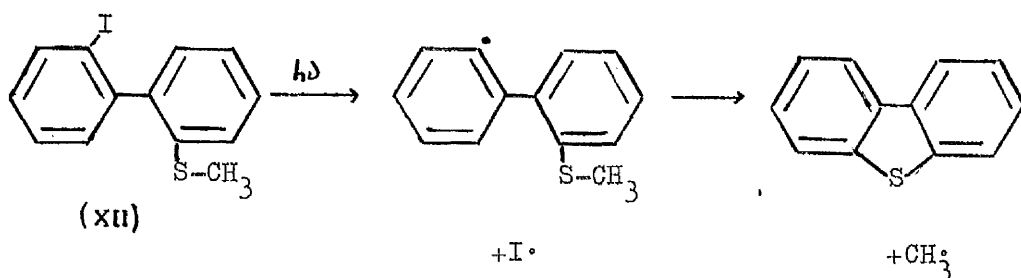


Mechanism C differs from mechanism A' in that the intermediate radical (VII) proposed in the latter is considered, in the former, to

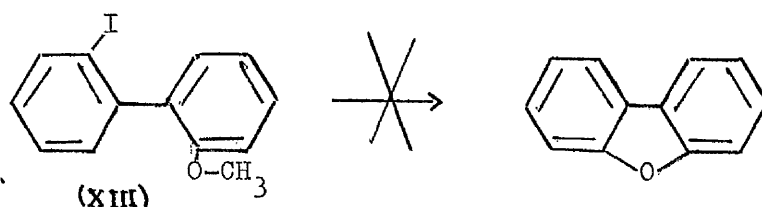
be a transition state (VIIa), i.e.,



In a study of the free-radical addition of trifluoroiodomethane<sup>30</sup> to trifluoroethylene in diethyl ether, Higginbottom<sup>30</sup> observed that the trifluoroiodomethane did not, in contrast to the reaction in dimethyl sulphide, react with the solvent. Similarly it has been shown that irradiation of 2-iodo-2'-methylthiobiphenyl (XII) in benzene solution gives a quantitative yield of dibenzothiophene; a free-radical mechanism has been proposed.



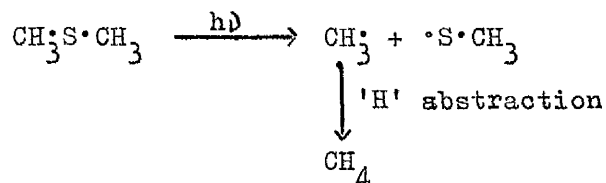
In contrast the corresponding methoxy compound (XIII) did not form dibenzofuran under similar conditions.



The failure of ethers to react under the same conditions as sulphides suggests the latter react through an expanded radical using the d orbitals of sulphur. Although indicative this evidence cannot be considered conclusive, since the C - O bond is stronger than the C - S bond. Therefore the successful reaction of sulphides, under conditions where ethers fail to react, may be a reflection of a

difference in bond strength rather than evidence in favour of an expanded radical. However, for simplicity mechanism C will not be considered further.

Returning to a consideration of mechanisms A' and B', it is not possible to distinguish between these mechanisms on the basis of the present evidence. The detection of methane in the reaction products could be cited as evidence against mechanism B', since this mechanism precludes the formation of methyl radicals. On the other hand an intensive study of the photochemical decomposition of dimethyl sulphide has shown that methane is one of the products. It is therefore possible that the small amounts of methane detected in the present work could arise from the photolytic decomposition of dimethyl sulphide, i.e.,



In view of the small quantities of methane detected (<5%), coupled with the uncertainty of its mode of formation, it is proposed to ignore its presence in the next section which is devoted to a comparison of experimental results with theoretical predictions.

Both mechanisms A' and B' require:

- (i) the only fluorine-containing products are the methyl polyfluoroalkyl sulphide and the H-polyfluoroalkane,
- (ii) the molar quantity of trimethylsulphonium iodide formed is equal to the molar quantity of polyfluoromonoiodoalkane consumed, and

(iii) the molar quantity of H-polyfluoroalkane formed is equal to the molar quantity of bis(methylthio)methane formed.

The results in Table 6 show that the first condition is mainly satisfied since the methyl polyfluoroalkyl sulphides and H-polyfluoroalkanes account for 91-98% of the polyfluoromonoiodoalkanes consumed. Trace quantities of compounds, believed to be formed by dimerisation of the polyfluoroalkyl radicals, were detected, as were trace quantities of silicon tetrafluoride and carbon monoxide. The latter compounds are decomposition products and may be explained by the reaction of polyfluoroalkyl radicals with the walls of the vessel and with small quantities of oxygen and water adsorbed on the walls.

86,87

TABLE 6

Reactions of polyfluoromonoiodoalkanes with dimethyl sulphide

$R_fI$	Irradiation period (days)	Extent of reaction (%)	*+Products, % yield			
			$R_fSMe$	$R_fH$	$Me_3S^+I^-$	$(MeS)_2CH_2$
$CF_3I$	14	100	63	33	87	24
$CF_3CF_2CF_2I$	28	100	50	46	91	29
$(CF_3)_2CFI$	24	78	32	66	92	53
$CF_2ClCF_2I$	28	100	45	52	86	25
$(CF_3)_2CF(CF_2)_4I$	28	83	46	45	83	15

\*Yields are based on polyfluoromonoiodoalkane consumed; the yields of methane have not been included because this was always contaminated with small amounts of carbon monoxide. However, the yields of methane were always low (<5%).

+Theoretically:  $yield\ of\ R_fSMe + R_fH = 100\%$   
 $yield\ of\ (Me_3S)^+I^- = 100\%$   
 $yield\ of\ R_fH = yield\ of\ (MeS)_2CH_2$

The second condition is also largely satisfied, the discrepancies may be explained by mechanical losses during the isolation of the trimethylsulphonium iodide.

The lack of correlation between the yield of 1H-polyfluoroalkane and the yield of bis(methylthio)methane isolated may be due, at least in part, to the difficulty of isolating small quantities of high-boiling liquids. In all of the reactions small quantities of tar remained in the reaction tubes and this probably contained some bis(methylthio)methane. Another possibility is that a certain fraction of the methylthiomethyl radicals,  $\text{CH}_3\text{S}\cdot\text{CH}_2$ , generated, reacted to give high-boiling products other than bis(methylthio)methane. This is consistent with the presence of tar in the reaction tube, and with the fact that the photochemical decomposition of dimethyl sulphide<sup>85</sup> was reported to give small quantities of involatile products which were not isolated in the present work.

a) Comparison of reactivities. An accurate comparison of the reactivities of the various polyfluoromonoiodoalkanes toward dimethyl sulphide is not justified because, in the present work, one of the primary objectives was to prevent excessive tar formation rather than to ensure that all the reactions received the same irradiation time. Despite the inexactitudes it is clear from Table 6 that trifluoroiodomethane reacted faster than the other polyfluoromonoiodoalkanes and that the yield of methyl trifluoromethyl sulphide is higher than those of the other methyl polyfluoroalkyl sulphides. A possible explanation for this is that the trifluoromethyl radical is less bulky than the other polyfluoroalkyl radicals and therefore the formation of the expanded radical (VII) would, in the former case, be less subject to steric inhibition. This would result in a faster attack on the sulphur atom and hence a reduction in the amount of hydrogen abstraction.

The lowest yield of methyl polyfluoroalkyl sulphide obtained, in the present work, was from the reaction of heptafluoro-2-iodopropane. This agrees reasonably well with the suggested steric inhibition, because the radical,  $(\text{CF}_3)_2\text{CF}\cdot$ , derived from this iodoalkane is a secondary radical and therefore probably more subject to steric interference than even the pentadecafluoro-5-methylhexyl radical,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\cdot$ .

In all the reactions trimethylsulphonium iodide was the only sulphonium iodide isolated. However, it might have been expected that toward the end of the reactions, when appreciable quantities of methyl polyfluoroalkyl sulphides were present, that these could compete with the dimethyl sulphide for the iodomethane generated. The failure to detect any dimethylpolyfluoroalkylsulphonium iodide may be due to deactivation of the sulphur atom by the inductive effect of the polyfluoroalkyl group (see p. 17). A comparison of the relative reactivities of dimethyl sulphide and methyl trifluoromethyl sulphide toward iodomethane was made; methyl trifluoromethyl sulphide was selected because this was the closest sulphide in size to dimethyl sulphide. The comparison showed that dimethyl sulphide and iodomethane reacted immediately in the dark, whereas no significant reaction between trifluoromethyl sulphide and iodomethane occurred after six months under the same conditions.

2. Polyfluorodiiodoalkanes. The two polyfluorodiiodoalkanes used showed a marked difference when irradiated in the presence of excess dimethyl sulphide. Thus the only product identified in the reaction of tetrafluoro-1,2-diiodoethane was tetrafluoroethylene (90% yield), whereas octafluoro-1,4-diiodobutane gave a number of products including polyfluoroalkyl sulphides (Table 7).



TABLE 7

Products from the reaction of octafluoro-1,4-diiodobutane with  
dimethyl sulphide

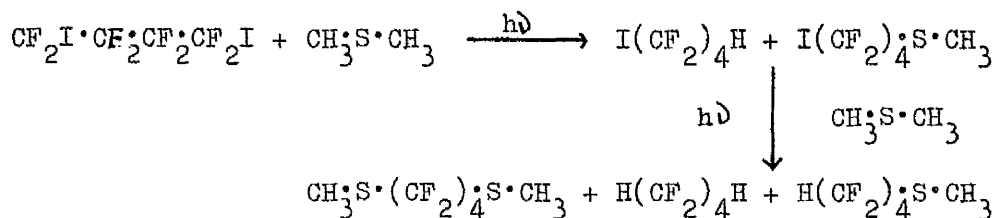
Product*	Yield %	Product*	Yield %
$C_2F_4$	trace	$H(CF_2)_4SMe$	6
$SiF_4$	trace	$MeS \cdot CH_2SMe$	54
$H(CF_2)_4H$	2	$MeS \cdot (CF_2)_4SMe$	2
$H(CF_2)_4I$	42	$(Me_3S)^+I^-$	90
$I(CF_2)_4SMe$	44	$CH_4$	trace

\*Theoretically total yield of octafluorobutyl compounds = 100%

yield of  $(Me_3S)^+I^-$  = 100%

yield of hydrogen abstraction products = yield of  $MeS \cdot CH_2SMe$

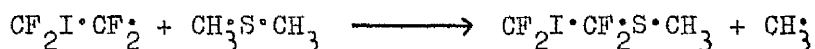
The formation of these products can be explained by similar mechanisms to those proposed for the reaction of polyfluoromonoiodoalkanes with dimethyl sulphide, e.g.,



Methyl 4H-octafluorobutyl sulphide,  $H(CF_2)_4S \cdot CH_3$ , was not positively identified but its identity was inferred from its g.l.c. elution order.

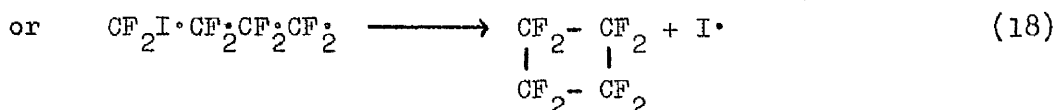
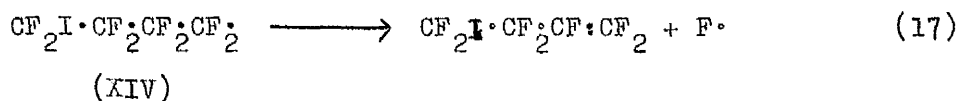
The differences in the products obtained from the reactions of the two polyfluorodiiodoalkanes may be rationalised in terms of the two intermediate radicals,  $CF_2I \cdot CF_2 \cdot$  and  $CF_2I \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot$ , formed by loss of an iodine atom. The radical,  $CF_2I \cdot CF_2 \cdot$ , derived from tetrafluoro-1,2-diiodoethane could attack dimethyl sulphide as predicted

by the mechanisms A' and B' previously described, e.g. (mechanism A'),



However this would necessitate breaking the fairly strong C - S bond, whereas expulsion of the second iodine atom, to give the observed tetrafluoroethylene, would only require fission of the relatively weak C - I bond.

The radical (XIV) derived from octafluoro-1,4-diiodobutane could theoretically stabilise itself in a number of ways, e.g.,



The first proposal (equation 17) seems improbable in view of the high strength of the C - F bond. The absence of the perfluorocyclobutane predicted by equation (18) is not as readily explained. It is possible that the negative entropy change necessary for the formation of a cyclic transition state precludes the formation of perfluorocyclobutane from radical (XIV) in favour of attack on the sulphur atom.

An alternative fate for radical (XIV) is loss of the second iodine atom to form a diradical (XV).



The latter could then cyclise to give perfluorocyclobutane, but this reaction would be subject to the same objection as raised against equation (18). The remaining possibility for the diradical (XV) is the formation of tetrafluoroethylene by homolytic fission of the 2,3-C - C bond, i.e.,

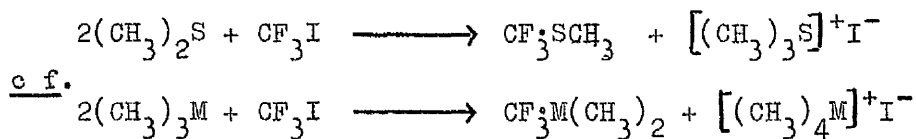


This process was considered to be unfavourable, however, the presence of trace amounts of tetrafluoroethylene and silicon tetrafluoride in the reaction products indicated a small amount of C - C bond fission had occurred.

In summary, the postulated intermediate radical,  $\text{CF}_2\text{I}\cdot\text{CF}_2^\bullet$ , obtained on irradiation of tetrafluoro-1,2-diiodoethane, stabilises itself by loss of the second iodine atom rather than by attack on the dimethyl sulphide. The radical,  $\text{CF}_2\text{I}\cdot\text{CF}_2\text{CF}_2\text{CF}_2^\bullet$ , derived from octafluoro-1,4-diiodobutane, however, is unable to stabilise itself easily by an intramolecular process and therefore attacks the dimethyl sulphide.

#### Reactions Related to the Photochemical Reaction of Dimethyl Sulphide with Polyfluoromonoiodoalkanes

1. General. The reaction of polyfluoromonoiodoalkanes with dimethyl sulphide is stoichiometrically similar to the reaction of trifluoro-<sup>88</sup>iodomethane with trimethylphosphine, -arsine, or -stibine, e.g.,



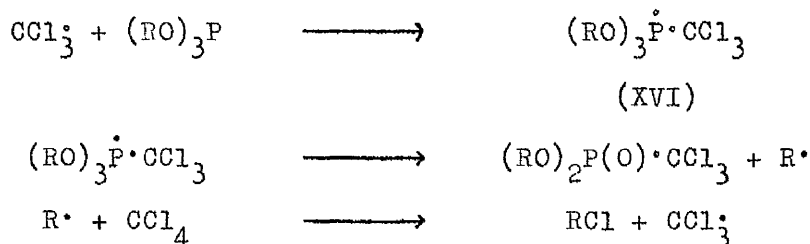
(where M = P, As, or Sb)

However, the latter reaction is probably ionic since it occurs rapidly and in the dark, whereas trifluoroiodomethane and dimethyl sulphide do not react under these conditions.

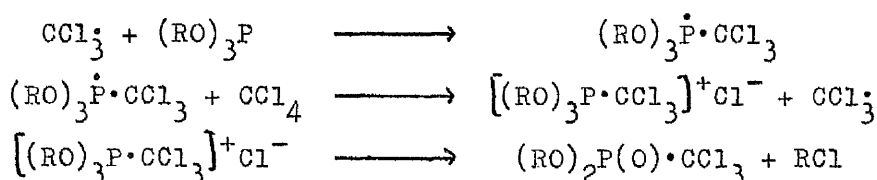
The reaction between carbon tetrachloride and trialkylphosphites, in the presence of benzoyl peroxide or ultraviolet light, is similar to the reaction of polyfluoromonoiodoalkanes with dimethyl sulphide in that the first step requires the formation of a phosphoranyl radical (XVI) with nine electrons in its valence shell. The following

reaction schemes have been proposed to explain the products:

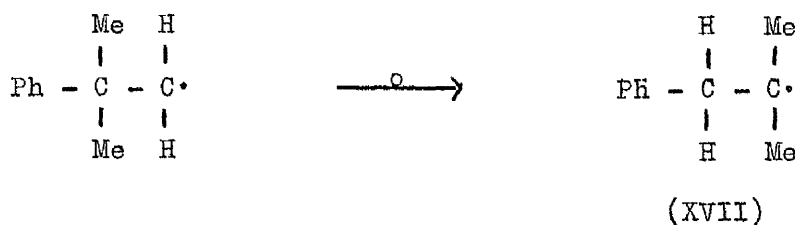
Scheme D



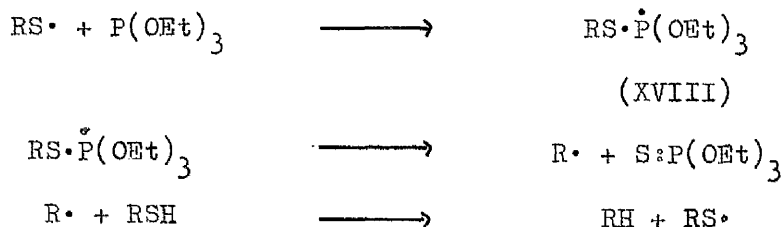
Scheme E



Cadogan proposed that the reaction of 2,2-dimethylphenethyl diethyl phosphite proceeded via scheme E because  $\beta,\beta$ -dimethylphenethyl chloride, or products derived from the readily formed rearranged radical (XVII), were not detected.



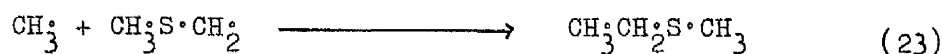
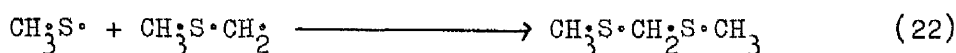
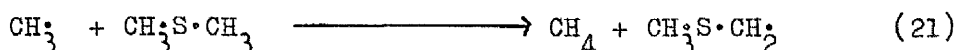
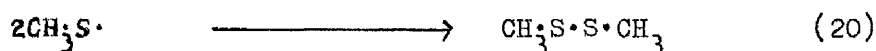
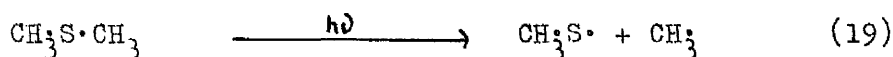
However the reaction of thiyl radicals with trialkyl phosphites is believed to involve decomposition of the intermediate phosphoranyl radical (XVIII).



Although free-radical displacements on disulphides are well known (p. 53), displacements on sulphides are rare. The reaction of phenyl radicals with *t*-butyl sulphide, for example, gives a number of

products which are believed to be formed via hydrogen abstraction rather than by free-radical displacement on sulphur.<sup>91</sup> Indeed the previously mentioned reaction of 2-iodo-2'-methylthiobiphenyl to give dibenzothiophene was claimed to be the first observed free-radical displacement on a sulphide.<sup>84</sup>

Of particular relevance to the reaction of polyfluoromonoiodoalkanes with dimethyl sulphide is the photochemical decomposition of dimethyl sulphide.<sup>85</sup> A free-radical mechanism has been proposed which requires a series of radical recombinations. In view of the large number of products obtained from this reaction only the major ones will be considered and related to the photochemical reaction of polyfluoromonoiodoalkanes with dimethyl sulphide. A simplified reaction scheme is given below.



It is apparent from the above reaction scheme, that the methane and bis(methylthio)methane detected in the present work could have arisen, at least in part, from the photolytic decomposition of dimethyl sulphide without the participation of polyfluoroalkyl radicals. The absence of significant quantities of methyl ethyl sulphide and dimethyl disulphide in the present work does not preclude this possibility because:

- (i) it was subsequently shown that dimethyl disulphide reacts with polyfluoroalkyl radicals to give the corresponding methyl polyfluoroalkyl sulphides, and

(ii) the methyl radicals necessary for the formation of methyl ethyl sulphide (equation 23) would preferentially abstract an iodine atom from the polyfluoromonoiodoalkane present to give iodomethane.

In connection with the last point, the presence of methane in the present reaction products shows that iodine abstraction by the methyl radicals does not occur exclusively. However, the ratio of trimethylsulphonium iodide to methane was always of the order of 20 : 1 which indicated that iodine abstraction by the methyl radicals was a far more favoured process than hydrogen abstraction.

In summary, the amount of independent photolytic dissociation, which probably occurs in the reaction of polyfluoromonoiodoalkanes with dimethyl sulphide, has not been assessed. However, for simplicity, this dissociation will be ignored in future discussions unless considered particularly pertinent.

2. Photochemical Reaction of Methyl Ethyl Sulphide with Heptafluoro-1-iodopropane. In this, and all future discussions, the heptafluoropropyl group,  $\text{CF}_3\text{CF}_2\text{CF}_2$ , is represented as  $\text{C}_3\text{F}_7$ .

The mechanisms proposed for the reaction of polyfluoromonoiodoalkanes with dimethyl sulphide are believed to operate in this reaction. However, the larger number of products obtained in this reaction indicates that secondary reactions play an important role. The fluorine-containing products obtained from the reactions of heptafluoro-1-iodopropane, both with dimethyl sulphide and with methyl ethyl sulphide, are shown in Table 8.

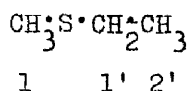
TABLE 8

Comparison of the reactions of dimethyl sulphide and methyl ethyl sulphide with heptafluoro-1-iodopropane

Sulphide	Irradiation period (days)	Extent of reaction (%)	*Products, yield %			
			C <sub>3</sub> F <sub>7</sub> H	C <sub>3</sub> F <sub>7</sub> SMe	C <sub>3</sub> F <sub>7</sub> SEt	C <sub>3</sub> F <sub>7</sub> Et
Me <sub>2</sub> S	28	100	46	50	-	-
MeSEt	49	95	58	7	21	6

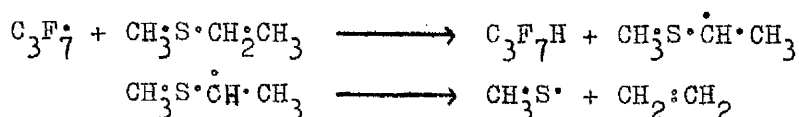
\*Other products obtained from the methyl ethyl sulphide reaction were: methane, ethane, ethylene, iodoethane, dimethyl sulphide, diethyl sulphide, a trialkylsulphonium iodide, unidentified high-boiling liquids, and a tar.

The results show that more hydrogen abstraction occurred in the methyl ethyl sulphide reaction than in the dimethyl sulphide reaction. This is consistent with the greater number of hydrogen atoms and the presence of a secondary carbon atom (1') in the former sulphide. It is likely that hydrogen abstraction would occur mainly at carbon atoms 1 and 1' (XIX) to form the more stable radicals.



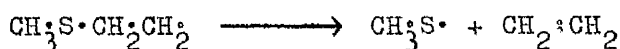
(XIX)

Attack at position 1' would be most preferred since the radical produced will have additional stabilisation from the 2' methyl group. The radical formed by hydrogen abstraction at the 1' position is the putative source of certain of the other products observed in the reaction, e.g.,

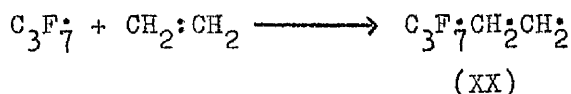


Attack at the 2' position would also give ethylene but this is

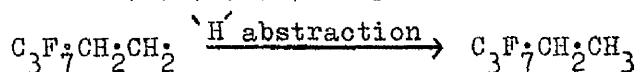
considered a less likely source.



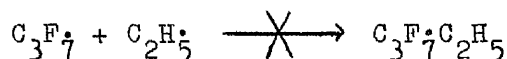
The ethylene formed may undergo attack by the heptafluoropropyl radical,



and the intermediate radical (XX) may then abstract a hydrogen atom to give the observed 1,1,1,2,2,3,3-heptafluoropentane.



The absence of any 1,1,1,2,2,3,3-heptafluorobutane in the reaction products indicates that the 1,1,1,2,2,3,3-heptafluoropentane is formed by attack on ethylene rather than by a free-radical combination process, e.g.,



The radical (XX) may also attack the sulphur atom to give the corresponding methyl or ethyl polyfluoroalkyl sulphide, e.g.,



or alternatively abstract an iodine atom,



However, it was expected that such products would be high-boiling liquids, in low yields, for which separation and identification would be difficult. Consequently no attempt was made to determine their presence.

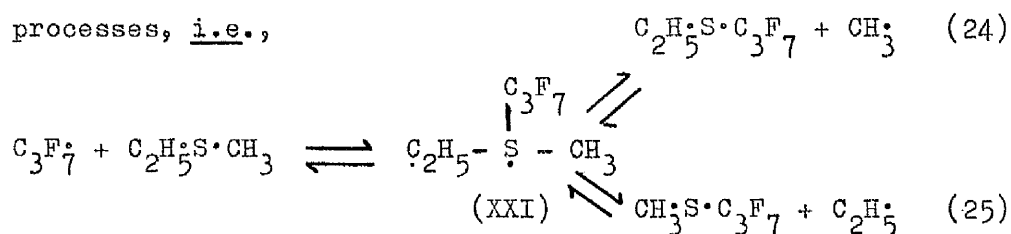
In addition to the preceding observations, the photochemical reaction of methyl ethyl sulphide with heptafluoro-1-iodopropane gave the following interesting results:

(i) the products methyl heptafluoropropyl sulphide and ethyl

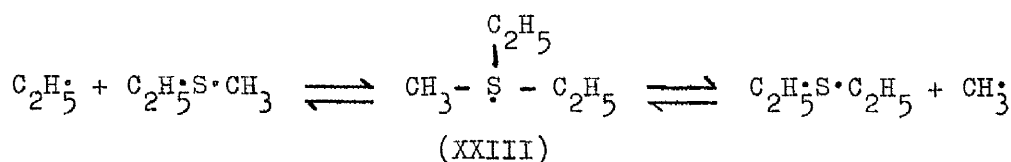
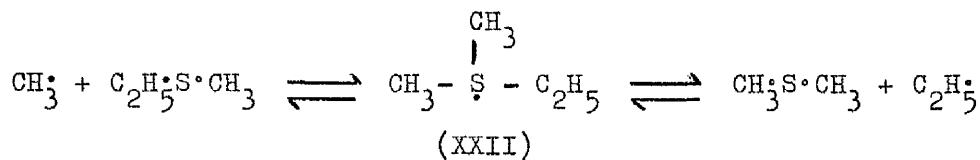


- heptafluoropropyl sulphide were present in the ratio 1:3, (ii) dimethyl sulphide and diethyl sulphide were present in the products, (iii) a small quantity of iodoethane was present, but iodo-methane was not detected in the products, and (iv) the analysis figures for the trialkylsulphonium iodide (C, 17.8; H, 4.2; I, 63.7%) correspond to those required for trimethylsulphonium iodide (C, 17.8; H, 4.2; I, 62.4%) rather than to those required for a mixture of methyldiethyl- and dimethylethylsulphonium iodides.

These observations may be rationalised by considering that the formation and decomposition of the expanded radical (XXI) are equilibrium processes, i.e.,

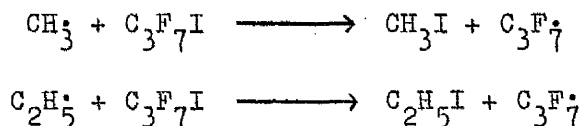


The methyl and ethyl radicals formed by decomposition of (XXI), apart from undergoing the reverse reaction, may either abstract an iodine atom or attack another molecule of methyl ethyl sulphide to give the expanded radicals (XXII) and (XXIII). These may decompose to give the observed dimethyl and diethyl sulphides.

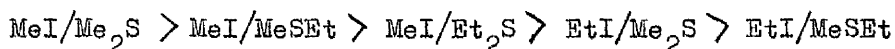


The most favourable alternative fate for the methyl and ethyl

radicals is iodine-abstraction, i.e.,



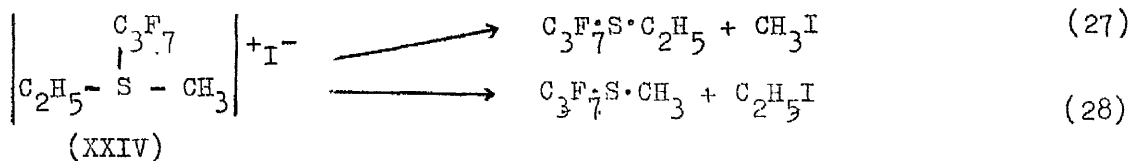
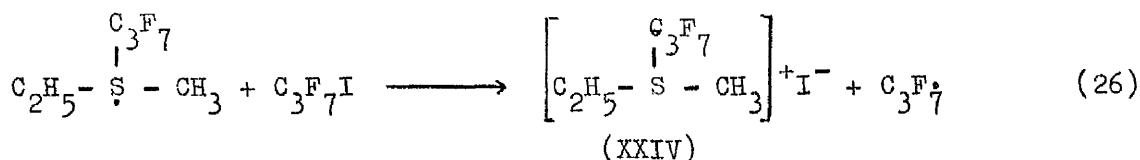
Now it is known that dialkyl sulphides react with iodoalkanes to give trialkylsulphonium iodides. The order of reactivity of certain iodoalkanes and dialkyl sulphides is given by the following sequence. 80



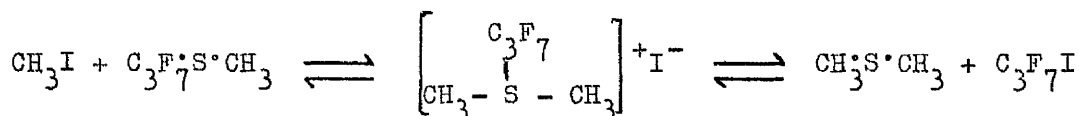
It is evident from this order of reactivity, that any dimethyl sulphide and iodomethane formed in the present reaction will react faster than any other combination of iodoalkane and dialkyl sulphide. Consequently trimethylsulphonium iodide will be formed in preference to any other trialkylsulphonium iodide. Further, the relatively fast reaction of dimethyl sulphide and iodomethane will cause the methyl radicals generated by the decomposition of the expanded radical (XXI) (equation 24) to be removed more rapidly than the ethyl radicals (equation 25). In consequence the equilibrium of the decomposition of the expanded radical (XXI) shown in equation (24) will be shifted further to the right (thus favouring the formation of ethyl heptafluoropropyl sulphide) compared with the equilibrium shown in equation (25). Hence ethyl heptafluoropropyl sulphide will be formed in preference to methyl heptafluoropropyl sulphide.

The above explanation presupposes that the formation of the products proceeds via the decomposition of the expanded radical (XXI). This is analogous to scheme A' proposed for the reaction of poly-fluoromonoiodoalkanes with dimethyl sulphide. However, it is also possible that the expanded radical abstracts an iodine atom to form an intermediate sulphonium iodide (XXIV) and that the products are

formed by the decomposition of the latter (analogous to scheme B'),  
i.e.,

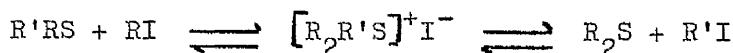


It has been shown in the present work that methyl trifluoromethyl sulphide does not react with iodomethane to give the corresponding sulphonium iodide. It therefore appears unlikely that equations (27) and (28) are reversible, hence reactions of the type,



will not occur. Consequently this mechanism as written, does not permit the formation of dimethyl sulphide, diethyl sulphide, or trimethylsulphonium iodide, nor does it explain why the yield of ethyl heptafluoropropyl sulphide is greater than that of methyl heptafluoropropyl sulphide.

Unfortunately the above arguments are only simplifications since it is probable that methyl ethyl sulphide dissociates on irradiation. Similarly the iodoalkanes formed in the reaction are known to <sup>92</sup>dissociate on irradiation, but in view of the low concentration of iodoalkanes, the effect of this would probably be small. In addition to these free-radical dissociations, trialkylsulphonium iodides are known to be <sup>in</sup>equilibrium with their components, <sup>93</sup>



It is therefore possible that trialkylsulphonium iodides, other than trimethylsulphonium iodide, could have been formed during the reaction, particularly in the early stages when the concentration of dimethyl sulphide was low, i.e.



However, these sulphonium iodides may have decomposed during the long reaction period (49 days) with the eventual formation of trimethylsulphonium iodide.

The full effect of these factors on the proposed reaction mechanisms is not known, but it can be shown that they may, in part, provide alternative explanations for certain of the observed products.

The results in Table 8 also show that heptafluoro-1-iodopropane reacts faster with dimethyl sulphide than with methyl ethyl sulphide. It is not possible to unequivocally explain this observation, since the rate-determining steps in the reactions are not known. However, it is probable that the differences in rate may be partly attributed to steric factors. The slow reaction of methyl ethyl sulphide may also be partly explained by the fact that appreciable quantities of tar were observed on the walls of the vessel during the reaction. This would have decreased the intensity of the radiation and would, consequently, retard the reaction.

3. Photochemical Reaction of Methyl Trifluoromethyl Sulphide with Heptafluoro-1-iodopropane. The products obtained from this reaction are presented in Table 9 together with the results obtained from the corresponding reaction of heptafluoro-1-iodopropane with dimethyl sulphide.

TABLE 9

Comparison of the reactions of heptafluoro-1-iodopropane with dimethyl sulphide and with methyl trifluoromethyl sulphide

Reactants (mole ratio)	Irradiation period (days)	Extent of reaction (%)	*Products, yield %		
			$C_3F_7SMe$	$C_3F_7H$	$C_6F_{14}$
$C_3F_7I$ , $Me_2S$ (1.0) (4.3)	28	100	50	46	trace
$C_3F_7I$ , $CF_3SMe$ (1.0) (1.8)	35	43	51	24	20

\*Other products from the methyl trifluoromethyl sulphide reaction were: trifluoroiodomethane (64%), trifluoromethane (trace), perfluorobutane (trace), and a trace of tar.

These results show that the methyl trifluoromethyl sulphide reaction differed from the dimethyl sulphide reaction in that:

- (i) attack on methyl trifluoromethyl sulphide was slower,
- (ii) despite the slower attack on the sulphur atom, the amount of hydrogen abstraction decreased; however, the yield of the dimerisation product, perfluorohexane, increased, and
- (iii) apart from the starting material, methyl trifluoromethyl sulphide, the only sulphide present in significant quantities was methyl heptafluoropropyl sulphide.

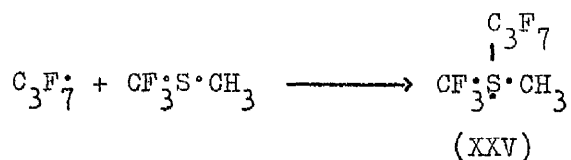
The first two points may be explained by the fact that the trifluoromethyl group withdraws electron density from the sulphur atom; this, coupled with the slightly greater size of the trifluoromethyl group, makes attack by the heptafluoropropyl radical on the sulphur atom more difficult. This does not lead to an increase in hydrogen abstraction by the radical, partly because of the presence of fewer hydrogen atoms in methyl trifluoromethyl sulphide relative to dimethyl

sulphide, and partly because of the withdrawal of electron density from the sulphur atom. The latter factor renders the radical formed by hydrogen abstraction from methyl trifluoromethyl sulphide less stable than that formed from dimethyl sulphide (see p.28 ). The slower attack on methyl trifluoromethyl sulphide will thus lead to an increase in dimerisation of the heptafluoropropyl radicals,

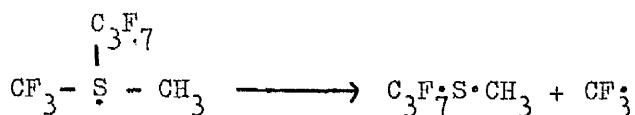


This tendency for dimerisation will be increased by the relatively low ratio of sulphide to heptafluoro-1-iodopropane compared with the corresponding reaction of dimethyl sulphide (1.8 : 1 compared with 4.3 : 1),

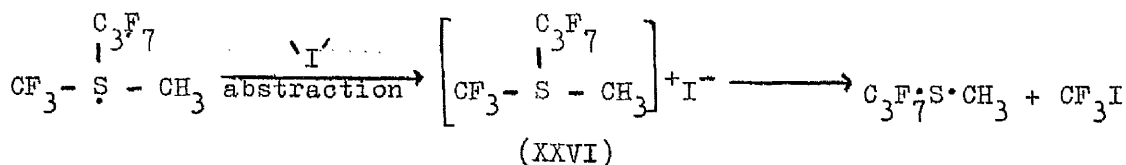
The absence of any sulphides apart from the starting material and methyl heptafluoropropyl sulphide has interesting implications if it is assumed that this reaction proceeds, initially at least, by similar routes to the dimethyl sulphide reaction. The two most probable schemes are given below.



Followed by EITHER

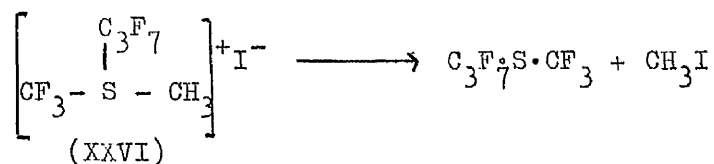


OR



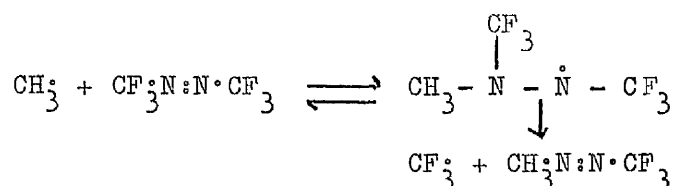
The postulated intermediate sulphonium iodide (XXVI) would

presumably decompose by nucleophilic attack of iodide ion upon one of the  $\alpha$ -carbon atoms. It seems improbable that attack would occur on a carbon atom in one of the fluoroalkyl chains because of the shielding effect of the fluorine atoms. On the other hand nucleophilic attack on the carbon atom of a methyl group is well known. On the basis of this reasoning intermediate (XXVI) should decompose to give iodomethane and trifluoromethyl heptafluoropropyl sulphide, i.e.,



However, these predicted products were not detected, and therefore it seems unlikely that the reaction proceeds via intermediate (XXVI).

If the methyl heptafluoropropyl sulphide observed in this reaction were formed by the decomposition of the expanded radical (XXV), it would be necessary to propose that, in the expanded radical, the  $\text{CF}_3 - \text{S}$  bond is cleaved more readily than the  $\text{CH}_3 - \text{S}$  bond. In this connection it is worthwhile to consider the reaction of methyl radicals with hexafluoroazomethane,  $\text{CF}_3\text{:N:N}\cdot\text{CF}_3$ , where it was found that methyl radicals partially displaced one of the trifluoromethyl groups. The authors proposed the following reaction scheme,<sup>94</sup>



in which it was required that the  $\text{CF}_3 - \text{N}$  bond should be weaker than the  $\text{CH}_3 - \text{N}$  bond for the second step to occur.

Consideration of the expanded radical (XXV) shows that fission of a  $\text{R}_f - \text{S}$  bond rather than a  $\text{CH}_3 - \text{S}$  bond could be favoured because of the greater electrostatic repulsions between two polyfluoroalkyl

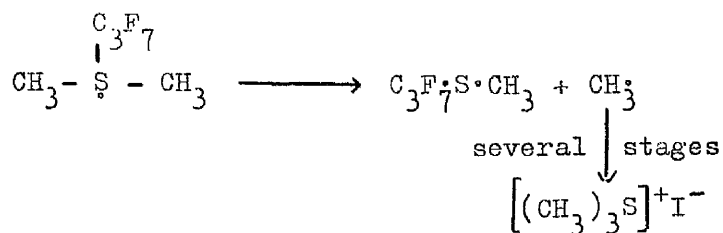
groups than between a polyfluoroalkyl and a methyl group. On the basis of this reasoning it would not be expected that any sulphide with two polyfluoroalkyl groups would be formed in the reaction; this is in accord with the experimental observations.

If, as inferred from the above reaction, the  $R_F-S$  bond is cleaved more readily than the  $CH_3-S$  bond, then it appears anomalous that the reaction of heptafluoro-1-iodopropane with dimethyl sulphide should favour the formation of methyl heptafluoropropyl sulphide.

However, the photochemical reaction of heptafluoro-1-iodopropane with ~~methyl~~ **trifluoromethyl** sulphide differs from that with dimethyl sulphide in at least two aspects.

(i) The expanded radical derived from methyl trifluoromethyl sulphide has two polyfluoroalkyl groups and electrostatic repulsions will favour the ejection of one of them rather than a methyl group. This is not the case with the expanded radical derived from dimethyl sulphide.

(ii) In the reaction of dimethyl sulphide with heptafluoro-1-iodopropane, trimethylsulphonium iodide is formed. The effect of the formation of a stable trialkylsulphonium iodide on the decomposition of the expanded radical has been discussed in the preceding experiment. By a similar reasoning it is expected that the expanded radical, derived from dimethyl sulphide would decompose to give methyl radicals and the observed methyl heptafluoropropyl sulphide, i.e.,





In the case of the methyl trifluoromethyl sulphide reaction, a stable sulphonium iodide is not formed; therefore the mode of decomposition of the expanded radical in this reaction will not be influenced by the factors that influence the decomposition of the radical derived from dimethyl sulphide.

4. Photochemical Reaction of Bis(chloromethyl) Sulphide with Trifluoriodomethane. This reaction was disappointing from a preparative standpoint. After 84 days irradiation ca. 70% of the trifluoriodomethane was recovered. The inside of the reaction vessel was observed to be covered with a hard black deposit, which undoubtedly diminished the intensity of the radiation. Although the products were not examined in detail, i.r. spectroscopy showed the presence of chlorotrifluoromethane, carbon disulphide, hydrogen chloride, and hexafluoroethane. It was therefore concluded that the reaction was of little preparative interest and it was not investigated further.

5. Thermal Reaction of Heptafluoro-1-iodopropane with Dimethyl Sulphide. The fluorine-containing products obtained from this reaction, along with the relevant data from the photochemical reaction, are presented in Table 10.

TABLE 10

Comparison of the photochemical and thermal reactions of  
heptafluoro-1-iodopropane with dimethyl sulphide

Reaction	Time (days)	Extent of reaction (%)	*Products, yield %	
			$C_3F_7SMe$	$C_3F_7H$
thermal (170°)	3	56	16	69
photochemical	28	100	50	46

\*Both reactions also gave trace quantities of silicon tetrafluoride.

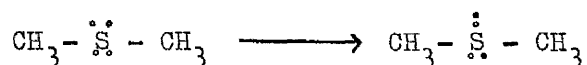
The low yield of methyl heptafluoropropyl sulphide obtained in the thermal reaction, compared to the photochemical reaction, may be explained in a number of ways.

(i) It is possible that methyl heptafluoropropyl sulphide was unstable under the reaction conditions and that once formed, it partly decomposed to 1H-heptafluoropropane. Although it was shown that methyl heptafluoropropyl sulphide is stable alone at 170°, it is not possible to predict the effect of the other components on the stability of the sulphide. Certain of these components were black intractable solids of unknown composition. The presence of small quantities of silicon tetrafluoride among the reaction products cannot be taken as evidence for the decomposition of the sulphide, since this may have arisen by decomposition of the heptafluoropropyl radicals prior to sulphide formation.

(ii) The second possibility is that the heptafluoropropyl radicals generated in the thermal reaction are more energetic

and therefore less selective than those generated in the photochemical reaction. However, work on the bidirectional additions of polyfluoroiodoalkanes to various unsymmetrical olefins has shown that the isomer ratio of the two possible 1:1 adducts, in general, shows only small variations with the method of formation of the polyfluoroalkyl radicals.<sup>95</sup>

(iii) A third possibility is that the substrate, dimethyl sulphide, may be differently activated toward radical attack in the photochemical reaction than it is in the thermal reaction. In this connection it is known that alkyl sulphides exhibit an absorption in the u.v. at ca. 210mμ. This has been attributed to promotion of one of the sulphur non-bonding electrons to a 3d orbital with the formation of a diradical, i.e.,<sup>96</sup>



It is therefore proposed that attack on the activated sulphur atom, by the heptafluoropropyl radical, is easier than attack on the sulphur atom in the ground state. It is further proposed that the energy absorbed by dimethyl sulphide in the thermal reaction does not effect an electronic transition but merely increases the vibrational energy of C - H and C - S bonds. Therefore, in view of the absence of selective excitation of the sulphur atom in the thermal reaction, the increase in the vibrational energy of the C - H bonds will favour hydrogen abstraction by the heptafluoropropyl radical.

## Photochemical Reactions of Polyfluoroiodoalkanes with Alkyl Disulphides

1. Polyfluoromonoiodoalkanes with Dimethyl Disulphide. Although the photochemical reaction of dimethyl sulphide with polyfluoromonoiodoalkanes was of mechanistic interest, the relatively low yields of polyfluoroalkyl sulphides obtained rendered the reaction unsuitable as a preparative route to these compounds. The susceptibility of the S - S<sup>83,97-99</sup> bond in disulphides to free-radical attack suggested that the reaction of alkyl disulphides with polyfluoroalkyl radicals might offer a convenient route to polyfluoroalkyl sulphides. The results (Table 11) from the photochemical reaction (21 days) of polyfluoromonoiodoalkanes with dimethyl disulphide show that this reaction gave excellent yields of the corresponding methyl polyfluoroalkyl sulphides.

The conditions in the first two experiments (Table 11) differed from the other experiments in that, in the former the upper portion of the reaction tube was 'blackened out' and the tube held vertically in front of the lamp so that only the liquid phase was irradiated. In the other experiments, the tube was held horizontally above the lamp and both the liquid and vapour phases irradiated. The difference in reaction conditions resulted in the reactants in the latter experiments being subjected to slightly more severe conditions. This caused a slight increase in the amounts of the side-products formed, e.g., methanethiol, dimethyl sulphide, carbon disulphide, and methane and a decrease in the ratio of methyl polyfluoroalkyl sulphide to H-polyfluoroalkane. However, these disadvantages were compensated for by the increased reaction rate.

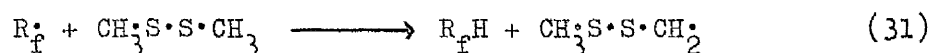
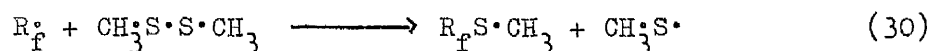
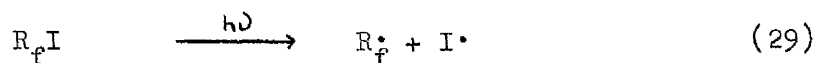
TABLE 11

Fluorine-containing products from the photochemical reactions of  
dimethyl disulphide with polyfluoromonoiodoalkanes

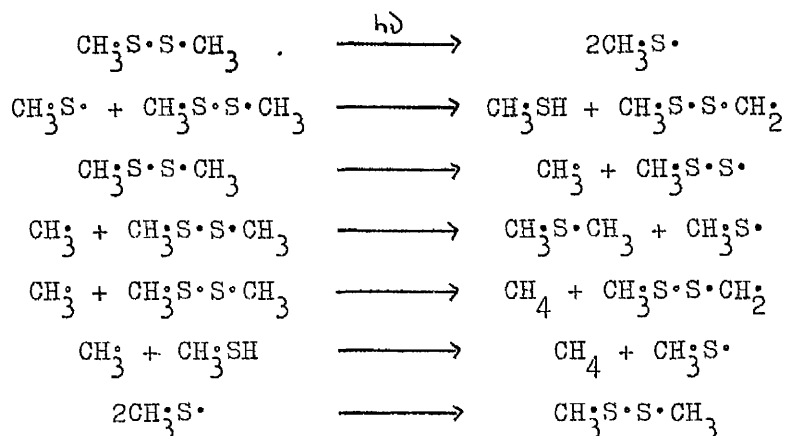
$R_fI$	Extent of reaction %	Products, yield %*	
		$R_fSMe$	$R_fH$
$CF_3I$	97	92	5
$CF_3\dot{C}F_2CF_2I$	92	93	6
$(CF_3)_2CFI$	100	83	12
$CF_2Cl\dot{C}F_2I$	100	82	14
$(CF_3)_2CF\dot{C}(CF_2)_4I$	100	80	17

\*Based on polyfluoroiodoalkane consumed.

A simplified scheme for the reaction is as follows:

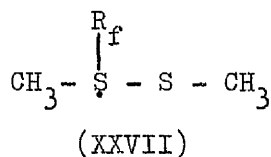


It was also observed that small quantities of side-products, arising from the decomposition of dimethyl disulphide, were also present. The formation of these was probably initiated, in part, by attack of the polyfluoroalkyl radicals on dimethyl disulphide (equations 30 and 31) and, in part, by the independent photolytic decomposition of dimethyl disulphide <sup>100</sup> (scheme F).

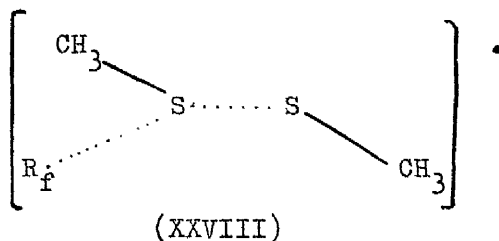
Scheme F

In addition to the products predicted by scheme F, small quantities of carbon disulphide were detected. It is very probable that other, undetected, products were present since the black, involatile oils, which were always formed in these reactions, were not examined. The methanethiol present in the reactions may have contributed to the formation of the H-polyfluoroalkanes, since it was shown, in the present work, that heptafluoropropyl radicals react readily with methanethiol to give 1H-heptafluoropropane. Fortunately the concentration of methanethiol was always low in the photochemical reactions.

The mechanism of polyfluoroalkyl radical attack on dimethyl disulphide can, as in the case of dimethyl sulphide, proceed through an expanded sulphur radical (XXVII),



or by an SH<sub>2</sub> mechanism where bond-formation and bond-breaking are concomitant (XXVIII),



Pryor has compared the rates of attack of nucleophiles and free radicals on various substrates and concludes that nucleophilic and free-radical attack on alkyl disulphides occur by a similar mechanism, i.e., by an  $\text{S}_\text{N}2$  and an  $\text{S}_\text{H}2$  attack on the sulphur atom <sup>83,97,101</sup> respectively. This inference is supported by the fact that free radicals react with benzoyl peroxide to give the corresponding ethers. Since oxygen is unable to expand its valence octet, it follows that bond-breaking and bond-making, in the formation of the ether, must be simultaneous. This reaction is used as an analogy for the free-radical attack on disulphides and is considered reasonable, though not unequivocal, evidence for an  $\text{S}_\text{H}2$  mechanism also occurring in the <sup>101</sup> latter reactions.

2. Polyfluoromonoiodoalkanes with Diethyl Disulphide. The results in Table 12 show that, although the polyfluoromonoiodoalkanes reacted with diethyl disulphide the yields of H-polyfluoroalkanes were much higher than in the corresponding reactions of diethyl disulphide (Table 11).

TABLE 12

Fluorine containing products from the reactions of diethyl disulphide  
with polyfluoromonoiodoalkanes

$*R_fI$	Products, yield %		
	$R_fSEt$	$R_fH$	$R_fEt$
$CF_3I$	43	40	7
$CF_3CF_2CF_2I$	45	41	6

\*Both reactions were carried out for 48 days and 100% reaction occurred.

The higher yields of H-polyfluoroalkanes obtained in the diethyl disulphide reactions may be explained partly in terms of the larger number of hydrogen atoms present, and partly by the fact that the carbon atom adjacent to the sulphur atom in diethyl disulphide is a secondary atom whereas that in dimethyl disulphide is only a primary carbon. In connection with the latter point Pryor has shown, using phenyl radicals and dialkyl disulphides, that hydrogen abstraction from primary and secondary carbon atoms adjacent to a sulphur atom is in the ratio,

$$\text{primary:secondary} = 1:3.2 \quad 97$$

The presence of compounds of the type  $R_fC_2H_5$  may be rationalised by similar explanations to those advanced for the formation of 1,1,1,2,2,3,3-heptafluoropentane in the photochemical reaction of heptafluoro-1-iodopropane with methyl ethyl sulphide (p. 41 ). Products which arose from the decomposition of diethyl disulphide were also observed in these reactions; this type of decomposition has already been discussed for dimethyl disulphide (p. 54 ).



3. Tetrafluoro-1,2-diiodoethane with Dimethyl Disulphide. The products obtained from this reaction are given in Table 13.

TABLE 13

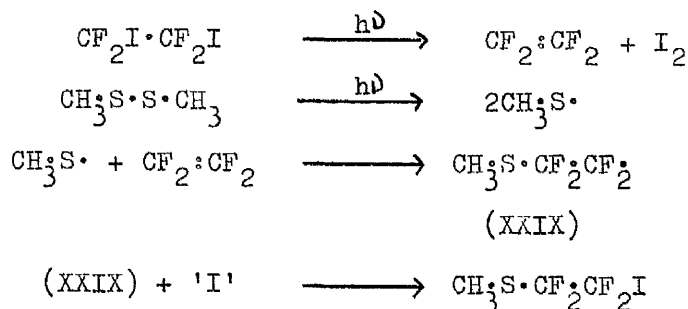
Fluorine-containing products from the photochemical reaction of tetrafluoro-1,2-diiodoethane with dimethyl disulphide

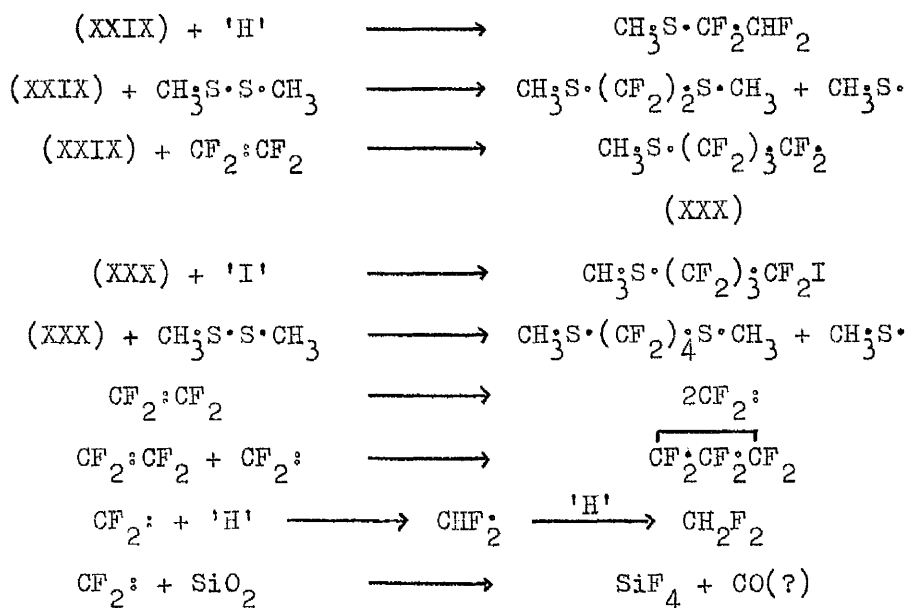
*Product	Yield %	*Product	Yield %
$C_2F_4$	5	$CF_2I \cdot CF_2S \cdot CH_3$	6
$SiF_4$	trace	$CH_3S \cdot (CF_2)_2S \cdot CH_3$	46
$CH_2F_2$	trace	$CF_2I \cdot (CF_2)_3S \cdot CH_3$	2
$CF_2CF_2CF_2$	not estimated	$CH_3S \cdot (CF_2)_4S \cdot CH_3$	15
$CHF_2CF_2S \cdot CH_3$	8		

\*In addition to the above products, decomposition products of dimethyl disulphide were detected as were small amounts of unidentified products.

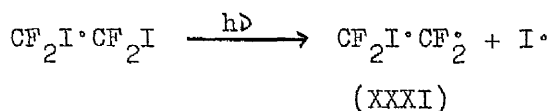
These products may be rationalised by scheme G which requires the decomposition of tetrafluoro-1,2-diiodoethane to tetrafluoroethylene followed by attack of methanethiyl radicals, arising from the photolytic decomposition of dimethyl disulphide, on the tetrafluoroethylene formed. In view of the large number of products formed, it is not possible <sup>to</sup> categorically define the sources of hydrogen and iodine for the abstraction processes. Consequently these are designated 'H' and 'I' respectively in the reaction scheme.

Scheme G



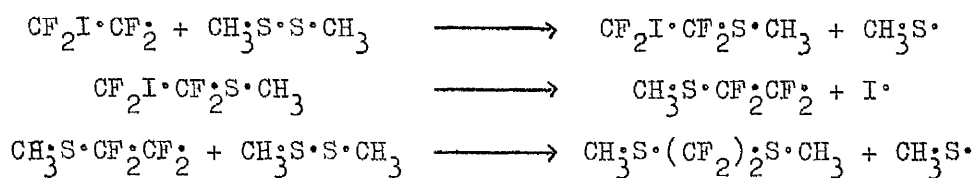


An alternative mechanism involves the initial loss of only one iodine atom, i.e.,



The intermediate radical (XXXI) may then attack dimethyl disulphide, as in the following scheme.

Scheme H



However, to explain the formation of  $\text{CH}_3\text{S}\cdot(\text{CF}_2)_4\text{S}\cdot\text{CH}_3$  and  $\text{CF}_2\text{I}\cdot(\text{CF}_2)_3\text{S}\cdot\text{CH}_3$  it is necessary to propose radical attack on tetrafluoroethylene as in scheme G.



Scheme G is preferred since in the reaction of tetrafluoro-1,2-diiodoethane, the only product isolated in significant yield, apart from tars, was tetrafluoroethylene. No evidence for anything but the most transient existence of the radical,  $\text{CF}_2\text{I}\cdot\text{CF}_2\cdot$ , was obtained. This,

however, does not completely preclude the participation of this radical in the disulphide reaction since radical displacements on sulphur in disulphides seem to occur more readily than in mono-sulphides.

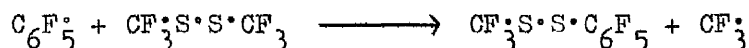
It has been reported that iodine can catalyse ionic additions<sup>102</sup> of disulphides to olefins. That this did not occur with dimethyl sulphide and tetrafluoroethylene was demonstrated by sealing dimethyl disulphide, tetrafluoroethylene, and iodine in a Pyrex tube and keeping the tube in the dark at room temperature (30 days). Tetrafluoroethylene (100%) was recovered unchanged.

#### Photochemical Reaction of Bis(trifluoromethyl) Disulphide with Pentafluoriodobenzene

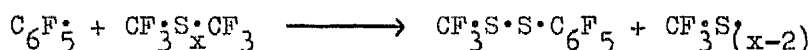
The successful preparation of methyl polyfluoroalkyl sulphides by the photochemical reaction of dimethyl disulphide with polyfluoromonoiodoalkanes suggested that this type of reaction might have further applications for the preparation of fluorine-containing sulphides. A preliminary investigation of the photochemical reaction of pentafluoriodobenzene with bis(trifluoromethyl) disulphide showed that the expected trifluoromethyl pentafluorophenyl sulphide was formed in fair yield (42%). However, in contrast to the reaction of dimethyl disulphide with polyfluoriodoalkanes, significant quantities of trifluoromethyl pentafluorophenyl disulphide (13%) were also isolated.

On the basis of the present evidence it is not possible to explain why a fluorine-containing disulphide was formed in this reaction, but not in the dimethyl disulphide reaction. However it is possible to speculate how the trifluoromethyl pentafluorophenyl disulphide might be formed. The formation of the disulphide could

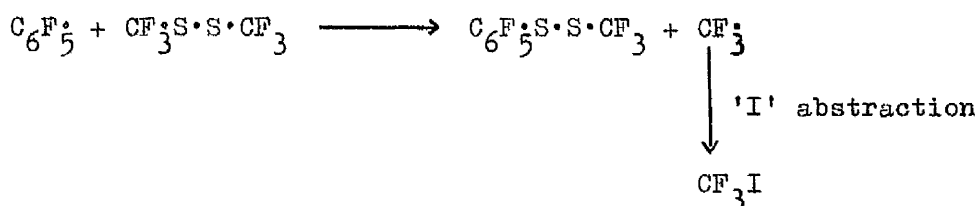
occur by attack of the pentafluorophenyl radical on bis(trifluoromethyl) disulphide with expulsion of a trifluoromethyl radical.



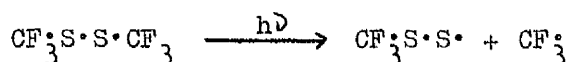
Alternatively it could be formed by attack of the pentafluorophenyl radical on one of the bis(trifluoromethyl)polysulphides believed to be formed on irradiation of bis(trifluoromethyl) disulphide. 12



The presence of trifluoroiodomethane in the reaction products suggests that the former mechanism is more likely, i.e.,



However, it is also possible that the formation of trifluoromethyl radicals is an independent process, e.g.,



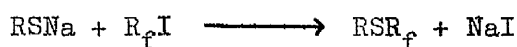
#### Comparison of the Photochemical and Thermal Reactions of Dimethyl Disulphide with Heptafluoro-1-iodopropane

The ratio of the yields of methyl heptafluoropropyl sulphide to 1H-heptafluoropropane obtained from the photochemical reaction (93:6) is significantly different from that obtained from the thermal reaction (31:61). These results are similar to those obtained from the corresponding reactions of heptafluoro-1-iodopropane with dimethyl sulphide (p. 50). However, the results from the disulphide reactions are complicated by the decomposition of dimethyl disulphide during the reactions. In the photochemical reaction the

decomposition was slight, whereas in the thermal reaction decomposition was extensive and large quantities of methanethiol were detected among the products. Because of the high reactivity of methanethiol with heptafluoropropyl radicals, it is probable that a certain proportion of the hydrogen abstraction by the heptafluoropropyl radicals occurred on the thiol. In view of the fact that the factors responsible for the high yield of methanethiol in the thermal reaction are not known, a comparison of the thermal and photochemical reactions is not justified.

#### Reactions of Heptafluoro-1-iodopropane with Sodium Alkanethiolates

It has already been suggested (p. 1 ) that reactions of the type,



where R = alkyl,

$\text{R}_f$  = polyfluoroalkyl

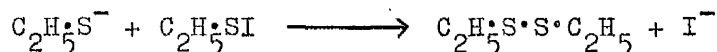
would not prove useful for the preparation of polyfluoroalkyl sulphides because polyfluoroiodoalkanes are polarised in the sense  $\delta^- \quad \delta^+$   
 $\text{R}_f - \text{I}$ . It was, nevertheless, decided to undertake preliminary investigations of this type of reaction to ascertain whether it was possible to modify the experimental conditions to induce polyfluoroalkyl sulphide formation.

In the first experiment an approximately equimolar mixture of sodium ethanethiolate and heptafluoro-1-iodopropane was heated (14 hr. at 100°) in dry dimethyl sulphoxide. After reaction 80% of the iodopropane was recovered unchanged. The product, 1H-heptafluoropropane (92% based on iodopropane consumed), indicates that this reaction is

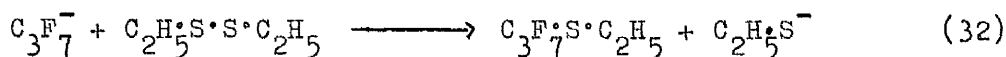
similar to the reaction of trifluoroiodomethane with alcoholic sodium hydroxide, where nucleophilic attack on the positively-polarised iodine atom is postulated to occur. On this basis it is proposed that nucleophilic attack by the ethanethiolate ion occurs on the iodine atom, i.e.,



The carbanion,  $\text{C}_3\text{F}_7^-$ , then abstracts a proton to give the observed 1H-heptafluoropropane. The source of the proton could be either the solvent, dimethyl sulphoxide, or impurities, e.g., traces of water or free ethanethiol. The fate of the ethanesulphenyl iodide formed is not known, but it is possible that it could react with a second ethanethiolate ion to give diethyl disulphide, i.e.,



It is further possible that, in addition to abstracting a proton, the heptafluoropropyl carbanion could attack any diethyl disulphide formed to give ethyl heptafluoropropyl sulphide.



However, the concentration of diethyl disulphide would be low and the results show the above reaction (equation 32) does not compete favourably with the hydrogen abstraction reaction. Nevertheless, the presence of small quantities of ethyl heptafluoropropyl sulphide could have remained undetected since the reaction products were not examined by g.l.c.

In the second reaction the possibility of the heptafluoropropyl carbanion reacting with a disulphide was investigated. Thus an approximately equimolar mixture of sodium methanethiolate and heptafluoro-1-iodopropane was heated (19 hr. at 100°) in dimethyl

sulphoxide (solvent), in the presence of excess dimethyl disulphide. The results (Table 14) show that attack by the carbanion on the disulphide occurs to give methyl heptafluoropropyl sulphide.

TABLE 14

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

Reactants (approx. mole ratio)	Extent of reaction %	Product, yield %	
		$C_3F_7SMe$	$C_3F_7H$
$C_3F_7I$ (1)  $Me_2S_2$ (6)	73	68	10

These results are not considered to realise the full potential of this reaction and it is probable that the reaction could be developed to give high yields of methyl polyfluoroalkyl sulphides.

It was considered possible, though unlikely, that the reaction could proceed via a free-radical mechanism. However, heptafluoro-1-iodopropane and dimethyl disulphide heated at  $100^\circ$  (20 hr.) did not react. This lack of reaction was considered to eliminate the possibility of a free-radical mechanism.

### Some Effects of the Polyfluoroalkyl Group on the Reactivity of Alkyl Sulphides

The reaction of alkyl sulphides with mercuric chloride to give complexes of the type  $R_2S \cdot yHgCl_2$  is believed to involve donation of an unshared electron pair on the sulphur atom.<sup>103</sup>

A series of polyfluoroalkyl sulphides were shaken with mercuric chloride at room temperature (15 hr.). After this time it was discovered that no reaction had occurred whereas a series of alkyl sulphides, treated in a similar manner, reacted almost quantitatively. The results are summarised in Tables 22 and 23 (p. 119).

The lack of reactivity of the polyfluoroalkyl sulphides may be attributed to the inductive effect of the polyfluoroalkyl group, which withdraws electron density from the sulphur atom, thus preventing the ready donation of a lone-pair of electrons to the mercury atom. The failure of methyl trifluoromethyl sulphide to react with iodomethane may be explained by similar reasoning (p. 17).<sup>20,24</sup> These results are in agreement with the findings of other authors.

### Oxidation of Polyfluoroalkyl Sulphides

The first three reagents provided excellent synthetic routes, in that reaction conditions could be so adjusted as to give only one of the possible oxidation products.

1. With Hydrogen Peroxide. The oxidations were carried out in glacial acetic acid and, depending on the ratio of peroxide to polyfluoroalkyl sulphide, either the corresponding sulfoxide or sulphone was obtained. The reactions did not give side-products but they suffered from the disadvantage that prolonged heating was required,

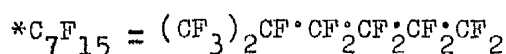


which necessitated the use of sealed tubes for low-boiling sulphides.

TABLE 15

Oxidation of polyfluoroalkyl sulphides with hydrogen peroxide

Approx. mole ratio $\text{H}_2\text{O}_2$ :sulphide	Reaction conditions	Sulphide	Product	Yield %
1:1	100°; 24 hr.	$\text{C}_3\text{F}_7\text{SMe}$	$\text{C}_3\text{F}_7\text{SOMe}$	71
9:1	100°; 216 hr.	$\text{C}_3\text{F}_7\text{SMe}$	$\text{C}_3\text{F}_7\text{SO}_2\text{Me}$	86
>10:1	reflux; 20 hr.	$^*\text{C}_{715}\text{SMe}$	$\text{C}_{715}\text{SO}_2\text{Me}$	83



2. With Fuming Nitric Acid. Oxidations with fuming nitric acid gave only the sulfoxides. These reactions were subject to the same experimental advantages and disadvantages as the hydrogen peroxide oxidations.

The first preparation of a polyfluoroalkyl sulfoxide was reported in 1965.<sup>72</sup> This involved the oxidation of methyl trifluoromethyl sulphide with concentrated nitric acid and gave a 30% yield of methyl trifluoromethyl sulfoxide. In the present work fuming nitric acid was used and the reaction period was increased. Oxidation under these conditions gave yields of ca. 70%.

TABLE 16

Oxidation of polyfluoroalkyl sulphides with fuming nitric acid

Reaction conditions	Sulphide	Product	Yield %
100°; 14 hr.	$\text{C}_3\text{F}_7\text{SMe}$	$\text{C}_3\text{F}_7\text{SOMe}$	70
100°; 14 hr.	$(\text{CF}_3)_2\text{CF}\cdot\text{SMe}$	$(\text{CF}_3)_2\text{CF}\cdot\text{SOMe}$	72

3. With Potassium Permanganate. The oxidations with potassium permanganate were carried out in glacial acetic acid and gave exclusively the sulphone. This reagent was favoured for the oxidation of low-boiling polyfluoroalkyl sulphides because oxidation occurred in the range 0-20° and so obviated the necessity of sealed-tube reactions.

TABLE 17

Oxidation of polyfluoroalkyl sulphides with potassium permanganate

Reaction conditions	Sulphide	Product	Yield %
0-20°; 5 hr.	$C_3F_7SMe$	$C_3F_7SO_2Me$	85
0-20°; 5 hr.	$(CF_3)_2CF \cdot SMe$	$(CF_3)_2CF \cdot SO_2Me$	59*
0-20°; 5 hr.	$CF_3SEt$	$CF_3SO_2Et$	78

\*The low yield obtained in this reaction is probably due to mechanical losses since only a small quantity of sulphide was used.

4. With Sodium Metaperiodate. The attempted oxidation of methyl heptafluoropropyl sulphide with aqueous sodium metaperiodate, in the temperature range 5°-20°, was unsuccessful and only unchanged starting material was obtained. This failure could be ascribed to the low miscibility of the two reactants and to the oxidant being insufficiently strong to effect oxidation of the deactivated sulphur atom under these mild conditions. In an attempt to "force" the reaction, the reactants were heated at 100° (7 days) and, although 80% of the sulphide was recovered unchanged, a small amount of methyl heptafluoropropyl sulphone was obtained. This was unexpected since it is generally accepted that the oxidation of sulfoxides to sulphones is more difficult than the oxidation of sulphides to sulfoxides. Although

exceptions to this generality are known,<sup>104</sup> sodium metaperiodate is regarded as a mild oxidising agent and has been used to oxidise a large number of sulphides to sulphoxides.<sup>105</sup> The preferential formation of sulphone in the present reaction may be due to:

- (i) initial formation of the sulphoxide followed by its decomposition into sulphone and sulphide, or
- (ii) the greater solubility of the sulphoxide in water, as compared with the reactant sulphide, made its rate of oxidation to the sulphone faster than the corresponding oxidation of sulphide to sulphoxide.

Certain sulphoxides have been reported to disproportionate into the corresponding sulphides and sulphones on heating.<sup>106</sup> That a similar disproportionation was not occurring with methyl heptafluoropropyl sulphoxide was demonstrated by heating the sulphoxide at 100° (7 days); only unreacted sulphoxide (95%) was recovered.

The presence of the oxygen atom in methyl heptafluoropropyl sulphoxide would make the latter more susceptible to hydrogen-bonding than the parent sulphide, and hence more soluble in water. If this solubility factor were responsible for the faster oxidation of the sulphoxide, then it could be expected that the presence of a suitable solvent, for both aqueous sodium metaperiodate and methyl heptafluoropropyl sulphoxide, would nullify the effect of the greater solubility of the sulphoxide in water. This would result in a faster reaction and permit isolation of the sulphoxide.

TABLE 18

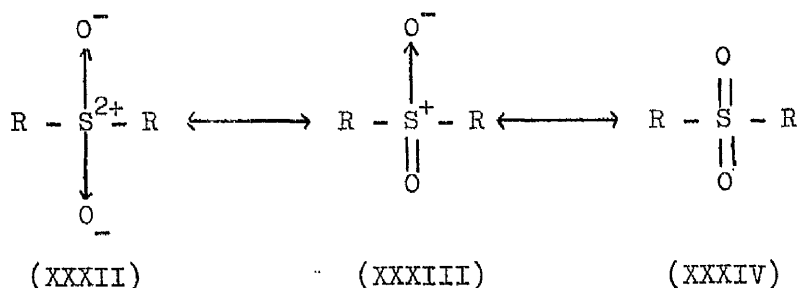
Oxidation of methyl heptafluoropropyl sulphide with aqueous sodium  
metaperiodate

Reaction conditions	Solvent	Product	Conversion %
5°; 1 day	none	none	nil
100°; 7 days	none	$C_3F_7SO_2Me$	12
100°; 1 day	methanol	$C_3F_7SOMe$	14

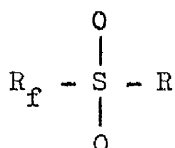
The results (Table 18) show that these expectations were realised. It was therefore concluded that the preferential formation of methyl heptafluoropropyl sulphone, in the second experiment, was due to the previously described solubility factors.

POLYFLUOROALKYL SULPHONES

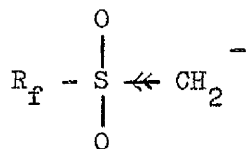
The sulphur-oxygen link in alkyl sulphones is considered to be a resonance hybrid of a semi-polar bond and a covalent double bond.



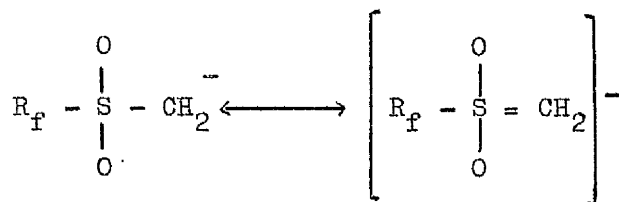
The relative contribution of each form is unknown, and although<sup>66</sup> a recent appraisal of the available evidence by Price and Oae suggests the hybrid lies very close to the semi-polar structure<sup>68,107</sup> (XXXII), the problem is not completely resolved. In view of the uncertainty as to the nature of the bonding, the structure of polyfluoroalkyl sulphones will be designated, non-committally, as



$\alpha$ -Carbanions in polyfluoroalkyl sulphones will be stabilised by the combined inductive effect of the sulphonyl group and the polyfluoroalkyl group.



This stabilisation will be augmented by a mesomeric effect which probably involves some sharing of the carbon 2p electrons with<sup>66</sup> the 3d orbitals of sulphur.



## Carbanion Reactions of Polyfluoroalkyl Sulphones

1. Deuterium-Exchange. The formation of  $\alpha$ -carbanions from polyfluoroalkyl sulphones was demonstrated by the fact that methyl heptafluoropropyl sulphone exchanged its hydrogen atoms for deuterium in the presence of deuterium oxide and sodium deuterioxide.

The exchange was demonstrated qualitatively by i.r. spectroscopy. The intensities of the bands at  $3.30$  and  $3.40\mu$ , ascribed to C - H stretching, were observed to have decreased and the appearance of bands in the region  $4.37$ - $4.65\mu$  was ascribed to the presence of C - D stretching vibrations.

The extent of ~~deuterium~~<sup>de</sup>-exchange was measured quantitatively by n.m.r. spectroscopy and mass spectrometry. In the first case the ratio of hydrogen to fluorine in the non-deuterated sulphone, as given by the n.m.r. integration curves, was compared with an internal standard, 1-bromo-1-chloro-2,2,2-trifluoroethane,  $\text{CF}_3\text{CHBrCl}$ . This was repeated for the deuterated mixture. The two results permitted a comparison of the amount of hydrogen present in the non-deuterated sulphone with the amount of hydrogen in the deuterated mixture. A ratio of 100:12 was obtained, which represented an 88% replacement of hydrogen by deuterium.

The extent of replacement was confirmed by mass spectrometry. Neither methyl heptafluoropropyl sulphone, nor its deuterated analogues gave parent-ion peaks so the peaks at  $m/e$  79, 80, 81 and 82 were used in the assessment. These peaks were assigned, respectively, to the positively-charged ions  $\text{CH}_3\text{SO}_2^+$ ,  $\text{CH}_2\text{D}\cdot\text{SO}_2^+$ ,  $\text{CHD}_2\cdot\text{SO}_2^+$ , and  $\text{CD}_3\text{SO}_2^+$ . In the calculation of the amount of deuteration that had occurred the following assumptions were made:

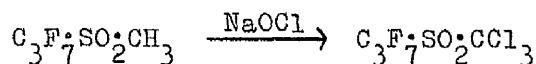
- (i) the breakdown patterns of the deuterated and non-deuterated

sulphones were the same, and

(ii) ions corresponding to  $\text{CH}_2\text{SO}_2^+$ ,  $\text{CHD}\cdot\text{SO}_2^+$ ,  $\text{CD}_2\cdot\text{SO}_2^+$  were not formed. This was true at least in the case of methyl heptafluoropropyl sulphone, since a peak at  $m/e$  78 ( $\text{CH}_2\text{SO}_2^+$ ) was absent.

Furthermore the contributions of the  $^{34}\text{S}$ ,  $^{13}\text{C}$ , and  $^{18}\text{O}$  isotopes were considered negligible and were ignored. On the basis of these assumptions the ratio of  $\text{CH}_3\text{SO}_2^+:\text{CH}_2\text{D}\cdot\text{SO}_2^+:\text{CHD}_2\text{SO}_2^+:\text{CD}_3\text{SO}_2^+$  was found to be 1.1 : 4.8 : 38 : 86. These ratios represented an overall exchange of hydrogen by deuterium of 87%. This is in excellent agreement with the value of 88% obtained from n.m.r. spectroscopy.

2. Under Haloform Conditions. A series of polyfluoroalkyl sulphones, which contained  $\alpha$ -hydrogen atoms, were shown to react with sodium hypochlorite to give chlorinated products, e.g.,



Similarly methyl heptafluoropropyl sulphone reacted with iodine, in the presence of sodium hydroxide, to give triiodomethyl heptafluoropropyl sulphone.

The reactions proceeded smoothly at room temperature and high yields of products were obtained (Table 19). The presence of a solvent was normally unnecessary, although aqueous methanol was used in the iodination reaction.

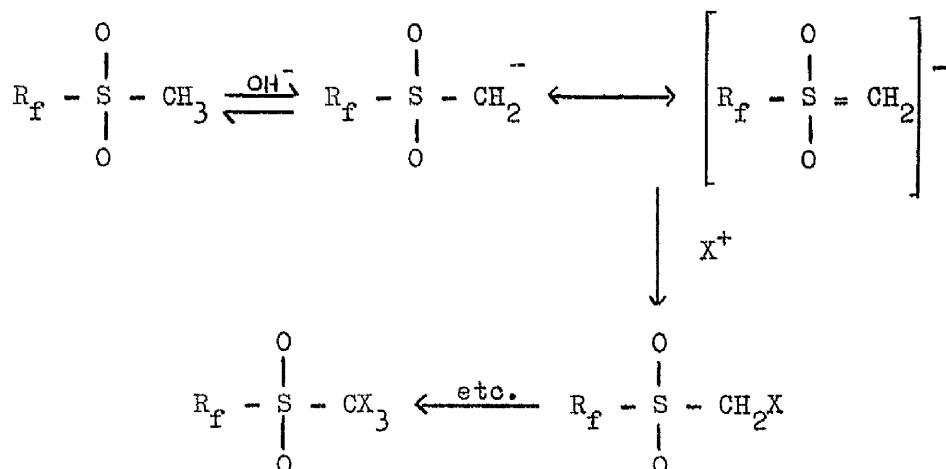
TABLE 19

Products from the halogenation of polyfluoroalkyl sulphones

Reactant	Product	Yield %
$\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_3$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CCl}_3$	98
$(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CH}_3$	$(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CCl}_3$	75
$*(\text{CF}_3)_2\text{CF}\cdot(\text{CF}_2)_4\text{SO}_2\text{CH}_3$	$(\text{CF}_3)_2\text{CF}\cdot(\text{CF}_2)_4\text{SO}_2\text{CCl}_3$	81
$\text{CF}_3\text{SO}_2\text{CH}_2\text{CH}_3$	$\text{CF}_3\text{SO}_2\text{CCl}_2\text{CH}_3$	90
$\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_3$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{Cl}_3$	84

\*An attempt to repeat this reaction was unsuccessful in that fluorinated products were not isolated and the solution gave a strong positive test for fluoride ion. The expected product,  $(\text{CF}_3)_2\text{CF}\cdot(\text{CF}_2)_4\text{SO}_2\text{CCl}_3$ , may possibly have decomposed since the reaction mixture stood in direct sunlight during the reaction.

The mechanism of the halogenation is believed to be similar, at least in the initial stages, to the haloform reaction, i.e.,



(where X = Cl or I)

The reaction of methyl heptafluoropropyl sulphone with sodium hypochlorite was terminated before reaction was complete and the organic layer was shown to consist of trichloromethyl heptafluoropropyl sulphone and unreacted methyl heptafluoropropyl sulphone. The absence of the corresponding monochloromethyl and dichloromethyl



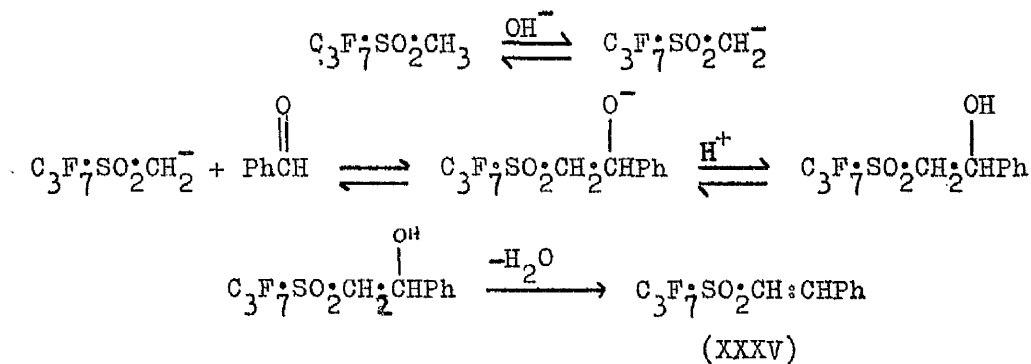
sulphones is consistent with the above mechanism, since the substitution of a chlorine atom for a hydrogen atom will further activate the remaining hydrogens towards base. The reactivities of the sulphones will thus lie in the order  $\text{CHCl}_2\text{SO}_2\text{R}_f > \text{CH}_2\text{Cl}\cdot\text{SO}_2\text{R}_f > \text{CH}_3\text{SO}_2\text{R}_f$ .

The  $\alpha$ -hydrogens of unsubstituted alkyl sulphones are not sufficiently acidic to react under the conditions employed in these experiments. However, the methylene hydrogens of  $\alpha,\beta$ -disulphones are sufficiently activated by the second sulphonyl group to undergo reaction.<sup>108,109</sup> This is also true of the methyl hydrogen atoms in chloromethyl trichloromethyl sulphone.<sup>109</sup>

3. With Benzaldehyde. Yagupol'skii and co-workers have reported that methyl trifluoromethyl sulphone condenses with aromatic aldehydes, in the presence of base, to give compounds of the type  $\text{CF}_3\text{SO}_2\text{CH}:\text{CHAr}$ .<sup>75</sup> The present work shows that methyl heptafluoropropyl sulphone undergoes a similar condensation with benzaldehyde.



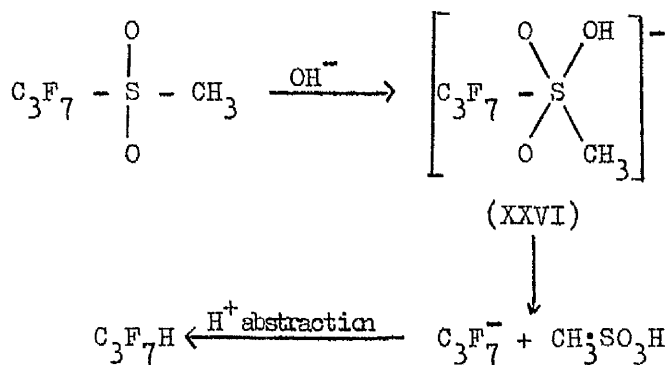
The reaction is believed to proceed via a mechanism similar to that proposed for the aldol condensation, i.e.,



The heptafluoropropyl styryl sulphone (XXXV) has been assigned the trans configuration on the basis of the large coupling constant of the olefinic protons ( $J_{H_1H_2}$ , 15.5 c./sec.). Typical coupling constants for olefinic  $\alpha, \beta$  protons are cis ( $J_{H_1H_2}$ , 6-12 c./sec) and trans ( $J_{H_1H_2}$ , 12-18 c./sec).<sup>110</sup>

### Nucleophilic Displacements on the Sulphur Atom of Polyfluoroalkyl Sulphones

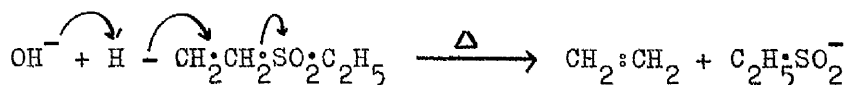
1. Methyl Heptafluoropropyl Sulphone. In contrast to alkyl sulphones,<sup>111</sup> which are resistant to nucleophilic attack on the sulphur atom, methyl heptafluoropropyl sulphone is readily cleaved by dilute aqueous sodium hydroxide at 100°. The ease of this reaction may be attributed to withdrawal of electron density from the sulphur atom by the heptafluoropropyl group. This would provide a highly electron-deficient site for attack by the hydroxide ion. The reaction may be represented by the following sequence.



Other workers have investigated the reaction of diphenyl sulphone with  $\text{O}^{18}$ -enriched potassium hydroxide and found that when the reaction was stopped before completion, sulphones containing  $\text{O}^{18}$ <sup>112</sup> were not present in the recovered diphenyl sulphone. This led the authors to conclude that the replacement of the phenyl group by the

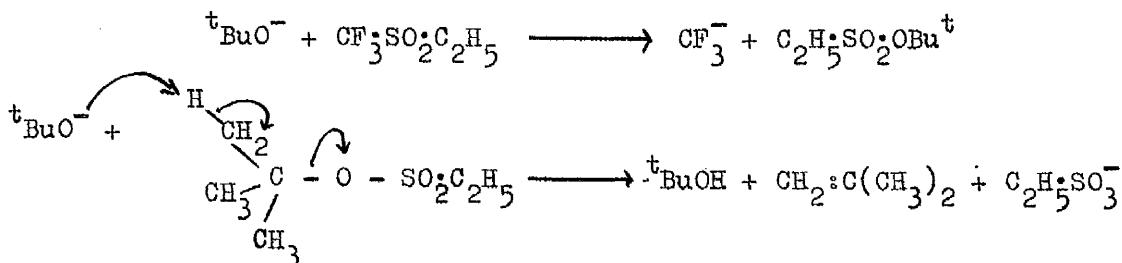
hydroxide group was a synchronous process involving a transition state rather than an intermediate complex. By analogy it seems probable that the hydrolysis of methyl heptafluoropropyl sulphone occurs by an  $S_N2$  process, similar to alkyl halides, and that the 'intermediate' (XXXVI) is merely a transition state.

2. Trifluoromethyl Ethyl Sulphone. Ingold showed that diethyl sulphone reacted with potassium hydroxide to give ethylene and potassium ethanesulphonate. A mechanism involving a  $\beta$ -elimination<sup>113</sup> was proposed.



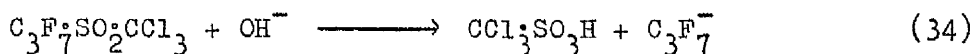
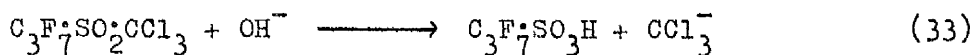
It was hoped to prepare sodium trifluoromethylsulphinate from trifluoromethyl ethyl sulphone and sodium hydroxide. The only products from this reaction were, however, trifluoromethane (92%) and sodium ethanesulphonate, which indicated that attack by the hydroxide ion had occurred on the sulphur atom.

In an attempt to prevent attack on the sulphur atom the bulky *t*-butoxide ion was used as the base and *t*-butanol as the solvent. The volatile products obtained from this reaction were trifluoromethane (85%) and isobutene. The presence of trifluoromethane suggests that, despite steric inhibition, nucleophilic attack had again occurred on the sulphur atom. A possible scheme to explain the observed products is given below.



3. Trichloromethyl Heptafluoropropyl Sulphone. Substitution of a trichloromethyl group for the methyl group, in methyl heptafluoropropyl sulphone, should render the sulphur atom more susceptible to nucleophilic attack. The subsequent failure of trichloromethyl heptafluoropropyl sulphone to react with aqueous potassium hydroxide was therefore ascribed to the low solubility of the sulphone in water. The reaction was repeated in aqueous dioxane and the anticipated potassium heptafluoropropanesulphonate (72%) was obtained. In addition 1H-heptafluoropropane (13%), carbon monoxide, and chloroform were obtained. The presence of carbon monoxide may be explained by hydrolysis of the chloroform formed.<sup>114</sup>

The ratio of potassium heptafluoropropanesulphonate indicates that the trichloromethyl anion is displaced (equation 33) in preference to the heptafluoropropyl anion (equation 34).

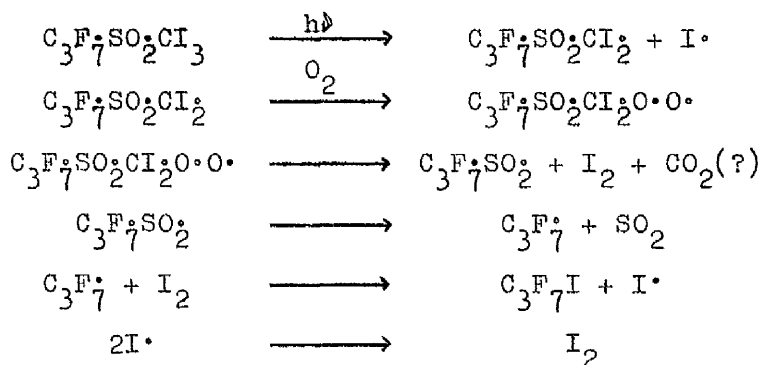


This may be rationalised on the basis that the presence of d orbitals on chlorine induces greater stabilisation of the trichloromethyl anion since the fluorine atoms in the heptafluoropropyl anion are unable to expand their valence shells to delocalise the negative charge.

The yield of potassium heptafluoropropanesulphonate quoted (72%) is an isolated yield. However, from the yield of 1H-heptafluoropropane (13%), it is probable that the actual yield of the former is higher than 72%. The aqueous solution of the products gave a negative test for fluoride ion, thus indicating the fluorinated products are stable under the reaction conditions.

## Miscellaneous Reactions of Polyfluoroalkyl Sulphones

1. Photolytic Decomposition of Triiodomethyl Heptafluoropropyl Sulphone. During the isolation of triiodomethyl heptafluoropropyl 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 photochemical-induced decomposition (sunlight) of the sulphone in the presence of oxygen were heptafluoro-1-iodopropane, sulphur dioxide, and iodine. Several free-radical mechanisms may be postulated to explain these products; one such mechanism is:



In addition to the above compounds, small quantities of carbonyl fluoride and silicon tetrafluoride were detected. The formation of these, by the reaction of perfluoroalkyl radicals with oxygen and glass, is known.<sup>86</sup>

2. Oxidation of Methyl Heptafluoropropyl Sulphone. The hydrolysis of trichloromethyl heptafluoropropyl sulphone with potassium hydroxide was considered to be the best route to potassium heptafluoro<sup>propane</sup>sulphonate. However, prior to the discovery of this route, potassium heptafluoropropanesulphonate was prepared, in 85% yield, by the oxidation of methyl heptafluoropropyl sulphone with potassium permanganate at

reflux temperature. This method has been previously reported for the oxidation of a mixture of  $\alpha, \omega$ -bis(methanesulphonyl)polyfluoroalkanes to the corresponding  $\alpha, \omega$ -disulphonic acid salts.<sup>40</sup>

Attempts to oxidise methyl heptafluoropropyl sulphone to heptafluoropropanesulphonic acid with fuming nitric acid were unsuccessful. (Table 20).

TABLE 20

Conditions	Recovery of sulphone %	Sulphonic acid, yield %
100°; 24 hr.	90	nil
150°; 72 hr.	74	nil
reflux; 9 days	nil	nil

At 100° (24 hr.) no significant reaction occurred whereas, after prolonged reflux, a gas was evolved which gave a precipitate with barium hydroxide solution; the gas was presumed to be carbon dioxide. Although no heptafluoropropanesulphonic acid was detected, it was observed that the reaction vessel was badly etched. It was concluded that, either the sulphone had decomposed to give carbon dioxide and hydrogen fluoride without the formation of the sulphonic acid, or that the latter had been formed but had decomposed under the reaction conditions. In view of the high stability of perfluoroalkanesulphonic acids,<sup>78</sup> the latter seems improbable. It is interesting to note that attempts to oxidise bis(trifluoromethyl) disulphide to trifluoromethanesulphonic acid, using concentrated nitric acid, have been reported to result in decomposition.<sup>79</sup>

3. Attempted Fluorination of Trichloromethyl Heptafluoropropyl Sulphone. Attempts to fluorinate trichloromethyl heptafluoropropyl sulphone with antimony trifluoride/antimony pentachloride were unsuccessful. At temperatures below  $100^{\circ}$  the sulphone (ca. 90%) was recovered unchanged. When the reactants were heated at  $140^{\circ}$  (7 days), breakdown of the sulphone occurred. The products were not examined in detail, but i.r. spectroscopy showed the presence of silicon tetrafluoride, sulphur dioxide, 1-chloroheptafluoropropane, pentafluoropropionyl chloride, pentafluoropropionic acid, and unidentified components. The breakdown was not investigated further.

The failure to fluorinate the trichloromethyl group is probably a result of the strong electron-withdrawing effect of the heptafluoropropanesulphonyl group. Although it is not known whether the mechanism of fluorination, with antimony trifluoride/antimony pentachloride, involves a free carbonium ion, e.g.,  $C_3F_7SO_2CCl_2^+$ , it is believed that the fluorination is an ionic process which involves the replacement of  $Cl^-$  by  $F^{115}$ . The withdrawal of electron density from the trichloromethyl group, by the heptafluoropropanesulphonyl group, will hinder the loss of chlorine as  $Cl^-$  and thus inhibit the fluorination.

### POLYFLUOROALKYL SULPHOXIDES

The bonding and carbanion stabilisation of polyfluoroalkyl sulphones have been discussed previously (p. 70) and the same factors apply also to polyfluoroalkyl sulfoxides. However, the presence of only one oxygen atom will reduce carbanion stabilisation in sulfoxides relative to sulphones.

#### Carbanion Reactions of Methyl Heptafluoropropyl Sulfoxide

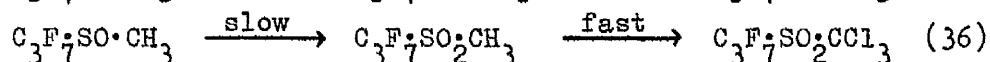
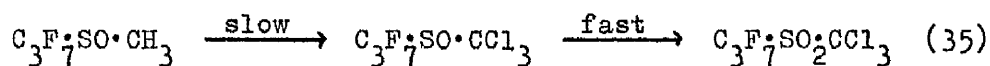
1. Deuterium-Exchange. Under similar conditions to those employed with the corresponding sulphone, methyl heptafluoropropyl sulfoxide underwent deuterium-exchange. The exchange was demonstrated, as before, by i.r. spectroscopy, n.m.r. spectroscopy, and mass spectrometry. The calculations based on n.m.r. spectroscopy showed a 90% exchange of hydrogen by deuterium had occurred.

The mass spectrum of the deuterated mixture showed parent-ion peaks at  $m/e$  232, 233, 234, and 235 corresponding to the ions  $C_3F_7SO \cdot CH_3^+$ ,  $C_3F_7SO \cdot CH_2D^+$ ,  $C_3F_7SO \cdot CHD_2^+$ , and  $C_3F_7SO \cdot CD_3^+$  respectively. The corresponding peak heights were in the ratio of 1.2 : 1.7 : 14 : 37, which, using approximations similar to those used for the sulphone, represented an 87% replacement of hydrogen by deuterium.

Methyl heptafluoropropyl sulphide failed to react under similar conditions. This was not a solubility effect because a reaction in ethanol was also unsuccessful. This result indicates the importance of electron-withdrawal by the oxygen atom in carbanion formation, since the sulphide can stabilise a carbanion by d-orbital interaction in the same way as can the sulfoxide and sulphone.



2. Under 'Haloform' Conditions. The reaction of methyl heptafluoropropyl sulphoxide and sodium hypochlorite, at room temperature, yielded a mixture of trichloromethyl heptafluoropropyl sulphone (82% based on sulphoxide consumed) and unreacted methyl heptafluoropropyl sulphoxide (21% recovered). The absence of any other high-boiling products 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. The possibilities for the two-stage reaction are given below.



Of the two possibilities (equations 35 and 36), the second, which involves oxidation before chlorination, is considered to be energetically preferable because:

(i) a carbanion in which the charge is  $\propto^-$  to a sulphonyl group will be more readily formed than a carbanion in which the charge is  $\propto^-$  to a sulphanyl group, because of the greater electron-withdrawing effect of the sulphonyl group; this will make the second step in equation (36) easier than the first step in equation (35).

(ii) the electron-withdrawing effect of the chlorine atoms will make the oxidation of the postulated trichloromethyl heptafluoropropyl sulphoxide more difficult than the oxidation of methyl heptafluoropropyl sulphoxide, consequently the first step in equation (36) will be easier than the second step in equation (35).

Although no direct evidence is available in support of the above argument, it is significant that alkyl sulphides have been

oxidised to the corresponding sulphones, without chlorination, by sodium hypochlorite at room temperature. It can therefore be inferred that the reported oxidation of dimethyl sulphoxide to bis(trichloromethyl) sulphone, with sodium hypochlorite at reflux temperature, proceeds via the initial formation of dimethyl sulphone and, by analogy, that the oxidative chlorination of methyl heptafluoropropyl sulphoxide proceeds via the formation of methyl heptafluoropropyl sulphone.

This is apparently contradicted by the report that the reaction of the sodium salt of thiobisacetic acid with sodium hypochlorite gives products of the type  $CX_3SO \cdot CX_3$  and  $CHX_2SO \cdot CHX_2$ . However, in addition to these products, incompletely halogenated sulphones were obtained, e.g.,  $CHBr_2SO \cdot CHBr_2$ . The isolation of these products is precluded by the 'haloform' type of mechanism proposed earlier, and it is therefore concluded that the reaction of thiobisacetic acid proceeds by a different mechanism.

An attempt to prepare triiodomethyl heptafluoropropyl sulphoxide by the iodination of methyl heptafluoropropyl sulphoxide with iodine in potassium iodide solution, in the presence of sodium hydroxide, was unsuccessful. This is further evidence against the intermediacy of trichloromethyl sulphoxide in the sodium hypochlorite reaction. The failure to react with iodine, however, is not readily reconcilable with carbanion formation by methyl heptafluoropropyl sulphoxide as evidenced by the deuterium-exchange experiment. It can only be suggested that the carbanion formed from methyl heptafluoropropyl sulphoxide is unstable and reacts with its 'solvent sheath' (water or deuterium oxide) before it can react with any other species present.

Nucleophilic Displacement on the Sulphur Atom of Methyl Heptafluoropropyl Sulphoxide

The reaction of methyl heptafluoropropyl sulphoxide with dilute sodium hydroxide parallels the reaction of the corresponding sulphone in that attack occurs on the sulphur atom to give 1H-heptafluoropropane (92%). This result confirms the results obtained by Russian workers from the alkaline hydrolysis of methyl trifluoromethyl sulphoxide. In the latter reaction, trifluoromethane and sodium ethanesulphinate were the observed products.<sup>71</sup>

### CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

Methyl polyfluoroalkyl sulphides were prepared in moderate yields (40-50%) by the general reaction of polyfluoromonoiodoalkanes with dimethyl sulphide under photochemical conditions. Better yields (>80%) were obtained from the corresponding reaction of polyfluoromonoiodoalkanes with dimethyl disulphide. Both of these preparative methods required long irradiation periods (3-4 weeks), which made them both costly and tedious. These difficulties were overcome in the corresponding thermally initiated, free-radical reactions but these reactions gave poor yields of methyl polyfluoroalkyl sulphides.

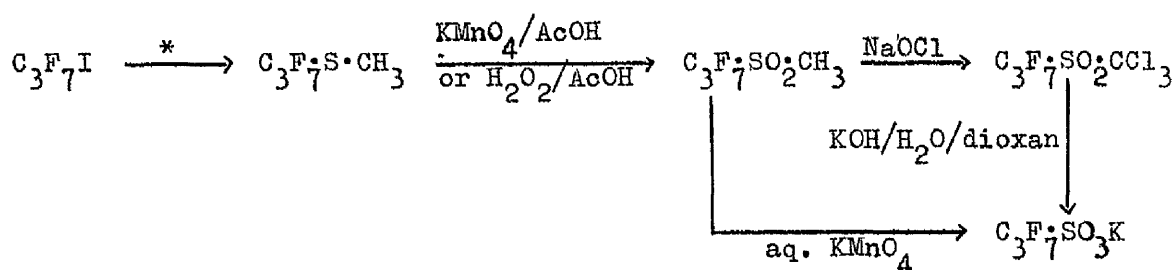
A preliminary investigation of the ionic reaction of heptafluoro-1-iodopropane with sodium methanethiolate, in the presence of excess dimethyl disulphide, showed that methyl heptafluoropropyl sulphide was formed in good yield (ca. 70%). The reaction was performed with dimethyl sulphoxide as solvent and was ca. 70% complete after 19 hr. at 100°. It is believed that this reaction could be developed as a general method of preparation of methyl polyfluoroalkyl sulphides from polyfluoromonoiodoalkanes. In view of the fact that the high yields of polyfluoroalkyl sulphides obtained from the photochemical reactions of disulphides were confined to methyl polyfluoroalkyl sulphides, it would be useful to determine whether the corresponding ionic reactions are subject to the same limitations.

The methyl polyfluoroalkyl sulphones prepared were shown to form carbanions of the type  $R_fSO_2\dot{C}H_2^-$ , and these could provide a convenient route of introducing the  $R_fSO_2CH_2$  group into other compounds. The methyl polyfluoroalkyl sulphoxides prepared were not investigated in great detail, although it was shown that these

compounds were capable of carbanion formation.

Both the polyfluoroalkyl sulphones and polyfluoroalkyl sulfoxides underwent attack on the sulphur atom by hydroxide ion. This attack, in the case of trichloromethyl heptafluoropropyl sulphone, gave rise to heptafluoropropanesulphonic acid (potassium salt).

From heptafluoro-1-iodopropane, the following routes to the corresponding sulphonic acid were devised. These routes are considered general for the preparation of polyfluoroalkanesulphonic acids from polyfluoromonoiodoalkanes.



\* $\text{Me}_2\text{S}_2/\text{h}\nu$ , or  $\text{Me}_2\text{S}/\text{h}\nu$ , or  $\text{MeSNa}/\text{Me}_2\text{S}_2$ .

The author wishes to express his thanks for a topic, which while providing interesting chemistry, possessed the more tangible incentive of being of possible commercial interest.

## EXPERIMENTAL

## EXPERIMENTAL

### General Techniques

Many of the compounds encountered during the course of this work were either gases or volatile liquids, certain of which possessed obnoxious odours. These materials were conveniently manipulated in a vacuum-system constructed from Pyrex glass. By this means air and moisture were excluded, toxicity hazards were minimized, and small quantities of material handled quantitatively.

The vacuum-system consisted of a storage system comprising five bulbs (1 to 25 litres), a distillation section consisting of a train of five traps, and a molecular-weight section equipped with two large-bore manometers for the accurate measurement of gas pressures. A detachable, thin-walled Pyrex bulb (237 ml.) was used in conjunction with the latter section for the measurement of molecular weights by the method of Regnault.

The distillation train was used for removing impurities from reactants, and for separating the reaction products into convenient fractions by the method of fractional condensation. The mixture to be separated was condensed in the first trap at the temperature of liquid nitrogen ( $-196^{\circ}$ ) and allowed to warm up slowly so that a pressure of ca. 2 mm. developed. The vapour of the warming mixture was passed through the remaining traps, each cooled to a successively lower temperature by slush baths. These were Dewar vessels containing a slush of a melting organic solvent maintained at its melting point by the addition of liquid nitrogen, a slush of solid carbon dioxide in methylated spirits, or liquid nitrogen with which the last trap in the series was cooled. The temperatures of the slush baths which were used are given in Table 20.

TABLE 20.

Slush bath temperatures

Liquid	Temp.	Liquid	Temp.
Carbon Tetrachloride	-22°	Toluene	-95°
Chlorobenzene	-45°	Light Petroleum (b.p. 30°-40°)	-130°
Carbon Dioxide/Meths.	-78°	Liquid Nitrogen	-196°

By repeated passage of each fraction through the distillation train, compounds whose boiling points differed by more than 30° could be separated. Throughout this dissertation compounds, or mixtures, are designated by the temperature of the trap in which they condensed, e.g., "-78° fraction".

Gases which did not condense at -196° were adsorbed onto charcoal, at -196°, which had previously been activated by heating in vacuo to 300° (20 min.). The gas was desorbed by heating the charcoal in vacuo to 300° (20 min.) and the volume of the desorbed gas was then measured at room temperature.

Low pressure reactions (<8 atm.) were carried out in sealed, evacuated, thick-walled, Pyrex tubes and photochemical reactions were carried out in sealed, evacuated, silica tubes held at a specified distance from a Hanovia S500 mercury-vapour lamp.

Reactions at higher pressures were carried out in stainless-steel autoclaves equipped with a pressure gauge and bursting disc.

The volatile reaction products were separated by fractional condensation and each fraction was either weighed, or measured as a gas volume, and then examined by some, or all of the following techniques: molecular-weight determination, gas-liquid chromatography (g.l.c.), infrared (i.r.) spectroscopy, nuclear magnetic resonance (n.m.r.)



spectroscopy, mass spectrometry, and elemental analysis.

In certain cases pure samples were isolated by g.l.c. separation and trapping. This was accomplished by allowing the vapour of the pure sample to enter a cooled, spiral trap fitted with a self-sealing rubber serum cap. These preparative-scale separations were carried out on Perkin-Elmer model 116,451, or 452 instruments.

Unless otherwise stated <sup>ti</sup>quantitative analysis of mixtures was carried out by g.l.c. using a Griffin and George D.6. instrument. This instrument incorporates a gas density balance detector, the response of which is related to the weight and molecular weight of the compound by the following equation.

$$\text{Weight of sample} = \text{Peak area} \cdot f \cdot M / (M - m)$$

M = molecular weight of sample

m = molecular weight of carrier gas

f = a constant of proportionality.

The quantities calculated from this equation gave excellent agreement with other checks, e.g., molecular weight of mixture, mass balance, or quantitative chemical separation. Both analytical and preparative-scale g.l.c. investigations were carried out using columns (2 - 8 m., 6 mm., i.d.) with Celite as the inert support. Unless otherwise stated, Silicone Oil M.S.550 (30%) was used as the stationary phase; the column length and operating temperature are given in the text.

High resolution i.r. spectra of pure compounds were recorded on Perkin-Elmer 21 or 257 instruments fitted with sodium chloride optics. Routine i.r. spectra were run on a Perkin-Elmer model 137 Infracord. Identification of known compounds by i.r. spectroscopy was made, unless otherwise stated, by a comparison of the i.r. spectrum obtained with that

of an authentic sample, recorded in the departmental files.

N.m.r. spectra were recorded on a Perkin-Elmer R10 permanent magnet machine operating at frequencies of 60.00 Mc./sec. for  $^1\text{H}$  and 56.46 Mc./sec. for  $^{19}\text{F}$ .

Mass spectra were recorded either on an A.E.I. MS/2H mass spectrometer, a single-focusing sector magnet instrument with a resolution of 1 in 700, or on an A.E.I. MS/9 mass spectrometer with a resolution of 1 in 1500.

Fluoride ion was detected by the alizarin/zirconium nitrate test.

### Preparation of Reactants

1. Silver Heptafluorobutyrate. To a solution of silver nitrate (200 g., 1.18 moles) in water (600 ml.), a slight excess of a solution of sodium carbonate (65 g., 0.62 mole) in water (200 ml.) was added with stirring. The yellow precipitate of silver carbonate was washed twelve times with water (12 x 1000 ml.), in a blackened beaker. The sludge of silver carbonate, so obtained, was treated with the theoretical quantity of 80% heptafluorobutyric acid and the resultant clear solution was evaporated at reduced pressure, with the temperature maintained below 50° to prevent decomposition, until crystallisation took place. The white crystals were dried over phosphoric oxide, in a darkened vacuum-desiccator (14 days),<sup>120</sup> to give silver heptafluorobutyrate (300 g., 1.04 moles, 90%).

2. Heptafluoro-1-iodopropane. Finely-powdered, dry silver heptafluorobutyrate (330 g., 1.04 moles) and finely-powdered, dry iodine (381 g., 1.50 moles) were intimately mixed and placed in a round-bottomed flask (3 l.) fitted with a nitrogen inlet.

The flask was connected to a vertical air condenser (ca. 20 cm., 3 cm. i.d.), for returning iodine to the reaction mixture, with its upper end connected to two traps (ca. 300 ml.) cooled to -78°.

Before pyrolysis the apparatus was flushed with dry nitrogen (1 hr.), the flask was then gently heated and the heptafluoro-1-iodopropane collected in the cooled traps. After the reaction was complete (3-4 hr.), the apparatus was again flushed with nitrogen to carry any remaining heptafluoro-1-iodopropane to the traps. The crude product was washed (3 x 100 ml.) with aqueous sodium hydroxide (30% w/v) at 0°, dried (phosphoric oxide), and distilled through a Vigreux column to give heptafluoro-1-iodopropane (266 g., 0.90 mole, 88%) (Found:  $\underline{M}$ , 295. Calc. for  $C_3F_7I$ :  $\underline{M}$ , 296)

b.p. 39-40° (<sup>120</sup>lit. 41). The product was shown to be pure by g.l.c. (8 m. column at 40°) and i.r. spectroscopy.

3. Trifluoroiodomethane.<sup>121</sup> Dry, powdered silver trifluoroacetate (193 g., 0.87 mole) and dry, powdered iodine (336 g., 1.32 moles) were intimately mixed and placed in a round-bottomed flask (2.5 l.) fitted with a nitrogen inlet. The flask was connected to a pyrolysis apparatus which consisted of a vertical air condenser (ca. 100 cm., 3 cm. i.d.) with its upper end leading to a scrubbing tower (5 cm. i.d.) packed with glass helices. During the pyrolysis a continuous flow of an aqueous solution of sodium hydroxide (30% w/v) and sodium thiosulphate (5% w/v) was passed down the tower against the gas stream. The gas outlet at the top of the tower was connected, via a Drechsel bottle which contained the same scrubbing solution (ca. 150 ml.), to two drying tubes (ca. 40 cm., 3 cm. i.d.) packed with phosphoric oxide.

The apparatus was flushed with dry nitrogen and gently heated, and the trifluoroiodomethane collected in two traps, cooled to -78°, connected to the drying tubes. The crude product was purified by fractional condensation in vacuo to give trifluoroiodomethane (151 g., 0.77 mole, 89%) (Found: M, 196. Calc. for CF<sub>3</sub>I: M, 196). The product was shown to be pure by g.l.c. (8 m. column at 20°) and i.r. spectroscopy.

4. Tetrafluoro-1,2-diiodoethane.<sup>122</sup> Tetrafluoroethylene (3.97 g., 39.7 mmoles) and iodine (15.2 g., 60.0 mmoles), sealed in vacuo in a Pyrex tube (300 ml.) and heated at 150° (14 hr.), gave, after fractional condensation in vacuo, unreacted tetrafluoroethylene (1.31 g., 13.1 mmoles, 33% recovered) (Found: M, 100. Calc. for C<sub>2</sub>F<sub>4</sub>: M, 100), condensing at -196°, and a fraction condensing at -22°.

The -22° fraction was shaken with mercury, to remove excess iodine,

and subsequently identified as tetrafluoro-1,2-diiodoethane (7.90 g., 22.3 mmoles, 84% based on tetrafluoroethylene consumed) by comparison of its g.l.c. retention time (4 m. column at 120°) with that of an authentic sample, and by i.r spectroscopy.

5. 1-Chlorotetrafluoro-2-iodoethane.<sup>123</sup> Tetrafluoroethylene (12.1 g., 0.121 mole) and iodine chloride (40.5 g., 0.248 mole), sealed in vacuo in a silica tube (1 l.) and heated at 90° (24 hr.), gave, on fractional condensation in vacuo, unreacted tetrafluoroethylene (3.42 g., 34.2 mmoles, 27% recovered), condensing at -196°, and a fraction condensing at -78°.

The -78° fraction was removed from the vacuum-system, washed with dilute sodium hydroxide solution (ca. 10 ml.), dried (phosphoric oxide), and distilled at atmospheric pressure to give 1-chloro-2-iodotetrafluoroethane (21.1 g., 80.2 mmoles, 92% based on tetrafluoroethylene consumed) (Found:  $\bar{M}$ , 264. Calc. for  $C_2ClF_3I$ :  $\bar{M}$ , 263) b.p. 56° (lit., 56.5°),<sup>123</sup> identified by i.r. spectroscopy.<sup>124</sup>

6. Bis(trifluoromethylthio)mercury.<sup>23</sup> Carbon disulphide (161 g., 2.12 moles) and mercuric fluoride (238 g., 1.00 mole) (prepared by passing fluorine gas, at 100°, over mercuric chloride for 24 hr.) were sealed in an autoclave (1 l., Hastalloy lined) and heated at 250° (5 hr.).

After reaction, the volatile material was vented off at room temperature and the residual carbon disulphide solution filtered from the red mercuric sulphide. The carbon disulphide was evaporated under reduced pressure (20°/17 mm.) and the resultant brown solid distilled under reduced pressure (83°/20 mm.) to yield a white solid identified as bis(trifluoromethylthio)mercury,  $(CF_3S)_2Hg$  (81.5 g., 0.203 mole, 61%) m.p. 37-39° (lit., 39-40°).<sup>23</sup>

7. Bis(chloromethyl) Sulphide.<sup>20</sup> S-Trithiane,  $\overline{S \cdot CH_2 \cdot S \cdot CH_2 \cdot S \cdot CH_2}$  (200 g.,

1.45 moles) was placed in a round-bottomed flask (2 l.) fitted with a reflux condenser, stirrer, and dropping funnel. Thionyl chloride (518 g., 4.35 moles) was added over a period of 1 hr., with stirring, and the resultant mixture was then heated under reflux (48 hr.).

The products were distilled under reduced pressure and the low-boiling products allowed to escape. A liquid, b.p.  $83^{\circ}/35$  mm., was collected and redistilled at atmospheric pressure to give yellow bis-(chloromethyl) sulphide (131 g., 1.00 mole, 69%) (Found: C, 18.0; H, 2.8%. Calc. for  $C_2H_4Cl_2S$ : C, 18.3; H, 3.1%) b.p.  $156^{\circ}$  (lit.,  $156-156.5^{\circ}$ ).

8. Trifluoromethyl Ethyl Sulphide. Bis(trifluoromethylthio)mercury (40.0 g., 99.5 mmoles) and iodoethane (29.6 g., 0.190 mole) were sealed in a Pyrex tube (300 ml.) and heated at  $100^{\circ}$  (24 hr.).

Fractionation of the volatile products in vacuo gave small quantities of carbonyl sulphide and silicon tetrafluoride, condensing at  $-196^{\circ}$ , and trifluoromethyl ethyl sulphide (19.5 g., 0.150 mole, 79%) (Found:  $\bar{M}$ , 130. Calc. for  $C_3H_5F_3S$ :  $\bar{M}$ , 130) b.p.  $39-41^{\circ}$  (lit.,  $40^{\circ}$ ), condensing at  $-78^{\circ}$  and identified by i.r. spectroscopy.

9. Bis(trifluoromethyl) Disulphide. a) From trifluoroiodomethane.<sup>12</sup> Trifluoroiodomethane (71.6 g., 0.365 mole) and sulphur (ca. 30 g., 0.94 mole) were sealed in an autoclave (1 l., Hastalloy lined), and heated at  $265^{\circ}$  (36 hr.). The products were separated by fractional condensation in vacuo, and the  $-78^{\circ}$  fraction was identified as bis(trifluoromethyl) disulphide (21.0 g., 0.104 mole, 56%) (Found:  $\bar{M}$ , 202. Calc. for  $C_2F_6S_2$ :  $\bar{M}$ , 202) b.p.  $36^{\circ}$  (lit.,  $34.6^{\circ}$ ). The i.r. spectrum was identical with that reported.<sup>125</sup>

b) From bis(trifluoromethylthio)mercury.<sup>25</sup> To a solution of bis(trifluoromethylthio)mercury (27.4 g., 67.6 mmoles) in tetrachloroethane

(50 ml.), contained in a round-bottomed flask (250 ml.), was added a solution of iodine (18.0 g., 70.9 mmoles) in tetrachloroethane (100 ml.). The mixture was stirred (8 hr.) during which time red mercuric iodide precipitated.

The volatile products were transferred to the vacuum-system and separated by fractional condensation in vacuo. The fraction condensing at  $-78^{\circ}$  was identified as bis(trifluoromethyl) disulphide (11.3 g., 56.1 mmoles, 83%) (Found:  $\bar{M}$ , 204. Calc. for  $C_2F_6S_2$ :  $\bar{M}$ , 202) by i.r. spectroscopy, and shown to be pure by g.l.c. (4 m. column at  $20^{\circ}$ ). The i.r. spectrum differed from that reported, and from the i.r. spectrum obtained in the previous experiment, in that a band at  $6.53\mu$  was absent.

10. Sodium Alkanethiolates. Ethanethiol (ca. 40 ml.) was dissolved in sodium-dried ether (ca. 100 ml.) contained in a round-bottomed flask (250 ml.) fitted with a total-reflux head, maintained at  $-78^{\circ}$ , and a drying tube (phosphoric oxide). Finely-diced sodium (8.12 g., 0.353 mole) was added with constant stirring (15 min.) and stirring was maintained for a further 4 hr. The resultant white precipitate was filtered and transferred to a round-bottomed flask (100 ml.). The flask was evacuated, to remove any volatile material, and gave sodium ethanethiolate (30.6 g., 0.326 mole, 90%).

The reaction between sodium and methanethiol, under the above conditions, was slow. After stirring (8 hr.), a mixture of ethanol and excess methanethiol was added to the reaction flask and the resultant mixture was heated under reflux (2 hr.). The precipitate of sodium methanethiolate was isolated by the procedure described above. The yield was not recorded.

11. Miscellaneous Reactants. Other reactants were either commercial

grade or pure research samples (checked by i.r. spectroscopy and g.l.c.), kindly donated by members of the department. Commercial samples were dried and purified by distillation or by fractional condensation in vacuo.

#### Photochemical Reactions of Dimethyl Sulphide with Polyfluoroiodoalkanes

The reactants were sealed in silica tubes (ca. 300 ml.) and irradiated at a distance of 6 in. from the lamp. During irradiation the tube was shaken vigorously and irradiation was continued until the formation of tar was observed on the sides of the reaction tube. After reaction the volatile products were transferred to the vacuum-system and separated by fractional condensation in vacuo.

1. With Trifluoriodomethane. Dimethyl sulphide (5.62 g., 90.7 mmoles) and trifluoriodomethane (4.25 g., 21.7 mmoles), sealed in a silica tube and irradiated (14 days), gave:

- (i) a non-condensable gas at  $-196^{\circ}$  (0.046 g., 2.3 mmoles;  $\bar{M}$ , 20), shown by i.r. spectroscopy to be a mixture of carbon monoxide and methane,
- (ii) trifluoromethane (0.51 g., 7.3 mmoles, 34%) (Found:  $\bar{M}$ , 70. Calc. for  $\text{CHF}_3$ :  $\bar{M}$ , 70), which condensed at  $-196^{\circ}$  and was shown by i.r. spectroscopy to be contaminated with small amounts of silicon tetrafluoride and hexafluoroethane,
- (iii) a combined  $-95^{\circ}$  and  $-78^{\circ}$  fraction (3.93 g., 51.6 mmoles;  $\bar{M}$ , 76), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $20^{\circ}$ ) to consist of unreacted dimethyl sulphide (2.34 g., 37.9 mmoles, 4.2% recovered) and methyl trifluoromethyl sulphide (1.59 g., 13.7 mmoles, 63%),
- (iv) a  $-22^{\circ}$  fraction (0.57 g., 5.3 mmoles), identified by i.r. spectroscopy, n.m.r. spectroscopy, and mass spectrometry (p.148)



as bis(methylthio)methane,  $\text{CH}_3\text{S}\cdot\text{CH}_2\text{S}\cdot\text{CH}_3$ , and

(v) a solid, non-volatile residue which was extracted with water.

The aqueous extract was evaporated, during which, an unpleasant odour ascribed to bis(methylthio)methane was evolved; a yellow-brown solid remained. The solid was recrystallised from ethanol to yield white crystals of trimethylsulphonium iodide (3.79 g., 18.6 mmoles, 86%) decomposition temp.  $210^\circ\text{--}211^\circ$  (lit.  $^{126} 215^\circ$ ), identified by comparison with an authentic sample. A positive test for iodide ion was obtained with aqueous silver nitrate.

A small residue of tar remained in the tube.

Trifluoriodomethane (100%) reacted to give trifluoromethane (33%) and methyl trifluoromethyl sulphide (63%). Trimethylsulphonium iodide was isolated in 87% yield.

2. With Heptafluoro-1-iodopropane. Dimethyl sulphide (5.74 g., 92.4 mmoles) and heptafluoro-1-iodopropane (6.31 g., 21.3 mmoles), sealed in a silica tube and irradiated (28 days), gave:

- (i) a non-condensable gas at  $-196^\circ$  (0.8 mmole), shown by i.r. spectroscopy to be a mixture of carbon monoxide and methane,
- (ii) a  $-196^\circ$  fraction (trace), shown by i.r. spectroscopy to be silicon tetrafluoride,
- (iii) a  $-130^\circ$  fraction (1.82 g., 12.2 mmoles;  $M_r$  149), shown by i.r. spectroscopy to consist of  $\text{1H-heptafluoropropane}$  and dimethyl sulphide,
- (iv) a  $-78^\circ$  fraction (4.98 g.), and
- (v) a  $-22^\circ$  fraction (0.72 g., 6.2 mmoles), shown by i.r. spectroscopy to be bis(methylthio)methane.

Trimethylsulphonium iodide (3.97 g., 19.4 mmoles, 91%) was extracted

from the residue in the tube; a small quantity of tar remained.

The  $-130^{\circ}$  fraction (1.82 g.) was shaken with mercuric chloride (ca. 10 g.) in a Pyrex ampoule (25 ml.) for 14 hr., and the volatile component was identified as 1H-heptafluoropropane (1.67 g., 9.8 mmoles, 46%) (Found:  $\underline{M}$ , 172. Calc. for  $C_3HF_7$ :  $\underline{M}$ , 170) by i.r. spectroscopy.

The  $-78^{\circ}$  fraction (4.98 g.) was shown by i.r. spectroscopy and g.l.c. (8 m. column at  $40^{\circ}$ ) to consist of unreacted dimethyl sulphide (2.65 g., 42.7 mmoles, 46% recovered), an unknown component A, and a trace of an unidentified component, possibly perfluorohexane.

Compound A was isolated by g.l.c. (4 m. column at  $40^{\circ}$ ) and identified as methyl heptafluoropropyl sulphide,  $CF_3CF_2CF_2S\cdot CH_3$  (2.30 g., 10.7 mmoles, 50%) (Found: C, 21.9; H, 1.4%;  $\underline{M}$ , 215.  $C_4H_5F_7S$  requires C, 22.2; H, 1.4%;  $\underline{M}$ , 216) b.p.  $61^{\circ}$ .

The mass spectrum (p. 144), n.m.r. spectrum (p. 173) and i.r. spectrum (p. 163) are consistent with the proposed structure.

Heptafluoro-1-iodopropane (100%) reacted to give 1H-heptafluoropropane (46%), methyl heptafluoropropyl sulphide (50%), and trimethylsulphonium iodide (91%).

3. With Heptafluoro-2-iodopropane. Dimethyl sulphide (6.52 g., 0.105 mole) and heptafluoro-2-iodopropane (8.12 g., 27.4 mmoles), sealed in a silica tube and irradiated (24 days), gave:

- (i) a non-condensable gas at  $-196^{\circ}$  (0.026 g., 1.3 mmoles;  $\underline{M}$ , 20), shown by i.r. spectroscopy to consist of carbon monoxide and methane,
- (ii) a  $-196^{\circ}$  fraction (trace), shown by i.r. spectroscopy to be silicon tetrafluoride,
- (iii) a  $-130^{\circ}$  fraction (2.53 g., 16.2 mmoles;  $\underline{M}$ , 157), shown by

i.r. spectroscopy and g.l.c. (8 m. column at  $20^{\circ}$ ) to consist of 2H-heptafluoropropane,  $\text{CF}_3\text{CHF}\cdot\text{CF}_3$  (2.40 g., 14.1 mmoles, 66%) and unreacted dimethyl sulphide (0.13 g., 2.1 mmoles, 2% recovered), (iv) a  $-78^{\circ}$  fraction (6.28 g.), and (v) a  $-22^{\circ}$  fraction (1.21 g., 11.2 mmoles), shown by i.r. spectroscopy to be bis(methylthio)methane.

Trimethylsulphonium iodide (4.00 g., 19.7 mmoles, 92%) was extracted from the reaction tube; a small residue of tar remained.

The  $-78^{\circ}$  fraction (6.28 g.) was examined by i.r. spectroscopy and g.l.c. (8 m. column at  $50^{\circ}$ ) and shown to consist of unreacted heptafluoro-2-iodopropane (1.80 g., 6.1 mmoles, 22% recovered), unreacted dimethyl sulphide (3.01 g., 48.6 mmoles, 46% recovered), an unknown component B, and a trace of an unidentified component, possibly perfluoro-(2,3-dimethylbutane).

Component B was isolated by g.l.c. (4 m. column at  $40^{\circ}$ ) and identified as methyl heptafluoro isopropyl sulphide,  $(\text{CF}_3)_2\text{CF}\cdot\text{S}\cdot\text{CH}_3$  (1.47 g., 6.8 mmoles, 32%) (Found: C, 22.4; H, 1.4%;  $\bar{M}$ , 214.  $\text{C}_4\text{H}_3\text{F}_7\text{S}$  requires C, 22.2; H, 1.4%;  $\bar{M}$ , 216) b.p.  $61^{\circ}$ .

The mass spectrum (p. 144), n.m.r. spectrum (p. 183), and i.r. spectrum (p. 166) are consistent with the proposed structure.

Heptafluoro-2-iodopropane (78%) reacted to give 2H-heptafluoropropane (66%), methyl heptafluoroisopropyl sulphide, (32%) and trimethylsulphonium iodide (92%) based on the iodopropane consumed.

4. With 1-Chlorotetrafluoro-2-iodoethane. 1-Chlorotetrafluoro-2-iodoethane (6.24 g., 23.8 mmoles) and dimethyl sulphide (5.42 g., 87.4 mmoles), sealed in a silica tube and irradiated (28 days) gave:

(i) a small quantity of a gas which did not condense at  $-196^{\circ}$ ,

(ii) a  $-196^{\circ}$  fraction (trace), shown by i.r. spectroscopy to be silicon tetrafluoride,

(iii) a  $-130^{\circ}$  fraction (2.00 g., 15.4 mmoles;  $\underline{M}$ , 130), which, after treatment with mercuric chloride, gave 1H-2-chlorotetrafluoroethane (1.70 g., 12.5 mmoles, 52%) (Found:  $\underline{M}$ , 138. Calc. for  $C_2HClF_4$ :  $\underline{M}$ , 136), identified by a comparison of its i.r. spectrum with that reported,<sup>127</sup>

(iv) a  $-78^{\circ}$  fraction (4.00 g.), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $50^{\circ}$ ) to consist of unreacted dimethyl sulphide (1.94 g., 31.3 mmoles, 36% recovered) and an unknown component C (2.06 g.), and

(v) a  $-22^{\circ}$  fraction (0.64 g., 5.9 mmoles), shown by i.r. spectroscopy to be bis(methylthio)methane contaminated with a trace of an unidentified component.

Trimethylsulphonium iodide (4.18 g., 20.3 mmoles, 86%) was extracted from the tube; a small residue of tar remained.

The  $-78^{\circ}$  fraction (4.00 g.) was shaken with mercuric chloride (ca. 40 g.) in a Pyrex tube (200 ml.) for 14 hr. to remove the dimethyl sulphide. The volatile component C was transferred to the vacuum-system via a drying tube (phosphoric oxide) and was identified as methyl 2-chlorotetrafluoroethyl sulphide,  $CF_2Cl \cdot CF_2S \cdot CH_3$  (1.96 g., 10.8 mmoles, 45%) (Found: C, 19.8; H, 1.9; F, 42.0; S, 17.7%;  $\underline{M}$ , 180.  $C_3H_3ClF_4S$  requires C, 19.7; H, 1.7; F, 41.6; S, 17.5%;  $\underline{M}$ , 182) b.p. (Siwoloboff)  $80^{\circ}$ .

The mass spectrum (p. 145), n.m.r. spectrum (p. 190), and i.r. spectrum (p. 163) are consistent with the proposed structure.

1-Chlorotetrafluoro-2-iodoethane (100%) reacted to give 1H-2-chlorotetrafluoroethane (52%), methyl 2-chlorotetrafluoroethyl sulphide (45%), and trimethylsulphonium iodide (86%).

5. With Pentadecafluoro-1-iodo-5-methylhexane. Dimethyl sulphide (5.26 g., 84.9 mmoles) and pentadecafluoro-1-iodo-5-methylhexane (10.29 g., 20.7 mmoles), sealed in a silica tube and irradiated (28 days), gave:

- (i) a non-condensable gas at  $-196^{\circ}$  (0.019 g., 1.0 mmole;  $\underline{M}$ , 19), shown by i.r. spectroscopy to be methane, possibly contaminated with carbon monoxide.
- (ii) dimethyl sulphide (0.49 g., 7.9 mmoles, 9% recovered) (Found:  $\underline{M}$ , 63. Calc. for  $C_2H_6S$ :  $\underline{M}$ , 62), which condensed at  $-95^{\circ}$  and was identified by i.r. spectroscopy, and
- (iii) a  $-78^{\circ}$  fraction (3.69 g., 37.5 mmoles;  $\underline{M}$ , 98), which, after reaction with mercuric chloride, gave a volatile component D, subsequently identified as 1H-pentadecafluoro-5-methylhexane,  $(CF_3)_2CF \cdot CF_2CF_2CF_2CHF_2$ . (2.84 g., 7.68 mmoles, 45%) (Found: C, 22.4; H, 0.5%;  $\underline{M}$ , 363.  $C_7H_{15}F_{15}$  requires C, 22.5; H, 0.3%;  $\underline{M}$ , 370) b.p. (Siwoloboff)  $90-92^{\circ}$ .

The mass spectrum (p. 161), n.m.r. spectrum (p. 172), and i.r. spectrum (p. 170) are consistent with the proposed structure.

A fraction condensing at  $-22^{\circ}$  (5.27 g.) was also isolated, and shown by i.r. spectroscopy and g.l.c. (8 m. column at  $135^{\circ}$ ) to consist of unreacted pentadecafluoro-1-iodo-5-methylhexane (1.72 g., 3.47 mmoles, 17% recovered), bis(methylthio)methane (0.27 g., 2.48 mmoles), and an unknown component E.

Component E was isolated by g.l.c. (as above) and identified as Methyl pentadecafluoro-5-methylhexyl sulphide,  $(CF_3)_2CF \cdot CF_2CF_2CF_2CF_2S \cdot CH_3$  (3.28 g., 7.97 mmoles, 46%) (Found: C, 23.0; H, 1.0; F, 68.5; S, 7.9%.  $C_8H_3F_{15}S$  requires C, 23.0; H, 0.7; F, 68.6; S, 7.7%) b.p.  $139^{\circ}$ .

The mass spectrum (p. 147), n.m.r. spectrum (p. 172), and i.r. spectrum (p. 164) are consistent with the proposed structure.

The non-volatile residue in the reaction tube was extracted to give an ether-soluble tar (0.41 g.) and trimethylsulphonium iodide (2.92 g., 14.3 mmoles, 83%).

Pentadecafluoro-1-iodo-5-methylhexane (83%) reacted to give 1H-pentadecafluoro-5-methylhexane (45%), methyl pentadecafluoro-5-methylhexyl sulphide (46%), and trimethylsulphonium iodide (83%) based on the iodoalkane consumed.

6. With Tetrafluoro-1,2-diiodoethane. Dimethyl sulphide (13.95 g., 0.225 mole) and tetrafluoro-1,2-diiodoethane (8.50 g., 24.0 mmoles), sealed in a silica tube and irradiated (14 days), gave:

(i) tetrafluoroethylene (1.89 g., 18.9 mmoles, 86%) (Found:  $\underline{M}$ , 100. Calc. for  $C_2F_4$ :  $\underline{M}$ , 100), which condensed at  $-196^\circ$  and was identified by i.r. spectroscopy,

(ii) a  $-130^\circ$  fraction (0.21 g., 2.7 mmoles;  $\underline{M}$ , 78), shown by i.r. spectroscopy to be a mixture of tetrafluoroethylene (0.12 g., 1.2 mmoles, 5%) and unreacted dimethyl sulphide (0.09 g., 1.5 mmoles, 1% recovered),

(iii) unreacted dimethyl sulphide (13.2 g., 0.213 mole, 94% recovered) (Found:  $\underline{M}$ , 62. Calc. for  $C_2H_6S$ :  $\underline{M}$ , 62), which condensed at  $-78^\circ$  and was identified by i.r. spectroscopy, and

(iv) a  $-22^\circ$  fraction (1.02 g.).

A tar, which contained a high proportion of iodine, remained in the tube.

The  $-22^\circ$  fraction (1.02 g.) was examined by i.r. spectroscopy and g.l.c. (2 m. column at  $120^\circ$ ) and was shown to consist of five components. The major component was identified as unchanged tetrafluoro-1,2-diiodoethane (ca. 0.75 g., 2.1 mmoles, 9% recovered). The other four components

(ca. 0.27 g.) were not identified. Exact quantities cannot be quoted for this fraction since the molecular weights of the unidentified components were not known.

Tetrafluoro-1,2-diiodoethane (91%) reacted to give tetrafluoroethylene (91% based on the diiodoethane consumed).

7. With Octafluoro-1,4-diiodobutane. Dimethyl sulphide (6.73 g., 0.108 mole) and octafluoro-1,4-diiodobutane (7.90 g., 17.4 mmoles), sealed in a silica tube and irradiated (14 days), gave:

- (i) a non-condensable gas at  $-196^{\circ}$  (0.8 mmole), shown by i.r. spectroscopy to be a mixture of methane and carbon monoxide,
- (ii) a  $-196^{\circ}$  fraction (trace), shown by i.r. spectroscopy to be a mixture of tetrafluoroethylene and silicon tetrafluoride,
- (iii) a  $-78^{\circ}$  fraction (4.34 g., 69.4 mmoles;  $M_r$  63), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $60^{\circ}$ ) to consist of 1H,4H-octafluorobutane,  $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$  (0.05 g., 0.25 mmole, 2%) and unreacted dimethyl sulphide (4.29 g., 69.2 mmoles, 64% recovered),
- (iv) a  $-45^{\circ}$  fraction (1.15 g.), and
- (v) a  $-22^{\circ}$  fraction (5.96 g.)

Trimethylsulphonium iodide (2.03 g., 10.0 mmoles, 90%) was extracted from the tube; a small quantity of tar remained.

The combined  $-45^{\circ}$  and  $-22^{\circ}$  fraction (7.11 g.) was examined by i.r. spectroscopy and g.l.c. (8 m. column at  $160^{\circ}$ ) and shown to consist of unreacted octafluoro-1,4-diiodobutane (3.16 g., 6.96 mmoles, 40% recovered), bis(methylthio)methane (0.60 g., 5.58 mmoles), and four unknown components F, G, H, and J which were subsequently isolated by g.l.c. (5 m. column at  $150^{\circ}$ )

Component F was identified as 1H-octafluoro-4-iodobutane,  $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$  (1.42 g., 4.33 mmoles, 42%) (Found: C, 14.6; H, 0.6%;  $\bar{M}$ , 323. Calc.  $\bar{M}$ , 328) b.p. (Siwoloboff)  $90^\circ$  (lit.,  $90-91^\circ$ ).

The mass spectrum (p. 160) and i.r. spectrum (p. 170) are consistent with the proposed structure.

Component G was not positively identified, but its elution order from g.l.c. suggested it was methyl 4H-octafluorobutyl sulphide,  $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (0.16 g., 0.65 mmoles, 6%) and calculations have been based on this assumption.

Compound H was identified as methyl octafluoro-4-iodobutyl sulphide,  $\text{CF}_2\text{I}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (1.71 g., 4.58 mmoles, 44%) (Found: C, 16.3; H, 0.8; I, 34.3%.  $\text{C}_5\text{H}_3\text{F}_8\text{I}$  requires C, 16.1; H, 0.8; I, 34.0%).

The mass spectrum (p. 146), n.m.r. spectrum (p. 191), and i.r. spectrum (p. 164) are consistent with the proposed structure.

Compound J was identified as 1,4-bis(methylthio)octafluorobutane,  $\text{CH}_3\text{S}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (0.06 g., 0.20 mmole, 2%) by mass spectral evidence only (p. 149).

Octafluoro-1,4-diiodobutane (60%) reacted to give 1H,4H-octafluorobutane (2%), 1H-octafluoro-4-iodobutane (42%), methyl octafluoro-4-iodobutyl sulphide (44%), 1,4-bis(methylthio)octafluorobutane (2%), an unidentified component, presumed to be methyl 4H-octafluorobutyl sulphide (6%), and trimethylsulphonium iodide (90%). The yields are based on the diiodobutane consumed.

#### Thermal Reaction of Dimethyl Sulphide with Heptafluoro-1-iodopropane

Dimethyl sulphide (2.06 g., 33.2 mmoles) and heptafluoro-1-iodopropane (3.42 g., 11.5 mmoles), sealed in a Pyrex tube (300 ml.) and heated at  $170^\circ$  (72 hr.), gave, after fractional condensation in vacuo:



- (i) a non-condensable gas at  $-196^{\circ}$  (0.9 mmole), which was not examined further,
- (ii) silicon tetrafluoride (0.15 mmole), which condensed at  $-196^{\circ}$  and was identified by i.r. spectroscopy,
- (iii) a  $-130^{\circ}$  fraction (1.00 g., 8.5 mmoles;  $\underline{M}$ , 118), which, after reaction with mercuric chloride, gave 1H-heptafluoropropane (0.74 g., 4.34 mmoles, 69%) (Found:  $\underline{M}$ , 167. Calc. for  $C_3HF_7$ :  $\underline{M}$ , 170), identified by i.r. spectroscopy, and
- (iv) a  $-78^{\circ}$  fraction (2.88 g.), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $50^{\circ}$ ) to consist of unreacted dimethyl sulphide (1.14 g., 18.4 mmoles, 55% recovered), unreacted heptafluoro-1-iodopropane (1.52 g., 5.14 mmoles, 45% recovered), and methyl heptafluoropropyl sulphide (0.22 g., 1.02 mmoles, 16%).

The involatile residue in the reaction tube was extracted to yield trimethylsulphonium iodide (0.26 g., 1.28 mmoles, 20%) and a tar (0.10 g.) which was soluble in ether. A black insoluble solid remained in the tube.

Heptafluoro-1-iodopropane (56%) reacted to give 1H-heptafluoropropane (69%), methyl heptafluoropropyl sulphide (16%), and trimethylsulphonium iodide (20%) based on the iodopropane consumed.

#### Photochemical Reaction of Methyl Ethyl Sulphide with Heptafluoro-1-iodopropane

Methyl ethyl sulphide (6.57 g., 86.5 mmoles) and heptafluoro-1-iodopropane (7.36 g., 24.9 mmoles) were sealed in a silica tube (300 ml.) and irradiated (28 days), with shaking, at a distance of 4 in. from the lamp. After this period a large quantity of tar was deposited on the sides of the tube. The volatile material was examined by i.r. spectroscopy and the presence of unreacted heptafluoro-1-iodopropane was observed. The

volatile material was transferred to another tube and irradiation was continued for a further 21 days. Fractional condensation of the products in vacuo gave:

- (i) a non-condensable gas at  $-196^{\circ}$  (1.8 mmoles), shown by i.r. spectroscopy to contain methane,
- (ii) a  $-196^{\circ}$  fraction (0.08 g., 2.7 mmoles;  $\underline{M}$ , 30), shown by i.r. spectroscopy to consist of ethane and ethylene which, on treatment with bromine and subsequent purification, gave ethane (0.06 g., 2.3 mmoles),
- (iii) 1H-heptafluoropropane (2.32 g., 13.6 mmoles, 58%) (Found:  $\underline{M}$ , 169. Calc. for  $C_3HF_7$ :  $\underline{M}$ , 170), which condensed at  $-130^{\circ}$  and was identified by i.r. spectroscopy,
- (iv) a  $-78^{\circ}$  fraction (5.04 g.), and
- (v) a  $-22^{\circ}$  fraction (0.874 g.) which was not investigated further.

The tar remaining in the tube was extracted with water to yield a mixture of trialkylsulphonium iodides (0.78 g.) (Found: C, 17.8; H, 4.2; I, 63.7%) decomposition temp.  $198^{\circ}$ .

The  $-78^{\circ}$  fraction (5.04 g.) was investigated by i.r. spectroscopy and g.l.c. (8 m. column at  $70^{\circ}$ ) and shown to consist of nine components. Two of these components were present only in trace quantities and were not positively identified, but were shown to correspond in retention times to perfluorohexane and iodoethane respectively. The remaining seven components were identified as unreacted heptafluoro-1-iodopropane (0.351 g., 1.19 mmoles, 5% recovered), unreacted methyl ethyl sulphide (1.94 g., 25.6 mmoles, 30% recovered), dimethyl sulphide (0.101 g., 1.63 mmoles), diethyl sulphide (0.775 g., 8.61 mmoles), methyl heptafluoropropyl sulphide (0.356 g., 1.65 mmoles, 7%), ethyl heptafluoropropyl sulphide (1.10 g.,

4.80 mmoles, 21%) (see p. 116), and 1,1,1,2,2,3,3-heptafluoropentane (0.267 g., 1.35 mmoles, 6%) (see p. 116).

Heptafluoro-1-iodopropane (95%) reacted to give 1H-heptafluoropropane (58%), methyl heptafluoropropyl sulphide (7%), ethyl heptafluoropropyl sulphide (21%), and 1,1,1,2,2,3,3-heptafluoropentane (6%) based on the iodopropane consumed.

Photochemical Reaction of Methyl Trifluoromethyl Sulphide with Heptafluoro-1-iodopropane

Methyl trifluoromethyl sulphide (1.15 g., 9.91 mmoles) and heptafluoro-1-iodopropane (1.61 g., 5.41 mmoles), sealed in a silica tube (100 ml.) and irradiated at a distance of 2 in. from the lamp (35 days), gave, after fractional condensation in vacuo:

- (i) trifluoromethane (trace), condensing at  $-196^{\circ}$  and identified by i.r. spectroscopy,
- (ii) a  $-130^{\circ}$  fraction (0.336 g., 1.75 mmoles; M, 192), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $20^{\circ}$ ) to consist of perfluorobutane (trace), 1H-heptafluoropropane (0.046 g., 0.27 mmole, 12%), and trifluoriodomethane (0.289 g., 1.47 mmoles, 64%),
- (iii) a  $-95^{\circ}$  fraction (0.989 g., 8.10 mmoles; M, 122), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $20^{\circ}$ ) to consist of 1H-heptafluoropropane (0.048 g., 0.28 mmoles, 12%), trifluoriodomethane (0.050 g., 0.25 mmoles, 11%), unreacted methyl trifluoromethyl sulphide (0.861 g., 7.41 mmoles, 75% recovered), and an unidentified component (0.03 g.), and
- (iv) a  $-78^{\circ}$  fraction (1.256 g.), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $40^{\circ}$ ) to consist of perfluorohexane (0.080 g., 0.23 mmoles, 20%), methyl heptafluoropropyl sulphide (0.254 g.,

1.17 mmoles, 51%), unreacted heptafluoro-1-iodopropane (0.920 g., 3.11 mmoles, 57% recovered), and a trace of an unidentified component.

A small quantity of tar remained in the reaction tube. Heptafluoro-1-iodopropane (43%) reacted to give perfluorohexane (20%), 1H-heptafluoropropane (24%), methyl heptafluoropropyl sulphide (51%), perfluorobutane (trace), and trifluoroiodomethane (64%) based on the iodopropane consumed.

#### Photochemical Reaction of Methanethiol with Heptafluoro-1-iodopropane

Methanethiol (1.10 g., 22.9 mmoles) and heptafluoro-1-iodopropane (6.76 g., 22.8 mmoles), sealed in a silica tube and irradiated (9 days), gave, on fractional condensation in vacuo:

- (i) a non-condensable gas at  $-196^{\circ}$  (0.008 g., 1.9 mmoles;  $\bar{M}$ , 4), which showed no i.r. absorption in the region 2.5 to  $15\mu$ ,
- (ii) 1H-heptafluoropropane (3.24 g., 19.0 mmoles, 85%) (Found:  $\bar{M}$ , 171. Calc. for  $C_3HF_7$ :  $\bar{M}$ , 170), which condensed at  $-130^{\circ}$  and was identified by i.r. spectroscopy,
- (iii) a  $-78^{\circ}$  fraction (0.82 g.), shown by i.r. spectroscopy and g.l.c. to consist of unreacted heptafluoro-1-iodopropane (0.11 g., 0.37 mmole, 2% recovered) and methyl heptafluoropropyl sulphide (0.71 g., 3.28 mmoles, 14%), and
- (iv) a  $-22^{\circ}$  fraction (0.12 g.), which was not investigated further.

An acetone-soluble, black tar remained in the tube. Heptafluoro-1-iodopropane (98%) reacted to give 1H-heptafluoropropane (85%) and methyl heptafluoropropyl sulphide (14%) based on the iodopropane consumed.

#### Photochemical Reaction of Bis(chloromethyl) Sulphide with Trifluoroiodomethane

The photochemical reaction of bis(chloromethyl) sulphide with

trifluoriodomethane was unsuccessful. After irradiation (84 days), trifluoriodomethane (70%) was recovered unchanged and the inside of the reaction tube was observed to be covered with a black deposit. The volatile products were shown, by i.r. spectroscopy, to include trifluoromethane, chlorotrifluoromethane, hexafluoroethane, carbon disulphide, hydrogen chloride, and small amounts of unknown products. The latter were not characterised and the reaction was not investigated further.

#### Photochemical Reactions of Dimethyl Disulphide with Polyfluoriodoalkanes

The reactions (1-5) were carried out under similar conditions. The irradiations were carried out at a distance of 4 in. from the lamp, for a period of 21 days. In experiments 1 and 2 the sealed silica tubes (300 ml.) were held in a vertical position and the liquid phase irradiated; in experiments 3-5 the tubes were held horizontally and the liquid and gas phases irradiated.

The products were identified by i.r. spectroscopy, g.l.c. retention times (4 m. column at appropriate temperature), and molecular-weight determinations (except experiment 5). Experiment 1 is given in detail, the other experiments are summarised in Tables 21a and 21b.

1. With Heptafluoro-1-iodopropane. Dimethyl disulphide (7.91 g., 84.3 mmoles) and heptafluoro-1-iodopropane (4.44 g., 15.0 mmoles), sealed in a silica tube and irradiated (21 days), gave, on fractional condensation in vacuo:

- (i) a trace of a non-condensable gas at  $-196^{\circ}$ , subsequently identified by i.r. spectroscopy as methane,
- (ii) a  $-130^{\circ}$  fraction (0.155 g., 1.0 mmole;  $M$ , 155), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $20^{\circ}$ ) to contain 1H-heptafluoropropane (0.15 g., 0.9 mmole, 6%) and methanethiol (0.005 g.,

0.1 mmole, < 1% based on dimethyl disulphide used), contaminated with a trace of an unidentified component,

(iii) a  $-78^{\circ}$  fraction (3.22 g., 15.3 mmoles;  $M$ , 210), and

(iv) a  $-45^{\circ}$  fraction (4.24 g.).

Large quantities of a black oil remained in the tube.

The  $-78^{\circ}$  fraction (3.22 g.) was examined by i.r. spectroscopy and g.l.c. (8 m. column at  $45^{\circ}$ ) and shown to consist of methyl heptafluoropropyl sulphide (2.82 g., 13.0 mmoles, 92%), unreacted heptafluoro-1-iodopropane (0.32 g., 1.1 mmoles, 7% recovered), dimethyl sulphide (0.05 g., 0.8 mmoles, 1% based on dimethyl disulphide), and carbon disulphide (trace).

The  $-45^{\circ}$  fraction (4.24 g.) was removed from the system and distilled through a Vigreux column (15 cm.). One fraction, only, was obtained and identified by i.r. spectroscopy as unreacted dimethyl disulphide (3.95 g., 42.0 mmoles, 51% recovered) b.p.  $107^{\circ}$ .

The oil remaining in the tube was distilled, with some decomposition, to yield a further quantity of dimethyl disulphide (1.62 g., 17.3 mmoles, 21% recovered).

Heptafluoro-1-iodopropane (93%) reacted to give 1H-heptafluoropropane (6%) and methyl heptafluoropropyl sulphide (93%) based on the iodopropane consumed.

Subsequent experiments, with the reaction tube held horizontally, gave methyl heptafluoropropyl sulphide (80-85%).

TABLE 21 a

Photochemical reactions of polyfluoromonoiodoalkanes with dimethyl disulphide

Experiment	Iodo compound		Me <sub>2</sub> S <sub>2</sub> mmoles	Extent of reaction %	Product R <sub>f</sub> SMe	
	R <sub>f</sub> I	mmoles			Yield %	Fraction
1	CF <sub>3</sub> •CF <sub>2</sub> •CF <sub>2</sub> I	15.0	84.3	93	93	-78°
2	CF <sub>3</sub> I	15.4	120	97	92	-95°
3	(CF <sub>3</sub> ) <sub>2</sub> CFI	28.5	126	100	83	-78°
4	CF <sub>2</sub> Cl•CF <sub>2</sub> I	25.9	68.7	100	82	-78°
5	(CF <sub>3</sub> ) <sub>2</sub> CF•(CF <sub>2</sub> ) <sub>4</sub> I	20.3	48.6	100	80	-22°

TABLE 21 b

Photochemical reactions of polyfluoromonoiodoalkanes with dimethyl disulphide

Experiment	Products Yield %					
	R <sub>f</sub> H		CS <sub>2</sub>	Me <sub>2</sub> S	MeSH	CH <sub>4</sub>
	Yield	fraction				
1	6	-130°	Trace	1	<1	<1
2	5	-;96°	Trace	1	1	<1
3	12	-130°	Trace	4	2	2
4	14	-130°	Trace	5	3	4
5	17	-45°	Trace	4	<1	5

6. With Tetrafluoro-1,2-diiodoethane. Tetrafluoro-1,2-diiodoethane (10.36 g., 29.3 mmoles) and dimethyl disulphide (11.23 g., 0.120 mole) were sealed in a silica tube (300 ml.), which was clamped horizontally above the lamp and irradiated (30 days). Fractional condensation of the products in vacuo gave:

- (i) a non-condensable gas at  $-196^{\circ}$  (ca. 1.5 mmoles), which was not examined,
  - (ii) a  $-196^{\circ}$  fraction (0.15 g., 1.5 mmoles;  $H$ , 98), shown by i.r. spectroscopy to be tetrafluoroethylene (ca. 5%), contaminated with silicon tetrafluoride and difluoromethane,
  - (iii) a  $-130^{\circ}$  fraction (0.22 g., 1.6 mmoles;  $M$ , 138), shown by i.r. spectroscopy to be a mixture of carbon disulphide, perfluorocyclopropane, and an unidentified component (or components) with i.r. bands at 3.40 m, 3.48 m, 3.52 w, 8.25 s, 10.05 s, 10.55 w, and 12.20  $w\mu$ , and
  - (iv) a  $-78^{\circ}$  fraction (0.41 g.), shown by i.r. spectroscopy to contain dimethyl sulphide, carbon disulphide, methyl 1,1,2,2-tetrafluoroethyl sulphide, and a trace of the unidentified component present in the  $-130^{\circ}$  fraction. The  $-78^{\circ}$  fraction was shaken with mercuric chloride (15 hr.) and gave methyl 1,1,2,2-tetrafluoroethyl sulphide (0.36 g., 2.4 mmoles, 8%) (Found:  $M$ , 146. Calc. for  $C_2H_4F_4S$ :  $M$ , 148), contaminated with a trace of the unidentified component.
- A  $-45^{\circ}$  fraction (2.32 g.) and a  $-22^{\circ}$  fraction (7.31 g.) were also isolated, and a black obnoxious oil remained in the tube.

The combined  $-22^{\circ}$  and  $-45^{\circ}$  fraction (9.63 g.) was examined by i.r. spectroscopy and g.l.c. (8 m. column at  $160^{\circ}$ ) and shown to consist of unreacted dimethyl disulphide (5.14 g., 54.7 mmoles, 46% recovered),



bis(methylthio)methane (0.43 g., 4.0 mmoles), methyl octafluoro-4-iodobutyl sulphide (0.10 g., 0.27 mmole, 2%) (identified by mass spectrometry), and three unknown components K, L, and M. Trace quantities of three unidentified components were also present.

Components K, L, and M were separated by g.l.c. (as above).

Component K was identified as 1,2-bis(methylthio)tetrafluoroethane,  $\text{CH}_3\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CH}_3$  (2.60 g., 13.4 mmoles, 46%) (Found: C, 24.7; H, 3.3; S, 32.7%.  $\text{C}_4\text{H}_6\text{F}_4\text{S}_2$  requires C, 24.7; H, 3.3; S, 33.0%) b.p. (Siwoloboff)  $150^\circ$ .

The mass spectrum (p. 148), n.m.r. spectrum (p. 189), and i.r. spectrum (p. 164) are consistent with the proposed structure.

Component L was identified as methyl tetrafluoro-2-iodoethyl sulphide,  $\text{CF}_2\text{I}\cdot\text{CF}_2\cdot\text{S}\cdot\text{CH}_3$  (0.45 g., 1.64 mmoles, 6%) by mass spectrometry only (p. 145). The i.r. spectrum is recorded (p. 164).

Component M was identified as 1,4-bis(methylthio)octafluorobutane,  $\text{CH}_3\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CH}_3$  (0.64 g., 2.18 mmoles, 15%) by mass spectrometry only (p. 149). The i.r. spectrum is recorded (p. 164).

Tetrafluoro-1,2-diiodoethane (100%) reacted to give tetrafluoroethylene (5%), difluoromethane (trace), perfluorocyclopropane, methyl 1,1,2,2-tetrafluoroethyl sulphide (8%), methyl octafluoro-4-iodobutyl sulphide (2%), 1,2-bis(methylthio)tetrafluoroethane (46%), methyl tetrafluoro-2-iodoethyl sulphide (6%), 1,4-bis(methylthio)octafluorobutane (15%), and at least four unidentified components.

#### Attempted Ionic Reaction of Dimethyl Disulphide with Tetrafluoroethylene

Dimethyl disulphide (11.10 g., 0.118 mole), iodine (7.61 g., 30.0 mmoles), and tetrafluoroethylene (3.00 g., 30.0 mmoles), were sealed in a Pyrex tube (300 ml.) and kept in the dark at room temperature (22 days),

Fractional condensation of the products in vacuo gave unreacted tetrafluoroethylene (3.00 g., 30.0 mmoles, 100%), which condensed at  $-196^{\circ}$  and was identified by i.r. spectroscopy. The high-boiling components were not investigated but a black oil was observed in the reaction tube.

Thermal Reaction of Dimethyl Disulphide with Heptafluoro-1-iodopropane

Dimethyl disulphide (1.97 g., 21.0 mmoles) and heptafluoro-1-iodopropane (5.80 g., 19.6 mmoles), sealed in a Pyrex tube (340 ml.) and heated at  $150^{\circ}$  (72 hr.), gave, on fractional condensation of the products in vacuo:

- (i) a non-condensable gas at  $-196^{\circ}$  (1.7 mmoles), shown by i.r. spectroscopy to contain carbonyl sulphide, silicon tetrafluoride, hydrogen sulphide, and an unidentified fluorocarbon.
- (ii) a  $-130^{\circ}$  fraction (1.20 g., 12.3 mmoles;  $M_r$ , 98), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $20^{\circ}$ ) to consist of 1H-heptafluoropropane (0.83 g., 4.9 mmoles, 61%) and methanethiol (0.36 g., 7.4 mmoles),
- (iii) a  $-78^{\circ}$  fraction (4.71 g.), and
- (iv) a  $-36^{\circ}$  fraction (0.11 g.), shown by i.r. spectroscopy to consist of dimethyl disulphide and an unknown component. This fraction was not investigated further.

A black tar remained in the tube.

The  $-78^{\circ}$  fraction (4.71 g.) was examined by i.r. spectroscopy and g.l.c. (8m. column at  $40^{\circ}$ ) and shown to consist of unreacted heptafluoro-1-iodopropane (3.40 g., 11.5 mmoles, 59% recovered), dimethyl sulphide (0.51 g., 8.3 mmoles), carbon disulphide (0.24 g., 3.2 mmoles), methyl heptafluoropropyl sulphide (0.54 g., 2.5 mmoles, 31%), and trace quantities of two unidentified components.

Heptafluoro-1-iodopropane (41%) reacted to give 1H-heptafluoropropane (61%) and methyl heptafluoropropyl sulphide (31%) based on the

iodopropane consumed.

### Photochemical Reactions of Diethyl Disulphide

1. With Heptafluoro-1-iodopropane. Diethyl disulphide (9.92 g., 81.2 mmoles) and heptafluoro-1-iodopropane (7.90 g., 26.6 mmoles) were sealed in a silica tube (300 ml.), which was clamped horizontally at a distance of 4 in. from the lamp, and irradiated (28 days). Subsequent examination of the volatile fraction, by i.r. spectroscopy, showed the presence of unreacted heptafluoro-1-iodopropane.

The volatile products were returned to the tube and irradiation continued (20 days). Fractional condensation of the products in vacuo gave:

- (i) a non-condensable gas at  $-196^{\circ}$  (0.4 mmole) which showed no i.r. absorption in the region of 2.5 to  $15\mu$ .
- (ii) a  $-196^{\circ}$  fraction (0.36 g., 12.0 mmoles;  $\bar{M}$ , 30), shown by i.r. spectroscopy to contain ethane and ethylene, contaminated with silicon tetrafluoride,
- (iii)  $1H$ -heptafluoropropane (1.86 g., 10.9 mmoles, 41%) (Found:  $\bar{M}$ , 168. Calc. for  $C_3HF_7$ :  $\bar{M}$ , 170), which condensed at  $-130^{\circ}$  and was identified by i.r. spectroscopy,
- (iv) a  $-78^{\circ}$  fraction (3.52 g.), and
- (v) a  $-22^{\circ}$  fraction (0.57 g.).

The residual black oil in the tube was heated to  $60^{\circ}$  in vacuo and a further 3.52 g. of liquid collected. This was combined with the  $-22^{\circ}$  fraction and identified by i.r. spectroscopy as unreacted diethyl disulphide (4.09 g., 33.5 mmoles, 40% recovered).

The  $-78^{\circ}$  fraction (3.52 g.) was examined by g.l.c. (8 m. column at  $70^{\circ}$ ) and shown to consist of ethanethiol (0.01 g., 0.5 mmole),

diethyl sulphide (0.22 g., 2.4 mmoles), and two unknown components N and O which were separated by g.l.c. (as above). Small quantities of two unidentified components were also detected.

Compound N was identified as 1,1,1,2,2,3,3-heptafluoropentane,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_3$  (0.30 g., 1.5 mmoles, 6%) (Found: C, 30.4; H, 2.5%;  $\bar{M}$ , 196.  $\text{C}_5\text{H}_5\text{F}_7$  requires C, 30.3; H, 2.5%;  $\bar{M}$ , 198) b.p. (isoteniscope)  $37.9^\circ$ .

The mass spectrum (p. 160), n.m.r. spectrum (p. 181), and i.r. spectrum (p. 170) are consistent with the proposed structure.

Compound O was identified as ethyl heptafluoropropyl sulphide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_2\text{CH}_3$  (2.88 g., 12.5 mmoles, 45%) (Found: C, 26.3; H, 2.4; F, 57.4%;  $\bar{M}$ , 230.  $\text{C}_5\text{H}_5\text{F}_7\text{S}$  requires C, 26.1, H, 2.2; F, 57.8%;  $\bar{M}$ , 230) b.p.  $78^\circ$ .

The mass spectrum (p. 150), n.m.r. spectrum (p. 174), and i.r. spectrum (p. 163) are consistent with the proposed structure.

Heptafluoro-1-iodopropane (100%) reacted to give 1H-heptafluoropropane (41%), ethyl heptafluoropropyl sulphide (47%), and 1,1,1,2,2,3,3-heptafluoropentane (6%).

2. With Trifluoriodomethane. Diethyl disulphide (9.75 g., 79.9 mmoles) and trifluoriodomethane (6.18 g., 31.5 mmoles) were sealed in a silica tube (300 ml.), which was held horizontally at a distance of 4 in. from the lamp, and irradiated (48 days). Fractional condensation of the products in vacuo gave:

- (i) a non-condensable gas at  $-196^\circ$ , which showed no i.r. absorption in the range 2.5 to  $15\mu$ ,
- (ii) a  $-196^\circ$  fraction (24.1 mmoles), shown by i.r. spectroscopy to contain ethane, ethylene, and trifluoromethane,
- (iii) 1,1,1-trifluoropropane (0.21 g., 2.1 mmoles, 7%) (Found:

$\bar{M}$ , 100. Calc. for  $C_3H_5F_3$ :  $\bar{M}$ , 98), which condensed at  $-130^\circ$  and was identified by i.r. spectroscopy, and

(iv) a  $-78^\circ$  fraction (1.98 g.), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $70^\circ$ ) to consist of ethyl trifluoromethyl sulphide (1.76 g., 13.5 mmoles, 43%), ethanethiol (0.02 g., 0.3 mmole), diethyl sulphide (0.14 g., 1.6 mmoles), and an unidentified component (trace).

The high-boiling residue was not investigated.

The  $-196^\circ$  fraction (24.1 mmoles) was condensed in vacuo into a hydrolysis bulb (1 l.) and treated with bromine (ca. 1 ml.). The excess bromine was destroyed with mercury and the volatile products (0.925 g., 14.0 mmoles;  $\bar{M}$ , 66) were shown, by i.r. spectroscopy and molecular-weight determinations, to consist of trifluoromethane (0.896 g., 12.8 mmoles, 40%) and ethane (0.026 g., 1.2 mmoles).

Trifluoroiodomethane (100%) reacted to give trifluoromethane (40%), ethyl trifluoromethyl sulphide (43%), and 1,1,1-trifluoropropane (7%).

#### Reactions of Sodium Alkanethiolates with Heptafluoro-1-iodopropane

1. With Sodium Ethanethiolate. Heptafluoro-1-iodopropane (7.25 g., 24.5 mmoles) and sodium ethanethiolate (2.04 g., 24.3 mmoles), in dimethyl sulphoxide (60 ml.), were sealed in a Pyrex tube (300 ml.) and heated at  $100^\circ$  (15 hr.). Fractionation of the volatile products in vacuo gave:

(i)  $1H$ -heptafluoropropane (0.83 g., 4.9 mmoles, 92% based on the iodopropane consumed) (Found:  $\bar{M}$ , 172. Calc. for  $C_3HF_7$ :  $\bar{M}$ , 170), which condensed at  $-130^\circ$  and was identified by i.r. spectroscopy, and

(ii) unreacted heptafluoro-1-iodopropane (5.76 g., 19.5 mmoles,

80% recovered) (Found:  $\underline{M}$ , 294. Calc. for  $C_3F_7I$ :  $\underline{M}$ , 296), which condensed at  $-78^\circ$  and was identified by i.r. spectroscopy.

The residue in the tube was not investigated.

## 2. With Sodium Methanethiolate in the presence of Dimethyl Disulphide.

Heptafluoro-1-iodopropane (5.92 g., 20.0 mmoles), sodium methanethiolate (1.61 g., 23.2 mmoles), and dimethyl disulphide (6.83 g., 72.8 mmoles), in dimethyl sulphoxide (60 ml.), were sealed in a Pyrex tube (300 ml.) and heated at  $100^\circ$  (19 hr.) Fractionation of the volatile products in vacuo gave:

- (i)  $1H$ -heptafluoropropane (0.26 g., 1.5 mmoles, 10%) (Found:  $\underline{M}$ , 170; Calc. for  $C_3HF_7$ :  $\underline{M}$  170), which condensed at  $-130^\circ$  and was identified by i.r. spectroscopy, and
- (ii) a  $-78^\circ$  fraction (3.76 g.), shown by i.r. spectroscopy and g.l.c. (8 m. column at  $40^\circ$ ) to consist of unreacted heptafluoro-1-iodopropane (1.60 g., 5.4 mmoles, 27% recovered), methylheptafluoropropyl sulphide (2.14 g., 9.9 mmoles, 68%), and dimethyl sulphide (trace).

The high-boiling material (mainly dimethyl disulphide and dimethyl sulphoxide) was not examined.

Heptafluoro-1-iodopropane (73%) reacted to give  $1H$ -heptafluoropropane (10%) and methyl heptafluoropropyl sulphide (68%) based on the iodopropane consumed.

In a separate experiment heptafluoro-1-iodopropane and dimethyl disulphide (excess), heated at  $100^\circ$  (20 hr.), failed to react.

Comparison of Certain Reactions of Alkyl and Polyfluoroalkyl Sulphides

1. With Mercuric Chloride. In a typical experiment methyl heptafluoropropyl sulphide (1.31 g., 6.06 mmoles) and mercuric chloride (ca. 5 g.) were sealed in a Pyrex ampoule (20 ml.) and shaken vigorously (15 hr.). The volatile material was transferred to the vacuum-system and identified as unchanged methyl heptafluoropropyl sulphide (1.29 g., 5.97 mmoles, 95% recovered) (Found: M, 216. Calc. for  $C_4H_3F_7S$ : M, 216) by i.r. spectroscopy.

The reaction was extended to a series of polyfluoroalkyl sulphides using similar conditions to those described above.

The results are summarised in Table 22.

TABLE 22

Attempted reaction of polyfluoroalkyl sulphides with mercuric chloride

Sulphide	Wt. (g.)	mmoles	Recovery %
$CF_3CF_2CF_2SMe$	1.31	6.06	95
$(CF_3)_2CF_2SMe$	1.09	5.05	93
$CF_3CF_2CF_2SEt$	1.02	4.44	91
$CF_3SEt$	1.91	14.7	96
$CF_2ClCF_2SMe$	1.10	6.05	95
$CF_3SMe$	1.05	9.05	98
$(CF_3)_2CF_2(CF_2)_4SMe$	3.23	7.84	85

The reaction was then repeated with alkyl sulphides. Thus dimethyl sulphide (0.36 g., 5.8 mmoles) and mercuric chloride (ca. 5 g.) were sealed in a Pyrex ampoule (20 ml.) and shaken (15 hr.). On opening the ampoule in vacuo no volatile material was detected. The solid residue was not examined.

The reaction was extended to other alkyl sulphides and the results obtained are summarised in Table 23.

TABLE 23

Reaction of alkyl sulphides with mercuric chloride

Sulphide	Wt. (g.)	mmoles	Recovery %
Me <sub>2</sub> S	0.36	5.8	0
MeSEt	0.51	6.7	0
Et <sub>2</sub> S	0.71	7.9	4

2. With Iodomethane. Methyl trifluoromethyl sulphide (0.12 g., 1.0 mmole) and iodomethane (0.14 g., 1.0 mmole) were sealed in a Pyrex ampoule (5 ml.) and kept in the dark (12 hr.). Fractional condensation of the products in vacuo gave an equimolar mixture of methyl trifluoromethyl sulphide and iodomethane (0.26 g., 2.0 mmoles, 100%) (Found:  $\bar{M}$ , 128. Calc. for equimolar mixture of C<sub>2</sub>H<sub>3</sub>F<sub>3</sub>S and CH<sub>3</sub>I:  $\bar{M}$ , 129), identified by i.r spectroscopy. The reactants were then resealed and left in the dark (6 months). On re-examination of the volatile material it was found that no reaction had occurred.

A similar reaction (12 hr.) between dimethyl sulphide (0.08 g., 1.3 mmoles) and iodomethane (0.17 g., 1.2 mmoles) gave trimethylsulphonium iodide (0.22 g., 1.10 mmoles, 92%).



## Oxidation of Polyfluoroalkyl Sulphides

### 1. Methyl Heptafluoropropyl Sulphide

a) With potassium permanganate. Methyl heptafluoropropyl sulphide (3.82 g., 17.7 mmoles) was dissolved in glacial acetic acid (60 ml.) contained in a round-bottomed flask which was fitted with a total reflux head maintained at  $-78^{\circ}$ . The flask was cooled in an ice-bath and potassium permanganate (4.18 g., 25.8 mmoles), dissolved in the minimum quantity of hot water, was slowly added (1 hr.) with vigorous stirring. Stirring was continued (4 hr.) during which time the flask attained room temperature.

An aqueous solution of sodium metabisulphite was then added, to destroy the manganese dioxide formed in the reaction, and the product separated as the lower, liquid layer. This was removed with a dropping pipette, washed with aqueous sodium bicarbonate, and dried over molecular sieve (type 4A).

The residue in the flask was partially neutralised with aqueous sodium bicarbonate and extracted with ether (3 x 100 ml.). The ether extract was separated, neutralised as before, dried ( $\text{MgSO}_4$ ), filtered, and the ether removed by distillation. The residual product was combined with that previously separated and distilled from a micro-distillation unit (5 ml.) to give methyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_3$  (3.73 g., 15.0 mmoles, 85%) (Found: C, 19.5; H, 1.2%.  $\text{C}_4\text{H}_3\text{F}_7\text{O}_2\text{S}$  requires C, 19.3; H, 1.2%) b.p.  $154^{\circ}$ .

The mass spectrum (p. 154), n.m.r. spectrum (p. 175), and i.r. spectrum (p. 167) are consistent with the proposed structure.

Subsequent preparations of the sulphone gave yields which varied from 62 to 88%.

b) With fuming nitric acid. Methyl heptafluoropropyl sulphide

(3.04 g., 14.2 mmoles) and fuming nitric acid (d. 1.51, 12 ml.) were sealed in a Pyrex tube (250 ml.) and heated at 100° (14 hr.).

After reaction the tube was cooled to -78°, and the contents transferred to a wide-necked vessel and neutralised by the careful addition of aqueous sodium bicarbonate. This caused the product to separate as a lower layer. The isolation and purification of the product was carried out as described in the preceding experiment, and gave methyl heptafluoropropyl sulphoxide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}\cdot\text{CH}_3$  (2.30 g., 9.9 mmoles, 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. 141-142°.

The mass spectrum (p. 152), n.m.r. spectrum (p. 179), and i.r. spectrum (p. 166) are consistent with the proposed structure.

c) With hydrogen peroxide (1 : 1 molar ratio). Methyl heptafluoropropyl sulphide (6.00 g., 27.8 mmoles) and 100 volume hydrogen peroxide (3.6 ml. 28.1 mmoles) were dissolved in glacial acetic acid (10 ml.), sealed in vacuo in a Pyrex tube (300 ml.), and heated at 100° (24 hr.).

After reaction the solution was transferred to a wide-necked vessel, neutralised with aqueous sodium bicarbonate, and extracted with ether (3 x 20 ml.). The ether extract was washed with water, dried ( $\text{MgSO}_4$ ), filtered, and the ether removed by distillation. The residue was distilled from a micro-distillation unit (10 ml.) and identified by i.r. spectroscopy as methyl heptafluoropropyl sulphoxide (4.60 g., 19.8 mmoles, 71%) b.p. 142°.

d) With an excess of hydrogen peroxide. Methyl heptafluoropropyl sulphide (2.92 g., 13.5 mmoles) and 100 volume hydrogen peroxide (15 ml. 117 mmoles) were dissolved in glacial acetic acid (20 ml.), sealed in vacuo in a Pyrex tube (300 ml.), and heated at 100° (9 days).

The product was isolated by the procedure described in the preceding experiment and identified by i.r. spectroscopy as methyl heptafluoropropyl sulphone (2.89 g., 11.7 mmoles, 86%) b.p.  $154^{\circ}$ .

e) With sodium metaperiodate at  $5^{\circ}$ . Methyl heptafluoropropyl sulphide (2.32 g., 10.7 mmoles) and aqueous 0.5 M-sodium metaperiodate (22.0 ml., 11.0 mmoles) were cooled to  $5^{\circ}$ , in a stoppered flask (100 ml.) and stirred vigorously (8 hr.). The flask and contents were allowed to attain room temperature and stirred for a further 15 hr.

The resultant lower layer of liquid was separated, dried (phosphoric oxide), and transferred to the vacuum-system. After fractional condensation in vacuo, the product was identified by i.r. spectroscopy as unreacted methyl heptafluoropropyl sulphide (2.00 g., 9.4 mmoles, 87% recovered) (Found:  $\underline{M}$ , 214. Calc. for  $C_4H_3F_7S$ :  $\underline{M}$ , 216), condensing at  $-78^{\circ}$ .

f) With sodium metaperiodate at  $100^{\circ}$ . Methyl heptafluoropropyl sulphide (2.16 g., 10.0 mmoles) and aqueous 0.5 M-sodium metaperiodate (20.0 ml. 10.0 mmoles), sealed in a Pyrex tube (300 ml.) and heated at  $100^{\circ}$  (7 days), gave, on fractional condensation of the products in vacuo:

- (i) unchanged methyl heptafluoropropyl sulphide (1.74 g., 8.0 mmoles, 80% recovered) (Found:  $\underline{M}$ , 216. Calc. for  $C_4H_3F_7S$ :  $\underline{M}$ , 216), which condensed at  $-78^{\circ}$  and was identified by i.r. spectroscopy, and
- (ii) a  $-45^{\circ}$  fraction which consisted of two layers. The upper aqueous layer was discarded. The lower layer was dried over molecular sieve (type 4A) to give methyl heptafluoropropyl sulphone (0.30 g., 1.2 mmoles, 60% based on the sulphide consumed),

identified by i.r. spectroscopy.

g) With sodium metaperiodate in methanol. Methyl heptafluoropropyl sulphide (2.41 g., 11.2 mmoles), aqueous 0.5 M-sodium metaperiodate (20.0 ml., 10.0 mmoles), and methanol (15 ml.) were sealed in vacuo in a Pyrex tube (300 ml.) and heated at 100° (24 hr.).

Isolation and identification of products, as described in the preceding experiment, gave unreacted methyl heptafluoropropyl-sulphide (1.83 g., 8.5 mmoles, 76% recovered), which condensed at -78°, and methyl heptafluoropropyl sulphoxide (0.38 g., 1.6 mmoles, 60% based on the sulphide consumed), which condensed at -45° and was shown by i.r. spectroscopy to be contaminated with a trace of the corresponding sulphone.

## 2. Methyl Heptafluoroisopropyl Sulphide

a) With potassium permanganate. Methyl heptafluoroisopropyl sulphide (1.83 g., 8.5 mmoles) and potassium permanganate (1.83 g., 11.5 mmoles) reacted, under the conditions previously described (p.121), to give methyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CH}_3$  (1.24 g., 5.0 mmoles, 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°.

The mass spectrum (p. 154), n.m.r. spectrum (p.183), and i.r. spectrum (p. 167) are consistent with the proposed structure.

b) With fuming nitric acid. Methyl heptafluoroisopropyl sulphide (5.24 g., 24.2 mmoles) and fuming nitric acid (d. 1.51, 20 ml.) reacted, under the conditions previously described (p.122), to give methyl heptafluoroisopropyl sulphoxide,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}\cdot\text{CH}_3$  (4.08 g., 17.6 mmoles, 72%) (Found: C, 20.6; H, 1.3%.  $\text{C}_4\text{H}_3\text{F}_7\text{OS}$  requires C, 20.8;

H, 1.3%) b.p.  $141^{\circ}$ .

The mass spectrum (p.152), n.m.r. spectrum (p.185), and i.r. spectrum (p.166) are consistent with the proposed structure.

### 3. Trifluoromethyl Ethyl Sulphide

With potassium permanganate. Trifluoromethyl ethyl sulphide (4.20 g., 32.3 mmoles) and potassium permanganate (8.00 g., 50.3 mmoles), reacted, under the conditions previously described (p.121), to give trifluoromethyl ethyl sulphone,  $\text{CF}_3\text{SO}_2\text{CH}_2\text{CH}_3$  (4.06 g., 25.2 mmoles, 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.  $142^{\circ}$ .

The mass spectrum (p. 158), n.m.r. spectrum (p.187) and i.r. spectrum (p. 168) are consistent with the proposed structure.

### 4. Methyl Pentadecafluoro-5-methylhexyl Sulphide

With hydrogen peroxide. Methyl pentadecafluoro-5-methyl hexyl sulphide (2.04 g., 4.90 mmoles) was dissolved in glacial acetic acid (10 ml.) and the solution was heated with 100 volume hydrogen peroxide (10 ml.) until the evolution of oxygen ceased. Two further portions of 100 volume hydrogen peroxide were added (2 x 10 ml.) and the solution heated under reflux (16 hr.).

The resultant solution was neutralised with aqueous sodium bicarbonate and extracted with ether (2 x 20 ml.). After separation the ether layer was dried ( $\text{MgSO}_4$ ), filtered, and the ether removed by distillation to leave a white solid. The solid was sublimed twice in vacuo ( $60^{\circ}$ ) to give methyl pentadecafluoro-5-methylhexyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\overset{\text{CF}_3}{\text{C}}\cdot\text{SO}_2\cdot\text{CH}_3$ , (1.82 g., 4.06 mmoles, 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.  $48^{\circ}$ .

The mass spectrum (p. 155), n.m.r. spectrum (p. 172), and i.r. spectrum (p. 167) are consistent with the proposed structure.

### Reactions of Polyfluoroalkyl Sulphones

#### 1. Methyl Heptafluoropropyl Sulphone

a) With sodium hydroxide. Methyl heptafluoropropyl sulphone (0.960 g., 3.87 mmoles) and aqueous 2M-sodium hydroxide (2.0 ml. 4.0 mmoles), sealed in a Pyrex tube (60 ml.) and heated at  $100^{\circ}$  (44 hr.), gave, on fractional condensation of the products in vacuo:

(i) 1H-heptafluoropropane (0.491 g., 2.88 mmoles, 96% based on the sulphone consumed) (Found:  $\underline{M}$ , 170. Calc. for  $C_3HF_7$ :  $\underline{M}$ , 170), which condensed at  $-130^{\circ}$  and was identified by i.r. spectroscopy, and

(ii) a  $-78^{\circ}$  fraction which consisted of two layers. The upper aqueous layer was discarded and the lower layer was identified by i.r. spectroscopy as unreacted methyl heptafluoropropyl sulphone (0.211 g., 0.85 mmole, 22% recovered).

The solid which remained in the tube was neutralised with hydrochloric acid, evaporated to dryness, and shown by i.r. spectroscopy to contain sodium methanesulphonate.

b) With deuterium oxide. Methyl heptafluoropropyl sulphone (2.01 g., 8.1 mmoles), deuterium oxide (3.00 g., 0.150 mole), and a catalytic quantity of sodium deuterioxide (ca. 0.001 g.), contained in a round-bottomed flask (25 ml.), were stirred vigorously at room temperature (72 hr.).

The resultant mixture consisted of two layers which were separated

with a dropping pipette. The lower layer was dried over molecular sieve (type 4A) and was shown by i.r. spectroscopy (p. 169), n.m.r. spectroscopy, and mass spectrometry (p. 159) to be a mixture of deuteromethyl heptafluoropropyl sulphones (1.69 g., ca. 6.6 mmoles, 82%). The extent of hydrogen replacement by deuterium was ca. 90% and the average molecular composition of the mixture may be represented by the formula  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_{0.3}\text{D}_{2.7}$ .

c) With sodium hypochlorite. Methyl heptafluoropropyl sulphone (3.04 g., 12.2 mmoles) and an aqueous solution of sodium hypochlorite (ca. 80 ml., 14% w/v available chlorine), contained in a round-bottomed flask (100 ml.), were stirred vigorously at room temperature (72 hr.).

The lower layer was separated with a dropping pipette, washed with water (2 x 5 ml.), dried over molecular sieve (type 4A), and identified as trichloromethyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CCl}_3$  (4.20 g., 12.0 mmoles, 98%) (Found: C, 13.6; Cl, 30.1%.  $\text{C}_4\text{Cl}_3\text{F}_7\text{O}_2\text{S}$  requires, C, 13.6; Cl, 30.2%) b.p.  $172^\circ$ .

The mass spectrum (p. 156), n.m.r. spectrum (p. 178), and i.r. spectrum (p. 168) are consistent with the proposed structure.

In a separate experiment the reaction was stopped after 12 hr., and the organic layer shown by g.l.c. (2 m. column at  $120^\circ$ ) to consist only of two components; the trichloromethyl sulphone and unreacted methyl heptafluoropropyl sulphone. The corresponding monochloromethyl and dichloromethyl sulphones were not detected.

d) With benzaldehyde. A mixture of methyl heptafluoropropyl sulphone (1.25 g., 5.01 mmoles), benzaldehyde (0.53 g., 5.00 mmoles), and ethanol (0.5 ml.), maintained at  $0^\circ$ , was treated with aqueous 5M-sodium hydroxide (ca. 1 ml., 5 mmoles). The mixture was vigorously

stirred (10 min.) during which time a heavy precipitate was formed which impeded the stirring. The suspension was diluted with water and stirring was continued (1 hr.). The solid was filtered off, washed with water, and recrystallised from ethanol. After drying over phosphoric oxide (48 hr.) in a vacuum-desiccator, white crystals of trans-heptafluoropropyl styryl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH:CHPh}$  (1.47 g., 4.25 mmoles, 85%) (Found: C, 39.0; H, 2.2; F, 39.6%.  $\text{C}_{11}\text{H}_7\text{F}_7\text{O}_2\text{S}$  requires C, 39.3; H, 2.1; F, 39.7%) m.p.  $37-39^\circ$ , were obtained.

The mass spectrum (p. 159), n.m.r. spectrum (p. 180), and i.r. spectrum (p. 167) are consistent with the proposed structure.

e) With iodine in the presence of base. A solution of iodine (3.56 g., 14.0 mmoles) and potassium iodide (ca. 5 g.), in water (20 ml.) was added dropwise to stirred solution of methyl heptafluoropropyl sulphone (0.904 g., 3.64 mmoles) in methanol (2 ml.), followed by dropwise addition of sodium hydroxide solution (ca. 10 ml.). A yellow solid precipitated, which was filtered under nitrogen and washed with water until free of iodide ion. The product was dried in a vacuum-desiccator, over phosphoric oxide, and identified as triiodomethyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CI}_3$  (1.92 g., 3.66 mmoles, 84%) (Found: C, 8.0; I, 60.9%.  $\text{C}_4\text{F}_7\text{I}_3\text{O}_2\text{S}$  requires C, 7.7; I, 61.0%) m.p. (with decomposition)  $100-110^\circ$ .

The n.m.r. spectrum (p. 176) and i.r. spectrum (p. 168) are consistent with the proposed structure.

No attempt was made to recrystallise the sulphone since other experiments showed that the compound decomposed in solution. An attempt to obtain a U.V. spectrum, in hexane and in ethanol, was unsuccessful due to decomposition.



f) With potassium permanganate. Methyl heptafluoropropyl sulphone (2.32 g., 9.35 mmoles), potassium permanganate (4.08 g., 27.0 mmoles), and water (5 ml.) were refluxed (24 hr.). Unreacted potassium permanganate was destroyed by addition of 100 volume hydrogen peroxide and the resultant suspension filtered through glass wool. The filtrate was neutralised with hydrochloric acid and evaporated to dryness. The solid residue was extracted with ethanol, filtered, and again evaporated to dryness to leave a white solid. This was dried over phosphoric oxide and identified as potassium heptafluoropropanesulphonate,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_3\text{K}$  (2.29 g., 7.93 mmoles, 85%) (Found: C, 12.3; S, 11.0%.  $\text{C}_3\text{F}_7\text{KO}_3\text{S}$  requires C, 12.5; S, 11.1%) m.p.  $278^\circ$ .

The n.m.r. spectrum (p. 177), and i.r. spectrum (p. 170) are consistent with the proposed structure.

A sample of potassium heptafluoropropanesulphonate was purified by dissolving it in the minimum quantity of acetone and reprecipitating by the addition of chloroform. The i.r. spectrum of the purified sample was identical with that of the crude sample and the pure sample had m.p.  $282^\circ$ .

g) With fuming nitric acid. Methyl heptafluoropropyl sulphone (2.44 g., 9.8 mmoles) and fuming nitric acid (d. 1.51, 12 ml.) were sealed in vacuo in a Pyrex tube (300 ml.) and heated at  $100^\circ$  (14 hr.). The resultant solution was neutralised with aqueous potassium bicarbonate at  $0^\circ$ , and extracted with ether (2 x 25 ml.). The ether extract was dried over molecular sieve (type 4A), filtered, and distilled. Only unreacted methyl heptafluoropropyl sulphone (2.18 g., 8.8 mmoles, 90% recovered) was obtained.

The aqueous phase was evaporated to dryness and extracted with ethanol. Examination of the ethanol extract showed only the presence

of potassium nitrate (trace).

In another experiment methyl heptafluoropropyl sulphone and nitric acid (d 1.51, 20 ml.) were heated at 150° (72 hr.). Examination of the solution (as above) showed only unreacted methyl heptafluoropropyl sulphone (1.81 g., 7.3 mmoles, 74% recovered).

In a third experiment methyl heptafluoropropyl sulphone (2.53 g., 10.2 mmoles) and nitric acid (d 1.51, 20 ml.) were refluxed (9 days). During the reaction a gas was evolved which gave a precipitate with barium hydroxide solution. Examination of the nitric acid solution (as above) showed that all of the sulphone had been consumed, but no solid or liquid products were detected.

## 2. Trifluoromethyl Ethyl Sulphone

a) With sodium hydroxide. Trifluoromethyl ethyl sulphone (0.851 g., 5.25 mmoles) and aqueous 5M-sodium hydroxide solution (5.0 ml., 25.0 mmoles), sealed in a Pyrex tube (80 ml.) and heated at 100° (36 hr.), gave, after fractional condensation of the products in vacuo, trifluoromethane (0.337 g., 4.85 mmoles, 92%) (Found: M, 70. Calc. for  $\text{CHF}_3$ : M, 70), which was identified by i.r. spectroscopy.

The residue in the tube was neutralised with hydrochloric acid, evaporated to dryness, and shown by i.r. spectroscopy to contain sodium ethanesulphonate.

b) With sodium t-butoxide. Trifluoromethyl ethyl sulphone (0.802 g., 4.94 mmoles) and a solution of t-butoxide (0.79 g., 8.2 mmoles) in hot t-butanol (15 ml.) (prepared by heating sodium in t-butanol) were sealed in a Pyrex tube (80 ml.) and heated at 100° (36 hr.). The volatile products were transferred to the vacuum-system and fractionated

to give:

- (i) trifluoromethane (0.295 g., 4.22 mmoles, 85%) (Found:  $\underline{M}$ , 69. Calc. for  $\text{CHF}_3$ :  $\underline{M}$ , 70), which condensed at  $-196^\circ$  and was identified by i.r. spectroscopy, and
- (ii) isobutane (0.190 g., 3.40 mmoles) (Found:  $\underline{M}$ , 58. Calc. for  $\text{C}_4\text{H}_{10}$ :  $\underline{M}$ , 56), which condensed at  $-130^\circ$  and was identified by i.r. spectroscopy.

c) With sodium hypochlorite. Trifluoromethyl ethyl sulphone (2.43 g., 15.0 mmoles) and an aqueous solution of sodium hypochlorite (ca. 80 ml., 14% w/v available chlorine), contained in a round-bottomed flask (100 ml.), were stirred vigorously at room temperature (36 hr.).

The lower layer was separated with a dropping pipette, washed with water (2 x 5 ml.), dried over molecular sieve (type 4A), and identified as trifluoromethyl 1,1-dichloroethyl sulphone,  $\text{CF}_3\text{SO}_2\text{CCl}_2\text{CH}_3$ . (3.14 g., 13.6 mmoles, 90%) (Found: C, 15.9; H, 1.3; Cl, 30.5; S, 14.0%.  $\text{C}_3\text{H}_3\text{F}_3\text{Cl}_2\text{O}_2\text{S}$  requires C, 15.6; H, 1.3; Cl, 30.7; S, 13.8%) b.p. (Siwoloboff)  $146^\circ$ .

The mass spectrum (p. 156), and i.r. spectrum (p. 169) are consistent with the proposed structure.

### 3. Methyl Heptafluoroisopropyl Sulphone.

With sodium hypochlorite. Methyl heptafluoroisopropyl sulphone (1.92 g., 7.74 mmoles) was vigorously stirred with aqueous sodium hypochlorite solution (50 ml., 14% w/v available chlorine) at room temperature. The product was isolated, as previously described (above), and identified as trichloromethyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CCl}_3$  (2.06 g., 5.85 mmoles, 75%) (Found: C, 14.1; Cl, 29.9; F, 37.5%.  $\text{C}_4\text{Cl}_3\text{F}_7\text{O}_2\text{S}$  requires C, 13.6; Cl, 30.2; F, 37.9%).

The mass spectrum (p. 158), n.m.r. spectrum (p. 172), and i.r. spectrum (p. 168) are consistent with the proposed structure.

#### 4. Methyl Pentadecafluoro-5-methylhexyl Sulphone

With sodium hypochlorite. Methyl pentadecafluoro-5-methylhexyl sulphone (0.981 g., 2.19 mmoles) was treated with aqueous sodium hypochlorite solution (50 ml.), as described in the preceding experiment. The reaction mixture was extracted with ether (3 x 20 ml.), washed with water (2 x 10 ml.), and dried over molecular sieve (type 4A). The resultant solution was filtered, and the ether removed by distillation to give a white solid. This was purified by sublimation in vacuo (30°) and identified as trichloromethyl pentadecafluoro-1-methylhexyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{CCl}_3$  (0.976 g., 1.77 mmoles, 81%) (Found: C, 17.4; Cl, 19.3%.  $\text{C}_8\text{Cl}_3\text{F}_{15}\text{O}_2\text{S}$  requires C, 17.7; Cl, 19.4%) m.p. 31-32°.

The mass spectrum (p. 157), n.m.r. spectrum (p. 172), and i.r. spectrum (p. 168) are consistent with the proposed structure.

An attempt to scale-up the reaction, using methanol as a solvent, was unsuccessful. The reaction mixture became hot and an examination of the solution showed the absence of any polyfluoroalkyl sulphone or polyfluoroalkanesulphonic acid. However, a strong positive test for fluoride ion was obtained. It was noted that the reaction mixture stood in direct sunlight during the reaction.

#### 5. Triiodomethyl Heptafluoropropyl Sulphone

Photolytic decomposition. A round-bottomed flask containing triiodomethyl heptafluoropropyl sulphone (ca. 0.5 g.) and oxygen (0.5 atm.) was placed on the bench in direct sunlight. The sulphone darkened rapidly and deposited elemental iodine on the sides of the

flask.

The volatile products were transferred to the vacuum-system and heptafluoro-1-iodopropane, silicon tetrafluoride, sulphur dioxide, and carbonyl fluoride were shown to be present by i.r. spectroscopy.

A control sample of triiodomethyl heptafluoropropyl sulphone, kept in the dark in vacuo, showed no decomposition.

#### 6. Trichloromethyl Heptafluoropropyl Sulphone

a) With potassium hydroxide. Trichloromethyl heptafluoropropyl sulphone (1.97 g., 5.60 mmoles), aqueous 2M-potassium hydroxide (8.0 ml., 16.0 mmoles), and dioxane (10 ml.), sealed in a Pyrex tube (80 ml.) and heated at 100° (7 days), gave, after fractional condensation in vacuo:

- (i) carbon monoxide (0.063 g., 2.3 mmoles) (Found: M, 28. Calc. for CO: M, 28) which did not condense at -196°, identified by i.r. spectroscopy,
- (ii) 1H-heptafluoropropane (0.119 g., 0.70 mmole, 13%) (Found: M, 170. Calc. for C<sub>3</sub>HF<sub>7</sub>: M, 170), which condensed at -196° and was identified by i.r. spectroscopy,
- (iii) chloroform (0.06 g., 0.51 mmole), which condensed at -78° and was identified by i.r. spectroscopy, and
- (iv) a -45° fraction which was not investigated.

The solid which remained in the tube was extracted with water, neutralised with hydrochloric acid, and the solution evaporated to dryness. The resultant solid was extracted with acetone to leave a solid residue which gave a negative result when tested for fluoride ion.

The acetone extract was centrifuged, to remove traces of a black solid, and evaporated to dryness to yield an off-white solid (1.25 g.)

which was redissolved in acetone and reprecipitated by the addition of chloroform. The solid was identified as potassium heptafluoropropanesulphonate (1.16 g., 4.02 mmoles, 72%) m.p.  $288^{\circ}$  (p. 129, m.p.  $282^{\circ}$ ) by i.r. spectroscopy.

In a separate experiment trichloromethyl heptafluoropropyl sulphone and aqueous 2M-potassium hydroxide were heated at  $100^{\circ}$  (14 days) in the absence of a solvent; 92% of the sulphone was recovered unchanged.

b) Attempted fluorination at  $100^{\circ}$ . Trichloromethyl heptafluoropropyl sulphone (2.39 g., 6.81 mmoles), dry antimony trifluoride (4.31 g., 24.0 mmoles), and antimony pentachloride (4 drops) were sealed in a Pyrex tube (80 ml.) and heated at  $100^{\circ}$  (48 hr.).

The products were separated by fractional condensation in vacuo to give silicon tetrafluoride (0.3 mmole), condensing at  $-196^{\circ}$ , and unchanged trichloromethyl heptafluoropropyl sulphone (2.33 g., 6.62 mmoles, 94% recovered), condensing at  $-22^{\circ}$ . The products were identified by i.r. spectroscopy.

c) Attempted fluorination at  $140^{\circ}$ . Trichloromethyl heptafluoropropyl sulphone (2.18 g., 6.21 mmoles), dry antimony trifluoride (4.46 g., 24.9 mmoles), and antimony pentafluoride (4 drops) were sealed in a Pyrex tube (80 ml.) and heated at  $140^{\circ}$  (7 days).

A qualitative examination of the volatile products by i.r. spectroscopy showed the presence of silicon tetrafluoride, sulphur dioxide, 1-chloroheptafluoropropane, <sup>129</sup>pentafluoropropionyl chloride, <sup>126</sup>and other decomposition products. The reaction was not investigated further.

### Reactions of Methyl Heptafluoropropyl Sulphoxide

1. With Sodium Hydroxide. Methyl heptafluoropropyl sulphoxide (1.73 g., 7.45 mmoles) and aqueous 2M-sodium hydroxide (3.8 ml., 7.6 mmoles), sealed in a Pyrex tube (80 ml.) and heated at 100° (44 hr.), gave, on fractional condensation of the products in vacuo, 1H-heptafluoropropane (1.16 g., 6.85 mmoles, 92%) (Found:  $\bar{M}$ , 170. Calc. for  $C_3HF_7$ :  $\bar{M}$ , 170), condensing at -196° and identified by i.r. spectroscopy, and water (3.56 g.) which condensed at -78°.

The residue in the tube was not examined.

2. With Deuterium Oxide. Methyl heptafluoropropyl sulphoxide (1.68 g., 7.25 mmoles), deuterium oxide (3.00 g., 0.150 mole), and a catalytic quantity of sodium deuterioxide (ca. 0.001 g.), contained in a round-bottomed flask (25 ml.), were stirred vigorously at room temperature (72 hr.).

The isolation of the products was identical to that employed for the corresponding sulphone (p.126). The products were shown by i.r. spectroscopy (p. 166), n.m.r. spectroscopy, and mass spectrometry (p.153) to be a mixture of deuteromethyl heptafluoropropyl sulphoxides (1.29 g., ca. 5.5 mmoles, 76%). The extent of hydrogen replacement by deuterium was ca. 90% and the average molecular composition of the products may be represented by the formula  $CF_3CF_2CF_2SO \cdot CH_{0.3}D_{2.7}$ .

3. With Sodium Hypochlorite. Methyl heptafluoropropyl sulphoxide (2.10 g., 9.05 mmoles) and aqueous sodium hypochlorite (75 ml., 14% w/v available chlorine), contained in a round-bottomed flask (100 ml.), were vigorously stirred at room temperature (6 days). The lower layer of liquid was separated with a dropping pipette and dried over molecular sieve (type 4A).

The resultant liquid was examined by i.r. spectroscopy and g.l.c. (8 m. column at 160°) and shown to consist of unreacted methyl heptafluoropropyl sulphoxide (0.45 g., 1.94 mmoles, 21% recovered), and trichloromethyl heptafluoropropyl sulphone (2.04 g., 5.80 mmoles, 82% based on the sulphoxide consumed.).

3a. Attempted Reaction with Iodine in the presence of Base. Methyl heptafluoropropyl sulphoxide (0.93 g., 4.00 mmoles) was added to an aqueous solution of iodine and potassium iodide. The resultant mixture was warmed to 50° and aqueous 2M-sodium hydroxide added until the yellow colour disappeared. The lower liquid layer was separated with a dropping pipette and identified as unreacted methyl heptafluoropropyl sulphoxide (0.86 g., 3.81 mmoles, 92% recovered) by i.r. spectroscopy.

4. Thermal Stability at 100°. Methyl heptafluoropropyl sulphoxide (2.06 g., 8.90 mmoles), sealed in a Pyrex tube (40 ml.) and heated at 100° (7 days), gave on fractional condensation of the products in vacuo, only unreacted methyl heptafluoropropyl sulphoxide (1.97 g., 8.50 mmoles, 95% recovered), which condensed at -45° and was identified by i.r. spectroscopy.

Attempted Reaction of Methyl Heptafluoropropyl Sulphide with Deuterium Oxide

Methyl heptafluoropropyl sulphide (2.00 g., 9.3 mmoles), deuterium oxide (3.00 g., 0.150 mole), and a catalytic quantity of sodium deuterioxide (ca. 0.001 g.) were sealed in a Pyrex ampoule (30 ml.) and shaken vigorously (36 hr.). The products were separated by fractional condensation in vacuo to give:

(i) unreacted methyl heptafluoropropyl sulphide (1.95 g., 9.1



mmoles, 95%), which condensed at  $-78^{\circ}$  and was identified by i.r. spectroscopy and mass spectrometry, and  
 (ii) a  $-45^{\circ}$  fraction (2.90 g.), which was not investigated but was presumed to be deuterium oxide.

The reactants were resealed in tube together with ethanol (1 ml.) and shaken vigorously (36 hr.). Examination of the products (as above) showed that no deuterium-exchange had occurred.

Photochemical Reaction of Bis(trifluoromethyl) Disulphide with Pentafluoriodobenzene

Bis(trifluoromethyl)disulphide (11.89 g., 58.6 mmoles) and pentafluoriodobenzene (5.20 g., 17.4 mmoles), sealed in a silica tube (300 ml.) and irradiated at a distance of 4 in. from the lamp (24 days), gave, on fractional condensation of the volatile products in vacuo:

- (i) trifluoriodomethane (1.30 g., 6.6 mmoles) (Found: M, 196. Calc. for  $\text{CF}_3\text{I}$ : M, 196), which condensed at  $-196^{\circ}$  and was identified by i.r. spectroscopy, and
- (ii) a combined  $-95^{\circ}$  and  $-78^{\circ}$  fraction (8.08 g.), shown by i.r. spectroscopy to be a mixture of bis(trifluoromethyl) sulphide and disulphide. This fraction was not investigated further.

The liquid remaining in the tube was extracted with ether (2 x 25 ml.), washed with aqueous sodium thiosulphate solution, separated, and dried over molecular sieve (type 4A). After filtration, the ether was removed by distillation and the residue distilled from a micro-distillation unit (5 ml.) to give:

- (iii) a fraction b.p.  $120-124^{\circ}$  (1.74 g.),
- (iv) a fraction b.p.  $130-160^{\circ}$  (1.28 g.), and
- (v) a high-boiling residue (2.01 g.), which was not investigated

further.

Fraction (iii) was identified as trifluoromethyl pentafluorophenyl sulphide,  $\text{CF}_3\text{S}\cdot\text{C}_6\text{F}_5$  (1.74 g., 6.5 mmoles, 42%) (Found: C, 30.5; F, 57.0; S, 11.8%.  $\text{C}_7\text{F}_8\text{S}$  requires C, 31.4; F, 56.8; S, 11.9).

The mass spectrum (p. 151), n.m.r. spectrum (p. 193), and i.r. spectrum (p. 165) are consistent with the proposed structure.

Fraction (iv) was shown by i.r. spectroscopy and g.l.c. (8 m. column at  $160^\circ$ ) to consist of unreacted pentafluoroiodobenzene (0.68 g., 2.3 mmole, 13% recovered) and an unknown component which was identified as trifluoromethyl pentafluorophenyl disulphide,  $\text{CF}_3\text{S}_2\text{C}_6\text{F}_5$  (0.60 g., 2.0 mmoles, 13%) (Found: C, 28.4; F, 50.2; S, 21.1%. Calc. for  $\text{C}_7\text{F}_8\text{S}_2$ : C, 28.0; F, 50.7; S, 21.3%).

The mass spectrum (p. 151), n.m.r. spectrum (p. 194), and i.r. spectrum (p. 165) are consistent with the proposed structure.

Pentafluoroiodobenzene (87%) reacted to give bis(trifluoromethyl) sulphide (42%) and bis(trifluoromethyl) disulphide (13%) based on the iodobenzene consumed.

A P P E N D I X    1

MASS SPECTRA

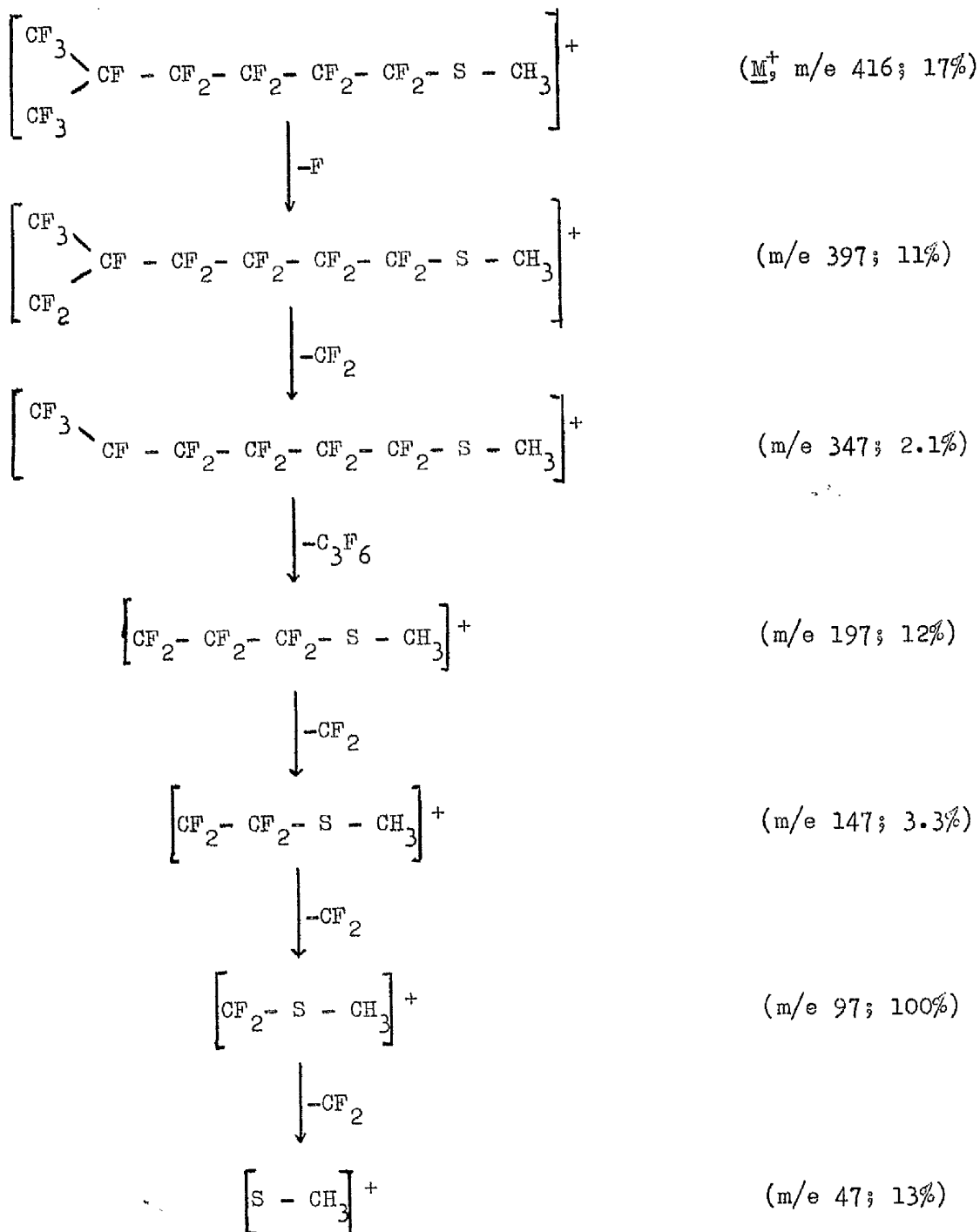
The mass spectra of the compounds prepared were, in all cases, consistent with the proposed structures. The full spectrum of each compound is given at the end of the appendix. It is not proposed to discuss each compound in detail but to discuss certain features common to a group of compounds.

All assignments made are for singly charged ions and only those peaks greater than a certain percentage of the base peak are recorded. This percentage has been determined by the complexity of the breakdown of the compound, and is given in parenthesis by the name of each compound. All spectra are 'isotope corrected', *i.e.*, although isotope peaks were observed, they have not been reported.

1. Compounds of the type  $R_fS \cdot CH_3$  where [ $R_f = CF_3CF_2CF_2$ ,  $(CF_3)_2CF$ ,  $CF_2Cl \cdot CF_2$ ,  $(CF_3)_2CF \cdot (CF_2)_4$ ,  $CF_2I \cdot CF_2$ , and  $CF_2I \cdot (CF_2)_3$ ]

All the methyl polyfluoroalkyl sulphides prepared gave a strong parent-ion peak ( $\underline{M}$ )<sup>+</sup>. Cleavage occurred at the  $CH_3-S$  bond to give the  $CH_3^+$  ion ( $m/e$  15) and at the  $R_f-S$  bond to give the  $[CH_3S]^+$  ion ( $m/e$  47). A particularly strong peak was obtained from cleavage of the  $\alpha-\beta$ , C - C bond of the polyfluoroalkyl chain. Where the  $\alpha$ -carbon possessed two fluorine atoms this peak occurred at  $m/e$  97 and was assigned to the  $[CF_2S \cdot CH_3]^+$  ion. In the absence of an  $\omega$ -iodine atom in the polyfluoroalkyl chain, cleavage of the  $\alpha-\beta$ , C - C bond gave the base peak. An  $(\underline{M} - X)^+$  peak (where  $X = F, Cl, \text{ or } I$ ) was always present; in the case of  $\omega$ -iodopolyfluoroalkyl sulphides, the ready loss of an iodine atom gave rise to the base peak. All compounds of the type  $R_fS \cdot CH_3$  showed breakdown by loss of successive fluoroalkyl

fragments, while maintaining the integrity of the  $\text{CH}_3\text{S}$  group, e.g.,



The arrows are merely used to show a decrease in molecular weight and not to signify each ion is derived exclusively from its

predecessor.

An alternative mode of cleavage of  $R_f-S$  bond (i.e., with retention of the positive charge on the  $R_f$  group, rather than on the  $CH_3S$  group) gave the  $R_f^+$  ion, or breakdown products derived from it.

2. Compounds of the type  $CH_3S \cdot (CF_2CF_2)_n \cdot S \cdot CH_3$  (where  $n = 1$  or  $2$ )

The spectra of these compounds showed a very similar breakdown pattern to the methyl polyfluoroalkyl sulphides described above. A strong parent-ion peak was observed, as were peaks corresponding to the ions,  $CH_3^+$  ( $m/e$  15) and  $[CH_3S]^+$  ( $m/e$  47). Cleavage of the  $\alpha - \beta$ , C - C bond also occurred and the resultant ion,  $[CF_2S \cdot CH_3]^+$  ( $m/e$  97) corresponded to the base peak. A small peak was observed at  $(M - 47)^+$ . Breakdown also occurred, as in the preceding group of compounds, by loss of fluoroalkyl fragments while the positive charge remained on the fragment carrying the  $CH_3S$  group

3. Compounds of the type  $R_fS \cdot C_2H_5$  (where  $R_f = CF_3CF_2CF_2$  or  $CF_3$ )

A strong parent-ion peak was observed and the breakdown pattern was again similar to the methyl polyfluoroalkyl sulphides. Cleavage of the carbon-sulphur bonds gave the ions  $C_2H_5^+$  ( $m/e$  29; base peak) and  $[C_2H_5S]^+$  ( $m/e$  61). Cleavage of the  $\alpha - \beta$ , C - C bond of the ethyl group in both compounds, and of the  $\alpha - \beta$ , C - C bond of the polyfluoroalkyl group, in the heptafluoropropyl sulphide, gave rise to ions of the type  $[CH_2SR_f]^+$  and  $[CF_2S \cdot C_2H_5]^+$  ( $m/e$  111) respectively. Peaks corresponding to perfluoroalkyl ions were again evident.

#### 4. Trifluoromethyl Pentafluorophenyl Sulphide and Disulphide

Both compounds gave a strong parent-ion peak. Cleavage of the  $\text{CF}_3\text{-S}$  bond gave the ion  $\text{CF}_3^+$  (m/e 69). A strong peak at m/e 199, assigned to the ion  $[\text{C}_6\text{F}_5\text{S}]^+$ , was present and the peak at m/e 147 was assigned to the ion  $[\text{C}_5\text{F}_5]^+$ .

#### 5. Compounds of the type $\text{R}_f\text{SO}\cdot\text{CH}_3$ [where $\text{R}_f = \text{CF}_3\text{CF}_2\text{CF}_2$ or $(\text{CF}_3)_2\text{CF}$ ]

These compounds gave a parent-ion peak of medium intensity. Cleavage of the  $\text{CH}_3\text{-S}$  bond gave a weak peak corresponding to the  $\text{CH}_3^+$  ion (m/e 15) and cleavage of the  $\text{R}_f\text{-S}$  bond gave rise to the base peak  $[\text{CH}_3\text{SO}]^+$  (m/e 63). The alternative mode of cleavage of the  $\text{R}_f\text{-S}$  bond gave a peak corresponding to the  $\text{R}_f^+$  ion. A weak peak at m/e 48 was assigned to the  $\text{SO}^+$  ion. 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 were observed.

#### 6. Compounds of the type $\text{R}_f\text{SO}_2\cdot\text{CH}_3$ [where $\text{R}_f = \text{CF}_3\text{CF}_2\text{CF}_2$ , $(\text{CF}_3)_2\text{CF}$ , or $(\text{CF}_3)_2\text{CF}\cdot(\text{CF}_2)_4$ ]

These compounds did not give a parent-ion peak. Cleavage of the  $\text{CH}_3\text{-S}$  bond gave a weak peak corresponding to the  $\text{CH}_3^+$  ion (m/e 15), and cleavage of the  $\text{R}_f\text{-S}$  bond gave the base peak  $[\text{CH}_3\text{SO}_2]^+$  (m/e 79). The alternative cleavage of this bond gave the  $\text{R}_f^+$  ion. Weak peaks were observed at m/e 64 and m/e 48 corresponding to the ions  $\text{SO}_2^+$  and  $\text{SO}^+$  respectively.

7. Compounds of the type  $R_fSO_2CCl_3$  [where  $R_f = CF_3CF_2CF_2$ ,  $(CF_3)_2CF$ , or  $(CF_3)_2CF(CF_2)_4$ ]

Again no parent-ion peak was observed for these sulphones.

Cleavage of the  $CCl_3-S$  bond gave rise to the base peak  $CCl_3^+$  ( $m/e$  117). A weak peak assigned to the  $[R_fSO]^+$  ion was also observed. Cleavage of the  $R_f-S$  bond gave a peak corresponding to the  $R_f^+$  ion. The spectra of these compounds consisted largely of the breakdown pattern of the trichloromethyl group and the polyfluoroalkyl groups, although peaks at  $m/e$  64 and  $m/e$  48 were present which corresponded to the ions  $SO_2^+$  and  $SO^+$  respectively.



SULPHIDES

Methyl heptafluoropropyl sulphide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	12	$\text{CH}_3$	100	5.0	$\text{C}_2\text{F}_4$
31	7.0	$\text{CF}$	113	9.4	$\text{C}_2\text{F}_3\text{S}$
35	14	$\text{H}_3\text{S}$	119	5.3	$\text{C}_2\text{F}_5$
45	37	$\text{CHS}$	127	5.0	$\text{C}_3\text{H}_2\text{F}_3\text{S}$
46	33	$\text{CH}_2\text{S}$	147	14	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
47	69	$\text{CH}_3\text{S}$	163	3.2	$\text{C}_3\text{F}_5\text{S}$
63	3.4	$\text{CFS}$	169	20	$\text{C}_3\text{F}_7$
69	24	$\text{CF}_3$	178	3.2	$\text{C}_4\text{H}_3\text{F}_5\text{S}$
82	4.9	$\text{CF}_2\text{S}$	197	12	$\text{C}_4\text{H}_3\text{F}_6\text{S}$
83	3.2	$\text{CHF}_2\text{S}$	216	79	$\text{C}_4\text{H}_3\text{F}_7\text{S}(\underline{\text{M}})$
97	100	$\text{C}_2\text{H}_3\text{F}_2\text{S}$			

Methyl heptafluoroisopropyl sulphide,  $(\text{CF}_3)_2\text{CF}\cdot\text{S}\cdot\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	10	$\text{CH}_3$	69	24	$\text{CF}_3$
31	5.6	$\text{CF}$	97	30	$\text{C}_2\text{H}_3\text{F}_2\text{S}$
44	3.1	$\text{CS}$	100	5.3	$\text{C}_2\text{F}_4$
45	31	$\text{CHS}$	113	26	$\text{C}_2\text{F}_3\text{S}$
46	23	$\text{CH}_2\text{S}$	127	4.7	$\text{C}_3\text{H}_2\text{F}_3\text{S}$
47	20	$\text{CH}_3\text{S}$	147	<u>100</u>	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
63	16	$\text{CFS}$	197	14	$\text{C}_3\text{H}_3\text{F}_6\text{S}$
65	4.5	$\text{C}_2\text{H}_3\text{F}_2$	216	68	$\text{C}_4\text{H}_3\text{F}_7\text{S}(\underline{\text{M}})$

Methyl 2-chlorotetrafluoroethyl sulphide,  $\text{CF}_2\text{Cl}\cdot\text{CF}_2\text{S}\cdot\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	5.3	$\text{CH}_3$	82	4.0	$\text{CF}_2\text{S}$
31	4.5	$\text{CF}$	85	9.3	$\text{CClF}_2$
44	4.2	$\text{CS}$	97	<u>100</u>	$\text{C}_2\text{H}_3\text{F}_2\text{S}$
45	20	$\text{CHS}$	100	3.2	$\text{C}_2\text{F}_4$
46	10	$\text{CH}_2\text{S}$	113	5.6	$\text{C}_2\text{F}_3\text{S}; \text{C}_2\text{H}_3\text{ClF}$
47	20	$\text{CH}_3\text{S}; \text{CCl}$	135	5.2	$\text{C}_2\text{ClF}_4$
50	3.2	$\text{CF}_2$	147	17	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
63	16	$\text{CFS}$	167	6.2	$\text{C}_2\text{ClF}_4\text{S}$
77	9.3	$\text{C}_2\text{H}_2\text{FS}$	182	36	$\text{C}_3\text{H}_3\text{ClF}_4\text{S}(\underline{\text{M}})$

Methyl tetrafluoro-2-iodoethyl sulphide,  $\text{CF}_2\text{I}\cdot\text{CF}_2\text{S}\cdot\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	6.4	$\text{CH}_3$	100	6.0	$\text{C}_2\text{F}_4$
31	3.7	$\text{CF}$	126	3.7	$\text{C}_3\text{HF}_3\text{S}$
45	13	$\text{CHS}$	127	5.2	$\text{I}; \text{C}_3\text{H}_2\text{F}_3\text{S}$
46	11	$\text{CH}_2\text{S}$	128	7.4	$\text{HI}; \text{C}_3\text{H}_3\text{F}_3\text{S}$
47	12	$\text{CH}_3\text{S}$	147	100	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
63	9.3	$\text{CFS}$	174	13	$\text{CH}_3\text{IS}$
76	6.8	$\text{C}_2\text{HFS}$	177	3.6	$\text{CF}_2\text{I}$
77	3.7	$\text{C}_2\text{H}_2\text{FS}$	274	15	$\text{C}_3\text{H}_3\text{F}_4\text{IS}(\underline{\text{M}})$
97	48	$\text{C}_2\text{H}_3\text{F}_2\text{S}$			

Methyl octafluoro-4-iodobutyl sulphide,  $\text{CF}_2\text{I}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	6.3	$\text{CH}_3$	127	15	$\text{I}; \text{C}_3\text{H}_2\text{F}_3\text{S}$
31	4.5	$\text{CF}$	128	25	$\text{HI}; \text{C}_3\text{H}_3\text{F}_3\text{S}$
45	11	$\text{CHS}$	147	7.8	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
46	7.5	$\text{CH}_2\text{S}$	177	16	$\text{CF}_2\text{I}$
47	17	$\text{CH}_3\text{S}$	197	14	$\text{C}_4\text{H}_3\text{F}_6\text{S}$
63	12	$\text{CFS}$	213	9.6	$\text{C}_4\text{F}_7\text{S}$
69	9.3	$\text{CF}_3$	227	43	$\text{C}_2\text{F}_4\text{I}$
77	5.4	$\text{C}_2\text{H}_2\text{FS}$	247	<u>100</u>	$\text{C}_5\text{H}_3\text{F}_8\text{S}$
97	53	$\text{C}_2\text{H}_3\text{F}_2\text{S}$	355	4.0	$\text{C}_5\text{H}_3\text{F}_7\text{IS}$
100	12	$\text{C}_2\text{F}_4$	374	14	$\text{C}_5\text{H}_3\text{F}_8\text{IS}(\underline{\text{M}})$

Methyl pentadecafluoro-5-methylhexyl sulphide,  $(\text{CF}_3)_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{S}\cdot$   
 $\text{CH}_3$  (>1%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	7.2	$\text{CH}_3$	128	6.9	$\text{C}_3\text{H}_3\text{F}_3\text{S}$
31	1.2	$\text{CF}^\bullet$	131	6.3	$\text{C}_3\text{F}_5$
45	13	$\text{CHS}$	147	3.3	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
46	7.2	$\text{CH}_2\text{S}$	150	1.2	$\text{C}_3\text{F}_6$
47	13	$\text{CH}_3\text{S}$	167	1.2	$\text{C}_3\text{H}_4\text{F}_5\text{S}$
50	1.2	$\text{CF}_2$	169	1.0	$\text{C}_3\text{F}_7$
51	1.8	$\text{CHF}_2$	178	1.8	$\text{C}_4\text{H}_3\text{F}_5\text{S}$
63	5.7	$\text{CFS}$	181	1.8	$\text{C}_4\text{F}_7$
69	29	$\text{CF}_3$	195	5.2	$\text{C}_4\text{HF}_6\text{S}$
77	1.8	$\text{C}_2\text{H}_2\text{F}_5\text{S}$	196	1.8	$\text{C}_4\text{H}_2\text{F}_6\text{S}$
79	1.8	$\text{C}_2\text{H}_4\text{F}_5\text{S}$	197	12	$\text{C}_4\text{H}_3\text{F}_6\text{S}$
94	1.2	$\text{C}_3\text{HF}_3$	347	2.1	$\text{C}_7\text{H}_3\text{F}_{12}\text{S}$
97	<u>100</u>	$\text{C}_2\text{H}_3\text{F}_2\text{S}$	364	12	$\text{C}_7\text{H}_4\text{F}_{13}\text{S}$
100	7.2	$\text{C}_2\text{F}_4$	397	11	$\text{C}_8\text{H}_3\text{F}_{14}\text{S}$
101	5.1	$\text{C}_2\text{HF}_4$	415	1.8	$\text{C}_8\text{H}_2\text{F}_{15}\text{S}$
119	2.7	$\text{C}_2\text{F}_5$	416	17	$\text{C}_8\text{H}_3\text{F}_{15}\text{S}(\underline{\text{M}})$

Bis(methylthio)methane,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_3$  (>1%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
27	8.2	$\text{C}_2\text{H}_3$	60	3.6	$\text{C}_2\text{H}_4\text{S}$
35	19	$\text{H}_3\text{S}$	61	<u>100</u>	$\text{C}_2\text{H}_5\text{S}$
45	22	$\text{CHS}$	76	1.4	$\text{CS}_2$
46	8.3	$\text{CH}_2\text{S}$	78	1.4	$\text{CH}_2\text{S}_2$
47	6.7	$\text{CH}_3\text{S}$	93	2.3	$\text{C}_2\text{H}_5\text{S}_2$
58	1.8	$\text{C}_2\text{H}_2\text{S}$	108	82	$\text{C}_3\text{H}_8\text{S}_2(\underline{\text{M}})$

1,2-Bis(methylthio)tetrafluoroethane,  $\text{CH}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CH}_3$  (>1%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	3.7	$\text{CH}_3$	77	3.6	$\text{C}_2\text{H}_2\text{FS}$
31	1.4	$\text{CF}$	79	6.9	$\text{CH}_3\text{S}_2$
44	1.4	$\text{CS}$	81	1.1	$\text{C}_2\text{F}_3$
45	13	$\text{CHS}$	94	4.1	$\text{C}_2\text{H}_6\text{S}_2$
46	6.9	$\text{CH}_2\text{S}$	97	<u>100</u>	$\text{C}_2\text{H}_3\text{F}_2\text{S}$
47	11	$\text{CH}_3\text{S}$	113	1.4	$\text{C}_2\text{F}_3\text{S}$
48	3.0	$\text{CH}_4\text{S}$	125	1.8	$\text{C}_3\text{F}_3\text{S}$
61	1.8	$\text{C}_2\text{H}_5\text{S}$	128	1.8	$\text{C}_3\text{H}_3\text{F}_3\text{S}$
63	13	$\text{CFS}$	147	5.1	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
69	1.1	$\text{CF}_3$	175	1.1	$\text{C}_4\text{H}_6\text{F}_3\text{S}_2$
76	2.2	$\text{CS}_2$ ; $\text{C}_2\text{HFS}$	194	26	$\text{C}_4\text{H}_6\text{F}_4\text{S}_2(\underline{\text{M}})$

1,4-Bis(methylthio)octafluorobutane,  $\text{CH}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CH}_3$  (>1%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	2.6	$\text{CH}_3$	113	1.5	$\text{C}_2\text{F}_3\text{S}$
45	7.9	$\text{CHS}$	128	4.7	$\text{C}_2\text{H}_3\text{F}_3\text{S}$
46	6.3	$\text{CH}_2\text{S}$	131	1.3	$\text{C}_3\text{F}_5$
47	14	$\text{CH}_3\text{S}$	147	3.8	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
63	5.2	$\text{CFS}$	197	1.8	$\text{C}_4\text{H}_3\text{F}_6\text{S}$
77	1.8	$\text{C}_2\text{H}_2\text{FS}$	247	3.8	$\text{C}_5\text{H}_3\text{F}_8\text{S}$
78	2.8	$\text{C}_2\text{H}_3\text{FS}$	275	2.3	$\text{C}_6\text{H}_6\text{F}_7\text{S}_2$
94	1.2	$\text{C}_2\text{H}_6\text{S}_2$	279	1.9	$\text{C}_5\text{H}_3\text{F}_8\text{S}_2$
97	<u>100</u>	$\text{C}_2\text{H}_3\text{F}_2\text{S}$	281	1.5	
100	1.8	$\text{C}_2\text{F}_4$	294	20	$\text{C}_6\text{H}_6\text{F}_8\text{S}_2(\underline{\text{M}})$

Trifluoromethyl ethyl sulphide,  $\text{CF}_3\cdot\text{S}\cdot\text{CH}_2\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
27	30	$\text{C}_2\text{H}_3$	59	6.8	$\text{C}_2\text{H}_3\text{S}$
29	<u>100</u>	$\text{C}_2\text{H}_5$	60	4.0	$\text{C}_2\text{H}_4\text{S}$
35	6.8	$\text{H}_3\text{S}$	61	11	$\text{C}_2\text{H}_5\text{S}$
45	10	$\text{CHS}$	63	8.0	$\text{CFS}$
46	4.4	$\text{CH}_2\text{S}$	69	28	$\text{CF}_3$
47	6.8	$\text{CH}_3\text{S}$	82	4.4	$\text{CF}_2\text{S}$
50	3.0	$\text{CF}_2$	83	10	$\text{CHF}_2\text{S}$
57	3.2	$\text{C}_2\text{HS}$	115	18	$\text{C}_2\text{H}_2\text{F}_3\text{S}$
58	4.6	$\text{C}_2\text{H}_2\text{S}$	130	33	$\text{C}_3\text{H}_5\text{F}_3\text{S}(\underline{\text{M}})$

Ethyl heptafluoropropyl sulphide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_2\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
14	4.0	$\text{CH}_2$	61	9.5	$\text{C}_2\text{H}_5\text{S}$
15	3.1	$\text{CH}_3$	63	9.5	$\text{CFS}$
27	30	$\text{C}_2\text{H}_3$	69	24	$\text{CF}_3$
29	<u>100</u>	$\text{C}_2\text{H}_5$	82	3.6	$\text{CF}_2\text{S}$
33	5.9	$\text{HS}$	83	18	$\text{CHF}_2\text{S}$
35	6.4	$\text{H}_3\text{S}$	100	4.3	$\text{C}_2\text{F}_4$
45	11	$\text{CHS}$	111	45	$\text{C}_3\text{H}_5\text{F}_2\text{S}$
46	7.7	$\text{CH}_2\text{S}$	119	3.6	$\text{C}_2\text{F}_5$
47	4.1	$\text{CH}_3\text{S}$	169	12	$\text{C}_3\text{F}_7$
58	4.8	$\text{C}_2\text{H}_2\text{S}$	183	3.5	$\text{C}_3\text{HF}_6\text{S}$
59	6.2	$\text{C}_2\text{H}_3\text{S}$	215	16	$\text{C}_5\text{H}_2\text{F}_7\text{S}$
60	8.4	$\text{C}_2\text{H}_4\text{S}$	230	50	$\text{C}_5\text{H}_5\text{F}_7\text{S}(\underline{\text{M}})$

Trifluoromethyl pentafluorophenyl sulphide,  $\text{CF}_3\text{S}\cdot\text{C}_6\text{F}_5$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	8.1	$\text{CF}$	117	17	$\text{C}_5\text{F}_3$
63	6.8	$\text{CFS}$	149	12	$\text{C}_5\text{F}_3\text{S}$
69	91	$\text{CF}_3$	155	47	$\text{C}_5\text{F}_5$
79	3.2	$\text{C}_5\text{F}$	167	4.7	$\text{C}_6\text{F}_5$
86	3.7	$\text{C}_4\text{F}_2$	180	6.7	$\text{C}_6\text{F}_4\text{S}$
87	19	$\text{C}_3\text{FS}$	199	91	$\text{C}_6\text{F}_5\text{S}$
93	9.3	$\text{C}_3\text{F}_3$	202	4.2	$\text{C}_2\text{F}_6\text{S}_2$
98	3.9	$\text{C}_5\text{F}_2$	249	13	$\text{C}_7\text{F}_7\text{S}$
105	3.5	$\text{C}_4\text{F}_3$	268	<u>100</u>	$\text{C}_7\text{F}_8\text{S}(\underline{\text{M}})$
111	6.7	$\text{C}_5\text{FS}$			

Trifluoromethyl pentafluorophenyl disulphide,  $\text{CF}_3\text{S}\cdot\text{S}\cdot\text{C}_6\text{F}_5$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	7.7	$\text{CF}$	117	15	$\text{C}_5\text{F}_3$
63	11	$\text{CFS}$	131	3.2	$\text{C}_3\text{F}_5$
64	11	$\text{S}_2$	149	14	$\text{C}_5\text{F}_3\text{S}$
69	63	$\text{CF}_3$	155	43	$\text{C}_5\text{F}_5$
76	3.5	$\text{CS}_2$	167	3.0	$\text{C}_6\text{F}_5$
82	10	$\text{CF}_2\text{S}$	168	17	
87	9.0	$\text{C}_3\text{FS}$	187	14	$\text{C}_5\text{F}_5\text{S}$
93	10	$\text{C}_3\text{F}_3$	199	<u>100</u>	$\text{C}_6\text{F}_5\text{S}$
98	4.3	$\text{C}_5\text{F}_2$	231	18	$\text{C}_6\text{F}_5\text{SS}$
99	3.4	$\text{C}_4\text{FS}$	268	6.3	$\text{C}_7\text{F}_8\text{S}$
101	3.3	$\text{CF}_3\text{S}$	294	3.0	
105	3.5	$\text{C}_4\text{F}_3$	300	61	$\text{C}_7\text{F}_8\text{S}_2(\underline{\text{M}})$
111	6.0	$\text{C}_5\text{FS}$			



SULPHOXIDES

Methyl heptafluoropropyl sulphoxide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}\cdot\text{CH}_3$  (>2%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	6.2	$\text{CH}_3$	63	<u>100</u>	$\text{CH}_3\text{OS}; (\text{CFS})$
31	8.4	$\text{CF}$	69	48	$\text{CF}_3$
34	2.7	$\text{H}_2\text{S}$	97	3.8	$\text{C}_2\text{H}_3\text{F}_2\text{S}$
45	10	$\text{CHS}$	100	6.4	$\text{C}_2\text{F}_4$
46	4.7	$\text{CH}_2\text{S}$	119	6.8	$\text{C}_2\text{F}_5$
47	19	$\text{CH}_3\text{S}$	169	14	$\text{C}_3\text{F}_7$
48	4.1	$\text{OS}$	232	37	$\text{C}_3\text{H}_3\text{F}_7\text{OS}(\underline{\text{M}})$
62	2.2	$\text{CH}_2\text{OS}$			

Methyl heptafluoroisopropyl sulphoxide,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}\cdot\text{CH}_3$  (>2%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	8.0	$\text{CH}_3$	62	2.2	$\text{CH}_2\text{OS}$
31	7.9	$\text{CF}$	63	<u>100</u>	$\text{CH}_3\text{OS}; (\text{CFS})$
33	2.2	$\text{HS}$	67	6.9	$\text{FOS}$
34	2.6	$\text{H}_2\text{S}$	69	29	$\text{CF}_3$
45	13	$\text{CHS}$	97	6.8	$\text{C}_2\text{H}_3\text{F}_2\text{S}$
46	6.2	$\text{CH}_2\text{S}$	100	5.3	$\text{C}_2\text{F}_4$
47	3.5	$\text{CH}_3\text{S}$	131	3.2	$\text{C}_3\text{F}_5$
48	6.3	$\text{OS}$	147	5.6	$\text{C}_3\text{H}_3\text{F}_4\text{S}$
50	2.5	$\text{CF}_2$	232	8.2	$\text{C}_3\text{H}_3\text{F}_7\text{OS}(\underline{\text{M}})$

Deuteromethyl heptafluoropropyl sulphoxides, (mixture)

(peaks below m/e 31 not included)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	7.1	CF	69	62	CF <sub>3</sub>
34	5.8	H <sub>2</sub> S; DS	100	13	C <sub>2</sub> F <sub>4</sub>
36	4.8	D <sub>2</sub> S	119	8.8	C <sub>2</sub> F <sub>5</sub>
46	11	CH <sub>2</sub> S; CDS	131	3.7	C <sub>3</sub> F <sub>5</sub>
48	3.2	CH <sub>2</sub> DS; CD <sub>2</sub> S	169	17	C <sub>3</sub> F <sub>7</sub>
50	23	CD <sub>3</sub> S; CF <sub>2</sub>	232	1.2	C <sub>4</sub> H <sub>3</sub> F <sub>7</sub> OS( <u>M</u> )
63	4.9	CH <sub>3</sub> OS; CFS	233	1.7	C <sub>4</sub> H <sub>2</sub> DF <sub>7</sub> OS( <u>M</u> )
64	5.5	CH <sub>2</sub> DOS; CD <sub>2</sub> OS	234	14	C <sub>4</sub> HD <sub>2</sub> F <sub>7</sub> OS( <u>M</u> )
65	37	CHD <sub>2</sub> OS	235	37	C <sub>4</sub> D <sub>3</sub> F <sub>7</sub> OS( <u>M</u> )
66	<u>100</u>	CD <sub>3</sub> OS; (CFS)			

SULPHONES

Methyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_3$  (>2%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	37	$\text{CH}_3$	69	86	$\text{CF}_3$
31	9.8	CF	79	<u>100</u>	$\text{CH}_3\text{O}_2\text{S}$
45	3.7	CHS	100	15	$\text{C}_2\text{F}_4$
48	5.5	OS	119	9.9	$\text{C}_2\text{F}_5$
50	3.0	$\text{CF}_2$	150	2.0	$\text{C}_3\text{F}_6$
63	22	$\text{CH}_3\text{OS}$ ; CFS	169	30	$\text{C}_3\text{F}_7$
64	3.6	$\text{O}_2\text{S}$			

Methyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CH}_3$  (>0.5%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	36	$\text{CH}_3$	67	1.6	FOS
31	4.4	CF	69	19	$\text{CF}_3$
44	0.5	CS	79	<u>100</u>	$\text{CH}_3\text{O}_2\text{S}$
45	1.5	CHS	100	7.0	$\text{C}_2\text{F}_4$
46	0.7	$\text{CH}_2\text{S}$	119	0.5	$\text{C}_2\text{F}_5$
48	2.3	OS	131	0.5	$\text{C}_3\text{F}_5$
50	0.6	$\text{CF}_2$	150	0.8	$\text{C}_3\text{F}_6$
63	4.0	$\text{CH}_3\text{OS}$ ; CFS	169	0.5	$\text{C}_3\text{F}_7$
64	1.3	$\text{O}_2\text{S}$			

Methyl pentadecafluoro-5-methylhexyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot$

$\text{SO}_2\text{CH}_3$  (>0.5%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
15	28	$\text{CH}_3$	112	2.7	$\text{C}_3\text{F}_4$
31	1.3	$\text{CF}$	119	3.9	$\text{C}_2\text{F}_5$
45	1.3	$\text{CHS}$	131	12	$\text{C}_3\text{F}_5$
46	0.5	$\text{CH}_2\text{S}$	150	0.6	$\text{C}_3\text{F}_6$
47	1.0	$\text{CH}_3\text{S}$	169	0.6	$\text{C}_3\text{F}_7$
48	1.1	$\text{OS}$	181	2.9	$\text{C}_4\text{F}_7$
63	24	$\text{CH}_3\text{OS}; \text{CFS}$	231	0.5	$\text{C}_5\text{F}_9$
64	0.8	$\text{O}_2\text{S}$	281	2.0	$\text{C}_6\text{F}_{11}$
69	49	$\text{CF}_3$	350	0.5	$\text{C}_7\text{F}_{14}$
79	<u>100</u>	$\text{CH}_3\text{O}_2\text{S}$	369	1.4	$\text{C}_7\text{F}_{15}$
93	1.5	$\text{C}_3\text{F}_3$	430	3.5	$\text{C}_7\text{F}_{15}\text{O}_2\text{S}$
97	1.7	$\text{C}_2\text{H}_3\text{F}_2\text{S}$	433	0.6	
100	7.4	$\text{C}_2\text{F}_4$			

Trichloromethyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CCl}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	3.5	CF	83	6.5	$\text{C}_2\text{ClOS}$
47	18	CCl	85	3.6	$\text{CClF}_2$
48	11	OS	100	14	$\text{C}_2\text{F}_4$
50	3.6	$\text{CF}_2$	117	<u>100</u>	$\text{CCl}_3$
63	20	CFS	131	6.4	$\text{C}_3\text{F}_5$
64	5.2	$\text{O}_2\text{S}$	150	4.9	$\text{C}_3\text{F}_6$
67	3.3	ClS; FOS	169	13	$\text{C}_3\text{F}_7$
69	73	$\text{CF}_3$	185	5.9	$\text{C}_3\text{ClF}_6$
79	4.7	$\text{CClS}$	217	9.4	$\text{C}_3\text{F}_7\text{OS}$
82	27	$\text{CCl}_2$	233	4.9	$\text{C}_3\text{F}_7\text{O}_2\text{S}$

Trifluoromethyl 1,1-dichloroethyl sulphone,  $\text{CF}_3\text{SO}_2\text{CCl}_2\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
36	14	HCl	64	32	$\text{O}_2\text{S}$
43	20	$\text{C}_2\text{F}$	65	12	$\text{HO}_2\text{S}$
44	4.1	$\text{C}_2\text{HF}$ ; CS	67	3.2	ClS; FOS
48	19	OS	69	45	$\text{CF}_3$
50	3.3	$\text{CF}_2$	82	8.4	$\text{CCl}_2$
60	11	$\text{C}_2\text{HCl}$	83	8.4	$\text{CHCl}_2$
61	70	$\text{C}_2\text{H}_2\text{Cl}$	91	6.5	
62	10	$\text{C}_2\text{H}_3\text{Cl}$	97	<u>100</u>	$\text{C}_2\text{H}_3\text{Cl}_2$

Trichloromethyl pentadecafluoro-5-methylhexyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2$

$\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{SO}_2\text{CCl}_3$  (>0.3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	4.0	CF	117	<u>100</u>	$\text{CCl}_3$
35	1.6	Cl	131	21	$\text{C}_3\text{F}_5$
44	0.7	CS	135	0.5	$\text{C}_2\text{ClF}_4$
47	8.2	$\text{ClS}$	143	0.5	$\text{C}_4\text{F}_5$
48	6.5	OS	147	0.5	$\text{C}_3\text{ClF}_4$
50	1.6	$\text{CF}_2$	150	1.5	$\text{C}_3\text{F}_6$
63	6.6	CFS	169	1.6	$\text{C}_3\text{F}_7$
64	8.9	$\text{O}_2\text{S}$	181	4.7	$\text{C}_4\text{F}_7$
65	2.3		182	2.8	$\text{C}_3\text{F}_6\text{S}$
67	2.4	$\text{ClS}$ ; FOS	185	0.3	$\text{C}_3\text{ClF}_6$
69	77	$\text{CF}_3$	193	0.3	$\text{C}_5\text{F}_7$
79	1.1	$\text{CClS}$	200	0.3	$\text{C}_4\text{F}_8$
81	2.5	$\text{C}_2\text{F}_3$	219	0.8	$\text{C}_4\text{F}_9$
82	21	$\text{CCl}_2$	231	0.6	$\text{C}_5\text{F}_9$
83	8.2	$\text{ClOS}$	269	0.4	$\text{C}_5\text{F}_{11}$
85	6.3	$\text{CClF}_2$	281	0.4	$\text{C}_6\text{F}_{11}$
93	2.4	$\text{C}_3\text{F}_3$	331	0.5	$\text{C}_7\text{F}_{13}$
100	16	$\text{C}_2\text{F}_4$	369	0.8	$\text{C}_7\text{F}_{15}$
112	0.7	$\text{C}_3\text{F}_4$	417	0.3	$\text{C}_7\text{F}_{15}\text{OS}$

Trichloromethyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CCl}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	12	CF	82	33	$\text{CCl}_2$
35	4.4	Cl	83	10	$\text{ClOS}$
44	4.0	CS	85	8.1	$\text{CClF}_2$
47	17	$\text{CCl}$	100	34	$\text{C}_2\text{F}_4$
48	21	OS	117	<u>100</u>	$\text{CCl}_3$
63	4.8	CFS	131	13	$\text{C}_3\text{F}_5$
64	20	$\text{O}_2\text{S}$	150	17	$\text{C}_3\text{F}_6$
67	14	$\text{ClS}$ ; $\text{FOS}$	169	6.4	$\text{C}_3\text{F}_7$
69	80	$\text{CF}_3$	251	4.8	$\text{C}_4\text{Cl}_2\text{F}_7$

Trifluoromethyl ethyl sulphone,  $\text{CF}_3\cdot\text{SO}_2\text{CH}_2\text{CH}_3$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
27	30	$\text{C}_2\text{H}_3$	64	6.2	$\text{O}_2\text{S}$
29	<u>100</u>	$\text{C}_2\text{H}_5$	65	15	$\text{HO}_2\text{S}$
48	9.2	OS	69	34	$\text{CF}_3$
50	3.6	$\text{CF}_2$	77	6.0	$\text{C}_2\text{H}_5\text{OS}$
51	3.1	$\text{CHF}_2$	93	78	$\text{C}_2\text{H}_5\text{O}_2\text{S}$

trans-Heptafluoropropyl styryl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}:\text{CHPh}$  (>1%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	1.8	$\text{CF}^+$	74	1.7	$\text{C}_6\text{H}_2^+$
39	2.3	$\text{C}_3\text{H}_3^+$	75	8.8	$\text{C}_6\text{H}_3^+$
45	3.1	$\text{CHS}^+$	76	4.8	$\text{C}_6\text{H}_4^+$
50	4.2	$\text{CF}_2^+$ ; $\text{C}_4\text{H}_2^+$	77	38	$\text{C}_6\text{H}_5^+$
51	13	$\text{CHF}_2^+$ ; $\text{C}_4\text{H}_3^+$	102	11	$\text{C}_8\text{H}_6^+$
52	7.2	$\text{C}_4\text{H}_4^+$	103	<u>100</u>	$\text{C}_8\text{H}_7^+$
63	2.6	$\text{CFS}^+$	167	88	$\text{C}_8\text{H}_7\text{O}_2\text{S}^+$
69	7.1	$\text{CF}_3^+$			

Deuteromethyl heptafluoropropyl sulphones (mixture)

(peaks below m/e 31 not included)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	9.8	$\text{CF}^+$	80	4.8	$\text{CH}_2\text{DO}_2\text{S}^+$
46	4.0	$\text{CH}_2\text{S}^+$ ; $\text{CDS}^+$	81	38	$\text{CHD}_2\text{O}_2\text{S}^+$
48	7.7	$\text{CH}_2\text{DS}^+$ ; $\text{CD}_2\text{S}^+$ ; $\text{OS}^+$	82	86	$\text{CD}_3\text{O}_2\text{S}^+$
50	4.8	$\text{CD}_3\text{S}^+$ ; $\text{CF}_2^+$	100	18	$\text{C}_2\text{F}_4^+$
65	16	$\text{HO}_2\text{S}^+$ ; $\text{CHD}_2\text{OS}^+$	119	11	$\text{C}_2\text{F}_5^+$
66	38	$\text{DO}_2\text{S}^+$ ; $\text{CD}_3\text{OS}^+$	150	3.0	$\text{C}_3\text{F}_6^+$
69	<u>100</u>	$\text{CF}_3^+$	169	28	$\text{C}_3\text{F}_7^+$
79	1.1	$\text{CH}_3\text{O}_2\text{S}^+$			



MISCELLANEOUS COMPOUNDS1H-octafluoro-4-iodobutane,  $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$  (>3%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	9.5	$\text{CF}^\bullet$	127	31	I
50	21	$\text{CF}_2^\bullet$	131	23	$\text{C}_3\text{F}_5^\bullet$
51	65	$\text{CHF}_2^\bullet$	163	7.1	$\text{C}_4\text{HF}_6^\bullet$
69	4.9	$\text{CF}_3^\bullet$	177	47	$\text{CF}_2\text{I}^\bullet$
82	3.4	$\text{C}_2\text{HF}_3^\bullet$	201	<u>100</u>	$\text{C}_4\text{HF}_8^\bullet$
100	14	$\text{C}_2\text{F}_4^\bullet$	208	6.0	$\text{C}_2\text{F}_3\text{I}^\bullet$
101	18	$\text{C}_2\text{HF}_4^\bullet$	227	8.4	$\text{C}_2\text{F}_4\text{I}^\bullet$
112	23	$\text{C}_3\text{F}_4^\bullet$	239	11	$\text{C}_3\text{F}_4\text{I}^\bullet$
119	10	$\text{C}_2\text{F}_5^\bullet$	328	50	$\text{CHF}_8\text{I}^\bullet(\underline{\text{M}})$

1,1,1,2,2,3,3-Heptafluoropentane,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_3$  (>1%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
14	2.1	$\text{CH}_2^\bullet$	77	13	$\text{C}_3\text{H}_3\text{F}_2^\bullet$
15	1.2	$\text{CH}_3^\bullet$	79	<u>100</u>	$\text{C}_3\text{H}_5\text{F}_2^\bullet$
27	20	$\text{C}_2\text{H}_3^\bullet$	89	3.1	$\text{C}_4\text{H}_3\text{F}_2^\bullet$
29	33	$\text{C}_2\text{H}_5^\bullet$	95	2.9	$\text{C}_3\text{H}_2\text{F}_3^\bullet$
31	3.1	$\text{CF}^\bullet$	109	19	$\text{C}_4\text{H}_4\text{F}_3^\bullet$
33	3.4	$\text{CH}_2\text{F}^\bullet$	113	2.6	$\text{C}_3\text{HF}_4^\bullet$
47	6.0	$\text{C}_2\text{H}_4\text{F}^\bullet$	119	3.7	$\text{C}_2\text{F}_5^\bullet$
51	43	$\text{CHF}_2^\bullet$	139	2.7	$\text{C}_5\text{H}_3\text{F}_4^\bullet$
59	18	$\text{C}_3\text{H}_4\text{F}^\bullet$	159	4.8	$\text{C}_5\text{H}_4\text{F}_5^\bullet$
65	4.7	$\text{C}_2\text{H}_3\text{F}_2^\bullet$	169	1.7	$\text{C}_3\text{F}_7^\bullet$
75	1.9	$\text{C}_3\text{HF}_2^\bullet$	178	1.6	$\text{C}_5\text{H}_4\text{F}_6^\bullet$

1H-pentadecafluoro-5-methylhexane,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$  (>0.5%)

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
31	6.5	CF	113	5.2	$\text{C}_3\text{HF}_4$
41	1.9		119	6.4	$\text{C}_2\text{F}_5$
43	1.2	$\text{C}_2\text{F}$	124	0.5	$\text{C}_4\text{F}_4$
44	3.6	$\text{C}_2\text{HF}$	131	18	$\text{C}_3\text{F}_5$
45	1.3		132	1.2	$\text{C}_3\text{HF}_5$
50	1.5	$\text{CF}_2$	143	0.8	$\text{C}_4\text{F}_5$
51	1.4	$\text{CHF}_2$	150	0.9	$\text{C}_3\text{F}_6$
55	1.3	$\text{C}_3\text{F}$	151	1.1	$\text{C}_3\text{HF}_6$
57	1.2		162	0.5	$\text{C}_4\text{F}_6$
59	1.2		163	0.5	$\text{C}_4\text{HF}_6$
60	2.0		169	1.0	$\text{C}_3\text{F}_7$
69	<u>100</u>	$\text{CF}_3$	181	6.5	$\text{C}_4\text{F}_7$
73	1.6		200	0.8	$\text{C}_4\text{F}_8$
74	0.7	$\text{C}_3\text{F}_2$	201	1.2	$\text{C}_4\text{HF}_8$
75	0.7	$\text{C}_3\text{HF}_2$	219	3.8	$\text{C}_4\text{F}_9$
81	0.7	$\text{C}_2\text{F}_3$	231	0.3	$\text{C}_5\text{F}_9$
82	3.0	$\text{C}_2\text{HF}_3$	262	1.1	$\text{C}_6\text{F}_{10}$
93	3.1	$\text{C}_3\text{F}_3$	269	0.5	$\text{C}_5\text{F}_{11}$
100	7.2	$\text{C}_2\text{F}_4$	281	3.1	$\text{C}_6\text{F}_{11}$
101	17	$\text{C}_2\text{HF}_4$	300	0.5	$\text{C}_6\text{F}_{12}$
112	1.0	$\text{C}_3\text{F}_4$			

A P P E N D I X    2

INFRARED SPECTRA

The i.r. spectra of the compounds prepared, apart from showing the presence of bands associated with C - H and C - F vibrations, were of little diagnostic value. The band associated with C - S stretching is known to be weak and variable in position. The bands associated with S - O stretching unfortunately coincide with the C - F stretching absorption region (ca. 7.1 - 10.0 $\mu$ )<sup>130</sup>. However, all the sulphones prepared showed a band in the region 7.12 - 7.35 $\mu$ . For compounds of the type  $R_fSO_2R$ , where R does not contain chlorine, the band was at 7.30( $\pm 0.05$ ) $\mu$ , while for compounds of the type  $R_fSO_2CCl_3$ , the band was observed at 7.13( $\pm 0.02$ ) $\mu$ .

Alkyl sulphones are reported to exhibit absorptions in the regions 8.62 - 8.93 $\mu$  and 7.41 - 7.70 $\mu$ . These bands have been assigned to S - O symmetric and asymmetric stretching respectively.<sup>131</sup> Replacement of one of the alkyl groups by a more electronegative substituent, e.g., Cl, causes a shift in the absorptions to lower wavelength ( $CH_3SO_2Cl$ , 8.55 $\mu$  and 7.14 $\mu$  respectively). On the basis of this evidence the bands observed for  $R_fSO_2R$  (7.30 $\mu$ ) and  $R_fSO_2CCl_3$  (7.13 $\mu$ ) have been assigned to asymmetric S - O stretching in these compounds.

The assignments are tentative because of the complexity of the spectra in this region. However, the value of 7.30( $\pm 0.05$ ) $\mu$  is in good agreement with the value of 7.36 $\mu$ ,<sup>72</sup> quoted by Gramstad and Haszeldine, for the S - O asymmetric stretching vibration in methyl trifluoromethyl sulphone.

The figures below represent the i.r. absorption bands, expressed in microns ( $\mu$ ), in the region 2.5 - 15.5 $\mu$ .

The following abbreviations have been used:

w = weak, m = medium, s = strong, vs = very strong, (sh) = shoulder, and (bd) = broad.

### SULPHIDES

Methyl heptafluoropropyl sulphide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (vapour)

3.37 m, 3.48 m, 6.93 m, 7.42 s, 7.91 s, 8.06 vs, 8.16 vs, 8.47 s, 8.93 vs, 9.12 s, 9.51 s, 10.25 s, 10.76 s, 11.57 s, 12.59 w, 12.95 m, 13.41 s, 13.93 w, 14.77 m, and 15.30 w.

Methyl heptafluoroisopropyl sulphide,  $(\text{CF}_3)_2\text{CF}\cdot\text{S}\cdot\text{CH}_3$  (vapour)

3.30 w, 3.31 w, 3.39 m, 3.47 w, 3.54 m, 3.95 w, 4.03 w, 4.17 w, 4.44 w, 4.57 w, 4.90 w, 5.00 w, 6.90 m, 7.30 w, 7.75 vs, 8.07 vs, 8.55 s, 9.09 s, 10.10 s, 10.33 s, 10.50 s, 11.22 w, 11.48 m, 13.76 s, and 13.89 s.

Ethyl heptafluoropropyl sulphide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_2\text{CH}_3$  (vapour)

3.34 w, 3.38 m, 3.44 m, 6.86 m, 7.20 w, 7.45 s, 7.80 s, 8.09 vs, 8.20 vs, 8.47s, 8.95 s, 9.15 s, 9.59 s, 10.30 w, 10.80 s, 11.16 m, 11.60 s, 13.40 s, 14.34 m, and 15.30 w.

Methyl 2-chlorotetrafluoroethyl sulphide,  $\text{CF}_2\text{Cl}\cdot\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (vapour)

3.31 w, 3.39 m, 3.50 w, 6.92 m, 7.50 w, 8.00 s, 8.55 vs, 8.74 s, 9.00 vs, 9.38 m, 9.60 vs, 10.28 s, 10.95 vs, 11.38 m, 12.04 vs, 14.03 w, 14.95 (sh)w, and 15.10 w.

Methyl pentadecafluoro-5-methylhexyl sulphide,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$   
(capillary film)

3.31 w, 3.39 w, 3.41 w, 3.50 w, 6.90 w, 6.94 w, 7.52 m, 7.78 s,  
7.95 s, 8.24 s, 8.37 s, 8.55 s, 8.84 s, 9.09 s, 9.63 m, 9.85 m, 10.15 s,  
10.76 w, 11.30 w, 11.56 w, 11.70 w, 12.20 m, 12.45 m, 12.85 m, 13.11 w,  
13.33 m, 13.50 m, 13.66 m, 13.79 m, 14.04 m, 14.49 m, and 14.81 m.

Methyl tetrafluoro-2-iodoethyl sulphide,  $\text{CF}_2\text{I}\cdot\text{CF}_2\text{S}\cdot\text{CH}_3$  (capillary film)

3.44 w, 3.50 m, 6.94 m, 6.99 m, 7.58 w, 7.70 w, 8.15 m, 8.26 m,  
8.44 m, 8.77 s, 9.13 s, 9.62 m, 9.85 s, 10.26 m, 11.63 s, 12.35 w,  
13.16 s, 14.08 w, and 14.71 w.

Methyl octafluoro-4-iodobutyl sulphide,  $\text{CF}_2\text{I}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$   
(capillary film)

3.39 w, 6.95 m, 6.99 (sh)m, 7.51 w, 7.75 m, 7.94 w, 8.42 vs,  
8.86 vs, 9.15 s, 9.46 s, 9.75 w, 9.91 w, 10.25 m, 10.70 m, 10.86 (sh)w,  
11.14 m, 11.65 w, 11.80 w, 12.24 w, 12.91 s, 13.30 w, 13.90 w, 14.32 w,  
14.96 (sh)s, 15.05 s, and 15.29 s.

1,2-Bis(methylthio)tetrafluoroethane,  $\text{CH}_3\text{S}\cdot\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (capillary film)

3.32 w, 3.38 m, 3.52 w, 6.94 m, 6.99 m, 7.53 m, 8.12 (sh)m,  
8.20 m, 8.33 m, 8.93 (sh)s, 9.26 s, 9.66 s, 10.26 m, 11.01 s, 11.24 (sh)m,  
11.63 w, 11.83 w, 12.32 s, 13.19 m, and 14.08 m.

1,4-Bis(methylthio)octafluorobutane,  $\text{CH}_3\text{S}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$  (capillary film)

3.34 w, 3.44 m, 3.52 w, 3.54 w, 6.99 m, 7.07 m, 7.53 w, 7.66 m,  
7.94 w, 8.30 m, 8.48 s, 8.73 m, 8.84 s, 9.17 s, 9.75 m, 10.20 w,  
10.53 m, 10.88 w, 12.05 w, 12.35 m, 13.14 m, 13.93 m, and 14.39 m.

Trifluoromethyl pentafluorophenyl sulphide,  $\text{CF}_3\text{S}\cdot\text{C}_6\text{F}_5$  (capillary film)

6.10 s, 6.49 (sh)s, 6.46 (sh)s, 6.60 s, 6.68 s, 7.07 w, 7.19 w, 7.26 w, 7.69 m, 7.75 (sh)m, 7.96 w, 8.20 w, 8.45 w, 8.61 s, 8.70 s, 9.01 s, 9.14 s, 9.30 m, 9.70 m, 10.10 s, 11.49 s, 12.41 w, 13.16 s, 13.66 m, and 15.41 m.

Trifluoromethyl pentafluorophenyl disulphide,  $\text{CF}_3\text{S}\cdot\text{S}\cdot\text{C}_6\text{F}_5$  (capillary film)

6.10 m, 6.53 (sh)m, 6.60 s, 6.68 s, 7.11 w, 7.23 w, 7.31 w, 7.68 w, 8.60 s, 8.69 s, 9.09 s, 9.80 w, 10.15 s, 11.49 w, 11.63 m, 12.41 w, 13.25 m, 13.70 w, and 15.60 w.

SULPHOXIDES

Methyl heptafluoropropyl sulphoxide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}\cdot\text{CH}_3$  (capillary film)

3.31 w, 3.40 w, 7.04 w, 7.09 m, 7.47 s, 7.80 m, 8.20 s, 8.44 s, 8.62 s, 8.85 s, 9.10 s, 9.22 s, 9.60 s, 10.45 m, 10.95 m, 11.90 s, 12.05 m, 13.34 m, 13.55 s, 14.65 m, and 15.05 m.

Methyl heptafluoroisopropyl sulphoxide,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}\cdot\text{CH}_3$  (capillary film)

3.31 w, 3.40 w, 6.99 w, 7.06 m, 7.13 m, 7.74 (sh)s, 7.81 s, 8.16 s, 8.41 s, 8.76 s, 8.97 s, 9.05 (sh)s, 9.26 m, 10.15 s, 10.21 s, 10.47 m, 10.99 m, 12.20 m, 12.82 w, 13.25 m, 13.68 w, 13.91 s, and 14.71 m.

Deuteromethyl heptafluoropropyl sulphoxides (mixture),  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\cdot\text{CH}_{0.3}\text{D}_{2.7}$  (capillary film)

3.36 w, 4.43 w, 4.63 w, 4.69 w, 7.46 s, 7.75 m, 8.00-8.41 (bd)s, 8.62 s, 8.85 s, 9.07 s, 9.18 s, 9.57 s, 9.63 m, 9.90 w, 10.42 w, 10.87 m, 11.63 w, 11.83 s, 12.99 w, 13.30 m, 13.51 s, 13.70 m, 14.71 m, 14.93 m, and 15.38 w.



SULPHONES

Methyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_3$  (capillary film)

3.30 w, 3.40 w, 7.09 w, 7.34 s, 7.46 s, 7.78 m, 8.05-8.55 (bd)s,  
8.83 s, 9.08 m, 9.46 m, 10.45 m, 10.64 m, 10.95 w, 11.35 m,  
11.72 m, 13.09 m, 13.55 s, 13.79 s, 14.78 m, and 14.91 m.

Methyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CH}_3$  (capillary film)

3.26 w, 3.29 w, 7.09 w, 7.27 s, 7.34 s, 7.52 s, 7.81-8.18 (bd)s,  
8.53 s, 8.64 s, 8.81 s, 10.16 s, 10.36 s, 10.64 s, 10.90 w, 13.05 w,  
13.50 s, and 13.59 s.

Methyl pentadecafluoro-5-methylhexyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_3$  (melt)

3.28 w, 3.31 w, 3.40 w, 7.07 w, 7.27 s, 7.69-8.05 (bd)s, 8.20-  
8.69 (bd)s, 8.81 s, 9.01 m, 9.63 w, 10.18 s, 10.42 , 11.30 w, 12.05 w,  
12.42 m, 13.33 m, 13.70 m, and 15.08 m.

trans-Heptafluoropropyl styryl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}:\text{CHPh}$  (melt)

3.24 m, 3.30 w, 6.21 s, 6.34 m, 7.67 w, 6.89 m, 7.30 s, 7.47 s,  
7.63 m, 7.75 m, 8.06-8.33 (bd)s, 8.62 s, 8.85 s, 9.09 m, 9.48 m,  
9.80 w, 9.98 w, 10.18 m, 10.53 w, 10.81 w, 11.24 m, 11.36 (sh)m,  
11.60 s, 11.70 s, 12.27 s, 12.50 (sh)m, 13.25 (sh)m, 13.42 s, 14.66 s,  
15.27 w, and 15.58 s.

Trichloromethyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CCl}_3$ 

(capillary film)

7.13 s, 7.50 s, 7.83 m, 8.00-8.41 (bd)s, 8.49 s, 8.80 s,  
9.20 m, 9.59 m, 10.75 w, 10.95 w, 11.60 s, 12.15 s, 12.45 s, 13.10 w,  
13.34 w, 13.54 s, 14.74 m, and 15.30 w.

Triiodomethyl heptafluoropropyl sulphone,  $\text{CH}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CI}_3$  (mull; nujol and hexachlorobutadiene)

7.24 m, 7.35 m, 7.52 m, 7.85 w, 8.09 s, 8.24 (sh)s, 8.30 s,  
8.43 (sh)s, 8.64 m, 8.80 s, 9.24 m, 9.60 w, 11.79 m, 13.39 m, 13.89 w,  
14.40 m, and 15.30 w.

Trichloromethyl pentadecafluoro-5-methylhexyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{CCl}_3$  (melt)

7.12 s, 7.51 m, 7.81 (sh)s, 7.97 s, 8.12 (sh)s, 8.30 s, 8.45 s,  
8.65 s, 8.77 s, 9.05 m, 9.75 w, 10.18 s, 11.36 w, 12.03 m, 12.42 m,  
12.95 w, 13.25 w, 13.33 w, 13.61 w, 13.70 w, 13.88 w, 14.08 w,  
14.49 w, 14.75 w, and 15.04 w.

Trichloromethyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CCl}_3$ 

(capillary film)

7.14 s, 7.77 s, 7.96 (sh)s, 8.07 s, 8.48 m, 8.61 m, 8.73 s,  
10.20 s, 10.66 m, 11.90 s, 12.42 s, 13.33 w, and 13.85 s.

Trifluoromethyl ethyl sulphone,  $\text{CF}_3\text{SO}_2\text{CH}_2\text{CH}_3$  (capillary film)

3.34 m, 3.38 m, 3.41 m, 6.85 m, 7.09 w, 7.17 m, 7.35 s, 7.58 w,  
7.75 w, 8.33 s, 8.90 s, 9.40 w, 9.56 m, 10.26 w, 12.74 m, 12.99 w,  
13.30 w, and 13.99 s.

Trifluoromethyl 1,1-dichloroethyl sulphone,  $\text{CF}_3\text{SO}_2\text{CCl}_2\text{CH}_3$  (capillary film)

3.31 w, 6.91 m, 7.18 s, 7.25 s, 8.26 s, 8.97 s, 9.22 s, 9.57 w, 13.16 m, and 13.62 m.

Deuteromethyl heptafluoropropyl sulphones (mixture),  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_{0.3}\text{D}_{2.7}$  (capillary film)

3.32 w, 3.36 w, 4.37 w, 4.42 w, 4.59 w, 4.65 w, 7.27 s, 7.47 s, 7.75 m, 8.13-8.44 (bd)s, 8.80 s, 9.03 m, 9.39 m, 9.76 w, 9.79 m, 10.52 w, 10.75 w, 11.36 m, 11.78 w, 12.03 w, 12.69 m, 13.35 m, 13.53 m, 13.89 m, 14.10 m, 14.71 w, and 15.15 m.

MISCELLANEOUS COMPOUNDS

1,1,1,2,2,3,3-Heptafluoropentane,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_3$  (vapour)

3.33 m, 3.38 m, 3.45 m, 6.79 m, 6.92 (sh)w, 7.02 w, 7.28 m, 7.41 s, 7.69 s, 7.80 (sh)m, 8.10 vs, 8.28 s, 8.45 s, 8.88 s, 9.35 s, 9.48 (sh)m, 9.80 m, 10.11 m, 10.58 m, 11.10 s, 11.55 (sh)s, 12.22 w, 12.63 w, 13.21 m, 14.08 s, and 15.31 w.

1H-pentadecafluoro-5-methylhexane,  $(\text{CF}_3)_2\text{CF}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CHF}_2$  (vapour)

3.26 w, 3.34 w, 7.06 (sh)m, 7.12 m, 7.38 m, 7.76 vs, 7.90 vs, 8.20 (sh)s, 8.32 s, 8.46 s, 8.65 (sh)s, 8.74 s, 9.01 s, 9.26 s, 10.10 s, 11.52 m, 11.68 m, 12.03 m, 12.27 m, 12.50 m, 12.69 m, 12.89 m, 13.33 s, 13.87 s, 14.06 (sh)m, 14.49 m, and 15.62 w.

1H-octafluoro-4-iodobutane,  $\text{CHF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\text{I}$  (vapour)

3.31 w, 3.34 (sh)w, 7.12 m, 7.36 w, 7.45 m, 7.70 m, 7.89 m, 8.10 (sh)s, 8.16 s, 8.37 vs, 8.74 vs, 8.98 s, 9.15 s, 9.45 w, 9.56 (sh)w, 9.82 w, 10.35 w, 10.80 w, 11.15 w, 11.35 w, 11.69 m, 11.95 m, 12.30 m, 12.48-12.62 (bd)m, 13.15 s, 13.39 w, 13.90 s, and 14.46 m.

Potassium heptafluoropropanesulphonate,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_3\text{K}$  (mull; nujol and hexachlorobutadiene)

2.30-2.95 (bd)w, 7.43 m, 7.80-8.45 (bd)s, 8.65 m, 8.86 (sh)m, 8.95 s, 9.49 m, 9.59 m, 11.44 m, 13.31 m, 13.87 w, 14.55 m, and 15.44 m.

A P P E N D I X    3

N.M.R. SPECTRA

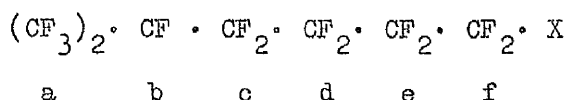
The author is indebted to Dr. M. G. Barlow for the measurement and interpretation of certain of these spectra.

All  $^1\text{H}$  spectra were recorded using internal tetramethyl silane as reference, and the  $^1\text{H}$  chemical shifts quoted are  $\tau$  values.

All  $^{19}\text{F}$  spectra were recorded using external trifluoroacetic acid as reference, and the  $^{19}\text{F}$  chemical shifts are quoted in p.p.m. from the resonance absorption of this compound; negative values are to low field of this compound and positive values are to high field.

Wherever possible 'neat' liquid samples were used for the determination of spectra. In certain cases, because of limited quantities of samples or because the sample was a solid, this was not possible and so a solvent was used. The solvent and solute concentration are given in parenthesis by the name of each compound.

In all cases the spectra obtained were consistent with the proposed structures.

Compounds Containing the Pentadecafluoro-5-methylhexyl Group

The spectra of these compounds were complex and the fine structure was poorly resolved. For these reasons the spectra are not reproduced in detail, however, certain assignments have been made.

In the  $^{19}\text{F}$  spectrum, the bands were assigned on the following basis:

- (i) integrated band intensities,

- (ii) the bands due to  $F_a$ ,  $F_b$ ,  $F_c$ , and  $F_d$  should show approximately the same chemical shift in all the compounds studied,
- (iii) branching at the adjacent carbon causes  $F_c$  to absorb at lower field than  $F_d$ ,
- (iv) the chemical shift of  $F_f$  will be the most variable, and
- (v) corresponding bands in the various compounds will have much fine structure in common.

On this basis the following chemical shifts were deduced (Table 24).

TABLE 24

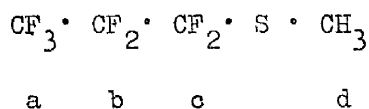
Chemical shifts in compounds of the type  $(CF_3)_2CF \cdot CF_2CF_2CF_2CF_2X$

Substituent X	Chemical shifts					
	$F_a$	$F_b$	$F_c$	$F_d$	$F_e$	$F_f$
I	-5.4	110.8	37.8	43.0	35.6	-19.9
H	-4.2	112.2	39.1	46.7	54.2	62.6
$S \cdot CH_3$	-6.0	111.1	38.9	43.6	43.6	14.1
$SO_2CH_3$	-6.6	110.4	<u>ca.</u> 37	<u>ca.</u> 43	<u>ca.</u> 43	<u>ca.</u> 37
$SO_2CCl_3$	-6.3	110.2	37.5	43.0	41.8	19.5

As previously stated the spectra were complex and assignment of individual coupling constants was not always possible. However, in every compound, the band system due to  $F_a$  appeared as a more or less clearly defined triplet of triplets of doublets, due to coupling with  $F_c$ ,  $F_d$ , and  $F_b$  respectively, typical magnitudes of coupling constants being 14.5, 8.9, and 6.1 c./sec.

Compounds Containing the Heptafluoropropyl Group,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{X}$

Methyl heptafluoropropyl sulphide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_3$



$^1\text{H}$  spectrum

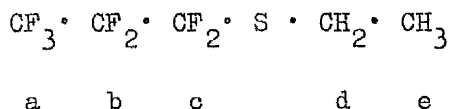
A single unresolved band centred at  $\tau$  7.60 was observed.

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	3.6	3	triplet	$J_{a-c}$ 9.4
$\text{F}_c$	14.7	2	quartet of triplets of quartets	$J_{c-a}$ 9.6 $J_{c-b}$ 3.3 $J_{c-d}$ 0.9
$\text{F}_b$	47.8	2	broad triplet	$J_{b-c}$ 3.3



Ethyl heptafluoropropyl sulphide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{S}\cdot\text{CH}_2\text{CH}_3$



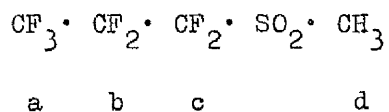
$^1\text{H}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{H}_d$	7.05	2	quartet	$J_{d-e}$ 7.6
$\text{H}_e$	8.65	3	triplet	$J_{e-d}$ 7.8

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	3.8	3	triplet	$J_{a-c}$ 9.4
$\text{F}_c$	11.8	2	quartet of triplets	$J_{c-a}$ 9.4 $J_{c-b}$ 3.9
$\text{F}_b$	47.8	2	triplet	$J_{b-c}$ 4.0

Methyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}_3$



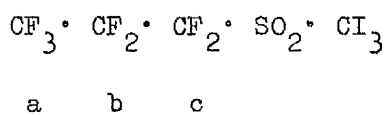
$^1\text{H}$  spectrum

A single unresolved band centred at  $\delta 6.81$  was observed.

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	5.0	3	triplet	$J_{a-c}$ 9.4
$\text{F}_c$	38.1	2	complex	
$\text{F}_b$	47.8	2	distorted triplet	$J_{b-c}$ 2.8

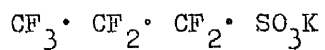
Triiodomethyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CI}_3$ , (40% solution in ether)



$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	4.2	3	triplet	$J_{a-c}$ 9.5
$\text{F}_c$	15.4	2	quartet of triplets	$J_{c-a}$ 9.5 $J_{c-b}$ 1.8
$\text{F}_b$	48.8	2	distorted triplet	$J_{b-c}$ 1.8

Potassium heptafluoropropanesulphonate,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_3\text{K}$  (25% solution in water).

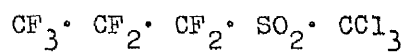


a      b      c

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	2.4	3	triplet	$J_{a-c}$ 8.9
$\text{F}_c$	37.5	2	quartet of triplets	$J_{c-a}$ 9.1 $J_{c-b}$ 1.0
$\text{F}_b$	47.6	2	unresolved multiplet	

Trichloromethyl heptafluoropropyl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CCl}_3$

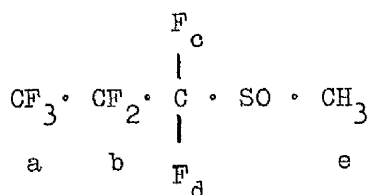


a      b      c

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	2.9	3	triplet	$J_{a-c}$ 9.2
$\text{F}_c$	20.5	2	quartet of triplets	$J_{c-a}$ 9.2 $J_{c-b}$ 2.5
$\text{F}_b$	46.6	2	distorted triplet	$J_{b-c}$ 2.3

Methyl heptafluoropropyl sulphoxide,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SOCH}_3$



The assignments c and d are arbitrary.

$^1\text{H}$  spectrum

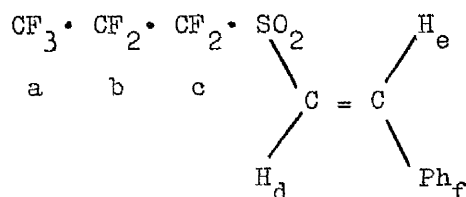
Band	Chemical shift	Multiplicity	Coupling constants (c./sec.)	
$\text{H}_e$	7.13	doublet of doublets of triplets	$J_{e-c}$	2.6
			$J_{e-d}$	1.3
			$J_{e-b}$	0.7

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)	
F <sub>a</sub>	4.9	3	unresolved	}	J <sub>c-d</sub> 270
*F <sub>c</sub>	41.3	1	doublet		
*F <sub>d</sub>	49.5	1	doublet		
F <sub>b</sub>	49.1	2	unresolved		

\*The geminal fluorines are rendered non-equivalent by asymmetry of the sulphoxide group and these bands appear as part of an AB quartet centred on 45.4 p.p.m. with internal chemical shift of 8.25 p.p.m.

trans-Heptafluoropropyl styryl sulphone,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{SO}_2\text{CH}=\text{CHPh}$   
(60% solution in carbon tetrachloride)



$^1\text{H}$  spectrum

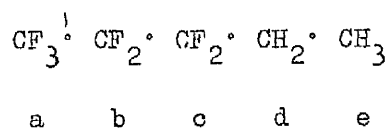
Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{H}_f$	<u>ca.</u> 2.46	5	complex	
* $\text{H}_e$	3.10	1	doublet	} $J_{d-e}$ 15.5
* $\text{H}_d$	2.10	1	doublet	

\*These bands appear as part of an AB quartet centred at  $\tau$  2.63 and with an internal chemical shift of 0.95 p.p.m.

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	2.7	3	broadened triplet	$J_{a-c}$ 9.6
$\text{F}_c$	36.1	2	broadened triplet	$J_{c-a}$ 9.6
$\text{F}_b$	46.6	2	unresolved multiplet	

1,1,1,2,2,3,3-Heptafluoropentane,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_3$  (30% solution in o-dichlorobenzene).



$^1\text{H}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
H <sub>e</sub>	8.97	3	triplet	J <sub>e-d</sub> 7.0
H <sub>d</sub>	8.04	2	triplet of quartets	J <sub>d-c</sub> 19 J <sub>d-e</sub> 7.0

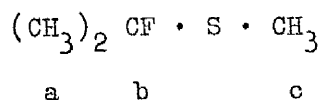
$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
F <sub>a</sub>	3.6	3	triplet	J <sub>a-c</sub> 9.6
F <sub>c</sub>	40.8	2	complex	
F <sub>b</sub>	51.4	2	complex	



Compounds Containing the Heptafluoroisopropyl Group,  $(\text{CF}_3)_2\text{CF}\cdot\text{X}$

Methyl heptafluoroisopropyl sulphide,  $(\text{CF}_3)_2\text{CF}\cdot\text{S}\cdot\text{CH}_3$



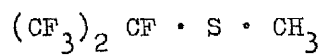
$^1\text{H}$  spectrum

Band	Chemical shift	Multiplicity	Coupling constants (c./sec.)	
$\text{H}_c$	7.60	doublet of septets	$J_{c-b}$	2.2
			$J_{c-a}$	1.1

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)	
$\text{F}_a$	-1.5	6	doublet of quartets	$J_{a-b}$	10.5
				$J_{a-c}$	1.0
$\text{F}_b$	90.0	1	septet of quartets	$J_{b-a}$	10.2
				$J_{b-c}$	2.4

Methyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\text{CH}_3$



a          b          c

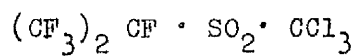
$^1\text{H}$  spectrum

Band	Chemical shift	Multiplicity	Coupling constants (c./sec.)	
$\text{H}_c$	6.69	doublet of septets	$J_{c-b}$	3.6
			$J_{c-a}$	0.5

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)	
$\text{F}_a$	-5.9	6	broadened doublet	$J_{a-b}$	7.2
$\text{F}_b$	95.8	1	overlapping septet of quartets	$J_{b-a}$	7.2
				$J_{b-a}$	3.6

Trichloromethyl heptafluoroisopropyl sulphone,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}_2\cdot\text{CCl}_3$

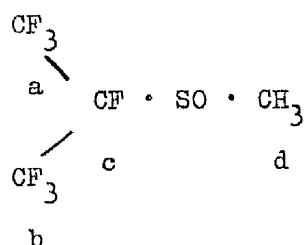


a      b

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	-7.1	6	doublet	$J_{a-b}$ 9.3
$\text{F}_b$	85.0	1	septet	$J_{b-a}$ 9.3

Methyl heptafluoroisopropyl sulphoxide,  $(\text{CF}_3)_2\text{CF}\cdot\text{SO}\cdot\text{CH}_3$



The assignments a and b are arbitrary.

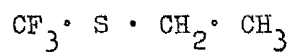
$^1\text{H}$  spectrum

Band	Chemical shift	Multiplicity	Coupling constants (c./sec.)
$\text{H}_d$	7.05	doublet of poorly resolved septets	$J_{d-c}$ 3.0 $J_{d-a}$ $J_{d-b}$ } 0.7

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	-6.2	3	broadened quintet	$J_{a-b}$ $J_{a-c}$ } 8.3
$*\text{F}_b$	-4.6	3	broadened quintet	$J_{b-a}$ $J_{b-c}$ } 8.3
$*\text{F}_c$	106.2	1	overlapping quartet of quartets of quartets	$J_{c-b}$ 8.5 $J_{c-a}$ 7.6 $J_{c-d}$ 3.2

\*The asymmetry of the sulphoxide group renders the geminal  $\text{CF}_3$  groups non-equivalent.

Miscellaneous CompoundsTrifluoromethyl ethyl sulphide,  $\text{CF}_3\text{S}\cdot\text{CH}_2\text{CH}_3$ 

a                      b              c

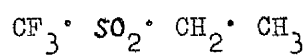
 $^1\text{H}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{H}_b$	7.10	2	quartet	$J_{b-c}$ 7.8
$\text{H}_c$	8.65	3	triplet	$J_{c-b}$ 8.1

 $^{19}\text{F}$  spectrum

A single unresolved band centred at 36.7 p.p.m. was observed.

Trifluoromethyl ethyl sulphone,  $\text{CF}_3\text{SO}_2\text{CH}_2\text{CH}_3$



a                      b      c

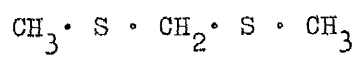
$^1\text{H}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{H}_b$	6.65	2	quartet	$J_{b-c}$ 7.2
$\text{H}_c$	8.55	3	triplet	$J_{c-b}$ 7.2

$^{19}\text{F}$  spectrum

A single broad band centred at 1.5 p.p.m. was observed showing poorly resolved fine structure.

Bis(methylthio)methane,  $\text{CH}_3\text{S}\cdot\text{CH}_2\text{S}\cdot\text{CH}_3$ , (30% solution in carbon tetrachloride)



a

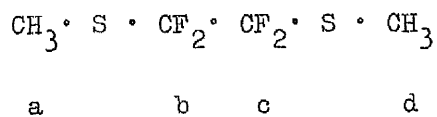
b

c

$^1\text{H}$  spectrum

Band	Chemical shift	Intensity	Multiplicity
$\text{H}_b$	6.45	1	singlet
$\text{H}_a$	7.90	3	singlet

1,2-Bis(methylthio)tetrafluoroethane,  $\text{CH}_3\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CH}_3$  (30% solution in chlorotrifluoromethane)



$^1\text{H}$  spectrum

Band	Chemical shift	Multiplicity	Coupling constants (c./sec.)
$\text{H}_a$	7.67	quintet	$*J_{a-b}$ 1.2

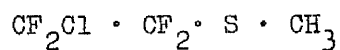
\*Average value

$^{19}\text{F}$  spectrum

A broad unresolved band centred at 12.8 p.p.m. was observed.



Methyl 1-chlorotetrafluoroethyl sulphide,  $\text{CF}_2\text{Cl} \cdot \text{CF}_2\text{S} \cdot \text{CH}_3$



a                      b                      c

$^1\text{H}$  spectrum

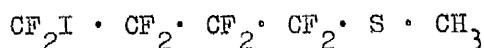
Band	Chemical shift	Multiplicity	Coupling constants (c./sec.)	
$\text{H}_c$	7.63	triplet of triplets	$J_{c-b}$	1.3
			$J_{c-a}$	0.8

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)	
$\text{F}_a$	-8.9	1	triplet of quartets	$J_{a-b}^*$	13.1
				$J_{a-c}$	0.7
$\text{F}_b$	14.0	1	triplet of quartets	$J_{b-a}^*$	13.1
				$J_{c-a}$	1.1

\*Average value.

Methyl tetrafluoro-4-iodobutyl sulphide,  $\text{CF}_2\text{I} \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{S} \cdot \text{CH}_3$



a            b            c            d            e

$^1\text{H}$  spectrum

Band	Chemical shift	Multiplicity	Coupling constants (c./sec.)	
$\text{H}_e$	7.65	triplet of triplets	$J_{e-d}$	1.2
			$J_{e-c}$	0.5

$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity
$\text{F}_a$	-19.9	1
$\text{F}_d$	12.9	1
$\text{F}_b$	34.8	1
$\text{F}_c$	41.2	1

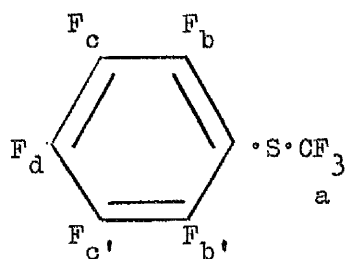
Because of the near equality of certain of the coupling constants, the poor resolution of certain of the bands, and the complexity of the fine structure (arising from 'second-order' effects) only a simplified interpretation of the spectrum of this compound was possible. The bands assigned to  $\text{F}_a$ ,  $\text{F}_b$ , and  $\text{F}_c$  all appeared as triplets of triplets of triplets with varying amounts of fine splitting and of varying resolution. The band assigned to

$F_d$  appeared as a triplet of triplets of quartets, the last splitting being due to coupling with the protons.

In view of the previously mentioned complexity, the following averaged values of the coupling constants (e.g. there are two a-b coupling constants and the average is quoted) are approximate and the assignments are somewhat tentative.

$J_{a-b}$ , 5.0;  $J_{a-c}$ , 15.0;  $J_{a-d}$ , 3.2;  $J_{b-c}$ , 5.7;  $J_{b-d}$ , 18.1; and  $J_{c-d}$ , 3.4.

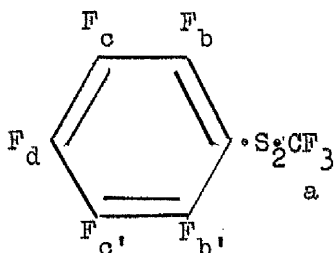
Trifluoromethyl pentafluorophenyl sulphide,  $\text{CF}_3\text{S}\cdot\text{C}_6\text{F}_5$



$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	-34.1	3	triplet	$J_{a-bb'}$ 5.1
$\text{F}_{bb'}$	54.6	2	complex	
$\text{F}_d$	72.6	1	triplet of triplets	$J_{d-cc'}$ 19.3 $J_{d-bb'}$ 5.4
$\text{F}_{cc'}$	86.5	2	complex	

Trifluoromethyl pentafluorophenyl disulphide,  $\text{CF}_3\text{S}_2\text{C}_6\text{F}_5$



$^{19}\text{F}$  spectrum

Band	Chemical shift	Intensity	Multiplicity	Coupling constants (c./sec.)
$\text{F}_a$	-30.7	3	triplet	$J_{a-bb'}$ 4.4
$\text{F}_{bb'}$	55.7	2	complex	
$\text{F}_d$	71.5	1	triplet of triplets	$J_{d-cc'}$ 19.6 $J_{d-bb'}$ 5.1
$\text{F}_{cc'}$	85.6	2	complex	

## REFERENCES

1. H. J. Emeléus, Angew. Chem. (Int. Ed.), 1962, 2, 129.
2. J. J. Lagowski, Quart. Rev., 1959, 13, 233.
3. A. Senning, Chem. Rev., 1965, 65, 385.
4. R. E. Banks and R. N. Haszeldine, 'The Chemistry of Organic Sulfur Compounds', N. Kharasch and C. A. Meyers, Ed., Pergamon Press Inc., New York, 1966, Vol. 2, p. 137.
5. W. J. Middleton, 'Organic Chemistry of Bivalent Sulfur', E. E. Reid, Ed., Chemical Publishing Co., Inc., New York, 1966, Vol. 6, p. 331.
6. J. Banus, H. J. Emeléus, and R. N. Haszeldine, J. Chem. Soc., 1951, 60.
7. G. C. Tesoro and R. N. Ring, U.S.P. 3,335,163/1967.
8. J. T. Barr and F. E. Lawlor, U.S.P. 2,894,991/1959;  
R. E. Oerstling, U.S.P. 3,006,964/1961.
9. R. C. Terrell, T. Ucciardi, and J. F. Vitcha, J. Org. Chem., 1965, 30, 4011.
10. E. T. McBee, C. W. Roberts, and G. Nilson, Jr., J. Amer. Chem. Soc., 1958, 80, 1719.
11. A. F. Clifford, H. K. El-Shamy, H. J. Emeléus, and R. N. Haszeldine, J. Chem. Soc., 1953, 2372.
12. G. A. R. Brandt, H. J. Emeléus, and R. N. Haszeldine, J. Chem. Soc., 1952, 2198.
13. M. Hauptschein and A. V. Grosse, J. Amer. Chem. Soc., 1951, 73, 5461.
14. G. V. D. Tiers, J. Org. Chem., 1961, 26, 3515.
15. R. D. Chambers, W. K. R. Musgrave, and J. Savory, J. Chem. Soc., 1962, 1993.

16. P. D. Faurote and J. G. O'Rear, J. Amer. Chem. Soc., 1956, 78, 4999.
17. F. Boberg, G. Winter, and G. R. Schultze, Annalen, 1959, 621, 8.
18. K. A. Petrov and G. A. Sokol'skii, J. Gen. Chem. (U.S.S.R.), 1957, 27, 2751.
19. C. T. Mason, U.S. Defence Doc., A.D.419526/1962.
20. W. E. Truce, B. H. Birum, and E. T. McBee, J. Amer. Chem. Soc., 1952, 74, 3594.
21. L. M. Yagupol'skii and M. S. Marenets, J. Gen. Chem. (U.S.S.R.), 1959, 29, 281.
22. L. M. Yagupol'skii and N. V. Kondratendo, J. Gen. Chem. (U.S.S.R.), 1967, 37, 1686.
23. E. H. Man, D. D. Coffman, and E. L. Muetterties, J. Amer. Chem. Soc., 1959, 81, 3575.
24. J. F. Harris, Jr., J. Org. Chem., 1967, 32, 2063.
25. H. J. Emeléus and H. Pugh, J. Chem. Soc., 1960, 1108.
26. H. J. Emeléus and D. E. Macduffie, J. Chem. Soc., 1961, 2597.
27. L. M. Yagupol'skii, V. F. Bystrov, and A. U. Stepanuyants, J. Gen. Chem. (U.S.S.R.), 1965, 35, 1631.
28. R. N. Haszeldine and J. M. Kidd, J. Chem. Soc., 1955, 3871.
29. F. W. Stacey and J. F. Harris, Jr., 'Organic Reactions', J. Wiley and Sons, Inc., 1963, Vol. 13, p. 150.
30. B. Higginbottom, Ph.D. Thesis, University of Manchester, 1964.
31. K. Inukai, T. Ueda, and H. Murmatsu, Bull. Chem. Soc. Japan, 1966, 39, 2191.
32. J. F. Harris, Jr. and F. W. Stacey, J. Amer. Chem. Soc., 1961, 83, 840.
33. J. F. Harris, Jr., U.S.P. 3,326,867/1967.

34. W. E. Hanford, U.S.P. 2,443,003/1948.
35. J. F. Harris, Jr. and F. W. Stacey, J. Amer. Chem. Soc., 1963, 85, 749.
36. A. V. Fokin, A. A. Skladnev, Y. N. Studnev, and I. L. Knunyants, Bull. Acad. Sci. U.S.S.R., 1967, 324.
37. V. S. Durrell, E. C. Stump, Jr., G. Westmoreland, and C. D. Padgett, J. Polymer Sci., 1965, 12, Part A, 4065.
38. J. F. Harris, Jr., J. Amer. Chem. Soc., 1962, 84, 3148.
39. N. Yarovenko and A. S. Vasil'eva, J. Gen. Chem. (U.S.S.R.), 1962, 31, 2816.
40. R. B. Ward, J. Org. Chem., 1965, 30, 3009; U.S.P. 3,346,606/1967.
41. S. F. Birch, T. V. Cullum, and R. A. Dean, J. Inst. Petroleum, 1953, 39, 206; Chem. Abs., 1954, 48, 4428.
42. K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., J. Amer. Chem. Soc., 1950, 72, 3642.
43. C. T. Bahner, U.S.P. 2,754,334/1956.
44. I. L. Knunyants, A. I. Schekotikin, and A. V. Fokin, Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk, 1953, 282; Chem. Abs., 1954, 48, 5787.
45. D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, Jr., J. Amer. Chem. Soc., 1960, 82, 5116.
46. G. Bier, H. Fritz, and H. H. Frey, G.P. 1,069,143/1961, Chem. Abs., 1961, 55, 7287.
47. W. T. Miller, U.S.P. 2,864,867/1958.
48. B.P. 896,373/1962.
49. A. W. Frank, J. Org. Chem., 1966, 31, 1917.
50. M. M. Schechter and R. F. Sweeney, U.S.P. 3,362,999/1968.
51. C. S. Scanley, U.S.P. 3,333,007/1967.



52. E. T. McBee, C. W. Roberts, and G. Wilson, Jr., J. Amer. Chem. Soc., 1957, 79, 2323.
53. I. L. Knunyants, I. N. Rozhkov, A. M. Alexansdrov, and L. M. Yagupol'skii, J. Gen. Chem. (U.S.S.R.), 1967, 37, 1210.
54. B.P. 926,573/1963.
55. I. L. Knunyants and E. G. Bykhovskaya, Izvest. Akad. Nauk S.S.R., Otdel Khim. Nauk, 1955, 852; Chem. Abs., 1956, 50, 9322.
56. S. Andreades, J. F. Harris, Jr., and W. A. Sheppard, J. Org. Chem., 1964, 29, 898.
57. W. A. Sheppard, J. Org. Chem., 1964, 29, 895.
58. J. Hine and J. J. Porter, J. Amer. Chem. Soc., 1960, 82, 6118.
59. A. H. de Cat, R. K. van Pouche, R. Pollet, and P. Schob, Bull. Soc. Chim. Belges, 1965, 74, 270; Chem. Abs., 1966, 64, 8065.
60. J. F. Harris, Jr., J. Org. Chem., 1966, 31, 931; U.S.P. 3,347,765/1967.
61. C. Walling and M. F. Mayahi, J. Amer. Chem. Soc., 1959, 81, 1485.
62. V. Prey, E. Gutschikin, and H. Berbalk, Monatsh., 1960, 91, 556.
63. F. W. Stacey and J. F. Harris, Jr., J. Amer. Chem. Soc., 1961, 83, 963.
64. W. J. Middleton, E. G. Howard, and W. H. Sharkey, J. Amer. Chem. Soc., 1961, 83, 2589.
65. K. Inukai, T. Ueda, and H. Murmatsu, Bull. Chem. Soc. Japan, 1967, 40, 1288; Chem. Abs., 1967, 67, 90892.
66. S. Oae and C. C. Price, 'Sulphur Bonding', The Ronald Press Co., New York, 1962.
67. C. C. Price and J. Zomlefer, J. Amer. Chem. Soc., 1950, 72, 14.
68. G. Cilento, Chem. Rev., 1960, 60, 147.
69. L. M. Yagupol'skii, V. F. Bystrov, A. U. Stepanuyants, and

- Y. A. Fialkov, J. Gen. Chem. (U.S.S.R.), 1964, 34, 3731.
70. L. M. Yagupol'skii, A. G. Panteleimonov, and V. U. Orda, J. Gen. Chem. (U.S.S.R.), 1964, 34, 3498.
71. L. M. Yagupol'skii and A. G. Panteleimonov, J. Gen. Chem. (U.S.S.R.), 1965, 35, 1123.
72. T. Gramstad and R. N. Haszeldine, J. Chem. Soc., 1957, 4069.
73. As reference 4, p. 145.
74. S. Temple, J. Org. Chem., 1968, 33, 344.
75. L. M. Yagupol'skii and A. G. Panteleimonov, J. Gen. Chem. (U.S.S.R.), 1966, 36, 433; Russ. P. 167,867/1965.
76. T. Gramstad and R. N. Haszeldine, J. Chem. Soc., 1956, 173.
77. J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, J. Chem. Soc., 1957, 2574.
78. T. Gramstad and R. N. Haszeldine, J. Chem. Soc., 1957, 2640.
79. R. N. Haszeldine and J. M. Kidd, J. Chem. Soc., 1954, 4228.
80. E. E. Reid, 'Organic Chemistry of Bivalent Sulfur', Chemical Publishing Co., Inc., New York, 1960, Vol. 2, p. 67.
81. C. E. Scott and C. C. Price, J. Amer. Chem. Soc., 1959, 81, 2672.
82. E. L. Eliel, 'Steric Effects in Organic Chemistry', J. Wiley and Sons, Inc., New York, 1956, p. 142.
83. W. A. Pryor, 'Mechanisms of Sulphur Reactions', McGraw Book Co., Inc., New York, 1962, p. 42.
84. J. A. Kampmeier and T. R. Evans, J. Amer. Chem. Soc., 1966, 88, 4096.
85. L. Hörner and J. Dorges, Tetrahedron Letters, 1963, 757.
86. W. C. Francis and R. N. Haszeldine, J. Chem. Soc., 1955, 2151.
87. D. W. Roberts, Ph.D. Thesis, University of Manchester 1965.

88. R. N. Haszeldine and B. O. West, J. Chem. Soc., 1956, 3631.
89. J. I. G. Cadogan and W. R. Foster, J. Chem. Soc., 1961, 3071.
90. C. Walling and R. Rabinowitz, J. Amer. Chem. Soc., 1959, 81, 1243; C. Walling, O. H. Basedow, and E. S. Savas, J. Amer. Chem. Soc., 1960, 82, 2181.
91. J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, J. Amer. Chem. Soc., 1966, 88, 1257.
92. S. Hacobian<sup>and</sup> T. Iredale, Nature, 1950, 166, 156, and references contained therein.
93. F. E. Ray and I. Levine, J. Org. Chem., 1937, 2, 267.
94. L. Batt and J. M. Pearson, Chem. Comm., 1965, 575.
95. A. E. Tipping, private communication.
96. H. H. Jaffe and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy', J. Wiley and Sons, Inc., New York, 1962, p. 476.
97. W. A. Pryor and H. Guard, J. Amer. Chem. Soc., 1964, 86, 1150.
98. K. H. Bückel and A. Conte, Chem. Ber., 1967,<sup>100</sup>1248.
99. W. J. Middleton, E. G. Howard, and W. H. Sharkey, J. Org. Chem., 1965, 30, 1375.
100. P. M. Rao, J. A. Copeck, and A. R. Knight, Canad. J. Chem., 1967, 45, 1369.
101. W. A. Pryor and T. L. Pickering, J. Amer. Chem. Soc., 1962, 84, 2705.
102. As reference 29, p. 207.
103. F. Challenger, 'Aspects of the Organic Chemistry of Sulphur', Butterworths, London, 1959, p. 9.

104. S. A. Kahn, Chem. Comm., 1968, 1036, and references quoted therein.
105. N. Leonard and C. R. Johnson, J. Org. Chem., 1961, 27, 282.
106. F. Ostermeyer and D. S. Tarbell, J. Amer. Chem. Soc., 1960, 82, 3752.
107. J. Strating, 'The Chemistry of Organic Sulphur Compounds', N. Kharasch, Ed., Pergamon Press Inc., New York, 1959, Vol. 1, p. 146.
108. D. T. Gibson, J. Chem. Soc., 1931, 2637.
109. R. J. Herschler and W. L. Shilling, Fr. P. 1,406,124/1965; Chem. Abs., 1965, 63, 11363.
110. R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds', J. Wiley and Sons, Inc., New York, 1967, p. 145.
111. L. A. Paquette, J. Amer. Chem. Soc., 1964, 86, 4085, and references quoted therein.
112. D. R. Christman and S. Oae, Chem. and Ind., 1959, 1251.
113. G. W. Fenton and C. K. Ingold, J. Chem. Soc., 1928, 3127.
114. E. S. Gould, 'Mechanism and Structure in Organic Chemistry', Holt, Rinehart, and Winston, Inc., New York, 1959, p. 389.
115. W. I. Bevan, Ph.D. Thesis, University of Manchester, 1963, and references quoted therein.
116. A. E. Wood and E. G. Travis, J. Amer. Chem. Soc., 1928, 50, 1226.
117. C. Di Santo, U.S.P. 3,304,331/1967.
118. W. V. Farrar, J. Chem. Soc., 1956, 508.
119. C. L. Guillemin and M. F. Auricourt, J. Gas Chromatog., 1964 2, 156.

120. M. A. Hauptschein and A. V. Grosse, J. Amer. Chem. Soc., 1951, 73, 2461.
121. R. N. Haszeldine, J. Chem. Soc., 1951, 584.
122. H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 1949, 2948.
123. R. N. Haszeldine, J. Chem. Soc., 1953, 2078.
124. R. D. Chambers, W. K. R. Musgrave, and J. Savory, J. Chem. Soc., 1961, 3779.
125. G. A. R. Brandt, H. J. Emeléus, and R. N. Haszeldine, J. Chem. Soc., 1952, 2549.
126. W. Steinkopf and S. Müller, Ber., 1923, 56, 1928.
127. P. Klaboe and J. R. Nielsen, J. Chem. Phys., 1961, 34, 1819.
128. C. G. Krespan, J. Org. Chem., 1958, 23, 2016.
129. M. Hauptschein, E. A. Nodiff, and A. V. Grosse, J. Amer. Chem. Soc., 1952, 74, 1347.
130. L. J. Bellamy, 'The Infrared Spectra of Complex Molecules', Methuen and Co., London, 1958, p. 329.
131. As reference 130, p. 350.