FLUOROALKYL DERIVATIVES

OF

SULPHUR

THESIS

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by

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ABSTRACT

The work of this thesis is concerned with the preparation, identification and some reactions of bis(trifluoromethylthio)alkanes and -fluoroalkanes and some reactions of trifluoromethylsulphur(VI) chloride tetrafluoride.

Bistrifluoromethyl disulphide reacts in a Pyrex vessel with olefins to give adducts which are best described as formed by attack of $CF_3S^{\bullet}$ radicals on the olefin. Ethylene gives $CF_3SCH_2CH_2SCF_3$; propene $CF_3SCH_2CH(CH_3)SCF_3$; tetrafluoroethylene $CF_3S(CF_2CF_2)_2SCF_3$ and $CF_3S(CF_2CF_2)_nSCF_3$ (n large); hexafluoropropene $CF_3S\left[CF(CF_3)CF_2\right]_nSCF_3$ (n = 1,2); 1,1-difluoroethylene $CF_3S(CF_2CH_2)_nSCF_3$ (n = 1-6); trifluoroethylene $CF_3S(CF_2CFH)_nSCF_3$ (n = 1-7); chlorotrifluoroethylene $CF_3S(CF_2CFCl)_nSCF_3$ (n = 1-4) and also $CF_3SCF_2CFClCF_3$ and $\overline{CF_2CFClCF_2CFClS}$; tetrachloroethylene $CF_3SCCl_2CCl_2SCF_3$, $CF_3SCCl{=}CCl_2$ and $CF_3SCCl_2CCl_3$. The infrared spectra of these adducts have been investigated but structure elucidation is obtained by a detailed investigation of the ^{19}F n.m.r. and mass spectra which are discussed at some length. An attempt is made to rationalise the mode of formation of the various isomers in the polymeric adducts in the light of current thinking on free radical addition to unsymmetrical olefins.

The reaction of $CF_3S\left[CF(CF_3)CF_2\right]_2SCF_3$ with chlorine monofluoride gives the new bis-sulphur(IV) compound $CF_3SF_2CF_2CF(CF_3)CF(CF_3)CF_2SF_2CF_3$ whose structure is established by ^{19}F n.m.r., i.r. and mass spectra and by elemental analysis.

The reaction of some of the adducts with liquid chlorine fails to give the S(IV) dichlorides.

Trifluoromethylsulphur(VI) chloride tetrafluoride adds to unsaturated carbon - carbon linkages under the influence of ultraviolet light in a manner best described by addition of $CF_3SF_4^{\bullet}$

radicals. Ethylene gives $CF_3SF_4CH_2CH_2Cl$; propene $CF_3SF_4CH_2CHClCH_3$; tetrafluoroethylene $CF_3SF_4CF_2CF_2Cl$; hexafluoropropene $CF_3SF_4CF(CF_3)CF_2Cl$ and $CF_3SF_4CF_2CFClCF_3$ (trace); 1,1-difluoroethylene $CF_3SF_4CH_2CF_2Cl$; trifluoroethylene $CF_3SF_4CFHCF_2Cl$; chlorotrifluoroethylene $CF_3SF_4CF_2CFCl_2$ and $CF_3SF_4(CF_2CFCl)_2Cl$; acetylene $CF_3SF_4CH{=}CHCl$. The ^{19}F n.m.r. spectra of the adducts establishes the trans structure about the sulphur atom. Some of the reactions also produce a compound which is thought to be $CF_3SF_4SF_4CF_3$.

The ultra-violet light induced reaction of CF_3SF_4Cl with hydrogen is also thought to produce $CF_3SF_4SF_4CF_3$ with HCl produced as a co-product, but the reaction of CF_3SF_4Cl with oxygen fails to give the oxide or peroxide, $CF_3SF_4OSF_4CF_3$ or $CF_3SF_4OOSF_4CF_3$, under the reaction conditions used.

CF_3SF_4Cl decomposes in the presence of mercury to give only CF_3Cl and SF_4 and a scheme is postulated to try to account for the specificity of the products observed.

ACKNOWLEDGEMENTS

I am especially grateful to Professor D.W.A. Sharp for his encouragement and supervision during the course of this work.

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CONTENTS

INTRODUCTION

The requirements of World War II for materials with unique and superior properties gave great impetus to research in fluorine chemistry in general and in sulphur - fluorine chemistry in particular. Research was hindered, however, by a lack of commercial availability of many fluorinated reagents. Progress was made mainly by industrial research chemists and by devotees in a limited number of universities.

In the last fifteen years the whole picture has changed and this is reflected in the number of reviews concerning various aspects of sulphur - fluorine chemistry (1 - 16) which have been published.

The chemistry discussed in this brief introduction is not intended to be comprehensive. On the contrary, a selection has been made purely on the basis of personal interest which is mainly in polyfluoroalkyl sulphur chemistry.

The ability of fluorine, with its high electronegativity and small atomic radius, to stabilise unusual chemical structures, and the ability of sulphur to exhibit several valence states enable many compounds containing sulphur and fluorine to exist, of which the polyfluoroalkyl sulphur derivatives are particularly interesting. It is convenient to discuss these under three main headings, viz. divalent, tetravalent and hexavalent sulphur compounds.

<u>Divalent Sulphur Compounds;</u>

CF_3SSCF_3, whose chemistry is discussed in more detail in Chapter I, Introduction, is easily converted to $(CF_3S)_2Hg$ by ultra - violet irradiation in the presence of mercury(17).

$$CF_3SSCF_3 + Hg \xrightarrow{u.v.} (CF_3S)_2Hg.$$

This mercurial, which can also be prepared from thiocarbonylfluoride (18) thus

$$HgF_2 + 2F_2C{=}S \longrightarrow (CF_3S)_2Hg$$

or from carbon disulphide (19),

$$CS_2 + HgF_2 \xrightarrow{250^\circ} (CF_3S)_2Hg$$

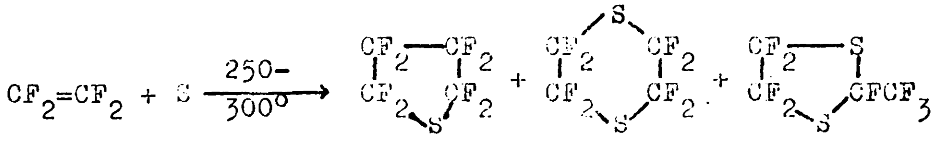
is an important reagent for introducing the CF_3S- grouping into a whole variety of compounds. Some examples are listed in Table I.1 while other chemistry of interest involving the mercurial is embodied in the following equations;

	Reference
$(CF_3S)_2Hg + 2SiH_3I \xrightarrow{20^\circ} CF_3SSiH_3$	(12)
$(CF_3S)_2Hg + AgNO_3 \xrightarrow{aq.} CF_3SAg$	(19)
$(CF_3S)_2Hg + Cu \xrightarrow{125^\circ} CF_3SCu$	(12)

Reagent	Products	Reference
CH_3COCl	$CF_3SC(O)CH_3$	(19)
CF_3COCl	$CF_3SC(O)CF_3$	(12)
CF_3SCl	$(CF_3S)_2 + CF_3SHgCl$	(20)
CCl_3SCl	$CF_3S_2CCl_3$	(19)
Cl_2CS	$(CF_3S)_2CS + CF_3SHgCl$	(21)
$CF_3SC(S)F$	$(CF_3S)_2CS + CF_3SHgF$	(21)
PCl_3	$(CF_3S)_3P + (CF_3S)_2PCl + CF_3SPCl_2$	(22)
$(CF_3)_2PI$	$(CF_3)_2PSCF_3$	(12)
$AsCl_3$	$(CF_3S)_3As + (CF_3S)_2AsCl + CF_3SAsCl_2$	(22)
$(CF_3)_2AsI$	$(CF_3)_2AsSCF_3$	(12)
C_2H_5I	$CF_3SC_2H_5$	(23)
CH_2I_2	$(CF_3S)_2CH_2$	(23)
CHI_3	$(CF_3S)_3CH$	(23)
CBr_4	$(CF_3S)_4C + (CF_3S)_2C{=}C(SCF_3)_2$	(23)
$BrCH_2CH_2Br$	$CF_3SCH_2CH_2SCF_3$	(23)

Table I.1 : Reactions of $(CF_3S)_2Hg$

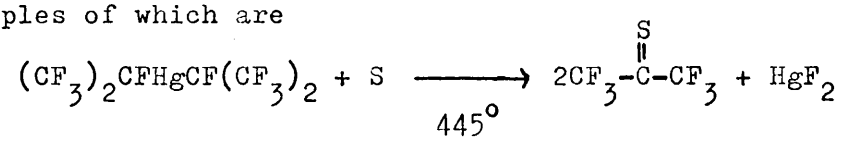
A large number of cyclic sulphides can be made by the reaction of sulphur with fluorinated olefins at elevated temperatures (24,25) e.g.



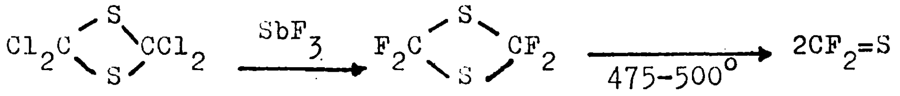
while acyclic sulphides may be prepared by the high temperature reactions of perfluoroalkyl iodides with sulphur (26) e.g.

$$C_3F_7I + S \xrightarrow[300^\circ]{} (C_3F_7)_2S$$

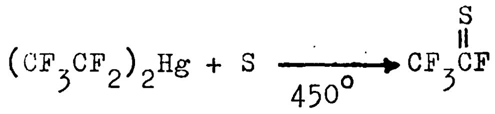
The preparation (27) of fluorothioketones has been investigated, some examples of which are



$$(CF_3)_2CFHgCF(CF_3)_2 + S \xrightarrow[445^\circ]{} 2CF_3-\overset{\overset{S}{\|}}{C}-CF_3 + HgF_2$$

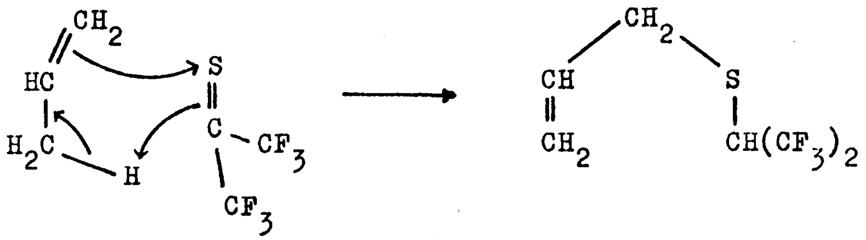


$$CF_2{=}CF_2 + S \xrightarrow[500-600^\circ]{} CF_2{=}S + CF_3CF{=}S + CF_3SSCF_3$$



$$(CF_3CF_2)_2Hg + S \xrightarrow[450^\circ]{} CF_3\overset{\overset{S}{\|}}{C}F$$

Hexafluorothioacetone reacts rapidly at low temperatures with olefins containing allylic hydrogen (28) to give 1 : 1 adducts that are allyl sulphides eg;



The number of divalent sulphur fluorides being prepared is steadily increasing: Sulphur difluoride, SF_2, whose existence was in some doubt for many years, has been characterised by its mass spectrum (29) and by its microwave spectrum (30). The mass spectrum of SF_2 was obtained when SCl_2 vapour was reacted with HgF_2 at a very low pressure while the microwave spectrum established SF_2 as having C_{2v} symmetry and a dipole moment of 1.05D. The values for the bond length and bond angle are shown in Fig. I.1.

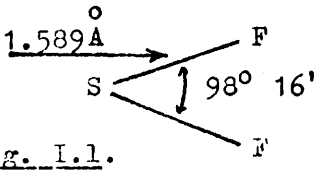


Fig. I.1.

Both disulphur difluoride, FSSF, and thiothionyl fluoride, $S{=}SF_2$, are formed by the reaction of sulphur vapour with AgF (31, 32, 33). Disulphur difluoride is a colourless liquid, b.p. 15 , which freezes to a white solid at -133° (33). FSSF is thermally less stable than the isomer $S{=}SF_2$. Alkali metal fluorides catalyse the isomerisation to $S{=}SF_2$ (32). The microwave spectrum (34) of FSSF shows the structure given in Fig. I.2.

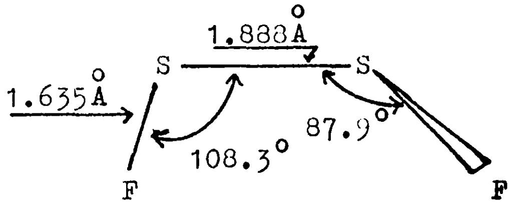


Fig. I.2.

For the sake of completeness, thiothionyl fluoride, $S{=}SF_2$, is included here rather than under " Tetravalent sulphur compounds". SSF_2 is formed by fluorination of S_2Cl_2(35) or by the passage of NF_3 through molten sulphur (36),

$$S_2Cl_2 + 2KSO_2F \longrightarrow S{=}SF_2 + 2KCl + SO_2$$

$$3S + NF_3 \xrightarrow[400^{\circ}]{} S{=}SF_2 + N{\equiv}SF$$

as well as from the isomerisation of FSSF. SSF_2 is a colourless gas, b.p. -10.6 whose structure was determined from the microwave spectrum (37) to be that given in Fig. I.3.

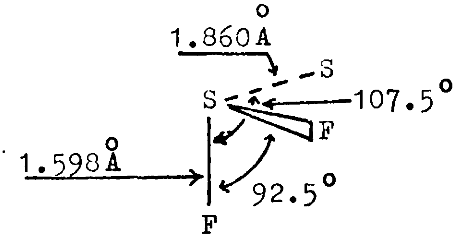


Fig. I.3.

Sulphenyl fluorides, R-SF, were first established in the form of $(CF_3)_2CFSF$ (38) which was identified by a detailed analysis of the ^{19}F n.m.r. spectrum. The compound claimed to be CCl_3SF (39) was revealed by subsequent work to be in fact CCl_2FSCl (40). The few sulphenyl fluorides known to date include F_2NCF_2SF (16), CF_3SF (41), SF_3-SF (42) (included here rather than under "Tetravalent sulphur compounds" for the sake of completeness) and F_2NCCl_2SF.(43). These sulphenyl fluorides are formed thus

$[(CF_3)_2CF]_2SF_2 \xrightarrow[200^\circ]{} (CF_3)_2CFSF$

$AgSCN + CaF_2 \longrightarrow F_2NCF_2SF$

$CF_3SCl + HgF_2 \longrightarrow CF_3SF$

$SCl_2 + KF \longrightarrow SF_3SF$

$NF_2CCl_2SCl + AgF_2 \longrightarrow NF_2CCl_2SF$

Tetravalent Sulphur Compounds.

Sulphur tetrafluoride, SF_4, was first made from the action of fluorine on a thin film of sulphur (44) and is now more conveniently prepared by the reaction of sulphur dichloride and sodium fluoride in a slurry of acetonitrile(45).

SF_4 derivatives containing S - N bonds belonging to the classes $R_2N - SF_3$, $R - N = SF_2$, $R - N = S(F) - NR'_2$, $R - N = S(F)R'$ and $N \equiv SF$ and SF_4 derivatives containing S - O bonds belonging to the classes $O=SF_2$, $O=S(F)R$, $O=S(F)NR_2$ and $O=S(F)OR$ are well established and discussed in the reviews cited. SF_4 derivatives of the class $F_nS(OR)_{4-n}$ have been established for $R= F(NO_2)_2CCH_2-$, n=1 (46) and R= Ph, n=1-4 (47).

Alkyl and aryl sulphur trifluorides, $R-SF_3$, have been prepared where $R=CF_3$ (48,49,50); $R=CF(CF_3)_2$ (38); $R=C_6H_5$,(50) ; and others (12).

The formation of $(CF_3)_2CFSF_3$, from the CsF catalysed addition of $CF_3CF=CF_2$ to SF_4 at 150°, is accompanied by formation of $[(CF_3)_2CF]_2SF_2$. This latter compound can be formed almost exclusively if the ratio of $CF_3CF=CF_2$ to SF_4 is increased to 2:1 from 1:1. Shreeve has observed a similar reaction (51) with $CF_2=CF_2$ which adds to SF_4, in the presence of CsF, to give $(CF_3CF_2)_2SF_2$ and $CF_3CF_2SF_3$. Other compounds of the class $R_fSF_2R'_f$ are formed by the fluorination of bis(perfluoroalkyl)sulphides with (a) ClF (51, 52) and (b) elemental F_2 (53) thus

$CF_3SR_f \longrightarrow CF_3SF_2R_f$ (a) $R_f=CF_3$, C_2F_5, $\underline{n}-C_3F_7$

(b) $R_f=CF_3$

$CF_3SF_2R_f$ with $R_f = \underline{i}-C_3F_7$ is obtained by the CsF catalysed reaction of

CF_3SF_3 with $CF_3CF=CF_2$ (38).

Hydrolysis of the R_fSF_3 compounds gives $R_fS(O)F$ (48, 54) while hydrolysis of the $R_fSF_2R_f'$ compounds gives $R_fS(O)R_f'$ (51-54).

The unique compound $(C_6F_5)_4S$ which is unstable above 0° and decomposes to $(C_6F_5)_2S$ and $C_6F_5-C_6F_5$, can be formed either by the action of C_6F_5Li on SF_4 or by the action of C_6F_5Li on $C_6F_5SF_3$ (55) thus

$$C_6F_5Li + SF_4 \xrightarrow{-80^\circ} (C_6F_5)_4S$$

$$C_6F_5Li + C_6F_5SF_3 \xrightarrow{-80^\circ} (C_6F_5)_4S$$

$C_6F_5SF_3$ is prepared by the fluorination of $(C_6F_5S)_2$ with AgF_2.

Hexavalent Sulphur Compounds.

Sulphur hexafluoride, SF_6, was first isolated and characterised in 1900 by Moissan and Lebeau (56). It was prepared by burning sulphur in an atmosphere of fluorine and removing lower fluorides by pyrolysis at 400° and washing with aqueous alkali.

By virtue of its dielectric properties and its chemical and physiological inertness, SF_6 is of importance in electrical and cooling techniques. The inactive behaviour of SF_6 is due less to its thermodynamic properties [the S-F bond dissociation energy is 76 kcals./mole (57)] but rather to its kinetic properties. Normal nucleophilic reagents cannot attack the highly symmetrical octahedral structure of six equal S-F bond distances, 1.564Å (58). However, the decomposition reactions at 200° of SF_6 with $AlCl_3$ yielding S_2Cl_2, or with SO_3 giving SO_2F_2 are known (59). The reaction of SF_6 with oxygen can be initiated by electrical explosion of extremely small masses of platinum or copper into SF_6/O_2 mixtures (60). e.g.

$$SF_6 + \tfrac{1}{2}O_2 \longrightarrow O{=}SF_4 + F_2$$

$$SF_6 + \tfrac{1}{2}O_2 \longrightarrow O{=}SF_2 + 2F_2$$

Of the mixed halides, only SF_5Br (9) and SF_5Cl (9) are known. The chemistry of the latter is discussed in more detail in the Introduction to Chapter II.

Structural studies (61) indicate slightly distorted octahedral symmetries for SF_5Cl and SF_5Br.

Disulphur decafluoride, S_2F_{10}, was first isolated and characterised (62) by Denbigh and Whytlaw - Gray as a high - boiling residue in the preparation of SF_6 by direct fluorination of sulphur. S_2F_{10} has an interesting structure (61) , consisting of two SF_5 units joined by a long S-S bond to retain an octahedral bond distribution about each S atom. The two halves of the molecule are staggered as shown in Fig.I.4.

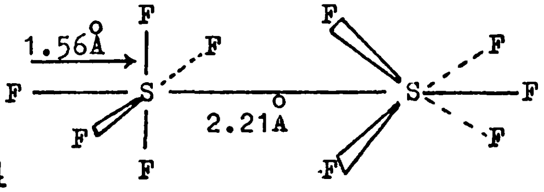


Fig.I.4

The first fluorocarbon derivative of SF_6, CF_3SF_5, was prepared by the reaction of CH_3SH with CoF_3 or F_2 in the presence of AgF_2 (63). The reaction of CS_2 with CoF_3 at 200° to 250° also produced CF_3SF_5 along with CF_4 and SF_6 (63) whilst use of elemental fluorine at 48° (64) resulted in a wide range of products including CF_3SF_5, $SF_5CF_2SF_5$, $SF_5CF_2SF_3$, CF_3SF_3 and S_2F_{10}. The electrochemical method of fluorinating compounds containing a C-S bond provides a convenient route to the preparation of fluorocarbon derivatives of SF_6. Table I.2 lists a few of the more unusual compounds prepared in this way.

Reagent	Products	Reference
$(CH_3)_2S$	CF_3SF_5, $(CF_3)_2SF_4$	(65)
$(CH_2S)_3$	CS_2, CF_3SF_5, $CF_2(SF_5)_2$, $(CF_2SF_4)_3$	(66)
$(C_3H_7)_2S$	$C_3F_7SF_5$, $(C_3F_7)_2SF_4$	(12)
$CH_3S(C_2H_4)SCH_3$	CF_3SF_5, $C_2F_5SF_4CF_3$, $(C_2F_5)_2SF_4$, $(C_2F_4SF_4)_2$, $CF_3SF_4C_2F_4SF_5$	(66)
$(CH_2)_4S$	$C_4F_9SF_5$, $(C_2F_5)_2SF_4$, $C_3F_7SF_4CF_3$	(12)

Table I.2. Electrochemical fluorination of C-S compounds.

A fuller list is to be found in Reference (12).

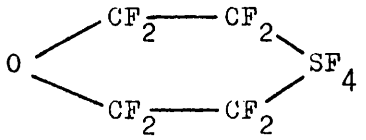
Fluorocarbon derivatives of SF_6 are chemically and pyrolytically quite stable, as might be expected of substances derived of fluorocarbons and SF_6 e.g. CF_3SF_5 is inert to water, KOH solution, and oxidising acids (12). However, pyrolytic decomposition of the perfluoroalkyl derivatives is reported to occur (65) via free radical mechanisms at temperatures between 400° and 500° in flow systems or closed reactors

$$R_fSF_5 \longrightarrow R_fF + R_f{-}R_f + SF_4$$

$$(R_f)_2SF_4 \longrightarrow R_f{-}R_f + SF_4$$

$(CF_3)_2SF_4$ has been copyrolysed with hexafluoropropene (67) to give SF_4 and a mixture of the C_5F_{12} isomers.

Most of the disubstituted fluorocarbon derivatives of SF_6 are <u>trans</u> about the central sulphur atom but the nature of the substituent group can force the molecule to take up a <u>cis</u> configuration e.g.



was established as <u>cis</u> about the sulphur by the ^{19}F n.m.r. spectrum (68) which showed two signals for the SF_4 group with an A_2B_2 fine structure.

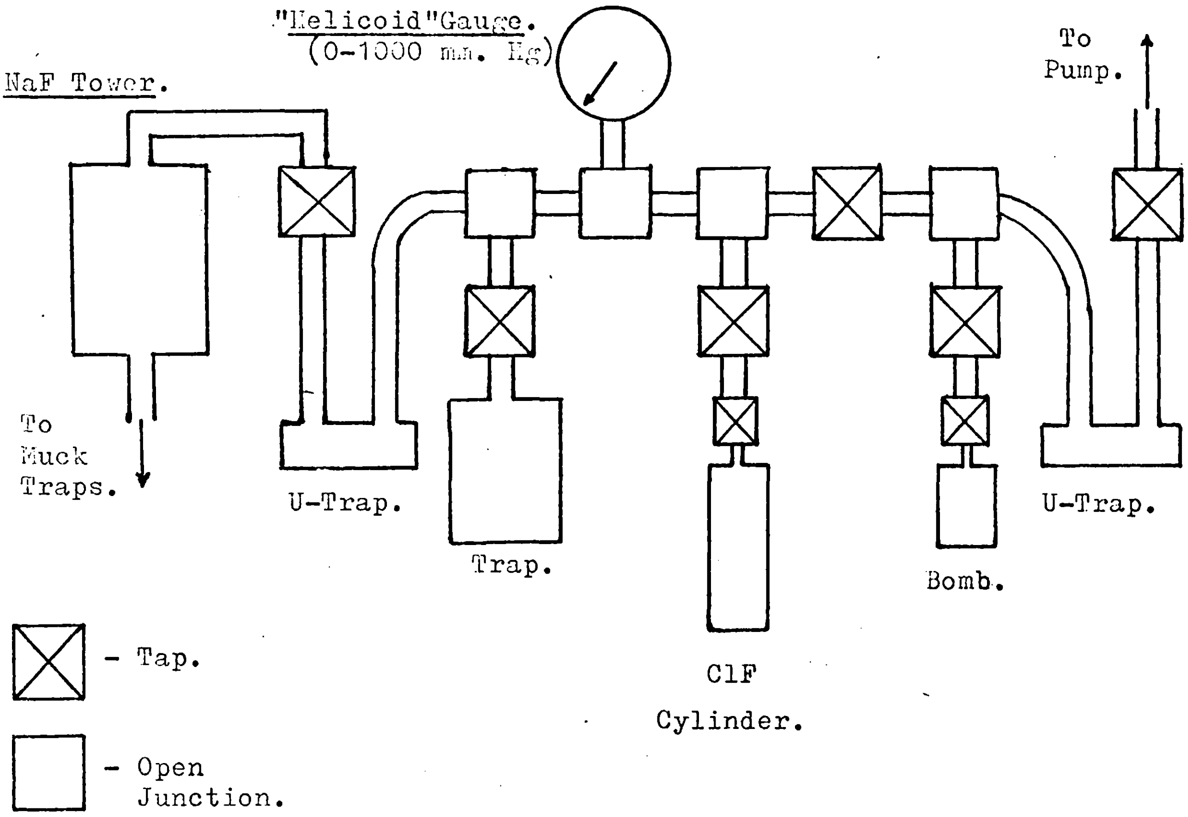
Recent years have produced the synthesis of compounds with sulphur atoms of mixed oxidation state bonded to one another with the preparation of $CF_3SSF_2CF_3$ (41) and $SF{-}SF_3$ (42) i.e. S (II) - S (IV). It would seem only a matter of time, therefore, till other compounds in this class, S (II) - S (VI) and S (IV) - S (VI), are produced. Also awaiting synthesis are the unknown classes of compounds :

(1) stable sulphur iodides

(2) sulphur hydrides, SH_4, SH_6, SF_5H etc.

(3) mixed halide sulphur compounds, SF_xCl_{4-x}, SOF_xCl_{4-x}, and SF_xCl_{6-x}, other than SF_5Cl.

GENERAL EXPERIMENTAL METHODS.



MONEL VACUUM LINE.

The figure illustrates the monel vacuum line used for transfer of chlorine monofluoride. Otherwise, standard vacuum techniques, using a Pyrex vacuum line, were used throughout. Hygroscopic solids were handled in a dry, oxygen - free, nitrogen atmosphere. Molecular weights were determined by the vapour density method or by mass spectrometry. Vapour pressures were measured at room temperature and corrected to 25^{0}C. Boiling points were measured in semi - micro apparatus at atmospheric pressure and corrected to 760.00 mm. Hg.

Elemental analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium.

Infrared spectra of gases were recorded in 5 or 10 cm. gas cells fitted with KBr windows. The spectra of involatile liquids or greases were taken as liquid films on KBr plates or as solutions using NaCl, semi - permanent cells obtained from R.I.I.C. All spectra were recorded on

Perkin - Elmer 237, 257 or 457 spectrophotometers. The following abbreviations have been used in the text : s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very; sym, symmetric; as, asymmetric; ν, stretch; δ, angle deformation.

Mass spectra were recorded at 70 eV (unless otherwise stated) using an A.E.I. MS 12 or an A.E.I. MS 9 spectrometer. For volatile liquids and gases, the cold gas inlet system was used while involatile liquids and greases were introduced into the ionisation chamber by means of the probe inlet. 1v spectra.

N.m.r. spectra were recorded on a Perkin - Elmer R. 10 spectrometer operating at 60.0 MHz., for ^{1}H and 56.4 MHz. for ^{19}F n.m.r. spectra. The probe temperature was 33°. The nuclear magnetic double resonance spectrum was recorded on a Varian T-60 N.M.R. spectrometer.

References (external) employed throughout were trichloro - fluoromethane for fluorine spectra and tetramethylsilane for proton spectra. The conversion factors for relating literature chemical shifts (in p.p.m.) to CCl_3F employed were (69).

$$\begin{aligned} \delta_F\ (CCl_3F) &= \delta_F\ (CF_3COOH) + 76.5 \\ &= \delta_F\ (CFCl_2CFCl_2) + 67.8 \\ &= \delta_F\ (F_2) - 430 \\ &= \delta_F\ (SF_6) - 56.8 \end{aligned}$$

CHAPTER I

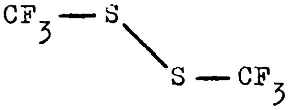
PREPARATION AND SOME REACTIONS
OF
BIS(TRIFLUOROMETHYLTHIO)ALKANES AND -FLUOROALKANES.

INTRODUCTION

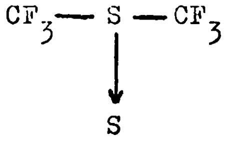
Bistrifluoromethyldisulphide, CF_3SSCF_3, was first reported in a preliminary communication in 1950 (70) and more fully later in 1952 (17). It was prepared by heating trifluoromethyl iodide and sulphur in glass or metal vessels at elevated temperatures e.g. at 310^0:

$$CF_3I + S \xrightarrow{310^0} \underset{(75\%)}{(CF_3S)_2} + \underset{(12\%)}{(CF_3S)_2S} + \underset{(1\%)}{(CF_3S)_2S_2}$$

The structure was established as A rather than B

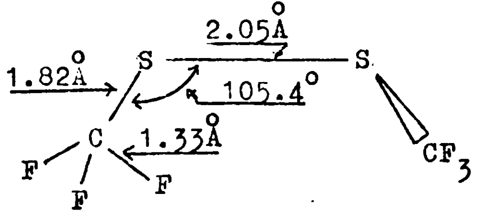


A



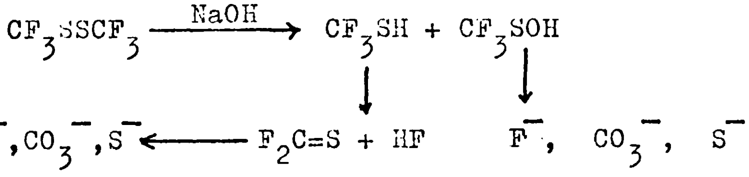
B

by an elegant series of reactions and this was confirmed in 1954 by an electron diffraction study (71) which gave the following parameters



for the trans, non - planar structure. The dihedral angle was not listed.

Bistrifluoromethyldisulphide is reported (17) to be insoluble in and unaffected by water or hydrochloric acid at room temperature although it is completely decomposed by dilute alkali in accord with the following scheme



i.e. involving hydrolytic fission of the S-S bond.

The i.r. (72) u.v. (72) ^{19}F n.m.r. (73) and mass (74) spectra of bistrifluoromethyldisulphide have all been reported and support the trans non - planar structure. Since the first preparation, from CF_3I and S, bistrifluoromethyldisulphide has been prepared in a variety of ways e.g.

	Reference
$CS_2 + IF_5 \xrightarrow{60\text{-}200^\circ} \underset{80\%}{CF_3SSCF_3} + SF_4 + \underset{7\%}{CF_3SSSCF_3}$	(20)
$CCl_3SCl \xrightarrow[CH_3CN]{NaF} CF_3SCl + CF_3SSCF_3$	(75)
$CCl_2S + NaF \xrightarrow[245^\circ]{TMS} CS_2 + \underset{37\%}{CF_3SSCF_3}$	(75)
$CCl_3SBr + 6KF \xrightarrow{\text{Solvent}} \underset{68\%}{CF_3SSCF_3} + Br_2$	(76)
$Cl_3CSSCCl_3 + 6KF \longrightarrow \underset{58\%}{CF_3SSCF_3} + 6KCl$	(76)

and other methods which are reported in the many review articles (4, 7, 11-14, 77, 78).

Bistrifluoromethyldisulphide also appears as a product in many reactions, for example;

	Reference
$UF_6 + CS_2 \longrightarrow UF_4 + SF_4 + (CF_3S)_2 + (CF_3S)_2S$	(79)
$VF_5 + CS_2 \longrightarrow VF_3 + (CF_3S)_2 + (CF_3S)_2S + SF_4$	(80)
$CF_3S(O)Cl + (CF_3S)_2Hg \longrightarrow CF_3SO_2SCF_3 + (CF_3S)_2$	(81)
$2NF_2SO_2Cl + (CF_3S)_2Hg \xrightarrow[CH_3CN]{} N_2F_4 + 2SO_2 + (CF_3S)_2 + HgCl_2$	(82)

Many others are mentioned in the reviews (4, 7, 11-14, 77).

Bistrifluoromethyldisulphide can be oxidised to CF_3SF_5 by CoF_3 (17), to CF_3SF_3 by F_2 (49), CF_3OF (49) and AgF_2 (48).

Homolytic cleavage of the S-S bond in RSSR compounds, R=alkyl, aryl, can be effected by u.v. irradiation and has been extensively reviewed (83-89). Bistrifluoromethyldisulphide is no exception and gives $(CF_3S)_2Hg$ on irradiation in the presence of Hg (17), trifluoromethylthiodifluoramine, CF_3SNF_2, on irradiation in the presence of tetrafluorohydrazine (90), and trifluoromethanesulphenyl chloride, CF_3SCl on irradiation in the presence of Cl_2 (20) or oxalyl chloride (91). All of these reactions are postulated to proceed through $CF_3S^\bullet$ radicals produced by homolytic cleavage of the S-S bond, $CF_3S^\bullet$ radicals also being postulated as intermediates in the formation of bistrifluoromethylsulphide, $(CF_3)_2S$, on irradiation of $(CF_3S)_2$ (20, 73), in the formation of transition metal trifluoromethylthio derivatives from transition metal carbonyls, cyclopentadienes or cyclopentadienyl carbonyls (92, 93) and in the formation of a $\left(SCF_2CF_2\right)_n$ polyomer on irradiation of $(CF_3S)_2$ with tetrafluorothiirane $\overline{CF_2CF_2S}$ in Pyrex (94). The reaction with bisdimethyldiarsine $(CH_3)_2AsAs(CH_3)_2$ proceeds in the absence of u.v. light to give dimethyl(trifluoromethyl)-arsine, $CF_3SAs(CH_3)_2$ (95). Other CF_3S- containing compounds are well reviewed (4, 7, 11-14, 77, 96-100).

The major part of this chapter deals with the preparation of bis(trifluoromethylthio)alkanes and - fluoroalkanes by the photochemically initiated addition of bistrifluoromethyldisulphide to olefins. The addition of free radicals to olefins has been comprehensively reviewed (85, 96, 101-106) and the direction of radical addition to unsymmetrical olefins discussed.

In this work, the direction of addition of the $CF_3S^{\bullet}$ radical from irradiation of $(CF_3S)_2$ to the unsymmetrical olefins examined will be discussed in the light of present thinking and the nature of the products observed.

The second part of this chapter is concerned with the fluorination of the bis(trifluoromethylthio)alkanes and - fluoroalkanes to the bis[sulphur (IV)] difluorides. Previous attempts to fluorinate bis-(perfluoroalkyl) sulphides using metal fluorides AgF_2, or CoF_3 did not yield bis(perfluoroalkyl) sulphur difluorides but rather cleaved the sulphur-carbon bond (73).

$(C_3F_7)_2SF_2$ and $(C_3F_7)SF_3$ are both formed by the CsF catalysed reaction of SF_4 with $CF_2{=}CFCF_3$ (38). With a 1:1 ratio of SF_4 to $CF_2{=}CFCF_3$, the trifluoride is the major product while with a 1:2 ratio of SF_4 to $CF_2{=}CFCF_3$ the difluoride is the major product. Fluorination by F_2 at -119° (73) and -78° (53) of $(CF_3)_2S$ is reported to produce $(CF_3)_2SF_2$ although the compound is not very well characterised and does not have the same chemical properties as $(CF_3)_2SF_2$ prepared from $(CF_3)_2S$ by the action of chlorine monofluoride (51, 52) and characterised by i.r., ^{19}F n.m.r. and mass spectra, elemental analysis. Other comparable reactions of chlorine monofluoride are listed in Table 1.1.

Table 1.1.

Reagent.	Product.	Reference.
SOF_2	SOF_4	107
SO_2	SO_2FCl	107
SO_3	$ClOSO_2F$	107
$R_fS(O)R'_f$	$R_fS(O)F_2R'_f$	108
$(R_f, R'_f = CF_3, C_2F_5)$		
$\overline{CF_2CF_2CF_2CF_2S}$	$\overline{CF_2CF_2CF_2CF_2S}F_2$	109
$\overline{CF_2CF_2CF_2CF_2S}(O)$	$\overline{CF_2CF_2CF_2CF_2S}(O)F_2$	109
SOF_4*	SF_5OCl	110, 111
SF_4**	SF_5Cl	112

* in the presence of BF_3 or KF or CsF

** in the presence of CsF

Iodine pentafluoride is a milder fluorinating agent than chlorine monofluoride and generally effects the transformation of $-CF_2I$ and $-CI_3$ groups to $-CF_3$ groups (96). However, it has been found to fluorinate tetrafluorodithietane, $\overline{CF_2SCF_2S}$, to trifluoromethylsulphur trifluoride i.e. an S (II) ⟶ S (IV) oxidation (27).

The last part of this chapter represents an attempt to prepare some stable S(IV) dichlorides. Diaryl sulphur dichlorides are well known (113), but the only alkyl sulphur dichloride to date is bis (2-chloroethyl)sulphur dichloride, $(ClCH_2CH_2)_2SCl_2$, prepared from the action of chlorine on mustard gas $(ClCH_2CH_2)_2S$ in CCl_4 solution (113). Alkyl and aryl sulphur trichlorides are well established (9, 114) being formed by the action of chlorine on disulphides or sulphenyl chlorides thus

$$RSCl \xrightarrow{Cl_2} RSCl_3$$

$$RSSR \xrightarrow{Cl_2} 2RSCl_3$$

but previous attempts at the chlorination of di-alkyl sulphides to the S(IV) compounds have resulted in the chlorination of the α - carbon and the elimination of HCl (115).

SUMMARY OF REACTIONS

A. Preparative Reactions.

1. $\mathrm{CF_3SSCF_3 + CH_2{=}CH_2 \xrightarrow{u.v.} CF_3SCH_2CH_2SCF_3}$
2. $\mathrm{CF_3SSCF_3 + CH_3CH{=}CH_2 \xrightarrow{u.v.} CF_3SCH(CH_3)CH_2SCF_3}$
3. $\mathrm{CF_3SSCF_3 + CF_2{=}CF_2 \xrightarrow{u.v.} CF_3S(CF_2CF_2)_2SCF_3 +}$
   $\mathrm{CF_3S(CF_2CF_2)_nSCF_3}$, n large
4. $\mathrm{CF_3SSCF_3 + CF_3CF{=}CF_2 \xrightarrow{u.v.} CF_3S\left[CF(CF_3)CF_2\right]_nSCF_3}$, $n=1,2$
5. $\mathrm{CF_3SSCF_3 + CF_2{=}CH_2 \xrightarrow{u.v.} CF_3S(CF_2CH_2)_nSCF_3}$, $n=1-6$
6. $\mathrm{CF_3SSCF_3 + CF_2{=}CFH \xrightarrow{u.v.} CF_3S(CF_2CFH)_nSCF_3}$, $n=1-7$
7. $\mathrm{CF_3SSCF_3 + CFCl{=}CF_2 \xrightarrow{u.v.} CF_3S(CFClCF_2)_nSCF_3}$, $n=1-4$
   $\mathrm{+ \ \overline{CF_2CFClCF_2CFClS}}$
   $\mathrm{+ \ CF_3SCF_2CFClCF_3}$
8. $\mathrm{CF_3SSCF_3 + CCl_2{=}CCl_2 \xrightarrow{u.v.} CF_3SCCl_2CCl_2SCF_3 + CF_3SCCl{=}CCl_2}$
   $\mathrm{+ \ CF_3SCCl_2CCl_3.}$

B. Reactions with Iodine Pentafluoride and Chlorine Monofluoride.

9. $\mathrm{CF_3SCH_2CH_2SCF_3 + IF_5 \longrightarrow CF_3I + CF_4}$ + solid products.
10. $\mathrm{CF_3SCH_2CH_2SCF_3 + ClF \longrightarrow HCl + CF_3Cl + Cl_2 + CF_4}$
    $\mathrm{+ \ CF_3SCCl_2CH_2SCF_3 + CF_3SCHClCH_2SCF_3}$
    + an unidentified S(VI) fluoride.
11. $\mathrm{CF_3SCF(CF_3)CF_2SCF_3 + ClF \longrightarrow CF_4 + CF_3Cl + Cl_2}$
    $\mathrm{+ \ CF_3SF_5 + \underline{trans}\text{-}\ CF_3SF_4Cl + CF_3SCF_2CFClCF_3}$
    $\mathrm{+ \ CF_3SCF(CF_3)CF_2Cl\ \ (CF_3)_2CFSCl}$
    $\mathrm{+ \ CF_3CFClCF_2SCl + CF_2Cl(CF_3)CFSCl}$
    $\mathrm{+ \ (CF_3)_2CFCl + \underline{trans}\text{-}(CF_3)_2CFSF_4Cl}$
    $\mathrm{+ \ \underline{trans}\text{-}CF_3CFClCF_2SF_4Cl}$
    $\mathrm{+ \ \underline{trans}\text{-}CF_3CFClCF_2SF_4CF_3}$
12. $\mathrm{CF_3S\left[CF(CF_3)CF_2\right]_2SCF_3 + ClF \longrightarrow HCl, SiF_4, CF_4, CF_3Cl, SF_4, SOF_2}$
    (all trace)
    $\mathrm{+ \ CF_3SF_2\left[CF(CF_3)CF_2\right]_2SF_2CF_3}$

C. Reactions with Chlorine.

13. $CF_3SCH_2CH_2SCF_3 + Cl_2 \longrightarrow CF_3SCHClCH_2SCF_3 + HCl$

14. $CF_3SCH(CH_3)CH_2SCF_3 + Cl_2 \longrightarrow CF_3SCCl(CH_3)CH_2SCF_3 + HCl$

15. $CF_3SCF(CF_3)CF_2SCF_3 + Cl_2 \longrightarrow$ no reaction.

RESULTS AND DISCUSSION

A. Preparation of Bis(trifluoromethylthio)alkanes and -Fluoroalkenes.

The ultra-violet spectrum of CF_3SSCF_3 (72) shows a λmax at 235nm. This, as well as the λmax at 250nm of alkyl disulphides (72, 116) is associated with conjugation between the unshared electrons of the two sulphur atoms, with a sulphur atom expanding its valence shell to ten or more electrons (72, 116). Expansion of the outer valence shell of sulphur has been shown to be possible (117). The homolytic rupture of the weak S-S bond is the major result of this light absorption (86). A mass spectrometric investigation of alkyl and perfluoroalkyl sulphides has been made and C-S and S-S bond energies for CF_3SSCF_3 and CH_3SSCH_3 calculated (74) and listed in Table 1.2.

Table 1.2 C-S and S-S bond energies (kcals./mole)

COMPOUND	C-S	S-S
CH_3SSCH_3	68.5	83.7
CF_3SSCF_3	45.5	89.8

These results indicate that the C-S bond is the weaker in both instances and that any bond rupture would preferentially take place at the C-S bond. With dimethyldisulphide, indirect evidence from experiments with ethylene and acetylene shows that S-S bond cleavage takes place (86) thus:

$$CH_3SSCH_3 \xrightarrow{h\nu} 2CH_3S^{\bullet}$$

Haszeldine showed that the C-S bond in CF_3SSCF_3 does not cleave directly on irradiation in a silica vessel, but S-S bond cleavage is the primary result of irradiation and C-S bond cleavage is a secondary process, effected by radical displacement by $CF_3S^{\bullet}$(17) thus:

$$CF_3SSCF_3 \xrightarrow{h\nu} 2CF_3S^{\bullet}$$

$$CF_3S^{\bullet} + CF_3SSCF_3 \qquad CF_3SCF_3 + CF_3SS^{\bullet}$$

$$CF_3SS^{\bullet} \qquad CF_3S^{\bullet} + S$$

Gee (118) has suggested that fragments containing more than one Sulphur atom may be stabilised by some sort of resonance interaction of the free electron with the sulphur chain and it is perhaps the stability of the

$CF_3SS^{\bullet}$ radical as much as the weakness of the C-S bond which is responsible for the secondary bond cleavage. Thus the bond energy data cannot be used here to predict products from irradiation involving disulphides. One suggestion (69) is that there is significant torsional strain in the S-S bond when the dihedral angle between the two substituents attached to a sulphur-sulphur bond is forced by geometric constraints to be smaller than the normal 90° and an effect of this sort may have some bearing on the relative ease of S-S bond cleavage described above.

Irradiation in Pyrex of CF_3SSCF_3 with organometallic complexes to give trifluoromethylthio derivatives (93) and with Cl_2 to give CF_3SCl (20) is thought to proceed via $CF_3S^{\bullet}$ radicals although in the latter case, C-S bond cleavage, probably of the CF_3SCl, was seen to take place when the reaction was carried out in silica. Now Pyrex only transmits light of wavelength >300 nm whilst silica or quartz will transmit light of wavelength >220 nm (86) therefore it is possible that the λmax at 235nm in the ultra-violet spectrum of CF_3SSCF_3 corresponds to the formation of excited $CF_3S^{\bullet}$ radicals whereas at higher wavelengths the extinction coefficient of CF_3SSCF_3 is very small and less energetic $CF_3S^{\bullet}$ radical are formed, which do not have sufficient energy to effect secondary C-S bond cleavage. To support this idea, it is noted that when dimethyldisulphide is exposed to ultra-violet light of wavelength 253.7nm and 360nm, in the presence of air the same products are formed in each case but the latter reaction takes <u>ca.</u> 5 times as long to reach completion (119). The λmax of $(CH_3)_2S_2$ is at 253 nm (4) and irradiation at that wavelength is known to produce $CH_3S^{\bullet}$ radicals (86) and it is possible that the irradiation at the higher wavelength does not produce such energetic radicals.

TABLE 1.3. Ultra-violet Output and Distribution for 100-watts Medium Pressure Arc Tube No. 12277

Wavelength.	Energy (kcal./mole).	% light transmitted
1367.3	20.9	1.18
1128.7		1.55
1014.0		4.95
578.0/590.0	49.5/48.4	9.58
546.1	52.4	16.41
435.8	65.7	13.34
404.5	70.7	7.51
366.0	78.1	16.40
334.1	85.6	1.36
320.5	88.0	4.56
....	....	....
313.0	91.3	9.20
296.7	96.3	3.31
289.4	98.8	1.00
280.4	101.8	1.16
275.2	104.0	.44
270.0	105.7	.53
265.2	107.9	2.55
257.1	111.2	.80
253.7	112.5	2.20
248.2	115.1	1.24
240.0	119.0	.77

Table 1.3 gives the ultra-violet output and distribution for the ultra-violet source used in this work. The dotted line shows where the filtering action of the Pyrex might be expected to act, cutting out all the energy below the line. When Pyrex vessels were used for the reaction of CF_3SSCF_3

with olefins C(AB)=C(XY), the "clean" products $CF_3SC(AB)C(XY)SCF_3$ described below were obtained, but when quartz vessels were used, the $CF_3SC(AB)C(XY)CF_3$ products were also obtained, showing that some C-S bond cleavage had indeed taken place due to the high energy radiation.

The preparation of the bis(trifluoromethylthio)alkane and fluoroalkanes was very smooth except in the case of the tetrachloro - compound. They were all clear liquids or greases. The liquids did not decompose during the recording of their boiling point in air. The preparation from CF_3SSCF_3 and olefin is described first with the characterisation being dealt with under the **i.r., n.m.r. and mass spectra headings.**

Reaction of Bistrifluoromethyldisulphide with Ethylene.

The addition of free radicals to ethylene is well established e.g. the radicals $CF_3^\bullet$ [from CF_3I (96)]. $Br^\bullet$; $Cl^\bullet$; $I^\bullet$ [from HBr, HCl, HI respectively (103)] $CCl_3^\bullet$ [from CCl_3Br (102, 120-122)] $CF_2Br^\bullet$ [from CF_2Br_2 (102, 123)] $C_3F_7^\bullet$ [from C_3F_7I (124)] $(CF_3)_2NO^\bullet$(125), $SF_2{=}N^\bullet$ [from SF_2N-Cl (126)], $SF_5^\bullet$ [from SF_5Cl (127, 128)], $(CF_3)_2P^\bullet$ [from $(CF_3)_2PP(CF_3)_2$ (129)] and $(CH_3)_2P^\bullet$ [from $(CH_3)_2PP(CH_3)_2$ (129)] all add to ethylene to give the 1:1 monomers although telomerisation is sometimes observed e.g. with SF_5Cl and CF_3I. Other examples of radical addition to ethylene are to be found in References (85) and (102). Bistrifluoromethyldisulphide and ethylene under the influence of ultra-violet light react to give 1,2 - bis(trifluoromethythio)ethane, $CF_3SCH_2CH_2SCF_3$. $CF_3SCH_2CH_2SCF_3$ is already known, having been formed by the reaction of bis(trifluoromethylthio)mercury with 1,2- dibromoethane (23) thus

$$(CF_3S)_2Hg + BrCH_2CH_2Br \xrightarrow[\text{20 hrs}]{\text{Reflux}} CF_3SCH_2CH_2SCF_3 + HgBr_2$$

and so identification of the product formed here was accomplished by comparison of b.p., **i.r.** and ^1H n.m.r. spectra (23). The compound is formed by **addition** of the $CF_3S^\bullet$ radical to ethylene to give the $CF_3SCH_2CH_2^\bullet$ radical with the termination step being either radical combination with

$CF_3S^\bullet$ or radical displacement of $CF_3S^\bullet$ from CF_3SSCF_3, both of which processes are well known for RSSR reactions (84). There is no reaction between CF_3SSCF_3 and ethylene in the absence of u.v. light and in a bomb at ca. 50 atmos. and 100° there is very little conversion to the bis(trifluoromethylthio) ethane. It was originally thought that all disulphides thermally dissociate at 100 - 150° since many colour reversibly when heated to temperatures in this range and this reversible colouration was incorrectly attributed to the formation of stable radicals. However, it has been shown that reversible colouration and homolytic cleavage may occur simultaneously but that they are not necessarily related phenomena. Although some diaryl disulphides do dissociate at 100-150° not all disulphides thermally dissociate at moderate temperatures (84). It may well be therefore that only a higher temperature will be necessary to bring about efficient conversion of the $CF_3SSCF_3/CH_2{=}CH_2$ mixture to $CF_3SCH_2CH_2SCF_3$.

The density/temperature relationship for $CF_3SCH_2CH_2SCF_3$ was recorded by measuring the volume of a weighed amount of the material in a mercury - calibrated capillary tube at various temperatures and is found to be

$$\rho = -1.956\times10^{-3}T + 2.014$$

where ρ = density in gms./ml.

and T = temperature in °K.

Two samples of the material were placed in small phials with strips of polished copper and sealed up, one in the presence of air and one anaerobically and left for 3 months. There was no visible discolouration of the copper strips in either case.

<u>Reaction of Bistrifluoromethyldisulphide with Propene.</u>

Bistrifluoromethyldisulphide undergoes free radical addition to propene under the influence of u.v. light to give the 1:1 adduct $CF_3SCH_2CH(CH_3)SCF_3$. Whether the initial attack of the $CF_3S^\bullet$ is at the =CH or $=CH_2$ of propene cannot be determined from the present results since the same final product would be formed in either case. The same situation is encountered in the free radical additions of $(CH_3)_2P^{\cdot}$ [from $(CH_3)_2PP(CH_3)_2$ (129)] and $(CF_3)_2P^{\cdot}$ [from $(CF_3)_2PP(CF_3)_2$, (129)] radicals to propene although the $SF_5^{\cdot}$ [from SF_5Cl (127)] and $CF_3^{\cdot}$ [from CF_3I (130)] radicals are believed to attack the $=CH_2$ group in radical addition to propene. Attack at the =CH- group in the addition of $(CF_3)_2N^{\cdot}$ [from $(CF_3)_2NCl$ (131)] to propene is believed to be due to an ionic mechanism and the free radical attack does takeplace at the $=CH_2$ group.

The density/temperature equation for $CF_3SCH_2CH(CH_3)SCF_3$ was measured as described in the $CF_3SSCF_3/CH_2{=}CH_2$ reaction above and is found to be

$$\rho = -1.658\times10^{-3}T + 1.859$$

where ρ = density in gms./ml.

and T = temperature in °K.

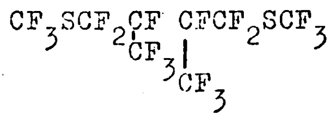
Two polished copper strips immersed in $CF_3SCH_2CH(CH_3)SCF_3$ under the conditions described in the previous reaction showed no visible contamination after 3 months.

Reaction of Bistrifluoromethyldisulphide with Tetrafluoroethylene.

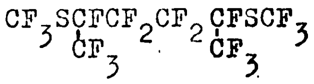
When bistrifluoromethyldisulphide reacts with tetrafluoroethylene under the influence of u.v. light, the only products are $CF_3S(CF_2CF_2)_nSCF_3$ with n=2 (3%) and n = a large number (97%). Even when the ratio of CF_3SSCF_3 to $CF_2{=}CF_2$ is increased to 5:1 the only liquid product isolated is $CF_3S(CF_2CF_2)_2SCF_3$ and $CF_3SCF_2CF_2SCF_3$ was never isolated from the reaction.. Radical additions to tetrafluoroethylene are adequately reviewed (85, 96, 102, 104, 106) though some examples bear individual mention here. 1:1 adducts are easily obtained in the addition to tetrafluoroethylene of the radicals $SF_2{=}N^{\cdot}$ [from SF_2NCl (132)], $(O)SF_2{=}N^{\cdot}$ [from $(O)SF_2{=}NCl$ (133)], $CF_{32}NO^{\cdot}$ [99% yield (125)], $PhS^{\cdot}$ [from PhSSPh (134, 135)] although $SF_5^{\cdot}$ [from SF_5Cl (136, 137)] also gives the telomer adducts $SF_5(CF_2CF_2)_nCl$ with n=2,3 plus some higher material. Haszeldine and Steele (138) noted that in reactions involving tetrafluoroethylene, it is difficult to suppress the propagation reaction with respect to chain transfer or combination steps as is certainly the case in the reaction between CF_3SSCF_3 and tetrafluoroethylene noted here, although not impossible as can be seen from the reactions cited above. The CF_3SSCF_3- induced polymerisation of tetrafluoroethylene (139) under high pressures and with high temperatures may well give trifluoromethylthio- containing polymers analogous to the telomers formed in the present reaction, and previous addition of the $CF_3S^{\cdot}$ radical [from CF_3SH (140)] was found to yield $CF_3S(CF_2CF_2)_nH$, n=1,2,3, etc. (from a 1.5:1.0 ratio of $CF_3SH_2CF_2CF_2$).

Reaction of Bistrifluoromethyldisulphide with Hexafluoropropene.

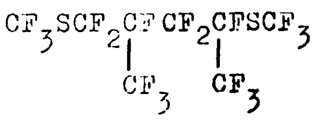
The reaction between bistrifluoromethyldisulphide and hexafluoropropene under the influence of u.v. light gives two liquid products, $CF_3S[CF(CF_3)CF_2]_nSCF_3$ with n=1(9.5%), 2(90.5%), although the high pressure/temperature reaction of bistrifluoromethyldisulphide with hexafluoropropene in an autoclave was found to give a solid white polyfluoropropene which may well contain CF_3S units (141). For the n=1 compound above, the structure is unambiguous and the ^{19}F n.m.r. spectrum is in agreement with that of the $CF_3SCF(CF_3)CF_2SCF_3$ found to the extent of 10% in the u.v. irradiation of a 1:1 mixture of trifluoromethanesulphenylchloride, CF_3SCl, and hexafluoropropene (142). The n=2 compound has three possible structures viz.


$CF_3SCF_2\underset{CF_3}{CF}\,\underset{CF_3}{CF}CF_2SCF_3$

VI(a)


$CF_3S\underset{CF_3}{CF}CF_2CF_2\underset{CF_3}{CF}SCF_3$

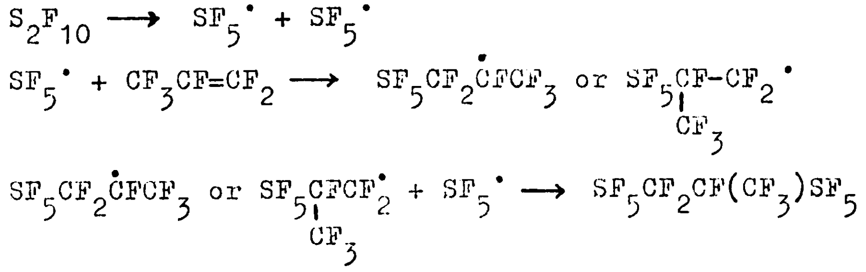
VI(b)


$CF_3SCF_2\underset{CF_3}{CF}CF_2\underset{CF_3}{CF}SCF_3$

VI(c)

but only VI(a) was isolated here. Characterisation was by ^{19}F n.m.r. and mass spectra and is discussed under these sections. $CF_3S[CF(CF_3)CF_2]_2SCF_3$ was obtained as a product in the u.v. irradiation of a ~4:1 mixture of hexafluoropropene and trifluoromethanethiol (140) although the structure of the compound was not established.

Hexafluoropropene, polarised thus $CF_3\overset{\delta-}{C}F{=}\overset{\delta+}{C}F_2$ (143), is very sensitive to nucleophilic attack (144) which is exclusively on the CF_2 group. Haszeldine, in reviewing free radical attack on hexafluoropropene (144), has suggested that the more nucleophilic the attacking radical, the more should radical attack be oriented towards the CF_2 group and, as in the case of hexafluoropropene, where the difference in stability of the intermediate radicals $RCF_2\dot{C}FCF_3$ and $RCF(CF_3)CF_2^{\bullet}$ (where R is the attacking radical), normally sufficient to determine the position of attack, is very small, the nucleophilic or electrophilic character of R could be important in determining the position of attack as well as determining the rate. This idea has been used to account for the formation in excess of the less favoured isomer when trifluoromethanethiol is reacted with hexafluoropropene:- 55% of $CF_3SCF(CF_3)CF_2H$ as opposed to 45% $CF_3SCF_2CFHCF_3$ is found, although the effect of the $H^{\bullet}$ radical is not taken into account (140). Tedder and Walton have suggested that a more logical method of determining the direction of addition to an unsymmetrical olefin is by considering the relative strengths of the bonds formed i.e. by assuming that the new bond will be formed at the carbon atom which forms the least stabilised radical (104, 145). While predicting the same direction of radical addition as before, this concept also draws into consideration the substituents of the carbon atom undergoing attack. With hexafluoropropene, therefore, the radical R will form a slightly more stable bond with $=CF_2$ than with $=CF(CF_3)$. On these bases, as well as on steric grounds, one would expect the $CF_3S^{\bullet}$ radical to attack the CF_2 group of hexafluoropropene although its relative electrophilic character (140), compared to $CH_3S^{\bullet}$ and $CF_3CH_2S^{\bullet}$, would tend to reduce the rate of addition to the olefin as well as direct some of the attack at the $CF(CF_3)$ group. In this work, where only $CF_3S^{\bullet}$ radicals are present, a 48% yield is obtained, after 184 hrs. reaction time; with CF_3SH where both $H^•$ and $CF_3S^•$ radicals are present, a 70% yield is obtained after 40 hrs. irradiation. This would suggest that the reaction involving CF_3SH is perhaps more complicated than at first it seems. In the present work, 90.5% of the reaction product is $CF_3S\left[CF(CF_3)CF_2\right]_2SCF_3$ and, having structure **VI(a)** above, this must necessarily result from initial attack of the $CF_3S^•$ radical at the CF_2 group of hexafluoropropene to give $CF_3SCF_2\dot{C}FCF_3$, i.e at least 90% of the radical attack of the $CF_3S^•$ radical, arising from CF_3SSCF_3, on hexafluoropropene occurs at the CF_2 group. The termination step is more likely to be a combination of two such radicals rather than further radical attack of $CF_3SCF_2\dot{C}FCF_3$ at the unfavoured end of another hexafluoropropene molecule, to give $CF_3SCF_2\underset{CF_3}{CF}\,\underset{CF_3}{CF}\,CF_2^•$ followed by either radical combination with a $CF_3S^•$ radical or radical displacement of $CF_3S^•$ from CF_3SSCF_3. Radical combination in the reaction between S_2F_{10} and hexafluoropropene (146) thus



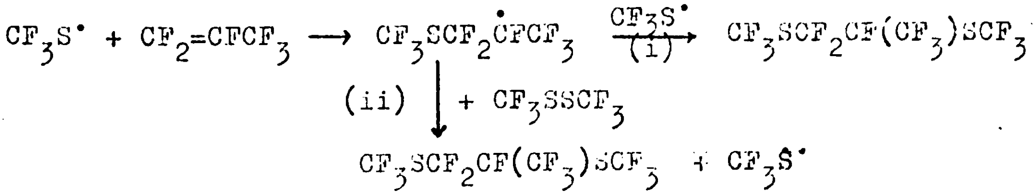
$$S_2F_{10} \longrightarrow SF_5^• + SF_5^•$$
$$SF_5^• + CF_3CF{=}CF_2 \longrightarrow SF_5CF_2\dot{C}FCF_3 \text{ or } SF_5\underset{CF_3}{\underset{|}{C}}F\text{-}CF_2^•$$
$$SF_5CF_2\dot{C}FCF_3 \text{ or } SF_5\underset{CF_3}{\underset{|}{C}}FCF_2^• + SF_5^• \longrightarrow SF_5CF_2CF(CF_3)SF_5$$

is thought to be the reason for the inefficient reaction of S_2F_{10} with hexafluoropropene compared with reaction of SF_5Cl with hexafluoropropene (136) where radical displacement of $Cl^•$ from SF_5Cl is the termination step thus

$$R^• + SF_5Cl \longrightarrow R\text{-}Cl + SF_5^•$$

The 1:1 product in the reaction of CF_3SSCF_3 with hexafluoropropene can arise in any of the following ways:

A.



$$\begin{tikzcd}
CF_3S^• + CF_2{=}CFCF_3 \arrow[r] & CF_3SCF_2\dot{C}FCF_3 \arrow[r, "CF_3S^•", "(i)"'] \arrow[d, "(ii)"', "+\ CF_3SSCF_3"] & CF_3SCF_2CF(CF_3)SCF_3 \\
& CF_3SCF_2CF(CF_3)SCF_3 + CF_3S^• &
\end{tikzcd}$$

$$\begin{tikzcd}
\text{B.}\quad CF_3S^\bullet + CF_2{=}CFCF_3 \arrow[r] & CF_3SCF(CF_3)CF_2^\bullet \arrow[r, "CF_3S^\bullet", "(i)"'] \arrow[d, "(ii)"', "+CF_3SSCF_3"] & CF_3SCF(CF_3)CF_2SCF_3 \\
 & CF_3SCF(CF_3)CF_2SCF_3 + CF_3S^\bullet &
\end{tikzcd}$$

Radical displacement steps at sulphur have been previously postulated e.g. in reactions involving trifluoromethanesulphenyl chloride (142), sulphur chloride pentafluoride (136) and dimethyltetrasulphide (87).

If scheme A is followed, this assumes that the $CF_3S^\bullet$ radical from CF_3SSCF_3 attacks the CF_2 group of hexafluoropropene exclusively. Exclusive addition at the $=CF_2$ end of the double bond in hexafluoropropene is not uncommon e.g. radical attack by the $CF_3^\bullet$ [from CF_3I (147)], by the $(CF_3)_2N^\bullet$ [from $(CF_3)_2NX$, X=Br or I (148)] and by the $CCl_3^\bullet$ [from CCl_3Br (149)] radicals all occur exclusively at the CF_2 group. If scheme B is obeyed, then there is 9.5% attack at the $CF(CF_3)$ group of hexafluoropropene by the $CF_3S^\bullet$ radical arising from CF_3SSCF_3 and is more in keeping with the suggested slight electrophilic character of the $CF_3S^\bullet$ radical (140) though probably $CF_3SCF_2CF(CF_3)SCF_3$ is formed via both schemes.

Reaction of Bistrifluoromethyldisulphide with 1,1- Difluoroethylene.

Work on the addition of the $CCl_3^\bullet$ radical [from CCl_3Br (120)], the $CH_3^\bullet$ radical [from $CH_3N{=}NCH_3$ (150)] and the $C_3F_7^\bullet$ radical [from C_3F_7I (124, 151)] to 1,1- difluoroethylene has shown that addition takes place almost exclusively at the CH_2 end of the molecule. This is in agreement with the concept of the site of attack being that at which the attacking radical will form the strongest bond (145) and is supported by the exclusive addition to the CH_2 of $CH_2{=}CF_2$ by the $SF_5^\bullet$ radical from [SF_5Cl (137) and SF_5Br (152)], the $PH_2^\bullet$ radical [from PH_3 (144)], the $CF_3NO^\bullet$ radical (125), the $(CF_3)_2N^\bullet$ radical [from $(CF_3)_2NBr$ (153)] and the $CF_3^\bullet$ radical [from CF_3I (154, 155)].

The reaction between bistrifluoromethyldisulphide and 1,1- difluoroethylene gives the series of adducts $CF_3S(CH_2CF_2)_nSCF_3$ with n=1-6. The n=1 adduct, $CF_3SCH_2CF_2SCF_3$, could arise from attack by the $CF_3S^\bullet$ radical at either end of the double bond, but in the light of the examples cited above plus the fact that the $CF_3SH/CH_2{=}CF_2$ reaction proceeds by exclusive attack of the $CF_3S^\bullet$ radical at the CH_2 group to give $CF_3SCH_2CF_2H$ (140), it is probable that $CF_3SCH_2CF_2SCF_3$ is formed by radical attack at CH_2 to give $CF_3SCH_2CF_2^\bullet$ with radical combination or displacement being the termination step. A similar situation exists in the reaction of both $(CH_3)_2PP(CH_3)_2$ and $(CF_3)_2PP(CF_3)_2$ with $CH_2{=}CF_2$ to give the corresponding 1:1 adducts (129). It is noteworthy that in the reaction of trifluoromethanesulphenyl chloride with 1,1- difluoroethylene (142), bistrifluoromethyldisulphide and " an unidentified component" were formed as by-products. It is quite possible that this " unidentified component" is $CF_3SCH_2CF_2SCF_3$.

There are three possible structures for the n=2 compound of $CF_3S(CH_2CF_2)_nSCF_3$, but only two of these **VIII(a)** and **VIII(b)** are found. **VIII(c)** was not identified.

$CF_3SCH_2CF_2CF_2CH_2SCF_3$

VIII(a)

$CF_3SCH_2CF_2CH_2CF_2SCF_3$

VIII(b)

$CF_3SCF_2CH_2CH_2CF_2SCF_3$

VIII(c)

The free radical additions of CF_2Br_2 (156), $CF_2BrCFClBr$ and CF_2ClCF_2ClI (157) to 1,1- difluoroethylene all proceed to give the adducts $R(CH_2CF_2)_nX$ (where R= the attacking radical, $CF_2Br^\bullet$, $CF_2BrCFCl^\bullet$ and $CF_2ClCF_2Cl^\bullet$; and X= Br, Br, and I respectively) with R attacking at the CH_2 group and with n=1 and 2. The structure of the n=2 compound in each case is $RCH_2CF_2CH_2CF_2X$ i.e. the "head to tail" telomerisation adduct:-

$$\begin{tikzcd} R^\bullet + CH_2{=}CF_2 \arrow[r] & RCH_2CF_2^\bullet \arrow[r, "+CH_2{=}CF_2"] & RCH_2CF_2CH_2CF_2^\bullet \arrow[d, "+RI"] \\ & & RCH_2CF_2CH_2CF_2I + R^\bullet \end{tikzcd}$$

If the $CF_3S^\bullet$ radical from CF_3SSCF_3 is assumed to attack the 1,1-difluoroethylene at the CH_2 group. Then the structures of the n=2 adducts identified can be rationalised thus: Initial attack of a $CF_3S^\bullet$ radical at the CH_2 group gives the radical $CF_3SCH_2CF_2^\bullet$; radical combination of two $CF_3SCH_2CF_2^\bullet$ radicals gives structure **VIII(a)** whilst attack of radical

$CF_3SCH_2CF_2^{\bullet}$ at the CH_2 group of 1,1- difluoroethylene, i.e. head - to - tail addition, followed by radical combination with a $CF_3S^{\bullet}$ radical or radical displacement of a $CF_3S^{\bullet}$ radical from CF_3SSCF_3 gives product VIII(b). Product VIII(c) is not formed as there is no initial radical attack at CF_2. Thus there is the scheme:-

$$\begin{tikzcd}
CF_3S^{\bullet} + CH_2{=}CF_2 \arrow[r] & CF_3SCH_2CF_2^{\bullet} \arrow[r, "+\overset{\bullet}{C}F_2CH_2SCF_3"] \arrow[d, "+CH_2{=}CF_2"] & \begin{array}{c} CF_3SCH_2CF_2CF_2CH_2SCF_3 \\ \text{VIII(a)} \end{array} \\
 & CF_3SCH_2CF_2CH_2\overset{\bullet}{C}F_2 \arrow[r, "+\overset{\bullet}{S}CF_3"] \arrow[d, "+CF_3SSCF_3"] & \begin{array}{c} CF_3SCH_2CF_2CH_2CF_2SCF_3 \\ \text{VIII(b)} \end{array} \\
 & \begin{array}{c} CF_3SCH_2CF_2CH_2CF_2SCF_3 + CF_3S^{\bullet} \\ \text{VIII(b)} \end{array} &
\end{tikzcd}$$

The n=3,4 and n=5,6 compounds occur as two separable fractions but it was not possible to separate the individual compounds completely.

The n=3 compound consists of the isomers IX(a) and IX(b) viz.,

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2SCF_3$$
IX(a)

$$CF_3SCH_2CF_2CH_2CF_2CF_2CH_2SCF_3$$
IX(b)

Addition of a $CF_3S^{\bullet}$ radical to the CH_2 group of 1,1- difluoroethylene with head - to - tail addition to give the radical $CF_3SCH_2CF_2CH_2CF_2CH_2CF_2^{\bullet}$ followed by either radical combination with $CF_3S^{\bullet}$ or radical displacement of $CF_3S^{\bullet}$ from CF_3SSCF_3 gives structure IX(a). Whilst radical combination of $CF_3SCH_2CF_2^{\bullet}$ and $CF_3SCH_2CF_2CH_2CF_2^{\bullet}$, both formed by addition of $CF_3S^{\bullet}$ to the CH_2 group of $CH_2{=}CF_2$ with head - to - tail addition of a $CH_2{=}CF_2$ unit in the latter case, gives rise to structure IX(b). No other structures were identified. The n=4 compound has the structures.

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2SCF_3$$
X(a)

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2SCF_3$$
X(b)

$$CF_3SCH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2SCF_3$$
X(c)

X(a) is formed by addition of $CF_3S^{\bullet}$ to the CH_2 group of $CH_2{=}CF_2$ followed by head - to - tail addition of $CH_2=CF_2$ to give the radical $CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2^{\bullet}$, i.e. the "4 - unit long" radical with either radical combination with $CF_3S^{\bullet}$ or radical displacement at CF_3SSCF_3 as the termination step. X(b) is formed by radical combination of a "3 - unit" radical with a "1 - unit" radical i.e.

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2^{\bullet} + {}^{\bullet}CF_2CH_2SCF_3$$

X(b)

and X(c) is formed by radical combination of two "2 - unit" radicals i.e.

$$CF_3SCH_2CF_2CH_2CF_2^{\bullet} + {}^{\bullet}CF_2CH_2CF_2CH_2SCF_3$$

X(c)

The n=5 compound consists of the isomers:-

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2SCF_3$$

XI(a)

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2SCF_3$$

XI(b)

XI(a) is formed by radical combination of a "4 - unit" radical with a "1 - unit" radical whilst XI(b) is formed by radical combination of a "3 - unit" radical with a "2 - unit" radical.

The n=6 compound consists of the isomers

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2SCF_3$$

XII(a)

$$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2CF_2CH_2SCF_3$$

XII(b)

XII(a) is formed by radical combination of a "4 - unit" radical with a "2 - unit" radical whilst XII(b) is formed by radical combination of two "3 - unit" radicals. The percentage distribution of products is

n	1	2	3,4	5,6
%	67.8	19.5	7.0	5.5

The density/temperature equation for $CF_3SCH_2CF_2SCF_3$ was measured as described in the $CF_3SSCF_3/CH_2=CH_2$ reaction above and is found to be

$$\rho = -1.970\times10^{-3}T + 2.132$$

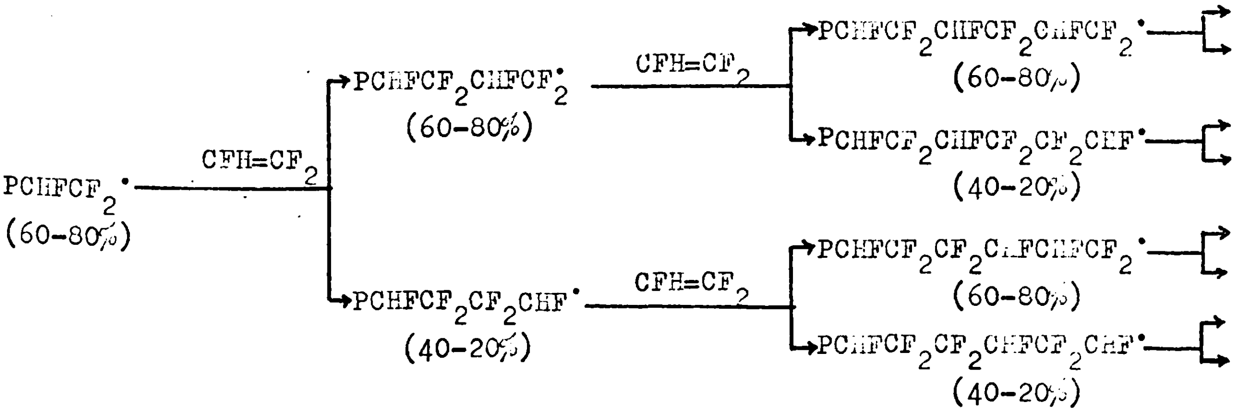
where ρ = density in gms./ml.

and T = temperature in °K.

Two polished copper strips were immersed in $CF_3SCH_2CF_2SCF_3$ under the conditions described in the $CF_3SSCF_3/CH_2{=}CH_2$ reaction above and left for 3 months whence it was found that although the strip of copper in the phial exposed to air was not corroded, there was extensive corrosion of the strip of copper sealed up with $CF_3SCH_2CF_2SCF_3$ under anaerobic conditions. The strip was considerably blackened and etched and there was a yellow deposit on the walls of the phial. A mass spectrometric examination revealed that although most of the $CF_3SCH_2CF_2SCF_3$ was unchanged, there had been some decomposition to sulphur and $CH_2{=}CF_2$. No trace of the CF_3 groups was found.

Reaction of Bistrifluoromethyldisulphide with Trifluoroethylene.

Table 1.4, which summarises the results of some previous work on the free radical addition to trifluoroethylene, serves to illustrate that trifluoroethylene undergoes bi-directional radical addition. This is to be expected from the similarity of the Arrhenius parameters for the addition to $=CHF$ and $=CF_2$ of trifluoroethylene of the $CF_2Br^{\bullet}$ (123), $CCl_3^{\bullet}$ (120) and $C_3F_7^{\bullet}$ (151) radicals. Haszeldine and Steele (161) have shown that homopolymerisation of trifluoroethylene by a free radical $P^{\bullet}$ will give both $PCHFCF_2^{\bullet}$ (*ca.* 60-80%) and $PCF_2CHF^{\bullet}$ (*ca.* 40-20%). The subsequent growth of these radicals by combination with further $CHF{=}CF_2$ molecules can be represented thus:-



with a similar sequence initiated by radical $PCF_2CFH^{\bullet}$ (40-20%). In the 1:1 reaction between bistrifluoromethyldisulphide and trifluoroethylene

Table 1.4.

			Reference.
CFH=CF$_2$	HBr, u.v. →	CHF$_2$CHFBr(58%)+CF$_2$BrCH$_2$F(42%)	(158)
	CF$_3$I, u.v. →	CF$_3$CHFCF$_2$I(80%) + CF$_3$CF$_2$CHFI(20%)	(158)
	CFCl$_2$I,Bz$_2$O$_2$ →	CFCl$_2$CHFCF$_2$I (predominant) +CFCl$_2$CF$_2$CHFI	(158)
	CF$_2$Br$_2$,Bz$_2$O$_2$,100° →	CF$_2$BrCHFCF$_2$Br(70%) +CF$_2$BrCF$_2$CHFBr(30%)	(158)
	CF$_2$Br$_2$,PhCO$_3$Bu^t,120° →	CF$_2$BrCHFCF$_2$Br(50%) +CF$_2$BrCF$_2$CHFBr(50%)	(158)
	CF$_2$Br, u.v. 150° →	CF$_2$BrCHFCF$_2$Br(70.4%) +CF$_2$BrCF$_2$CHFBr(29.6%)	(123)
	(CF$_3$)$_2$NBr →	(CF$_3$)$_2$NCFHCF$_2$Br(78%) +(CF$_3$)$_2$NCF$_2$CFHBr(22%)	(153)
	CH$_3$SH, x-ray →	CH$_3$SCHFCHF$_2$(75%) +CH$_3$SCF$_2$CH$_2$F(25%)	(158)
	CF$_3$SH, u.v. →	CF$_3$SCHFCHF$_2$(98%) +CH$_3$SCF$_2$CH$_2$F(2%)	(158)
	SiHCl$_3$ u.v. →	Cl$_3$SiCHFCHF$_2$(99%) +Cl$_3$SiCF$_2$CH$_2$F(1%)	(158)
	SF$_5$Cl, Bz$_2$O$_2$ →	SF$_5$CHFCF$_2$Cl(95%) +SF$_5$CF$_2$CHFCl(5%)	(159)
	SF$_5$Cl u.v. 63-160° →	SF$_5$CHFCF$_2$Cl(92-96%) +SF$_5$CF$_2$CFHCl(8-4%)	(160)
	SF$_5$Cl u.v. 63-160° →	SF$_5$CHFCF$_2$Cl(predominant) +SF$_5$CF$_2$CFHCl	(137)
	SF$_5$Cl u.v. →	SF$_5$CHFCF$_2$Cl(73%) +SF$_5$CF$_2$CFHCl(27%)	(159)
	SF$_5$Br →	SF$_5$CHFCF$_2$Br(100%)	(152)
	CF$_3$F$_7$I u.v. 85-154° →	C$_3$F$_7$CFHCF$_2$I(80%) +C$_3$F$_7$CF$_2$CFHI(20%)	(124,151)
	CCl$_3$Br u.v. 100° →	CCl$_3$CFHCF$_2$Br(78%) +CCl$_3$CF$_2$CFHBr(22%)	(120)

products $CF_3S(CFHCF_2)_nSCF_3$, n = 1-7, are obtained. The n = 1 compound, $CF_3SCFHCF_2SCF_3$, can arise in two ways, viz. by attack of $CF_3S^\bullet$ at either end of $CFH{=}CF_2$ to give the radicals $CF_3SCFHCF_2^\bullet$ and $CF_3SCF_2CFH^\bullet$ with termination occurring by radical combination with $CF_3S^\bullet$ or by radical displacement at CF_3SSCF_3. The n = 2 compound is found to consist of two, XIV(a) and XIV(b), of the three possible isomers;

$CF_3SCFHCF_2CFHCF_2SCF_3$
XIV(a)

$CF_3SCFHCF_2CF_2CFHSCF_3$
XIV(b)

$CF_3SCF_2CFHCFHCF_2SCF_3$
XIV(c)

XIV(c) is not detected although there is no reason why it should not be formed as evidenced by the reaction scheme drawn up by Haszeldine and Steele and reproduced above. If it is formed here, it must be in such a small quantity as to not be detected by the technique used. In view of the complexity of the system, it is not possible to make a positive identification of all the higher telomers, i.e. n = 3-7, formed in this reaction. Suffice it to say that the only constraints on the nature of the structures of these higher telomers are the concentrations of the higher radicals and the probabilities of combination or transfer, to give an adduct, and addition of a further $CFH{=}CF_2$ unit, to give a higher radical.

The percentage distribution of products is

n	1	2	3	4	5,6,7
%	36.8	25.6	16.8	12.5	8.3

When the ratio of trifluoroethylene to disulphide is increased to 2 : 1, the product distribution is

n	1	2	3	4	5,6,7,>7
%	10.7	24.7	28.6	21.6	14.4

The most noticeable result of the increased ratio is that products (unidentified) with n >7 are observed. Also, the relative amount of higher telomer is increased as the relative amount of lower telomer is decreased.

Reaction of Bistrifluoromethyldisulphide with Chlorotrifluoroethylene.

Many of the free radical additions to chlorotrifluoroethylene occur exclusively at the CF_2 group; e.g. additions ofthe SF_2=N$^\bullet$ [from SF_2=NBr (162)], $CF_3^\bullet$ [from CF_3I (163,164)], $R'_2P^\bullet$ [R' = CF_3, CH_3; from R'_2PR (R = H etc.) (165)], Br$^\bullet$ [from HBr (138)], $PH_2^\bullet$ [from PH_3 (144)] and $SF_5^\bullet$ [from SF_5Cl (136)] radicals.

In the reaction between bistrifluoromethyldisulphide and chlorotrifluoroethylene, the n = 1 adduct, $CF_3SCF_2CFClSCF_3$, is not formed in any great quantity, even when the ratio of disulphide to olefin is raised to 5 : 1. $CF_3SCF_2CFClSCF_3$ could be formed by radical attack of $CF_3S^\bullet$ at either end of the double bond followed by radical combination with $CF_3S^\bullet$ or radical displacement at CF_3SSCF_3 as termination steps, a situation similar to that found for the reaction

$$2(CF_3)_2NO^\bullet + CF_2{=}CFCl \longrightarrow (CF_3)_2NOCF_2CFClON(CF_3)_2 \quad (125).$$

However, evidence for exclusive attack of the $CF_3S^\bullet$ radical, arising from CF_3SSCF_3, at the CF_2 group of CF_2=CFCl is found from the higher telomers which are formed in the 1 : 1 reaction, viz. $CF_3S(CF_2CFCl)_nSCF_3$ with n = 2-4. Telomerisation is also found when CF_3SH adds to chlorotrifluoroethylene under the influence of u.v. light (140). Formation of the 1 : 1 adduct occurs by exclusive addition of the $CF_3S^\bullet$ at the CF_2 group to give CF_3SCF_2CFClH but the structures of the higher telomers $CF_3S(CF_2CFCl)_nH$, n = 2,3, etc., are not known. The reaction of ethanol with chlorotrifluoroethylene, catalysed by di-tert-butylperoxide and azobis-isobutyronitrile (166) or initiated by gamma-irradiation (166) and u.v. irradiation (167), has been well investigated. Radical addition of $CH_3(OH)CH^\bullet$ occurs exclusively at the CF_2 group of chlorotrifluoroethylene to give the radical $CH_3(OH)CHCF_2CFCl^\bullet$ which can terminate by displacement of $CH_3(OH)CH^\bullet$ from ethanol or can add another olefin unit, addition again taking place at the CF_2 group of chlorotrifluoroethylene, to give the $CH_3(OH)CHCF_2CFClCF_2CFCl^\bullet$ radical, and so on. Although minor products are formed by various rearrangement reactions, the main products are formed by this process. A very similar reaction sequence is found for the reaction of methanol with chlorotrifluoroethylene (168) (initiated by di-tert-butylperoxide, gamma-irradiation or u.v. irradiation) although trace quantities of the unfavoured compounds (formed by radical addition at CFCl) are found.

For $CF_3S(CF_2CFCl)_2SCF_3$, there are three possible structures viz. :-

$CF_3SCF_2CFClCF_2CFClSCF_3$
XXIII(a)

$CF_3SCF_2CFClCFClCF_2SCF_3$
XXIII(b)

$CF_3SCFClCF_2CF_2CFClSCF_3$
XXIII(c)

The n = 2 compound consists of isomers XXIII(a) and XXIII(b), XXIII(c) being absent as would be expected if initial attack of the $CF_3S^{\bullet}$ radical is in the direction indicated by the literature citations above, i.e. at the CF_2 group. The formation of structures XXIII(a) and XXIII(b) can be rationalised in terms of radical addition at CF_2 thus :- attack of a $CF_3S^{\bullet}$ radical on $CF_2{=}CFCl$ to give the radical $CF_3SCF_2CFCl^{\bullet}$ which can undergo radical combination with another $CF_3SCF_2CFCl^{\bullet}$ radical to give the isomer XXIII(b) or can attack a $CF_2{=}CFCl$ molecule to give the radical $CF_3SCF_2CFClCF_2CFCl^{\bullet}$ which can undergo radical combination with $CF_3S^{\bullet}$ or radical displacement of $CF_3S^{\bullet}$ from CF_3SSCF_3 to give isomer XXIII(a).

The n = 3 and n = 4 components have the structures :-

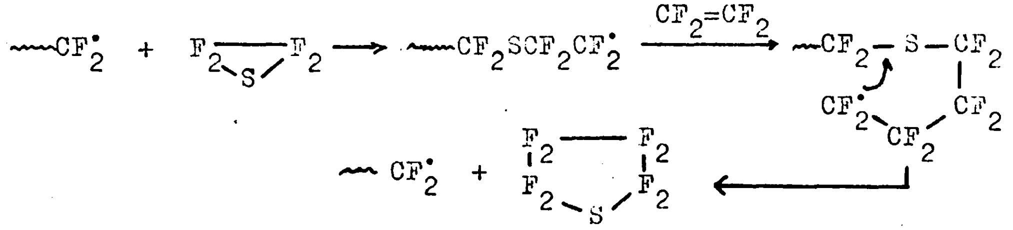
XXIV(a) $CF_3SCF_2CFClCF_2CFClCF_2CFClSCF_3$
XXIV(b) $CF_3SCF_2CFClCF_2CFClCFClCF_2SCF_3$ n = 3

XXV(a) $CF_3SCF_2CFClCF_2CFClCF_2CFClCF_2CFClSCF_3$
XXV(b) $CF_3SCF_2CFClCF_2CFClCF_2CFClCFClCF_2SCF_3$ n = 4
XXV(c) $CF_3SCF_2CFClCF_2CFClCFClCF_2CFClCF_2SCF_3$

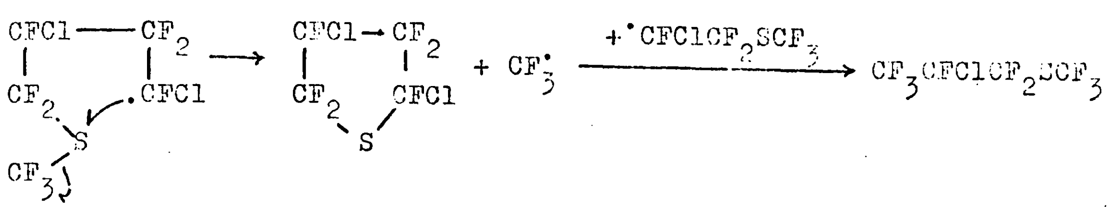
A trace amount of higher telomers was found but was not separated or identified.

In the same way as was done for the n = 2 isomers, the formation of the isomers making up the n = 3 and n = 4 telomers, of which there is a preponderance of XXIV(b) and XXV(c) respectively, can be rationalised in terms of free radical attack exclusively at the CF_2 group of chlorotrifluoroethylene. Thus addition of two $CF_2=CFCl$ units gives the radical $CF_3SCF_2CFClCF_2CFCl^{\bullet}$ which can undergo radical combination with another such radical to give isomer XXV(c) or radical combination with a $CF_3SCF_2CFCl^{\bullet}$ to give isomer XXIV(b); or can add another olefin unit to give the radical $CF_3SCF_2CFClCF_2CFClCF_2CFCl^{\bullet}$ which can combine with a $CF_3SCF_2CFCl^{\bullet}$ radical to give isomer XXV(b), radical combination with a $CF_3S^{\bullet}$ radical or radical displacement at CF_3SSCF_3 giving isomer XXIV(a); or can add another olefin unit to give $CF_3SCF_2CFClCF_2CFClCF_2CFClCF_2CFCl^{\bullet}$ which can undergo radical combination with $CF_3S^{\bullet}$ or radical displacement at CF_3SSCF_3 to give XXV(a). The higher telomers would be produced by radical combinations of the higher radicals.

The n = 1 compound is found as the least component of a mixture of 1,2-bis(trifluoromethylthio),1-chlorotrifluoroethane, $CF_3SCF_2CFClSCF_3$, 1,3-dichlorohexafluorothiolan, $\overline{CF_2CFClCF_2CFClS}$, and 1-trifluoromethylthio, 2-chlorohexafluoropropane, $CF_3SCF_2CFClCF_3$. The presence of the latter two, perhaps unexpected products can be accounted for by a mechanism similar to that invoked to explain the surprisingly large amounts of octafluorothiolan produced during the copolymerisation of tetrafluoroethylene with tetrafluorothiiran (169). Octafluorothiolan is formed thus :-



A $CF_3SCF_2CFClCF_2CFCl^{\bullet}$ radical can therefore undergo the conventional reactions as already indicated but can also undergo intramolecular radical attack on sulphur to form the thiolan with elimination of a $CF_3^{\bullet}$ radical which can combine with a $CF_3SCF_2CFCl^{\bullet}$ radical to give $CF_3SCF_2CFClCF_3$ thus :-



The product distribution for the 1 : 1 reaction is

n	2	3	4	>4
%	24.8	22.2	19.9	7.0

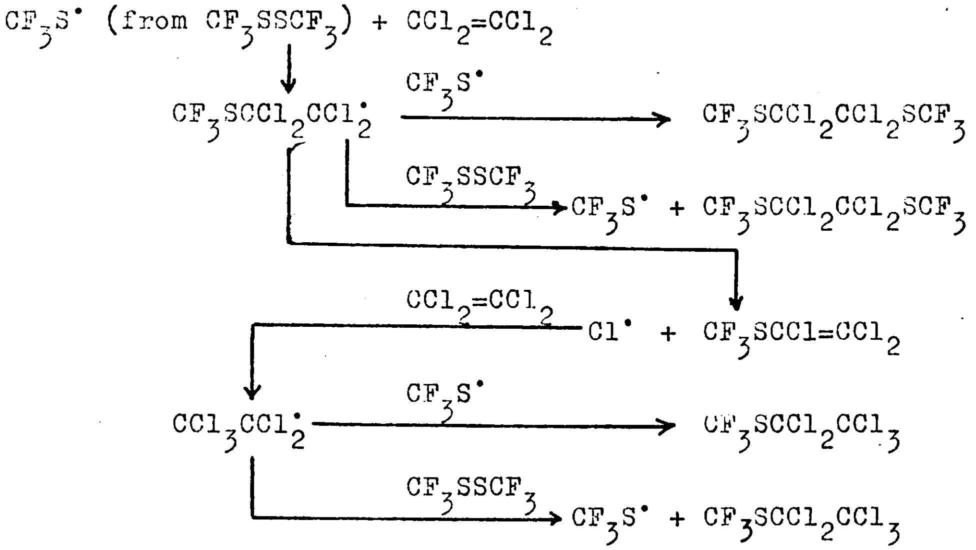
with $\overline{CF_2CFClCF_2CFClS}$, $CF_3SCF_2CFClCF_3$, and $CF_3SCF_2CFClSCF_3$ forming an inseparable mixture to the extent of 26.0% of the products.

Increasing the ratio of bistrifluoromethyldisulphide to chlorotrifluoroethylene to 5 : 1 serves only to increase the amount of low molecular weight material with respect to the higher telomers, the thiolan $\overline{CF_2CFClCF_2CFClS}$ still being formed in large quantities.

Reaction of Bistrifluoromethyldisulphide with Tetrachloroethylene.

Free radical addition to tetrachloroethylene to give the saturated 1 : 1 adduct $R'CCl_2CCl_2R$ has been observed for SF_5OF (170), $BrNSF_2$ (126), and $(CF_3)_2NO^\bullet$ [which gives $(CF_3)_2NOCCl_2CCl_2ON(CF_3)_2$ (125)]. In other cases, e.g. addition of the radicals $Cl_3Si^\bullet$ [from Cl_3SiH (85)], $HOCH_2^\bullet$, $CH_3(OH)CH^\bullet$, $C_2H_5(OH)CH^\bullet$, and $C_3H_7(OH)CH^\bullet$ [from $HOCH_3$, $CH_3(OH)CH_2$, $C_2H_5(OH)CH_2$, and $C_3H_7(OH)CH_2$ respectively (171)] , formation of the saturated compound $R'CCl_2CCl_2R$ is accompanied by formation of the unsaturated compound $R'CCl{=}CCl_2$ and in yet other instances, e.g. addition of the radicals $CH_3SiCl_2^\bullet$ [from CH_3SiCl_2H (85)], $ClCH_2CO_2(CH_3)CH^\bullet$ and $^\bullet CHClCO_2C_2H_5$ [both from $ClCH_2CO_2CH_2CH_3$ (172)], the saturated compound is not formed at all and only the unsaturated compound is obtained. This last situation was observed by Tedder in the addition of the trichloromethyl radical [from CCl_3Br (173)] to tetrachloroethylene where the compounds formed were CCl_2BrCCl_2Br, $CClBr{=}CCl_2$, CCl_3CCl_2Br, and C_2Cl_6. It is suggested that the unsaturated compound may be formed by $Cl^\bullet$ elimination from the radical $CCl_2BrCCl_2^\bullet$, the $Cl^\bullet$ atom being picked up by a tetrachloroethylene molecule to give $CCl_3CCl_2^\bullet$ which then undergoes radical displacement at CCl_3Br to give CCl_3CCl_2Br and $CCl_3^\bullet$.

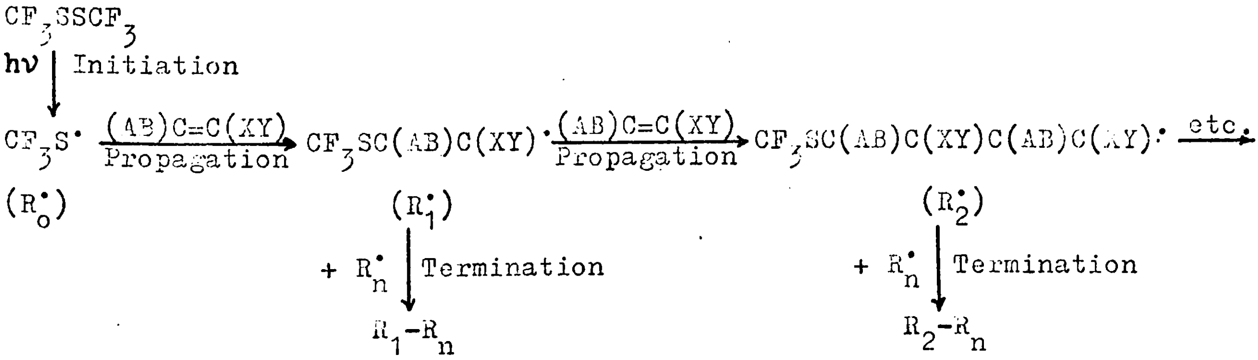
In the reaction of bistrifluoromethyldisulphide with tetrachloroethylene, the products **obtained** are $CF_3SCCl_2CCl_2SCF_3$, $CF_3SCCl=CCl_2$, and $CF_3SCCl_2CCl_3$. These would be formed in accord with the above scheme thus :-



The reaction is extremely slow and the yields are very low. As a preparation of $CF_3SCCl_2CCl_2SCF_3$, the reaction is very inefficient.

<u>General Reaction Scheme.</u>

From the products observed in all the preceding reactions, the following general reaction scheme can be established.



Radical combination is postulated as the main termination process although termination processes involving $R_o^{\bullet}$ radicals (i.e. $CF_3S^{\bullet}$) can occur by radical displacement at R_o-R_o (i.e. CF_3SSCF_3). The stuctures of all the isomers formed can be readily rationalised by this scheme and are shown in Table 1.5.

<u>Note 1.</u> The anomalous compounds found with the chlorotrifluoroethylene and tetrachloroethylene reactions cannot be accounted for by this scheme

No.	COMPOUND	n	ISOMERIC STRUCTURES	A B X Y
I	$CF_3S(CH_2CH_2)_nSCF_3$	1	R_1-R_0	H H H H
II	$CF_3S\left[CH(CH_3)CH_2\right]_nSCF_3$	1	R_1-R_0	H H H CH_3
III	$CF_3S(CF_2CF_2)_nSCF_3$	2	R_1-R_1 or R_2-R_0	F F F F
IV		large	unknown	F F F F
V	$CF_3S\left[CF(CF_3)CF_2\right]_nSCF_3$	1	R_1-R_0	F F F CF_3
VI		2	R_1-R_1	F F F CF_3
VII	$CF_3S(CF_2CH_2)_nSCF_3$	1	R_1-R_0	H H F F
VIII	"	2	R_2-R_0(a), R_1-R_1(b)	H H F F
IX		3	R_3-R_0(a), R_2-R_1(b)	H H F F
X		4	R_4-R_0(a), R_3-R_1(b), R_2-R_2(c)	H H F F
XI		5	R_4-R_1(a), R_3-R_2(b)	H H F F
XII		6	R_4-R_2(a), R_3-R_3(b)	H H F F
XIII	$CF_3S(CF_2CFH)_nSCF_3$	1	R_1-R_0	H F F F F F F H
XIV		2		" " " "
XV		3		" " " "
XVI		4		" " " "
XVII		5		" " " "
XVIII		6		" " " "
XIX		7		" " " "
XX	$\overline{CF_2CFClCF_2CFClS}$	-		
XXI	$CF_3SCF_2CFClCF_3$	-		
XXII	$CF_3S(CF_2CFCl)_nSCF_3$	1	R_1-R_0	F F F Cl
XXIII		2	R_2-R_0(a), R_1-R_1(b)	F F F Cl
XXIV		3	R_3-R_0(a), R_2-R_1(b)	F F F Cl
XXV		4	R_4-R_0(a), R_3-R_1(b), R_2-R_2(c)	F F F Cl
XXVI		>4	unknown	F F F Cl
XXVII	$CF_3S(CCl_2CCl_2)_nSCF_3$	1	R_1-R_0	Cl Cl Cl Cl
XXVIII	$CF_3SCCl{=}CCl_2$	-		
XXIX	$CF_3SCCl_2CCl_3$	-		

Table 1.5

but their formation is given in the text.

Note 2. The "Isomeric Structures" column in Table 1.5 for the compounds $CF_3S(CF_2CFH)_nSCF_3$, n >1, has been deliberately left blank since even the n = 2 compound can have three different isomers formed in four different ways whilst the n = 7 compound has 128 different ways of being formed (although some of these lead to the same isomers and others will not be followed due to the small concentrations of the radicals involved). In fact, there are 2^n ways of forming a $CF_3S(CF_2CFH)_nSCF_3$ adduct and Table 1.5 is not large enough to accommodate all of them.

Note 3. Since the major part of this work was published (174), a Patent (175) has appeared describing the u.v. induced addition of bistrifluoromethyldisulphide to tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene, 1,1-difluoroethylene, and hexafluoropropene. Although the reactions were carried out under the influence of u.v. light, as reported in this work, a different experimental technique was used. Bistrifluoromethyldisulphide was refluxed into the reaction zone, a quartz well in the reactor which housed the u.v. source. The olefin was passed into the reactor at a constant rate and the mixture irradiated. The reaction was monitored by means of the temperature of the boiling liquid. By employing this technique, Dear and Gilbert were able to isolate $CF_3SCF_2CF_2SCF_3$, as well as $CF_3S(CF_2CF_2)_2SCF_3$, from the reaction between CF_3SSCF_3 and $CF_2{=}CF_2$ whereas $CF_3SCF_2CF_2SCF_3$ is not prepared by the static conditions used in this work.

Also significant was the isolation of $CF_3SCF(CF_3)CF_2SCF_3$ as the only product in the $CF_3SSCF_3/CF_2{=}CFCF_3$ reaction. In the present work, the main product (90.5%) is the 1 : 2 adduct, $CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3$.

With chlorotrifluoroethylene, Dear and Gilbert report the formation of the compounds $CF_3S(CF_2CFCl)_nSCF_3$, n = 2-4, from the reaction of CF_3SSCF_3, as is found in the present work. However, this work also produced the compounds $CF_3SCF_2CFClSCF_3$, $CF_3SCF_2CFClCF_3$, and $\overline{CF_2CFClCF_2CFClS}$ from the reaction of CF_3SSCF_3 and $CF_2{=}CFCl$, no mention of which is made by Dear and

Gilbert.

With $CH_2=CF_2$, the 1 : 1 adduct again was not prepared by the method of Dear and Gilbert and only $CF_3S(CH_2CF_2)_2SCF_3$ was mentioned. Of the three possible isomers,

$CF_3SCH_2CF_2CF_2CH_2SCF_3$
VIII(a)

$CF_3SCH_2CF_2CH_2CF_2SCF_3$
VIII(b)

$CF_3SCF_2CH_2CH_2CF_2SCF_3$
VIII(c)

only VIII(c), the unfavoured isomer, was produced. In the present work, the isomers VIII(a), VIII(b) are detected with no trace of VIII(c). This is perhaps a consequence of the different experimental technique employed though it is noteworthy that the ^{19}F n.m.r. parameters reported by Dear and Gilbert for isomer VIII(c) are almost identical to those found here for isomer VIII(a) (which is also characterised by the mass spectrum).

Very interesting is the thermal conversion of $CF_3S(CF_2CF_2)_2SCF_3$ (350°/7 days) to $\overline{CF_2CF_2CF_2CF_2S}$ reported by Dear and Gilbert and it is possible that some of the n = 2 adducts prepared in this work may undergo a similar conversion.

Infrared Spectra of Bis(trifluoromethylthio)alkanes and -fluoroalkanes.

The characterisation and identification of CF_3S- derivatives is greatly facilitated by the use of infrared spectroscopy. From the infrared spectra of a large number of compounds containing CF_3S- groups, it has been possible to establish a number of group frequency assignments. This is because the sulphur atom in the bridging position serves to break down coupling between the groups bonded to it as a result of its relatively large mass. Nabi and Sheppard (176) were able to assign the vibrations of the CF_3S- group to the following frequency regions on the basis of a study of a number of trifluoromethanesulphenyl derivatives :- $\nu_{as}(C-F)$ 1205 - 1155 cm^{-1}, $\nu_s(C-F)$ 1135 - 1095 cm^{-1}, $\delta_s(CF_3)$ 765 -750 cm^{-1},

No.	X	Gas Press. (a)/Solvent	n	ν_{as} & ν_s(C-F)	$\delta_s(CF_3)$	$\delta_{as}(CF_3)$	ν(C-S)
I	CH_2CH_2	11 & 1		1172vs 1131vs 1112vs	757s	522w	465m
II	$CH(CH_3)CH_2$	15 & 1		1173vs 1132vs	759s	546w	461m
III	$(CF_2CF_2)_n$	4	2	1190vs 1140vs,br 1118vs 1104vs	763s	533m	451m
V	$[CF(CF_3)CF_2]_n$	3	1	1189vs 1160s 1122vs,br 1101vs	762s	550w	454w
VI		<1	2	1189vs 1169s,sh 1140vs 1105vs	762s	542w	452w
VII	$(CF_2CH_2)_n$	23 & 2	1	1180vs 1159vs 1114vs	762s	545w	455m
VIII		<1 & liq. film	2	1189vs 1145vs,br 1121vs	759s	540w	452m
IX X		CCl_4 & dioxan	3 4	1189vs 1169vs 1140vs 1112vs	759s	(b)	(b)
XI XII		CCl_4 & dioxan	5 6	1190vs 1169vs 1141vs 1113vs	757s	(b)	(b)
XIII	$(CF_2CFH)_n$	26 & 3	1	1192vs 1163vs 1130vs 1109s	762s	522s	471m
XIV		5 & 3	2	1193vs 1167vs 1146vs 1130vs	762s	520w	474m
XV		<1 & liq.film	3	1191vs 1163vs 1140vs 1127vs	759m	518w	470m
XVI		CCl_4 & dioxan	4	1179vs 1152vs 1138vs 1117vs	758m	(b)	(b)
XVII XVIII XIX		CCl_4 & dioxan	5 6 7	1187vs,sh 1176vs 1150vs 1116vs	757m	(b)	(b)
XXIII	$(CF_2CFCl)_n$	<1	2	1188vs 1156s 1138s,sh 1131vs 1120vs	762m	537w	481w
XXIV		liq. film & CCl_4	3	1174vs 1145vs 1119vs 1109vs	761s	545w	474w
XXV		CCl_4 & dioxan	4	1164vs 1141vs 1123vs,br	759s	(b)	(b)
XXVII	CCl_2CCl_2	liq. film		1187vs 1172vs 1118vs 1100vs	756m	538w	456w

(a) recorded in mm. Hg.
(b) region not investigated.

Table 1.6 : CF_3S- vibrations of the CF_3S-X-SCF_3 compounds.

$\delta_{as}(CF_3)$ 540 - 510 cm.$^{-1}$, and ν(C-S) 495 -445 cm.$^{-1}$ In a much more extensive study of compounds containing the CF_3S- group (177,178), these assignments were confirmed. Although no assignments are made, the same group frequencies are observed in the infrared spectra of $(CF_3S)_2N$-derivatives (179) and in the derivatives CF_3S-CAB-$SSCAB_2$ (with A and B,

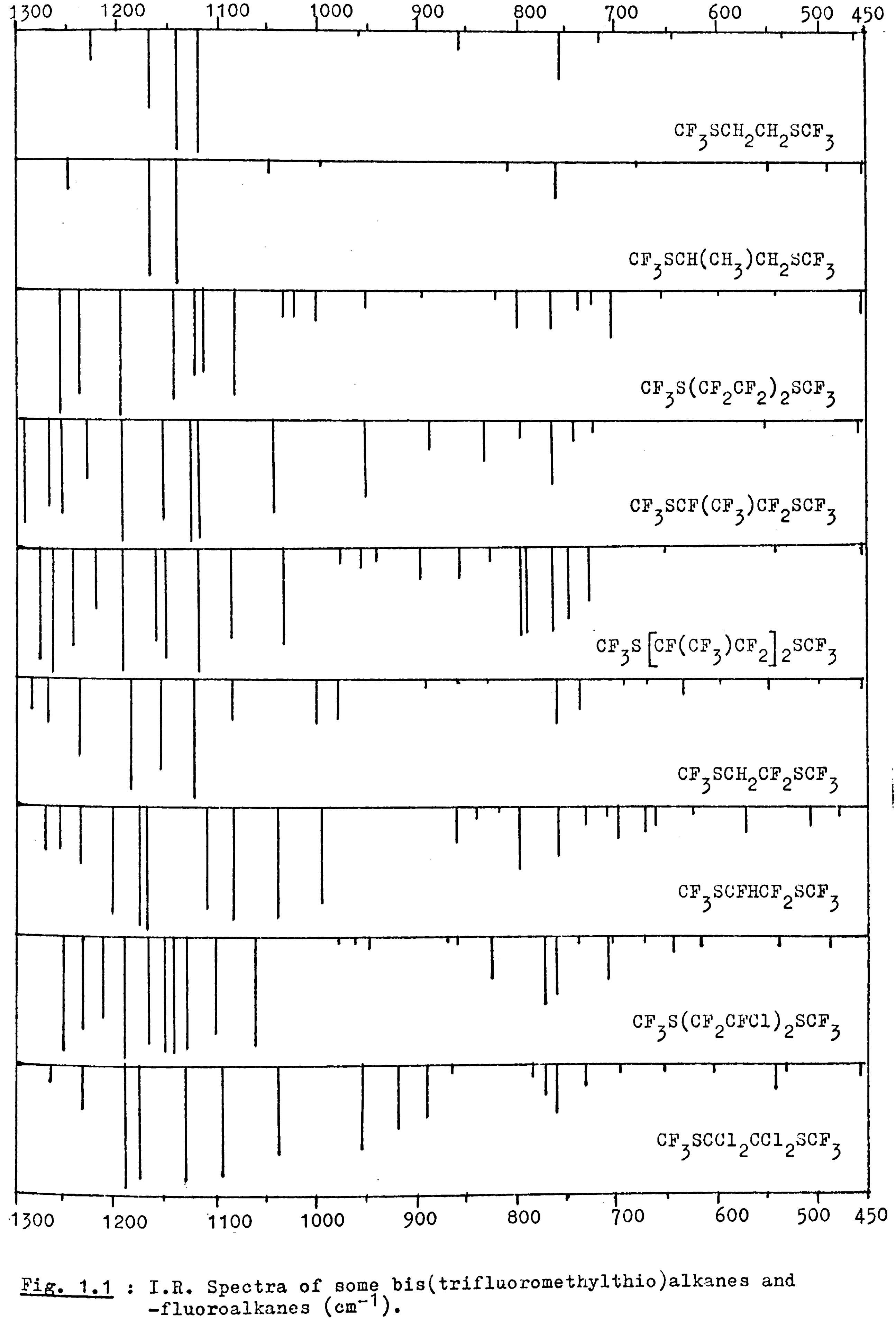
No.	X	Gas Press. (a)/Solvent	ν(C-H)	C-H Deformation.
I	CH_2CH_2	11 and 1	2980w	1431s
II	$CH_2CH(CH_3)$	15 and 1	2984s 2947s 2893m	1462s 1426m 1384s
VII	CF_2CH_2	23 and 2	2965w	1369s
VIII	$(CF_2CH_2)_2$	<1 and liq. film	3010w 2970w	1392m
IX	$(CF_2CH_2)_3$	CCl_4 and	3007w 2965w	1427m
X	$(CF_2CH_2)_4$	dioxan		1392s
XI	$(CF_2CH_2)_5$	CCl_4	3006w 2964w 2922w	1425m
XII	$(CF_2CH_2)_6$	and dioxan	2870w 2850w	1392s
XIII	CF_2CFH	26 and 3	2998m	1383s 1349s
XIV	$(CF_2CFH)_2$	5 and 3	2999w	1393m 1348m
XV	$(CF_2CFH)_3$	<1 and liq. film	2998w	1339m 1345m 1387m
XVI	$(CF_2CFH)_4$	CCl_4 and dioxan	2982w	1342m
XVII XVIII	$(CF_2CFH)_n$	CCl_4 and	2992w	1389m
XIX	n=5,6,7	dioxan		1344m

(a) recorded in mm. Hg.

Table 1.7 : ν(C-H) and deformation C-H of the $CF_3S-X-SCF_3$ compounds.

F or Cl) prepared from the reaction of RC(S)F (R=Cl, F, CF_3S) with the sulphenyl chlorides $CF_3S-CClF-SCl$, CF_3S-CCl_2-SCl and $(CF_3)_2CCl-SCl$ (180) Table 1.6. lists the CF_3S- group frequencies for the bis(trifluoromethylthio) alkanes and -fluoroalkanes. The ν_{as}(C-F) and ν_s(C-F) are grouped together since identification of some of the bands as ν_{as} or ν_s was not possible.

The frequencies observed here are very similar to those found by Harris in the compounds $CF_3SC_2H_5$, $CF_3S(CH_2)_nSCF_3$ n=1,2,3,5, $(CF_3S)_2CHCH_3$, $(CF_3S)_2CHCH_2SCF_3$, $(CF_3S)_3CH$ and $(CF_3S)_4C$ (23). As is found here, Harris only observed one $\delta_s(CF_3)$ frequency for each compound although there are several different CF_3S- groups in the compounds. Also, the number of ν (C-F) frequencies observed was less than one would anticipate for compounds containing several CF_3S- groups. Although Harris did not identify $\delta_{as}(CF_3)$



<u>Fig. 1.1</u> : I.R. Spectra of some bis(trifluoromethylthio)alkanes and -fluoroalkanes (cm^{-1}).

and ν(C-S) frequencies with his studies, the compounds examined here all showed only one frequency for each vibration. Table 1.7. shows the ν(C-H) and C-H deformation vibrations observed here.

A survey of ν(C-F) vibrations in fluorinated hydrocarbons (181) has shown that they can occur anywhere in the range 1400-1000cm^{-1} and are very difficult to assign. No attempt therefore has been made here to assign ν(C-F) bands or δ(CF) bands (for the same reason) in the i.r. spectra of the bis(trifluoromethylthio)alkanes and -fluoroalkanes.

Fig.1.1 gives an illustration of the infrared spectra of a few of the bis(trifluoromethylthio)alkanes and -fluoroalkanes. From this it can be seen that the observation of ν_{as}(C-F), ν_{s}(C-F), $\delta_{s}(CF_3)$, $\delta_{as}(CF_3)$ and ν(C-S) vibrations in the infrared spectrum of any one of these compounds serves to show that the compound contains the CF_3S- group, but attention has to be paid to the rest of the spectrum in order to determine the rest of the structure of the compound.

Some other bands in the i.r. spectra are worth noting :- the band at 640cm^{-1} for $CF_3SCH_2CH_2SCF_3$ and at 647cm^{-1} for $CF_3SCH_2CF_2SCF_3$ compare well with that at 643cm^{-1} for $CF_3SC_2H_5$ (119) which is assigned to νS-C(H). The ν(C=C) of $CF_3SCCl=CCl_2$ is observed at 1541cm^{-1}.

N.m.r. Spectra of Bis(trifluoromethylthio)alkanes and -fluoroalkanes.

^{19}F Chemical Shifts.

It has been shown (182) that variations in the local paramagnetic circulations of the fluorine atom are the dominant cause of chemical shifts in fluorine compounds. The paramagnetic contribution which represents a shift toward low field is greatest in covalently bonded fluorine and is zero in the spherically symmetric F^- ion. The magnitude of this effect is dependent on the degree of ionic character in the bond and this has been shown to be consistant with observations on the ^{19}F chemical shifts found in an extensive series of binary fluorides (Table 1.8) where, generally speaking, the more electronegative the atom (A) bound to fluorine, the more

Compound	δCF_3COOH ext. p.p.m.	δF_2 ext. p.p.m.	Electronegativity (183)
F_2	-	0.0	4.00
ClF_3	-193.0,-81.0	+343.4	3.25
NF_3	-219.0	+285.0	3.15
BrF_5	-349.0,-219.0	+290.5,+152.9	3.05
IF_5	-138.0,-95.8	+418.2,+368.9	2.80
SF_6	-127.0	+375.6	2.75
SeF_6	-128.0	+372.7	2.55
CF_4	-11.9	+491.0	2.45
AsF_3	-35.0	+469.1	2.20
PF_5	-0.7	+502.1	2.20
GeF_4	+99.0	+608.8	2.20
SbF_5	+6.8,+26.2,+52.0	+537.3	2.10
BF_3	+54.2	+555.5	1.90
HF	-	+625.0	2.20

Table 1.8: ^{19}F n.m.r. chemical shifts of some binary fluorides (69)

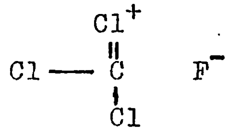
covalent the A-F bond, and hence the less ionic the bond. Thus the increasing electronegativity of the bonded atom destroys the symmetrical charge distribution, characteristic of the F^- ion, to a greater extent, thus increasing the paramagnetic contributions and causing the resonance to be displaced to lower field.

Attempts to rationalise the shielding of nuclei in aliphatic fluorocarbons however, have not generally been successful. The influences governing the chemical shifts in the halomethanes (Table 1.9) are explained in the case of the fluoromethanes, as successive replacement of the H atoms by the more electronegative F atoms causing a progressive displacement of the fluorine resonance to lower field. This type of reasoning in the case of the chlorofluoromethanes leads to a prediction of the chemical shift progression opposite to that found .

Compound.	δF(p.p.m.)
CF_4	0
CF_3H	18.2
CF_2H_2	80.9
CFH_3	210.0
CF_3Cl	-36.8
CF_2Cl_2	-60.4
$CFCl_3$	-76.7

Table 1.9: ^{19}F n.m.r. chemical shifts of the fluoromethanes and chlorofluoromethanes (184).

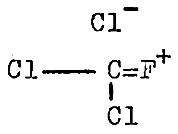
Structures of the form;



$\mathrm{Cl-\underset{Cl}{\underset{|}{\overset{Cl^+}{\overset{\|}{C}}}}\quad F^-}$

A

and



$\mathrm{Cl-\underset{Cl}{\underset{|}{\overset{Cl^-}{C}}}=F^+}$

B

with B favoured over A, are postulated as contributing to the overall molecular structure and therefore leading to less shielding of the F nucleus. In fluoroethanes and higher alkanes, the effects of vicinal substituents are not well understood. The progressive displacement of the ^{19}F resonance to lower field in the series CF, CF_2, CF_3 in fluorocarbons is thought to be due to the amount of charge which fluorine is able to draw from a carbon atom and this decreases as the number of competing fluorines bonded to that carbon increases (184). In the case of the CF_2 group, the apparent electron withdrawing power of the adjacent substituents is in the following order of effectiveness: CCl_3, $CH_2I > COCl$, $CH_2Br > CH_2Cl > CF_3 > CF_2H$ (184). Another order of apparent electron withdrawing power is deduced (185) to be : $I > Br > Cl > F \gg CF_2I > CF_2Br > CF_2Cl > CF_3$, both series exhibiting a trend contrary to that expected from group electronegativity consideration. A "repulsive unshielding effect has been suggested (185) to explain this anomalous trend, i.e. very large groups give rise to steric interactions which tend to increase their apparent electron withdrawing power . Characteristic ^{19}F chemical shifts are reported (13,186,187,188) for a large number of fluoroorganic compounds and in general the correlation tables given have been used to help assign chemical shifts in the bis(trifluoromethylthio)alkanes and -fluoroalkanes when there has been some doubt.

^{19}F Spin-Spin Coupling Constants.

The apparently random size of F-F coupling constants in fluoroorganic compounds is rationalised by a dual mechanism i.e. the "through-bond", "through-space" mechanism (189). As the name implies, the "through-bond" mechanism proceeds through the electronic structure in the intervening bonds whereas the "through-space" mechanism becomes operative only when there is direct overlap of the electronic clouds of the fluorine atoms, proceeding through an electronic structure where there is "no bond". In geminal fluorines, i.e. fluorine nuclei separated by two bonds, the two mechanisms may both be operating at once and this may explain the extremely large coupling constants observed (150-400 Hz.). In the case of vicinal fluorines only the "through bond" mechanism is important normally since the structure does not usually allow for sufficient fluorine-fluorine electron cloud interaction. The magnitude of the "through-bond" coupling is hence governed by the electron withdrawing power of the other substituents attached to the carbon skeleton and may therefore decrease to zero or almost zero in certain instances. When the fluorine nuclei are separated by more than three bonds, the "through-bond" coupling is very small indeed, but the geometry of the molecule may allow "through-space" interactions to occur due to the close proximity of the respective fluorines. Thus the observed spin-spin coupling constants in fluoroorganic compounds are not so anomalous as they first seem in the light of this mechanism e.g. in perfluorobutyric acid the following coupling

$$\underset{3}{CF_3}\text{—}\underset{2}{CF_2}\text{—}\underset{1}{CF_2}\text{—}COOH$$

constants are observed:- $J_{12}=J_{23} \leqslant 1$H . and $J_{13}=9.9$ Hz.(188) and can be explained by the dual mechanism above.

The CF_3S- group is particularly sensitive in its chemical shift to the nature of the group immediately attached to the sulphur e.g. Haas has shown (97) that all the compounds of the CF_3SN- family of compounds have a chemical shift in the range 51± 4 p.p.m. while the CF_3SC- family has a chemical shift in the region 49± 5 p.p.m.(97,180).

No.	COMPOUND	δCF_3S	δCF_2	δCF	δCF_3
I	$CF_3SCH_2CH_2SCF_3$	+41.9			
II	$CF_3SCH(CH_3)CH_2SCF_3$	i +42.1			
	i ii	ii +40.3			
III	$CF_3S(CF_2CF_2)_2SCF_3$	i +35.3	ii +85.5		
	i ii iii		iii +118.7		
V	$CF_3SCF(CF_3)CF_2SCF_3$	i +33.6	+78.2	+156.9	+74.1
	i ii	ii +35.2			
VI(a)	$CF_3S[CF(CF_3)CFF]_2SCF_3$	+36.4	A+71.5	+164.7	+69.1
	AB		B+73.7		
VII	$CF_3SCF_2CH_2SCF_3$	i +37.2	+71.3		
	i ii	ii +42.4			
VIII(a)	$CF_3SCH_2CF_2CF_2CH_2SCF_3$	+42.4	+113.0		
VIII(b)	$CF_3SCH_2CF_2CH_2CF_2SCF_3$	i +42.0	ii +62.1		
	i ii iii iv	iv +36.0	iii +89.9		
XIII	$CF_3SCF_2CFHSCF_3$	i +36.2	+74.7	+221.1	
	i ii	ii +40.6			
XIV(a)	$CF_3SCFHCF_2CFHCF_2SCF_3$	i +36.7	iii +117.5	ii+198.9	
	i ii iii iv v vi	vi +41.7	v +75.4	iv+212.1	
XIV(b)	$CF_3SCFHCF_2CF_2CFHSCF_3$	+41.3	+121.5	+222.2	
XXI	$CF_3SCF_2CFClCF_3$	+35.4	+80.5	+127.4	+78.7
XXIII(a)	$CF_3SCF_2CFClCF_2CFClSCF_3$	i +37.1	ii +73.6	iii +73.4	
	i ii iii iv v vi	vi +33.4	iv +113.7	v +80.3	
XXIII(b)	$CF_3SCF_2CFClCFClCF_2SCF_3$	+35.5	+76.5	+78.4	
XXIV(b)	$CF_3SCF_2CFClCF_2CFClCFClCF_2SCF_3$	+35.0	+76.6 +119.8	+78.2	
XXV(c)	$CF_3S(CF_2CFCl)_2(CFClCF_2)_2SCF_3$	+34.8	+71.5 +125.6		
XXVII	$CF_3SCCl_2CCl_2SCF_3$	+42.4			
XXVIII	$CF_3SCCl=CCl_2$	+39.5			
XXIX	$CF_3SCCl_2CCl_3$	+36.8			

Table 1.10: ^{19}F n.m.r. Chemical Shifts of the CF_3S- derivatives.

From Table 1.10 the following categories for δCF_3S- in the bis(trifluoromethylthio)alkanes and -fluoroalkanes can be distinguished:-

Group	δ range (p.p.m.)
CF_3SCHX- $X=H,F,CH_3$	40.3-42.4
CF_3SCF_2-	34.8-37.2
CF_3SCFX- $X=Cl, CF_3$	33.5± 0.1

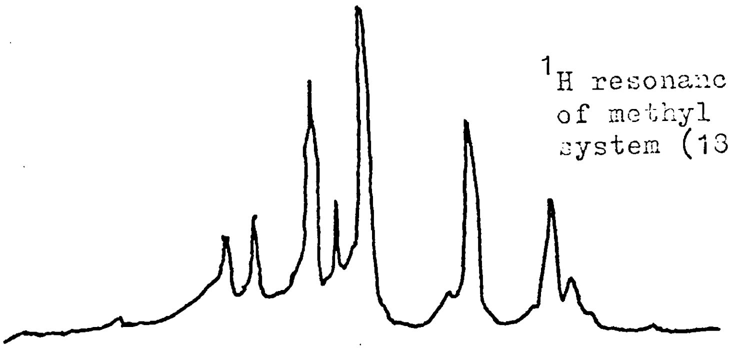
Table 1.11.

The ^{19}F n.m.r. spectra of the bis(trifluoromethylthio)alkanes, $CF_3SCH_2CH_2SCF_3$ and $CF_3SCH_2CH(CH_3)SCF_3$, show one and two singlets respectively. The HF coupling, if any, is less than 0.25Hz. The ^1H n.m.r. spectrum of $CF_3SCH_2CH_2SCF_3$ consists of a singlet showing that all the protons are equivalent (see Table 1.12).

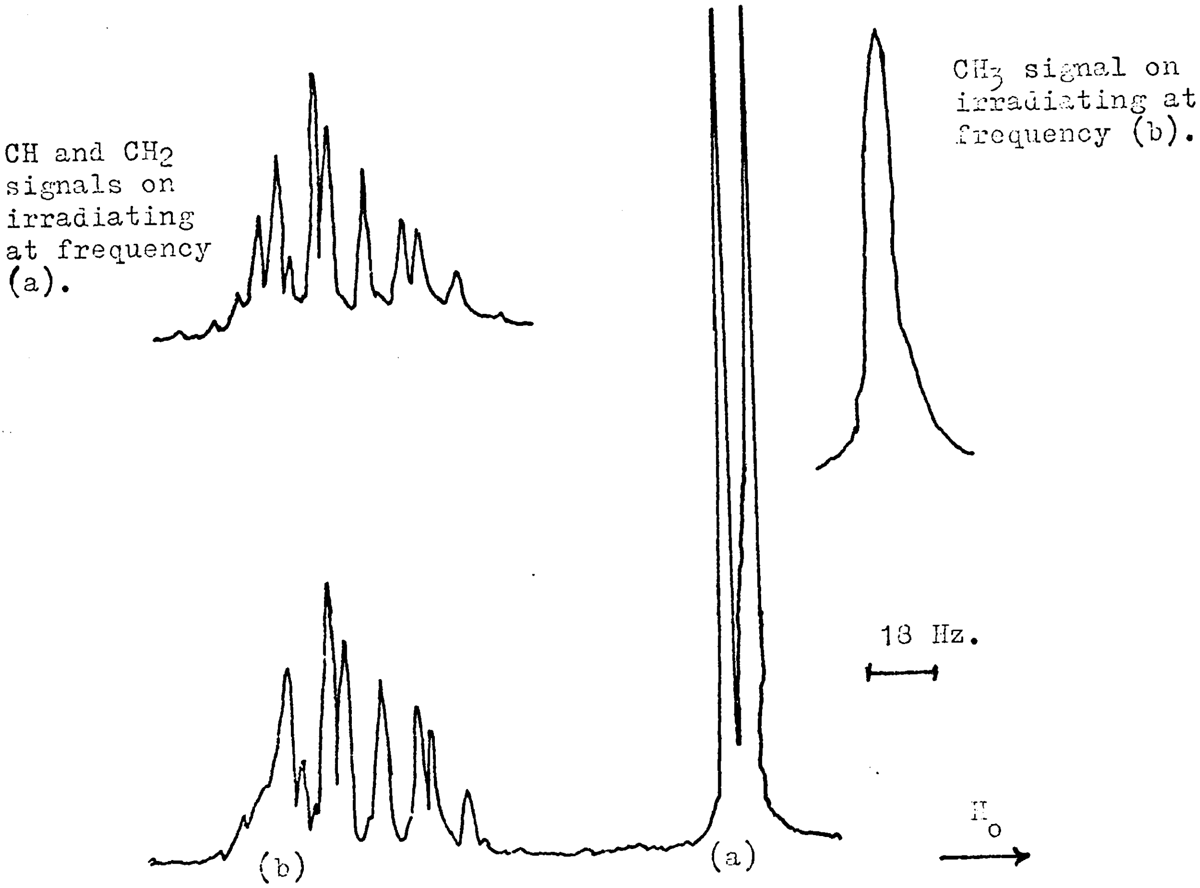
No.	COMPOUND	δCH_2	δCH	δCH_3
I	$CF_3SCH_2CH_2SCF_3$	+2.94		
II	$CF_3SCH(CH_3)CH_2SCF_3$	see text	see text	+1.33
VII	$CF_3SCH_2CF_2SCF_3$	+3.65		
VIII(a)	$CF_3SCH_2CF_2CF_2CH_2SCF_3$	+3.48		
VIII(b)	$CF_3SCH_2CF_2CH_2CF_2SCF_3$	+3.78 - +2.41		
XIII	$CF_3SCF_2CFHSCF_3$		+6.32	
XIV(a)	$CF_3SCFHCF_2CFHCF_2SCF_3$		+7.02 - +6.30 +6.17 - +5.15	
XIV(b)	$CF_3SCFHCF_2CF_2CFHSCF_3$		+5.02 - +4.23	

Table 1.12 : ^1H n.m.r. Chemical Shifts of the CF_3S- derivatives

The ^1H n.m.r. spectrum of $CF_3SCH(CH_3)CH_2SCF_3$, on the other hand, is very complex and compares with the ^1H n.m.r. spectrum of $SF_5CH_2CHClCH_3$, which was analysed as an AB_4P_3XYZ system (190), and trans-$CF_3SF_4CH_2CHClCH_3$ described in Chapter II. Thus $CF_3SCH(CH_3)CH_2SCF_3$ may possibly be regarded as an $A_3D_3P_3XYZ$ system with no detected coupling between A_3 and D_3 or between A_3D_3 and P_3XYZ. The ^1H n.m.r. spectrum is shown in Fig. 1.2.



^{1}H resonance of the vinyl group of methyl acrylate - an ABC spin system (137).



CH and CH_2 signals on irradiating at frequency (a).

CH_3 signal on irradiating at frequency (b).

Fig. 1.2 : ^{1}H n.m.r. spectrum of $CF_3SCH(CH_3)CH_2SCF_3$.

The CH_3 signal is easily identified but the CH and CH_2 signals cannot be picked out. The CH_3 signal is a doublet (J = 6.9 Hz.) suggesting that coupling to CH alone takes place. To try to clarify the interactions giving rise to the fine structure of the spectrum, recourse to double irradiation was made. When two non-equivalent nuclei, A and X, are coupled together by indirect spin-spin interaction, the resonance spectrum of each nucleus is split into a multiplet structure. If one of these nuclei jumps rapidly between the various spin states corresponding to the multiplet lin of the other nucleus, then only a single average resonance absorption frequency will be observed at the centre of the original multiplet. Spin multiplets in the X resonance absorption are observed when the nucleus A spends a longer time in a given spin state than the time corresponding to the reciprocal of the frequency separation of the multiplets. Partial or complete spin decoupling can occur naturally if one of the nuclei possesses an electric quadrupole moment. Here the lifetime of such a nucleus in a particular spin state is limited by rapid spin-lattice relaxation; e.g. in the case of nitrogen coupled to hydrogen nuclei, the hydrogen resonance absorption bands can be made considerably sharper by irradiating with the nitrogen resonance frequency. Spin-spin decoupling can also be promoted without the necessity of one of the nuclei concerned possessing a quadrupole moment. In applications where different magnetic nuclei are being dealt with, the multiplet of one nucleus can be collapsed by irradiating the other interacting nucleus with the appropriate resonance frequency.

Thus secondary irradiation of $CF_3SCH(CH_3)CH_2SCF_3$ with a frequency corresponding to the centre of the CH_3 doublet, (a) in Fig. 1.2, sharpens up the low field part of the complex multiplet whilst the high field part of this multiplet is left unaffected, supporting the suggestion that the CH_3 protons couple only with the CH proton and not with the CH_2 protons. Confirmation of this is achieved by secondary irradiation of $CF_3SCH(CH_3)CH_2SCF_3$ with a frequency corresponding to the centre of the low field part of the complex multiplet, i.e. the CH resonance frequency (b), whence the CH_3 signal collapses to a broad singlet (Fig. 1.2). The decoupling of the CH and CH_2 protons could not be observed since the signals are too close together. Hence the $CHCH_2$ part of the spectrum is reduced to an ABC spectrum. The ABC spin system is very complicated (69) and no attempt was made to solve it here, but Fig. 1.2 shows an ABC spectrum, that of the vinyl group of methyl acrylate (187), and the similarity between the two spectra is evident.

The ^{19}F n.m.r. spectrum of $CF_3S(CF_2CF_2)_2SCF_3$ is relatively simple, showing only three signals (chemical shifts are to be found in Table 1.10),

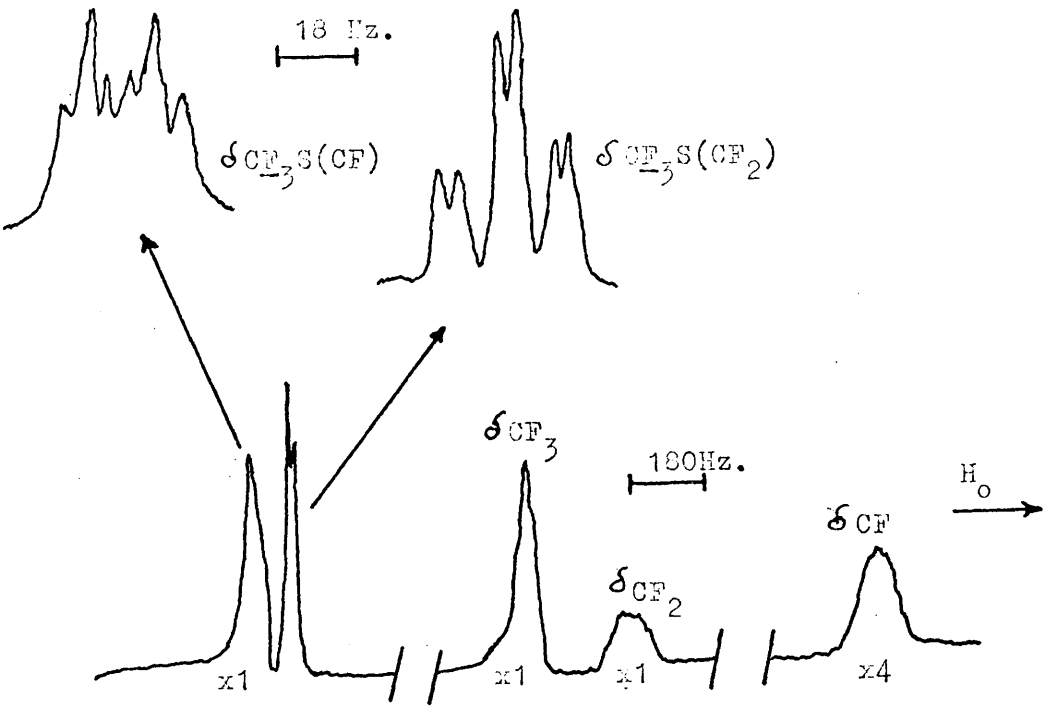


Fig. 1.3 : ^{19}F n.m.r. Spectrum of $CF_3SCF(CF_3)CF_2SCF_3$

but the coupling was too complicated for any J values to be calculated save that the CF_3S signal was a broad triplet on expansion. The spectrum is identical to that found by Dear and Gilbert for $CF_3S(CF_2CF_2)_2SCF_3$ (175).

Fig. 1.3 shows the ^{19}F n.m.r. spectrum of $CF_3SCF(CF_3)CF_2SCF_3$; the chemical shifts and coupling constants (as far as they could be determined) are given in Tables 1.10 and 1.13 respectively. Expansion of the two CF_3S signals shows the low field one to be a doublet of triplets while the higher field signal is a triplet of doublets, establishing them as CF_3SCF and CF_3SCF_2 respectively. The CF_3, CF_2, and CF signals are too complex for

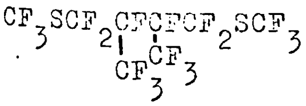
COMPOUND	$J_{C\underline{F}_3SC\underline{F}_2}$	$J_{C\underline{F}_3SCC\underline{F}_2}$	$J_{C\underline{F}_3SC\underline{F}}$	$J_{C\underline{F}_3SCC\underline{F}}$	$J_{H_1F_2}$	$J_{H_1F_1}$	$J_{F_1F_2}$
$CF_3SCF(CF_3)CF_2SCF_3$	10.4	3.8	11.2	5.5			
 $CF_3SCF_2\underset{CF_3}{CF}\underset{CF_3}{CF}CF_2SCF_3$	10.3						
$CF_3SCF_2CH_2SCF_3$	10.9	5.8			14.1		
$CF_3SCF_2CFHSCF_3$	10.7	3.6	10.9	3.7	5.8	56.4	13.1

Table 1.13 : Coupling Constants (Hz.).

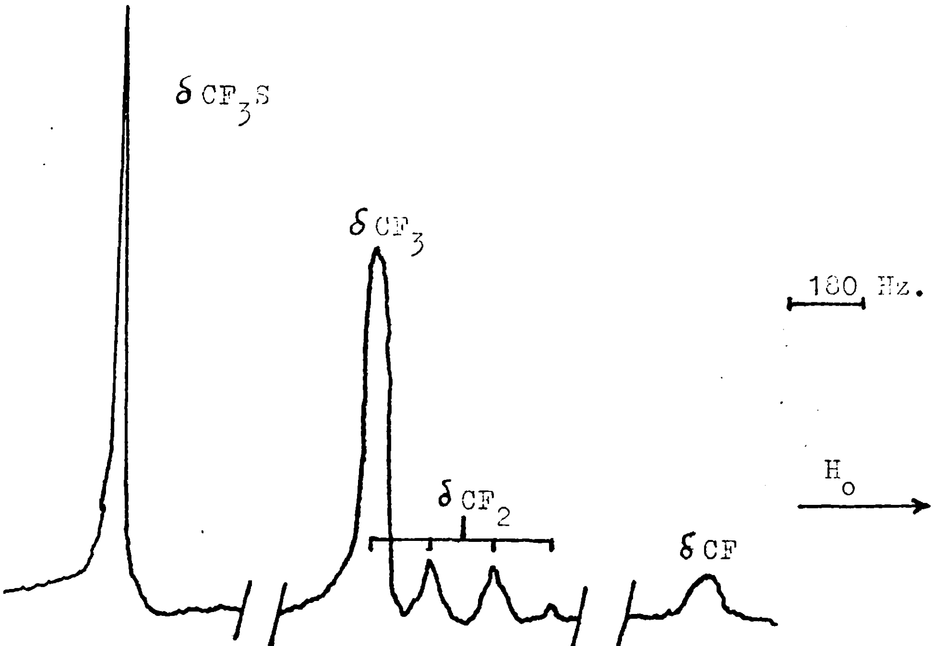
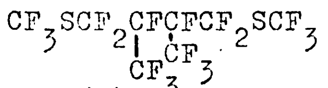


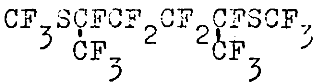
Fig. 1.4 : ^{19}F n.m.r. spectrum of $CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3$

any coupling constant data to be obtained. Again, the spectrum is identical to that recorded by Dear and Gilbert (175) and also to the published spectrum (142).

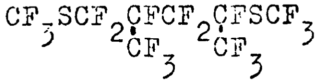
Fig. 1.4 shows the ^{19}F n.m.r. spectrum of $CF_3S[CF(CF_3)CF_2]_2SCF_3$, the chemical shifts being given in Table 1.10. There is only one CF_3S signal and three other signals with an intensity ratio of 3 : 3 : 2 : 1; i.e. CF_3S, CF_3, CF_2, and CF signals. The CF_3S signal has a chemical shift typical of a CF_3SCF_2 group by comparison with $CF_3SCF(CF_3)CF_2SCF_3$ and from Table 1.11. The signal is a broad triplet on expansion with J = 10.3 Hz., again suggesting CF_3SCF_2. The simplicity of the spectrum suggests that a symmetrical structure such as VI(a) or VI(b) is present since VI(c) would be expected to give a much more complicated spectrum with at least two CF_3S signals.


$CF_3SCF_2\underset{CF_3}{C}F\underset{CF_3}{C}FCF_2SCF_3$

VI(a)

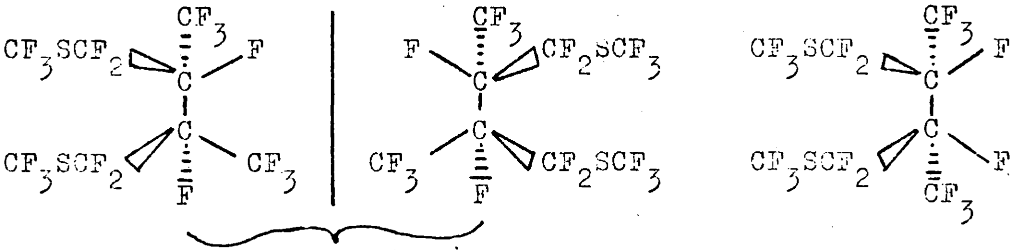

$CF_3S\underset{CF_3}{C}FCF_2CF_2\underset{CF_3}{C}FSCF_3$

VI(b)


$CF_3SCF_2\underset{CF_3}{C}FCF_2\underset{CF_3}{C}FSCF_3$

VI(c)

VI(a) is suggested by the presence of CF_3SCF_2 and the chemical shift of the CF_2 signal confirms this; CF_2 in the environment of VI(b) would appear at ca. 120 p.p.m. (191). The CF_2 signal appears as an AB type spectrum with one of the weaker bands hidden by the CF_3 signal. Analysis of the CF_2 signal as an AB spectrum (69) gives the parameters δ_A = +71.5 p.p.m., δ_B = +73.7 p.p.m., $|J_{AB}|$ = 144 Hz. The CF_2 chemical shift agrees with the SCF range found by Tiers(191) The CF chemical shift is more appropriate to VI(a) than VI(b). Hence the overall suggestion is that VI(a) is the probable structure for $CF_3S[CF(CF_3)CF_2]_2SCF_3$, a result which is confirmed by the mass spectrum. The non-equivalence of the CF_2 fluorines, found also in compounds such as $CF_2BrCFBrSO_2F$ (192) and $CF_2ClCFClSO_2F$ (192), is probably due to restricted rotation about the $CF(CF_3)$-$CF(CF_3)$ C-C bond. These two carbons each have four different substituents and therefore such a structure should give rise to optical activity with the dl racemic mixture and the meso form all being possible isomers :-

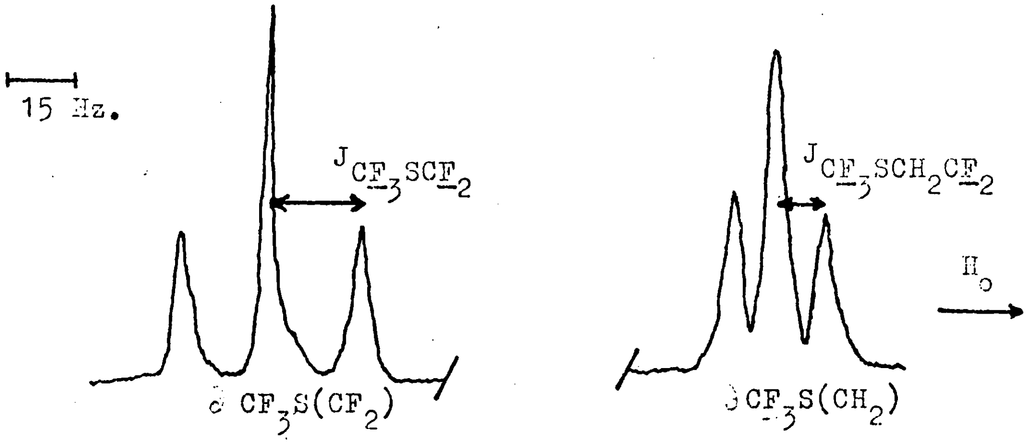


dl racemic mixture

meso

The ^{1}H n.m.r. spectrum of $CF_3SCH_2CF_2SCF_3$ (see Tables 1.12 and 1.13) consists of a triplet from coupling with the CF_2 group. There does not appear to be any coupling with the CF_3 groups. Harris has shown that the CH_2 signal in $CF_3SCH_2CF_2Cl$ is at +3.48 p.p.m. with a triplet fine structure due to coupling with CF_2 (142). The ^{19}F n.m.r. spectrum shows two 1 : 1 CF_3S signals (see Fig. 1.5). By comparison with the CF_3S chemical shifts

Fig. 1.5 : CF_3S signals of $CF_3SCF_2CH_2SCF_3$



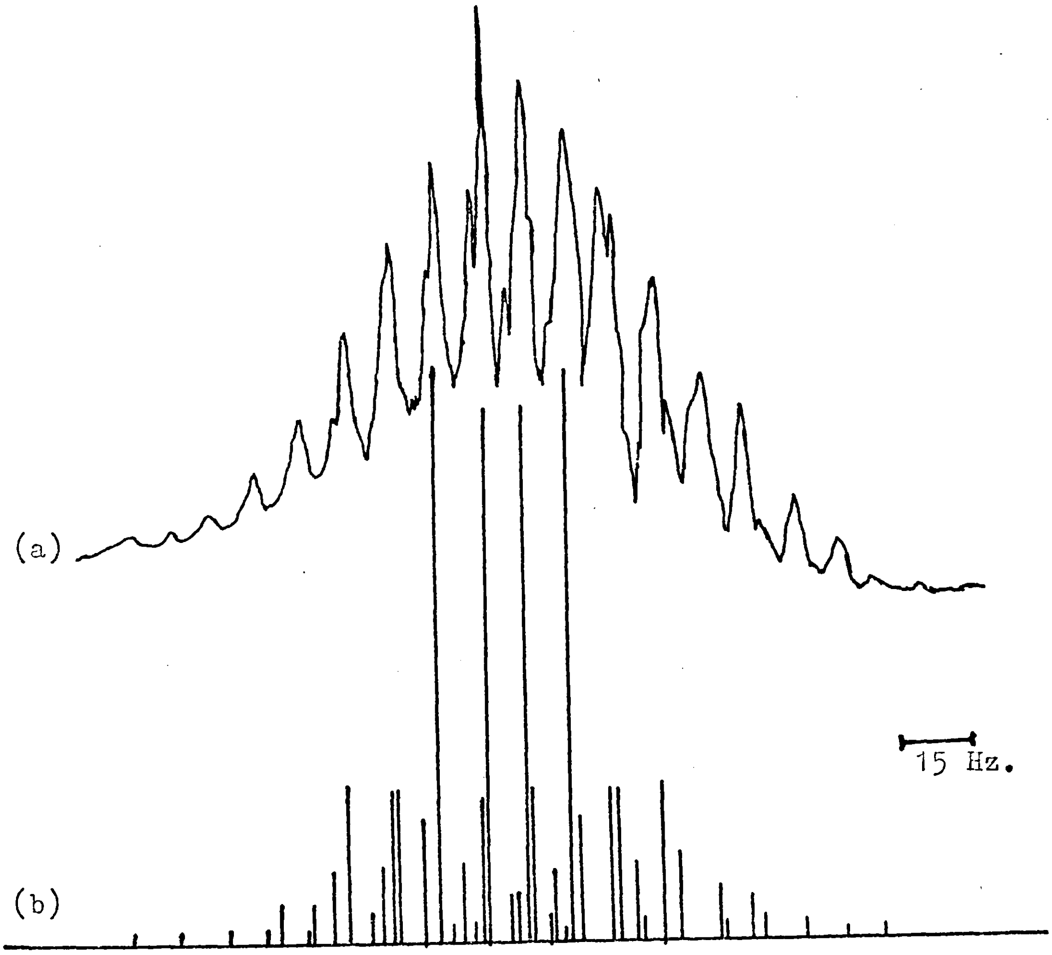


Fig. 1.6 : (a) observed and (b) calculated CF_2 resonance in the ^{19}F n.m.r. spectrum of $CF_3SCF_2CH_2SCF_3$

of $CF_3S(CF_2CF_2)_2SCF_3$ and $CF_3SCH_2CH_2SCF_3$, the low field signal is assigned to $\underline{CF_3}SCF_2$ while the higher field signal is assigned to $\underline{CF_3}SCH_2$. Fig. 1.5 shows that not only does the CF_3S of CF_3SCF_2 couple with CF_2, but so does the CF_3S of CF_3SCH_2. $J_{\underline{CF_3}S\underline{CF_2}}$ is larger than $J_{\underline{CF_3}SCH_2\underline{CF_2}}$ (Table 1.13). From the known coupling constants, the fine structure expected for the CF_2 signal is calculated and shown together with the observed spectrum in Fig. 1.6. As can be seen, the agreement is quite good.

The ^{19}F n.m.r. spectrum of $CF_3S(CH_2CF_2)_2SCF_3$ gives three CF_3S signals (Table 1.10); two of approximately the same height and the third about 3x the height of the other two together. From Table 1.11, these are assigned as CF_3SCH_2 with CF_3SCF_2 : CF_3SCH_2 as 1 : 3. There are also three CF_2 signals; one about 3x the height of the other two combined. Assignment is made with the help of Reference (136). This suggests the presence of two compounds; one symmetrical giving rise to just one $C\underline{F}_3S(CH_2)$ signal and one CF_2 signal, i.e. $CF_3SCH_2CF_2CF_2CH_2SCF_3$, and the other not symmetrical, i.e. $CF_3SCH_2CF_2CH_2CF_2SCF_3$. The former shows the CF_3S signal as a triplet with $J_{C\underline{F}_3SCH_2C\underline{F}_2}$ = 3.2 Hz. No other coupling constants could be determined from the ^{19}F n.m.r. spectrum. The ^1H n.m.r. spectrum shows a complex multiplet between +3.78 and +2.41 p.p.m. but a large triplet, with $J_{C\underline{H}_2C\underline{F}_2}$ = 14.2 Hz., can be picked out at +3.48 p.p.m.. This latter signal supports the $CF_3SCH_2CF_2CF_2CH_2SCF_3$ structure. The remainder of the spectrum is too complex for further analysis, as would be expected for a compound such as $CF_3SCH_2CF_2CH_2CF_2SCF_3$.

The ^1H n.m.r. spectrum of a $CF_3S(CF_2CH_2)_nSCF_3$, n = 3,4, mixture shows a broad absorption from +3.78 to +2.15 p.p.m. and no details could be determined. Only one signal, that of a CF_3S group, at +41.2 p.p.m. and typical of CF_3SCH_2 could be found in the ^{19}F n.m.r. spectrum. This was due to an insuffiency of material and no structural data could be determined from the n.m.r. spectra. A similar situation, i.e. an insufficiency of material, existed for the n = 5,6 mixture of $CF_3S(CF_2CH_2)_nSCF_3$. The ^1H n.m.r. spectrum shows a broad absorption from +3.50 to +1.16 p.p.m. while only one signal (Table 1.14) could be picked out in the ^{19}F n.m.r. spectrum.

<u>Table 1.14</u> : Supplementary Table of CF_3S signals.

COMPOUND	n	$\delta\, CF_3S^{(a)}$
$CF_3S(CF_2CH_2)_nSCF_3$	3,4	41.2
	5,6	41.4
$CF_3S(CF_2CFH)_nSCF_3$	3	36.3, 41.5 41.2, 41.1
	4	35.1, 41.5 41.2
	5,6,7	39.6, 40.2
$CF_3S(CF_2CFCl)_nSCF_3$	3	35.0
	4	34.8

(a) all chemical shifts are positive with respect to CCl_3F (ext.).

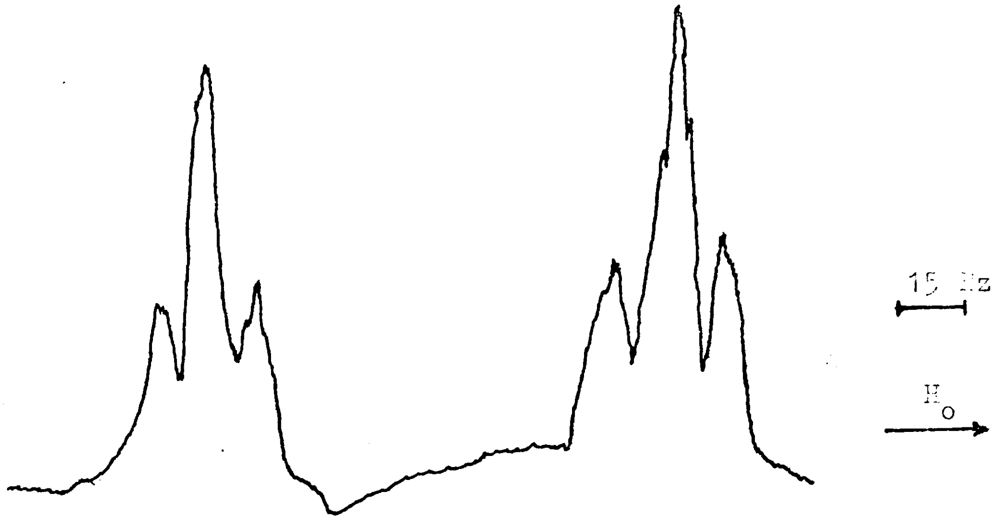


Fig. 1.7 : CH resonance in the ^1H n.m.r. spectrum of $CF_3SCF_2CFHSCF_3$

The ^1H n.m.r. spectrum of $CF_3SCF_2CFHSCF_3$ is shown in Fig. 1.7 with the chemical shift given in Table 1.12. The signal is a doublet (from geminal HF coupling) of triplets (from vicinal HF coupling) with coupling constants given in Table 1.13. The ^1H n.m.r. spectrum of $CF_3SCFHCF_2Cl$ (142) is a doublet of triplets centred at $\delta = +5.92$ p.p.m. with $J_{H_1F_1} \approx 54$Hz. and $J_{H_1F_2} \approx 10$Hz. The two CF_3S signals in the ^{19}F n.m.r. spectrum of $CF_3SCF_2CFHSCF_3$ are shown in Fig. 1.8. The lower field signal is identified as the $C\underline{F}_3S(CF_2)$ signal from Table 1.11 and from the fine structure which is a triplet (from CF_2 coupling) of doublets (from CF coupling). The higher field CF_3S signal is identified as the $CF_3S(CFH)$ resonance from Table 1.11 and from the fine structure which is a doublet (from CF coupling) of triplets (from CF_2 coupling). J values are given in

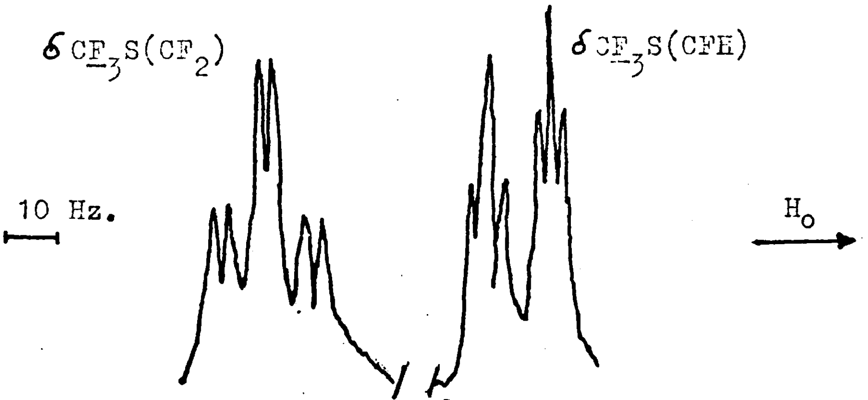


Fig. 1.8 : CF_3S resonances in the ^{19}F n.m.r. spectrum of $CF_3SCF_2CFHSCF_3$

Table 1.13. The CF signal is a well defined doublet from geminal HF coupling, but on expansion gives a doublet of broad triplets (from CF_2 coupling) with further fine structure unidentifiable, as is the fine structure of the CF_2 signal.

The ^1H n.m.r. spectrum of $CF_3S(CF_2CFH)_2SCF_3$ is very complicated. It consists of three complex multiplets with chemical shift ranges +4.22 to +5.01 p.p.m., +5.19 to +6.21 p.p.m., and +6.32 to +7.18 p.p.m. and analysis is not possible, especially since the compound is a mixture of isomers. The ^{19}F n.m.r. spectrum (Table 1.10) of $CF_3S(CF_2CFH)_2SCF_3$ shows three CF_3S signals; one at +41.3 p.p.m. which is 3x the height of the other two together. There are three CF_2 signals and three CF signals; in each case there is one signal 3x the height of the other two signals combined. Thus there is, as in the case of $CF_3S(CF_2CH_2)_2SCF_3$, one symmetrical and one unsymmetrical structure for $CF_3S(CF_2CFH)_2SCF_3$. From Table 1.11, the CF_3S signal of the symmetrical structure is due to $\underline{CF_3}SCFH$. This is confirmed by the CF_2 chemical shift and. to a lesser extent, by the CF chemical shift. The symmetrical stucture is therefore suggested to be $CF_3SCFHCF_2CF_2CFHSCF_3$. There is only one structure for the unsymmetrical compound, viz. $CF_3SCFHCF_2CFHCF_2SCF_3$. The CF_3S signal at +36.7 p.p.m. is assigned to $\underline{CF_3}S(CF_2)$ on the basis of Table 1.11 and on the fine structure which is a broad triplet with $J_{\underline{CF_3}S\underline{CF_2}} = 9.2$ Hz. and the CF_3S signal at +40.6 p.p.m. is assigned to $\underline{CF_3}S(CFH)$. No other coupling constants could be determined due to the complexity of the fine structure of the signals. The other possible isomer, $CF_3SCF_2CFHCFHCF_2SCF_3$ is not observed in the ^{19}F n.m.r. spectrum. The CF_3S signal is a sensitive probe, but no trace of CF_3S signals for this structure are found, although it may have been present in minute quantities.

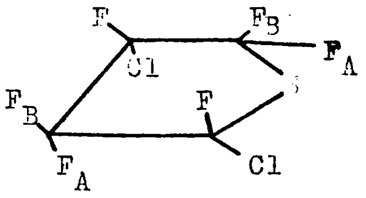
Table 1.14 summarises the information that can be gained from the ^{19}F n.m.r. spectra of the compounds $CF_3S(CF_2CFH)_nSCF_3$, n = 3,4,5,6,7; i.e. the CF_3S signals. Although there are signals detected due to CF_2 and CF groups, assignment of these to isomeric stuctures is well nigh impossible due to the sheer complexity of the systems. The ^1H n.m.r. spectra are also not very helpful; all bear a very great resemblance to that of $CF_3S(CF_2CFH)_2SCF_3$.

The ^{19}F n.m.r. spectrum of $CF_3S(CF_2CFCl)_2SCF_3$ shows three CF_3S signals one of which is 1/3 of the height of the other two signals combined. There are also three CF_2 signals and three CF signals, with one being 1/3 of the height of the other two combined in each case. This would suggest a symmetrical compound and an unsymmetrical compound as in the earlier cases of $CF_3S(CF_2CFH)_2SCF_3$ and $CF_3S(CF_2CH_2)_2SCF_3$, but this time the symmetrical structure is present in the smaller amount. The chemical shifts are given in Table 1.10. By comparison with Table 1.11, the CF_3S signal of the symmetrical structure is assigned to $C\underline{F}_3S(CF_2)$. This is confirmed by the fine structure of the signal which shows a broad triplet with $J_{C\underline{F}_3SC\underline{F}_2}$ = 10.2 Hz. Thus, the symmetrical structure is thought to be $CF_3SCF_2CFClCFClCF_2SCF_3$. The unsymmetrical structure can only be $CF_3SCF_2CFClCF_2CFClSCF_3$ and the chemical shifts of the CF_3S groups agree with the ranges in Table 1.11.

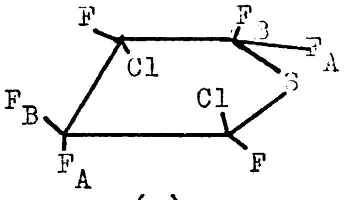
For the $CF_3S(CF_2CFCl)_nSCF_3$, n = 3,4, compounds, the ^{19}F n.m.r. data are given in Table 1.10. Obviously not all the signals are recorded in the table; insufficient material precludes all the signals being detected. From Table 1.11, the CF_3S signals in both cases would appear to be due to $C\underline{F}_3S(CF_2)$, but no **coupling constants to confirm or deny this could be calculated, the signals being too complex.**

The chemical shifts of the signals in the ^{19}F n.m.r. spectrum of $CF_3SCF_2CFClCF_3$ are given in Table 1.10.

For $\overline{SCF_2CFClCF_2C}FCl$, there are two possible structures, (a) or (b) :-



(a)



(b)

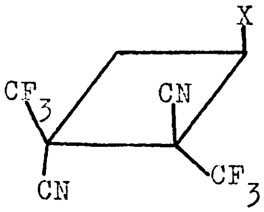
The ^{19}F n.m.r. spectrum can be explained in terms of (a), more readily than in terms of (b), being the preferred structure. The ^{19}F spectral parameters

	S-CF$_2$-C (1)	C-CF$_2$-C (2)	S-CClF-C (3)	C-CClF-C (4)
δA(p.p.m.)	+67.7	+105.7	+75.7	+116.1
δB(p.p.m.)	+92.3	+133.1		
$\lvert J_{AB}\rvert$ (Hz.)	214.2	248.1		

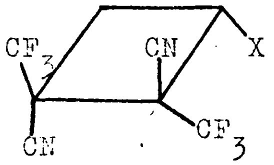
Table 1.15 : ^{19}F n.m.r. parameters of $\overline{CF_2CFClCF_2CFClS}$

are listed in Table 1.15. The fluorines of the CF$_2$ groups are analysed as AB spin systems(69). Reference is made to similar compounds such as $\overline{SCF_2CFClCCl_2C}FCl$, investigated by Tatlow et al.(193), in assigning signals. The $F_{(1)B}$ signal is basically a doublet with J = 16.2 Hz., probably from coupling with $F_{(4)}$. $F_{(2)B}$ is a triplet with J = 14.1 Hz.; this is most probably due to equal coupling to $F_{(3)}$ and $F_{(4)}$ to give an overlapping doublet of doublets with $J_{(1)B(3)}$ and $J_{(1)B(4)}$ both 14.1 Hz. Further coupling of both $F_{(1)B}$ and $F_{(2)B}$ is observed but is too complex for a full analysis, as are the $F_{(3)}$ and $F_{(4)}$ signals. The $F_{(2)A}$ signal has both branches as extremely sharp lines with very little coupling evident in the expanded signal.

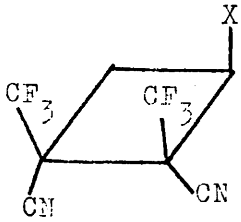
Ng and Sederholm have studied the following systems (189).



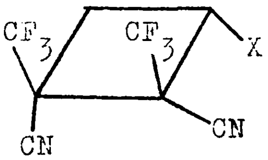
I(i)



I(ii)



II(i)



II(ii)

Although they found coupling between the two CF$_3$ groups in both the cis conformations II(i) and II(ii), they found no coupling in the trans conformations. There are too many bonds beyween the CF_3 groups, they argued, so that any coupling would have to be "through - space" coupling, no "through - bond" coupling being possible. In the trans forms, there is no way that the two CF_3 electron clouds can interact, hence there is no "through - space" coupling. This is evidenced by the single line resonances. In the cis forms on the other hand, the electron clouds of the two CF_3 groups can interact and "through - space" coupling is observed.

Thus, only in structure (a) of $\overline{CF_2CFClCF_2CFClS}$ can there be no coupling to the $F_{(2)A}$ fluorine and can the $F_{(1)B}$ and $F_{(2)B}$ signals show the splittings observed. The slight anomaly is the $F_{(1)A}$ fluorine which does not give as sharp a signal as that of the $F_{(2)A}$ fluorine. There must be slight interaction with other fluorines, but how this can occur is not exactly clear.

Table 1.10 lists the ^{19}F n.m.r. chemical shifts of the CF_3S signals of the products of the reaction between CF_3SSCF_3 and $CCl_2{=}CCl_2$. The signal for $CF_3SCCl_2CCl_3$ would appear to be somewhat lower than one would expect, but identification by its mass spectrum is positive and the reason for the signal value being low must be put down to the greater electron withdrawing power of the CCl_3 group compared to the CF_3S group (in $CF_3SCCl_2CCl_2SCF_3$).

Mass Spectra of Bis(trifluoromethylthio)alkanes and -fluoroalkanes.

Theoretical considerations show that the ionisation process in mass spectrometry is not simply the removal of an electron from a single bond in a molecule (194); the redistribution of electronic charge between the bonds takes place so rapidly that all the bonds are weakened simultaneously, but there will often be some bond which is weakened much more than others and bond ionisation can be interpreted in that sense. For large polyatomic molecules, it is thought that there is a mechanism whereby the "weak - point" can "wander about" in the molecule, dissociation occurring when the electronic configuration enables it to take place most easily (194). In saturated hydrocarbons, the above ideas hold very well such that the subsequent decomposition can often be evaluated statistically, but when heteroatoms are present in the molecule, this theory tends to break down (195). As far as decomposition of a molecular ion is concerned, it is neither necessary nor important to know how and from where the initial electron is removed. A preferred charge localisation concept is suggested whereby the charge is preferentially localised on one atom just before decomposition of the molecular ion (195). Frequently, this atom turns out to be the heteroatom in heteroatom - containing hydrocarbons. The real significance of this localised charge concept is in its ability to predict which bonds are most likely to break in a given molecular ion.

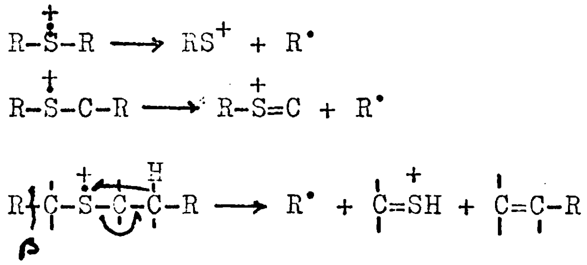
Although the stability of the fragments, both charged and uncharged, which are formed in a fragmentation process may often play an important part in determining the mode of fragmentation (194), the major fragments in mass spectra are best rationalised by bearing in mind that the most stable ion products are those which are formed by the most favourable reaction pathways (196).

Certain modes of fragmentation are confirmed by the observation in the mass spectrum of metastable peaks. These are usually weak diffuse signals and often appear in the mass spectrum at non - integral masses. How these peaks arise is well understood. Some of the ions formed in the ionisation chamber of the mass spectrometer are metastable. That is to say, they are sufficiently stable to be withdrawn in large numbers from the ionisation chamber but their half - life is extremely short (ca. 1 micro-second) and many of them will dissociate during their passage towards the collector. Some of these ions, of original mass m_1 will of course reach the collector without decomposition. Others will decompose to give ions of mass m_2 (plus neutral fragments) before leaving the ion chamber. Hence peaks corresponding to both the initial and final masses, m_1 and m_2 respectively, will be observed in the mass spectrum. It is the metastable transition $m_1 \longrightarrow m_2$ occurring between the ionisation chamber and the collector which gives rise to metastable peaks in the mass spectrum.

Thus, a metastable peak, m^*, is entirely characteristic of the metastable transition which gives rise to it and the position of m^* in the mass spectrum is calculated from the equation $m^* = (m_2)^2/m_1$.

In contrast to hydrocarbon compounds, which normally give rise to positive ions on electron bombardment, the high electronegativity of fluorine would suggest that negative ions could be formed as well as positive ions on electron bombardment of fluorine containing compounds. Negative ion mass spectrometric studies have shown that this is indeed the case e.g. SF_6 and $CF_3C(O)CF_3$ both show negative ion mass spectra (197).

It has been shown (198) that the fragmentation modes of the dithioethers $R-S-(CH_2)_n-S-R$ follow closely those established for simple thioethers (199). For simple thioethers, it was found that α cleavage, β cleavage, and α, β cleavage with hydrogen rearrangement are the three important fragmentation processes. In this work, the definition of α and β cleavage given by Levy and Stahl (199) rather than that used by Budzikiewicz et al. (195) will be used, viz. :-



α cleavage $R-\overset{+\cdot}{S}-R \longrightarrow RS^{+} + R^{\cdot}$

β cleavage $R-\overset{+\cdot}{S}-C-R \longrightarrow R-\overset{+}{S}=C + R^{\cdot}$

α, β cleavage with hydrogen rearrangement $R-C-\overset{+\cdot}{S}-C-\overset{H}{C}-R \longrightarrow R^{\cdot} + C=\overset{+}{S}H + C=C-R$

(Note: a single headed arrow is used to denote a one electron transfer and a double headed arrow to denote a two electron transfer.)

Six major fragmentation pathways were established for the aliphatic thioethers (199) and these are listed in Table 1.16.

SERIES	N	ION TYPE
M-14N-1	0,1,2,3, etc.	$(CH_2)_nSH$ or R-S
M-14N	1,2,3,4, etc.	R-SH
M-14N+1	1,2,3,4, etc.	$R-SH_2$
M-14N-5	2,3,4,5.	C_nH_{2n+1}
M-14N-6	2,3,4,5.	C_nH_{2n}
M-14N-7	2,3,4,5.	C_nH_{2n-1}

Table 1.16.

The mass spectra of the bis(trifluoromethylthio)alkanes and -fluoroalkanes and related compounds are given in Table 1.17. In the case of ions containing two sulphur atoms, the ions listed refer to $S^{32}S^{32}$ contributions. Similarly, ions containing chlorine are quoted only for those containing the Cl^{35} isotope. Where more than one chlorine atom is present, characteristic isotope patterns are observed (194); e.g. :-

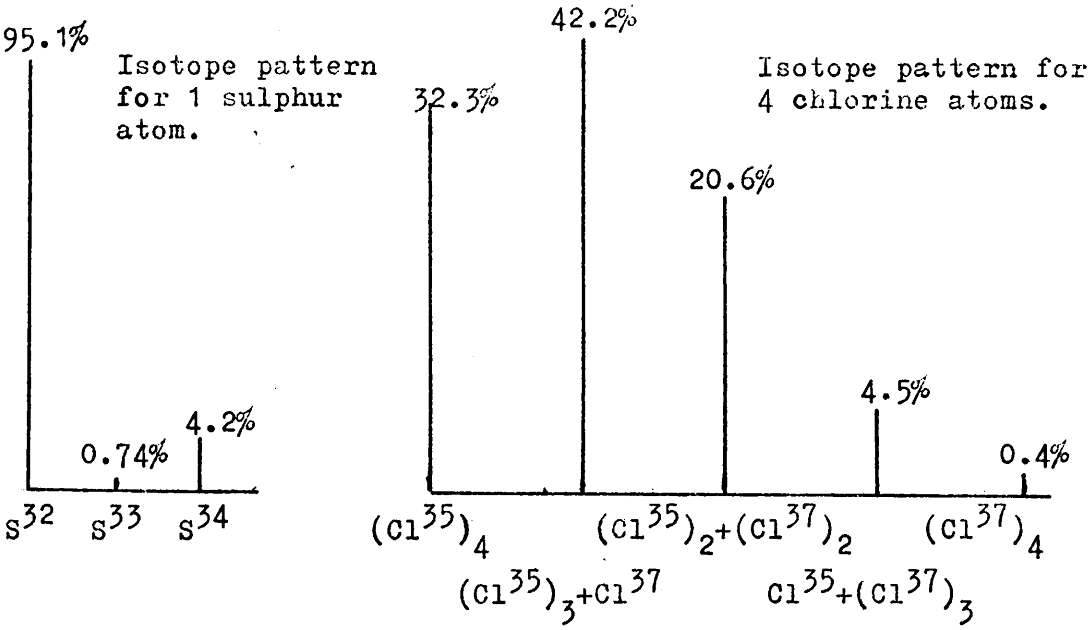


Fig. 1.10

Except for $CF_3SCCl_2CCl_2SCF_3$, all the bis(trifluoromethylthio)alkanes and -fluoroalkanes show molecular ions, as is found with aliphatic dithioethers (198) and thioethers (199), although increasing the amount of halogen with respect to hydrogen decreases the relative abundance of the molecular ion eg. $CF_3SCH_2CH_2SCF_3$ has a relative abundance of 46% for the molecular ion whilst the relative abundance of the molecular ion of $CF_3S(CF_2CF_2)_2SCF_3$ is less than 1% and the molecular ion of $CF_3SCCl_2CCl_2SCF_3$ is not observed at all. A similar trend is shown in the fluoroethanes (145) as shown in Table 1.18.

Fluoroethane	Relative abundance of Molecular Ion (%)
C_2F_6	0.15
CF_3CH_3	1.16
CFH_2CH_3	10.0

Table 1.18.

(continued on page 84)

Table 1.17

(1) $\underline{CF_3SCH_2CH_2SCF_3}$:

230, 46, $CF_3SCH_2CH_2SCF_3^+$; 161, 6, $CF_3SCH_2CH_2S^+$; 129, 72, $CF_3SCH_2CH_2^+$; 128, 10, $CF_3SC_2H_3^+$; 115, 100, $CF_3SCH_2^+$; 101, 1, CF_3S^+; 82, 5, CF_2S^+; 69, 65, CF_3^+; 63, 19, CFS^+; 60, 17, $SC_2H_4^+$; 59, 32, $SC_2H_3^+$; 58, 17, $SC_2H_2^+$; 57, 6, SC_2H^+; 47, 41, SCH_3^+; 46, 15.5, SCH_2^+; 45, 30, SCH^+; 44, 7, SC^+; 32, 5.5, S^+; 31, 4, CF^+; 28, 17, $C_2H_4^+$; 27, 26, $C_2H_3^+$; 26, 9, $C_2H_2^+$.

(2) $\underline{CF_3SCH(CH_3)CH_2SCF_3}$:

244, 28, $CF_3\ SCH(CH_3)CH_2SCF_3^+$; 175, 2, $SCH(CH_3)CH_2SCF_3^+$; 143, 8, $CF_3S(CH_2CHCH_3)^+$; 142, 32, $CF_3SC_3H_5^+$; 141, 3, $CF_3SC_3H_4^+$; 129, 100, $CF_3SCHCH_3^+$; 115, 41, $CF_3SCH_2^+$; 101, 1, CF_3S^+; 91, 6, $SCHCH_2S^+$ or $CFSCHCH_3^+$; 82, 5, CF_2S^+; 76, 2, $CFSCH^+$; 74, 5, $SCH(CH_3)CH_2^+$; 73, 12, $SC_3H_5^+$; 72, 3, $SC_3H_4^+$; 71, 6, $SC_3H_3^+$; 69, 88, CF_3^+; 63, 11, CFS^+; 61, 16, $SCH_2CH_3^+$; 60, 11, $SC_2H_4^+$; 59, 17, $SC_2H_3^+$; 58, 10, $SC_2H_2^+$; 57, 3, SC_2H^+; 47, 43, SCH_3^+; 46, 12, SCH_2^+; 45, 37, SCH^+; 44, 1, SC^+; 42, 23, $CH_3CHCH_2^+$; 41, 83, $C_3H_5^+$; 40, 7, $C_3H_4^+$; 39, 39, $C_3H_3^+$; 38, 6, $C_3H_2^+$; 37, 3, C_3H^+; 32, 7, S^+; 31, 6, CF^+; 29, 2, $CH_3CH_2^+$; 28, 15.5, $C_2H_4^+$; 27, 23.5, $C_2H_3^+$; 26, 2, $C_2H_2^+$; 15, 2, CH_3^+.

(3) $\underline{CF_3S(CF_2CF_2)_2SCF_3}$:

402, <1, $CF_3S(CF_2CF_2)_2SCF_3^+$; 333, 1, $CF_3S(CF_2CF_2)_2S^+$; 301, <1, $CF_3S(CF_2CF_2)_2^+$; 251, <1, $CF_3SCF_2CF_2CF_2^+$; 201, <1, $CF_3SCF_2CF_2^+$; 181, 1, $C_4F_7^+$; 151, 20, $CF_3SCF_2^+$; 131, 10, $C_3F_5^+$; 113, 3, $SC_2F_3^+$; 100, 9, $C_2F_4^+$; 82, 5, CF_2S^+; 69, 100, CF_3^+; 63, 13, CFS^+; 50, 1, CF_2^+; 32, 1, S^+; 31, 5, CF^+.

(5) $\underline{CF_3SCF(CF_3)CF_2SCF_3}$

352, 1, $CF_3SCF(CF_3)CF_2SCF_3^+$; 251, 10.5, $CF_3SC_3F_6^+$; 245, 3, $S_2C_4F_7^+$; 201, 1, $CF_3SCFCF_3^+$; 163, 9, $CF_3SC_2F_2^+$; 151, 39, $CF_3SCF_2^+$; 150, 2, $CF_3CFCF_2^+$; 131, 3, $C_3F_5^+$; 113, 10, $SC_2F_3^+$; 101, 2, CF_3S^+; 100, 5.5, $CFCF_3^+$; 94, 3, $SC_2F_2^+$; 82, 6.5, CF_2S^+; 69, 100, CF_3^+; 63, 23, CFS^+; 50, 1, CF_2^+; 32, 1, S^+; 31, 6, CF^+.

Table 1.17 (cont.)

(6) $\underline{CF_3S[CF_2CF(CF_3)]_2SCF_3}$:

502, 1, $CF_3S[CF_2CF(CF_3)]_2SCF_3^+$ (M^+); 433, 8, $(M-CF_3)^+$; 401, 2, $(M-CF_3S)^+$; 395, 2, ($M-CF_3$ and 2F$)^+$; 313, 1, $CF_3SCF_2CF(CF_3)CF{=}CF^+$; 181, 4, $C_4F_7^+$; 151, 10, $CF_3SCF_2^+$; 150, 1, $C_3F_6^+$; 144, 1, $SC_3F_4^+$; 131, 5, $C_3F_5^+$; 113, 3, $SC_2F_3^+$; 100, 3, $CFCF_3^+$; 93, 1.5, $C_3F_3^+$; 82, 5.5, CF_2S^+; 69, 100, CF_3^+; 63, 20, CFS^+; 32, 2, S^+; 31, 1, CF^+.

(7) $\underline{CF_3SCF_2CH_2SCF_3}$:

266, 11, $CF_3SCF_2CH_2SCF_3^+$; 165, 64.5, $CF_3S(CF_2CH_2)^+$; 151, 4, $CF_3SCF_2^+$; 145, 9, CF_3SCHCF^+; 127, 6, $SC_3H_2F_3^+$; 115, 41, $CF_3SCH_2^+$; 114, 1, CF_3SCH^+; 113, 12, CF_3SC^+; 101, 3.5, CF_3S^+; 96, 8, $S(CH_2CF_2)^+$; 95, 7, $S(CHCF_2)^+$; 94, 2, $SC_2F_2^+$; 83, 5, CF_2SH^+; 82, 9, CF_2S^+; 77, 23, $SC_2H_2F^+$; 76, 2, SC_2HF; 75, 1, SC_2F^+; 69, 100, CF_3^+; 64, 26, $CF_2CH_2^+$; 63, 24, CFS^+ or CF_2CH^+; 58, 4, $SC_2H_2^+$; 57, 4, SC_2H^+; 51, 4.5, SF^+; 50, 5, CF_2^+; 47, 13, SCH_3^+; 46, 23, SCH_2^+; 45, 44.5, SCH^+ or $CFCH_2^+$; 44, 5, SC^+ or $CFCH^+$; 33, 8, SH^+; 32, 4.5, S^+; 31, 11, CF^+.

(8) $\underline{CF_3S(CF_2CH_2)_2SCF_3}$:

330, 8, $CF_3S(CF_2CH_2)_2SCF_3^+$ (M^+); 310, 11, $(M-HF)^+$; 261, 13, $CF_3S(CF_2CH_2)_2S^+$ 229, 14, $CF_3S(CF_2CH_2)_2^+$; 209, 9, $CF_3S(CH_2CF_2)(CH{=}CF)^+$; 195, 21, $CF_3S(CH{=}CF)CF_2^+$; 192, 8, $S(CF_2CH_2)_2S^+$; 165, 17, $CF_3S(CF_2CH_2)^+$; 164, 3, $CF_3S(CF_2CH)^+$; 159, 5.5, $S{=}CHCF_2CF_2CH_2^+$; 151, 1, $CF_3SCF_2^+$; 145, 5, $CF_3S(CH{=}CF)^+$; 141, 1.5, $S(CFCH_2)(CF_2CH_2)^+$; 127, 5, $SC_3H_2F_3^+$; 121, 1, $SC_4H_3F_2^+$; 115, 100, $CF_3SCH_2^+$; 113, 7, $SC_2F_3^+$; 100, 1, $CF_2CF_2^+$; 96, 5, $S(CH_2CF_2)^+$; 95, 8, $S(CHCF_2)^+$; 82, 3, CF_2S^+; 77, 13, $S(CH_2CF)^+$; 76, 3, $S(CFCH)$; 69, 72.5, CF_3^+; 64, 15, $CF_2CH_2^+$; 63, 16.5, CFS^+ or CF_2CH^+; 51, 4, SF^+; 50, 1, CF_2^+; 47, 3, SCH_3^+; 46, 19, SCH_2^+; 45, 32, SCH^+ or $CFCH_2^+$; 44, 2, SC^+ or $CFCH^+$; 33, 5, SH^+; 32, 1.5, S^+; 31, 4, CF^+.

Table 1.17 (cont.)

(9) $CF_3S(CF_2CH_2)_3SCF_3$

394, 4, $CF_3S(CF_2CH_2)_3SCF_3^+$ (M^+); 375, 2.5, $(M-F)^+$; 374, 13, $(M-HF)^+$; 355, 6, $(M-H,2F)^+$; 354, 3, $(M-2HF)^+$; 335, 2, $(M-2H,3F)^+$; 325, 1, $(M-CF_3)^+$; 305, 4, $(M-CF_3,HF)^+$; 293, 2, $(M-CF_3S)^+$; 285, 1, $(M-CF_3,2HF)^+$; 279, 1, $(M-CF_3SCH_2)^+$; 273, 6, $(M-CF_3S,HF)^+$; 259, 2, $(M-CF_3SCH_2,HF)^+$; 253, 2, $(M-CF_3S,2HF)^+$; 229, 1, $CF_3S(CF_2CH_2)_2^+$; 215, <1, $CF_3S(CF_2CH_2)CF_2^+$; 209, 4, $CF_3S(CH{=}CF)(CH_2CF_2)^+$; 195, <1, $CF_3SCH{=}CFCF_2^+$; 189, 1, $CF_3S(CH{=}CF)_2^+$; 179, <1, $CF_3SCH_2CF_2CH_2^+$; 165, 14.5, $CF_3S(CH_2CF_2)^+$; 159, 5, $CF_3SCH{=}CFCH_2^+$; 151, 2.5, $CF_3SCF_2^+$; 145, 4, $CF_3S(CH{=}CF)^+$; 141, 1, $SC_4H_4F_3^+$; 139, 3, $SC_4H_2F_3^+$; 127, 7, $SC_3H_2F_3^+$; 121, 3, $SC_4H_3F_2^+$; 115, 100, $CF_3SCH_2^+$; 113, 16, $SC_2F_3^+$; 108, 2, $CF_2CH_2CF{=}CH^+$; 107, 1, $CF_2CHCF{=}CH^+$; 101, 2, CF_3S^+; 100, <1, $CF_2CF_2^+$; 96, 2, $S(CH_2CF_2)^+$; 95, 11, $S(CHCF_2)^+$; 89, 3, $CFCH_2CF{=}CH^+$; 82, 3, CF_2S^+; 77, 24, $S(CH_2CF)^+$; 76, 1, $S(CH{=}CF)^+$; 75, 2, SC_2F^+; 69, 44, CF_3^+; 64, 4, $CF_2CH_2^+$; 63, 10, CF_2CH^+ or CFS^+; 59, 4, $CH_2CFCH_2^+$; 57, 2, $CHCFCH^+$; 51, 5, SF^+; 50, 1.5, CF_2^+; 47, 4, SCH_3^+; 46, 11, SCH_2^+; 45, 19, SCH^+; 44, 3, CFCH or SC^+; 39, 4, $C_3H_4^+$; 33, 3, SH^+; 32, 3, S^+; 31, 2.5, CF^+.

(10) $CF_3S(CF_2CH_2)_4SCF_3$:

458, 4, $CF_3S(CF_2CH_2)_4SCF_3$ (M^+); 438, 5.5, $(M-HF)^+$; 419, 1.5, $(M-H,2F)^+$; 389, 10.5, $(M-CF_3)^+$; 357, 7, $(M-CF_3S)^+$; 343, 2, $CF_3S(CF_2CH_2)_3CF_2^+$; 337, 3, $(M-CF_3S,HF)^+$; 323, 16, $(M-CF_3SCH_2,HF)^+$; 320, 2, $S(CF_2CH_2)_4S^+$; 293, 2, $CF_3S(CF_2CH_2)_3^+$; 279, 1, $CF_3S(CF_2CH_2)_2CF_2^+$; 273, 6, $C_7H_5F_8S^+$; 259, 2, $C_6H_3F_8S^+$; 253, 2, $CF_3S(CH_2CF_2)(CH{=}CF)_2^+$; 229, 1, $CF_3S(CH_2CF_2)_2^+$; 223, 5.5, $CF_3S(CH_2CF_2)(CH{=}CF)CH_2^+$; 215, <1, $CF_3S(CH_2CF_2)CF_2^+$; 209, 4, $CF_3S(CH_2CF_2)(CH{=}CF)^+$; 203, 4, $CF_3S(CH{=}CF)_2CH_2^+$; 189, 1, $CF_3S(CH{=}CF)_2^+$; 179, <1, $CF_3SCH_2CF_2CH_2^+$; 165, 14, $CF_3S(CH_2CF_2)^+$; 159, 5, $CF_3SCH{=}CFCH_2^+$; 151, 3.5, $CF_3SCF_2^+$; 145, 3.5, $CF_3S(CHCF)^+$; 141, 1, $SCH_2CFCH_2CF_2^+$; 139, 3, $SCH{=}CFCHCF_2^+$; 127, 7, $SC_3H_2F_3^+$; 121, 2, $SCH{=}CFCH_2CF^+$; 115, 100, $CF_3SCH_2^+$; 113, 15, $SC_2F_3^+$; 108, 2, $CF_2CH_2CF{=}CH^+$; 107, 1, $CF_2CHCF{=}CH^+$; 101, 2, CF_3S^+; 100, <1, $CF_2CF_2^+$; 96, 2, $S(CH_2CF_2)^+$; 95, 11, $S(CHCF_2)^+$; 89, 3, $CFCH_2CF{=}CH^+$; 82, 3, CF_2S^+; 77, 10.5, $S(CH_2CF)^+$; 76, 1, $S(CH{=}CF)^+$; 75, 2, SC_2F^+; 69, 44, CF_3^+; 64, 15, $CF_2CH_2^+$; 63, 10, CF_2CH^+ or CFS^+; 59, 4, $CH_2CFCH_2^+$; 57, 2, $CHCFCH^+$; 51, 5, SF^+; 50, 1, CF_2^+; 47, 4, SCH_3^+; 46, 11, SCH_2^+; 45, 17.5, SCH^+ or CH_2CF^+; 44, 3, SC^+ or $CHCF^+$; 39, 4, $C_3H_3^+$; 33, 2, SH^+; 32, 3, S^+; 31, 2, CF^+.

Table 1.17 (cont.)

(11) $\underline{CF_3S(CF_2CH_2)_5SCF_3}$:

522, 5, $CF_3S(CF_2CH_2)_5SCF_3^+$ (M^+); 502, 8, $(M-HF)^+$; 483, 5, $(M-H,2F)^+$; 463, 2, $(M-2HF,F)^+$; 453, 1, $(M-CF_3)^+$; 433, 1, $(M-CF_3,HF)^+$; 421, <1, $(M-CF_3S)^+$; 407, <1, $(M-CF_3SCH_2)^+$; 401, 3, $(M-CF_3S,HF)^+$; 387, 6, $(M-CF_3SCH_2,HF)^+$; 381, 1.5, $(M-CF_3S,2HF)^+$; 375, 2, $(M-CF_3,2HF,F_2)^+$; 367, 3, $(M-CF_3SCH_2,2HF)^+$; 357, <1, $(M-CF_3SCH_2CF_2)^+$; 343, <1, $CF_3S(CF_2CH_2)_3CF_2^+$; 337, 2, $(M-CF_3SCH_2CF_2;HF)^+$; 323, 3, $CF_3S(CF_2CH_2)_2(CF{=}CH)CF_2^+$; 293, 1, $CF_3S(CH_2CF_2)_3^+$; 279, <1, $CF_3S(CF_2CH_2)_2CF_2^+$; 273, 4, $CF_3S(CH_2CF_2)_2(CH{=}CF)^+$; 259, 4, $CF_3S(CH_2CF_2)(CH{=}CF)CF_2^+$; 243, <1, $CF_3S(CH_2CF_2)_2CH_2^+$; 229, 3, $CF_3S(CH_2CF_2)_2^+$; 223, 1, $CF_3S(CH_2CF_2)(CH{=}CF)CH_2^+$; 215, <1, $CF_3S(CH_2CF_2)CF_2^+$; 209, 6, $CF_3S(CH_2CF_2)(CH{=}CF)^+$; 203, 2, $CF_3S(CH{=}CF)_2CH_2^+$; 195, 1, $CF_3S(CH{=}CF)CF_2^+$; 179, 2, $CF_3SCH_2CF_2CH_2^+$; 165, 13, $CF_3S(CH_2CF_2)^+$; 164, 4, $CF_3S(CHCF_2)^+$ or $CF_2CF_2CH_2CF_2^+$; 159, 8, $CF_3SCH{=}CFCH_2^+$; 145, 3, $CF_3S(CH{=}CF)^+$; 141, 1, $SCH_2CFCH_2CF_2^+$; 140, <1, $SCH{=}CFCH_2CF_2^+$; 139, 2, $SCH{=}CFCHCF_2^+$; 127, 6, $SC_3H_2F_3^+$; 121, 2, $SCH{=}CFCH_2CF^+$; 115, 100, $CF_3SCH_2^+$; 113, 20, $SC_2F_3^+$; 109, 8, $CF_2CH_2CFCH_2^+$; 108, 2, $CF_2CH_2CF{=}CH^+$; 101, 1, CF_3S^+; 100, <1, $CF_2CF_2^+$; 96, 1, $S(CH_2CF_2)^+$; 95, 12, $S(CHCF_2)^+$; 89, 3, $CFCH_2CF{=}CH^+$; 82, 4, CF_2S^+; 77, 8, $S(CH_2CF)^+$; 76, 1, $S(CH{=}CF)^+$; 75, 1, SC_2F^+; 69, 30, CF_3^+; 64, 14, $CF_2CH_2^+$; 63, 5, CF_2CH^+ or CFS^+; 59, 4, $CH_2CFCH_2^+$; 57, 1, $CHCFCH^+$; 51, 4, SF^+; 50, 1.5, CF_2^+; 47, 3, SCH_3^+; 46, 5, SCH_2^+; 45, 10, SCH^+ or CH_2CF^+; 44, 2, SC^+ or $CHCF^+$; 33, 2, SH^+; 32, 2, S^+; 31, 2, CF^+.

Table 1.17 (cont.)

(12) $\mathrm{CF_3S(CF_2CH_2)_6SCF_3}$:

586, 4.5, $\mathrm{CF_3S(CF_2CH_2)_6SCF_3^+}$ $(\mathrm{M^+})$; 566, 11, $\mathrm{(M{-}HF)^+}$; 547, 7, $\mathrm{(M{-}H,2F)^+}$;
546, 2, $\mathrm{(M{-}2HF)^+}$; 517, 5, $\mathrm{(M{-}CF_3)^+}$; 485, <1, $\mathrm{(M{-}CF_3S)^+}$; 471, <1;
$\mathrm{(M{-}CF_3SCH_2)^+}$; 451, 2.5, $\mathrm{(M{-}CF_3SCH_2,HF)^+}$; 431, 2, $\mathrm{(M{-}CF_3SCH_2,2HF)^+}$;
421, <1, $\mathrm{(M{-}CF_3SCH_2CF_2)^+}$; 407, <1, $\mathrm{(M{-}CF_3SCH_2CF_2CH_2)^+}$; 401, 3,
$\mathrm{(M{-}CF_3SCH_2CF_2,HF)^+}$; 387, 5, $\mathrm{(M{-}CF_3SCH_2CF_2CH_2,HF)^+}$; 381, 1,
$\mathrm{(M{-}CF_3SCH_2CF_2,2HF)^+}$; 367, 2, $\mathrm{(M{-}CF_3SCH_2CF_2CH_2,2HF)^+}$; 357, <1,
$\mathrm{CF_3S(CH_2CF_2)_4^+}$; 343, <1, $\mathrm{CF_3S(CH_2CF_2)_3CF_2^+}$; 323, 3, $\mathrm{CF_3S(CH_2CF_2)_2(CH{=}CF)CF_2^+}$;
293, 1, $\mathrm{CF_3S(CH_2CF_2)_3^+}$; 279, 1, $\mathrm{CF_3S(CH_2CF_2)_2CF_2^+}$; 273, 4,
$\mathrm{CF_3S(CH_2CF_2)_2(CH{=}CF)^+}$; 259, 3, $\mathrm{CF_3S(CH_2CF_2)(CH{=}CF)CF_2^+}$; 243, <1,
$\mathrm{CF_3S(CH_2CF_2)_2CH_2^+}$; 229, 3, $\mathrm{CF_3S(CH_2CF_2)_2^+}$; 223, 1, $\mathrm{CF_3S(CH_2CF_2)(CH{=}CF)CH_2^+}$;
209, 6, $\mathrm{CF_3S(CH_2CF_2)(CH{=}CF)^+}$; 203, 2, $\mathrm{CF_3S(CH{=}CF)_2CH_2^+}$; 179, 2,
$\mathrm{CF_3SCH_2CF_2CH_2^+}$; 165, 13, $\mathrm{CF_3S(CH_2CF_2)^+}$; 164, 4, $\mathrm{CF_3S(CHCF_2)^+}$ or
$\mathrm{CF_2CF_2CH_2CF_2^+}$; 159, 8, $\mathrm{CF_3SCH{=}CFCH_2^+}$; 145, 3, $\mathrm{CF_3SCH{=}CF^+}$; 141, 1,
$\mathrm{SCH_2CFCH_2CF_2^+}$; 139, 2, $\mathrm{SCH{=}CFCHCF_2^+}$; 127, 6, $\mathrm{SC_3H_2F_3^+}$; 121, 2,
$\mathrm{SCH{=}CFCH_2CF^+}$; 115, 100, $\mathrm{CF_3SCH_2^+}$; 113, 18, $\mathrm{CF_3SC^+}$; 109, 4.5, $\mathrm{CF_2CH_2CFCH_2^+}$;
108, 2, $\mathrm{CF_2CH_2CFCH^+}$; 101, 1, $\mathrm{CF_3S^+}$; 95, 11, $\mathrm{SCHCF_2^+}$; 91, 1, $\mathrm{SCH_2CFCH_2^+}$;
89, 3, $\mathrm{CFCH_2CFCH^+}$; 82, 3, $\mathrm{CF_2S^+}$; 77, 8, $\mathrm{SCH_2CF^+}$; 76, 1, $\mathrm{SCH{=}CF^+}$;
75, 1, $\mathrm{SCCF^+}$; 69, 27, $\mathrm{CF_3^+}$; 64, 13, $\mathrm{CF_2CH_2^+}$; 63, 4.5, $\mathrm{CF_2CH^+}$ or $\mathrm{CFS^+}$;
59, 4, $\mathrm{CH_2CFCH_2^+}$; 57, 1, $\mathrm{CFCHCF^+}$; 51, 4, $\mathrm{SF^+}$; 50, 1, $\mathrm{CF_2^+}$; 47, 3,
$\mathrm{SCH_3^+}$; 46, 4.5, $\mathrm{SCH_2^+}$; 45, 9, $\mathrm{SCH^+}$ or $\mathrm{CH_2CF^+}$; 44, 2, $\mathrm{SC^+}$ or $\mathrm{CH{=}CF^+}$;
33, 2, $\mathrm{SH^+}$; 32, 2, $\mathrm{S^+}$; 31, 1, $\mathrm{CF^+}$.

Table 1.17 (cont.)

(13) $\underline{CF_3SCF_2CFHSCF_3}$:

284, 1, $CF_3SCF_2CFHSCF_3^+$; 196, 27, $CF_3SCFHCF{=}S^+$; 183, 5, $CF_3S(CF_2CFH)^+$; 177, 10, $CF_3S(CF{=}CH)S^+$; 163, 3, $CF_3SCF{=}CF^+$; 157, 5, CF_3SCCS^+; 151, 14, $CF_3SCF_2^+$; 145, 3, $CF_3S(CFCH)^+$; 133, 23, CF_3SCFH^+; 132, 3, CF_3SCF^+; 127, 2, $SCFHCFS^+$; 114, 4, CF_3SCH^+; 113, 41, CF_3SC^+; 107, 6, $SCFCS^+$; 101, 5, CF_3S^+; 95, 36, $SC_2F_2H^+$; 94, 5, $SC_2F_2^+$; 87, 2, SC_3F^+; 83, 3, $SCHF_2^+$; 82, 53, CF_2S^+ or CF_2CFH^+; 76, 5, SC_2FH^+; 75, 9, SC_2F^+; 69, 78, CF_3^+; 64, 35, $SCFH^+$; 63, 36, SCF^+; 57, 3, SC_2H^+; 56, 2, SC_2^+; 51, 30, SF^+; 50, 3, CF_2^+; 45, 100, SCH^+; 44, 4.5, SC^+ or C_2FH^+; 32, 3, S^+ or CFH^+; 31, 20.5, CF^+.

(14) $\underline{CF_3S(CF_2CFH)_2SCF_3}$:

366, 4, $CF_3S(CF_2CFH)_2SCF_3^+$; 297, 6, $CF_3S(CF_2CFH)_2S^+$; 277, <1, $CF_3S(CF_2CFH)(CF{=}CF)S^+$; 265, 3, $CF_3S(CF_2CFH)_2^+$; 259, 1, $CF_3S(CF_2CFH)(CF{=}CH)S^+$; 233, 2, $CF_3S(CF_2CFH)CF_2^+$; 227, 1, $CF_3S(CF_2CFH)(CF{=}CH)^+$; 213, 2, $CF_3SC_3F_4^+$; 209, 1, $S(CF_2CFH)CFHCF{=}S^+$; 196, 2, $CF_3SCFHCF_2CH^+$; 195, 3, $CF_3S(CF{=}CH)CF_2^+$; 183, 6, $CF_3S(CFHCF_2)^+$; 177, 9, $S(CFCFH)(CF_2CFH)^+$; 164, 2, $CF_3S(CFHCF)^+$; 163, 3, $CF_3SCF{=}CF^+$; 151, 14, $CF_3SCF_2^+$; 145, 4, $CF_3S(CF{=}CH)^+$; 133, 50, CF_3SCFH^+; 132, 1, $(CF_2CFH)CF_2^+$ or CF_3SCF^+; 131, 2, $CF_2CFCF_2^+$; 114, 1, SC_2HF_3 or $C_3H_2F_4^+$; 113, 14, $SC_2F_3^+$; 107, 2, $SC_3HF_2^+$; 101, 6, CF_3S^+; 95, 16, $SC_2F_2H^+$; 94, 2, $SC_2F_2^+$; 83, 1, $SCHF_2^+$; 82, 16, CF_2S^+ or CF_2CFH^+; 76, 2, $C_3H_2F_2^+$ or SC_2FH^+; 75, 3, $C_3HF_2^+$ or SC_2F^+; 69, 100, CF_3^+; 64, 7, $SCFH^+$; 63, 7, CFS^+ or $C_2F_2H^+$; 57, 16, $C_3FH_2^+$ or SC_2H^+; 51, 20, SF^+; 45, 42, SCH^+; 32, 2, S^+ or CFH^+; 31, 5, CF^+.

Table 1.17 (cont.)

(15) $CF_3S(CF_2CFH)_3SCF_3$:

448, 1, $CF_3S(CF_2CFH)_3SCF_3^+$ (M^+); 429, 1, $(M-F)^+$; 428, 1, $(M-HF)^+$; 379, 1, $(M-CF_3)^+$; 347, 2, $CF_3S(CF_2CFH)_3^+$; 315, 1, $CF_3S(CF_2CFH)_2CF_2^+$; 309, 2, $CF_3S(CF_2CFH)_2(CF{=}CH)^+$; 297, <1, $CF_3S(CF_2CFH)_2CFH^+$; 295, 3, $CF_3S(CF_2CFH)(CF{=}CF)CF_2^+$; 265, 2, $CF_3S(CFHCF_2)_2^+$; 259, 2, $CF_3S(CFHCF_2)(CH{=}CF)CFH^+$; 245, 1.5, $CF_3S(CFHCF_2)(CF{=}CF)^+$; 233, 3, $CF_3S(CF_2CFH)CF_2^+$; 227, 1, $CF_3S(CF_2CFH)(CF{=}CH)^+$; 213, 2, $CF_3S(CF{=}CF)CF_2^+$; 195, 2, $CF_3S(CF{=}CH)CF_2^+$; 183, 9, $CF_3S(CF_2CFH)^+$; 177, 5, $S(CFCFH)(CF_2CFH)^+$ or $C_5H_3F_6^+$; 164, 1.5, $CF_3S(CFHCF)^+$; 163, 3, $CF_3SCF{=}CF^+$; 151, 18, $CF_3SCF_2^+$; 145, 5.5, $CF_3S(CF{=}CH)^+$; 133, 91.5, CF_3SCFH^+; 131, 2, $CF_2CFCF_2^+$; 113, 15.5, $SC_2F_3^+$ or $C_3HF_4^+$; 107, 1, $SC_3HF_2^+$ or $C_4H_2F_3^+$; 101, 7, CF_3S^+; 100, 1, $CF_2CF_2^+$; 95, 16, $SC_2F_2H^+$ or $C_3H_2F_3^+$; 94, 1, $SC_2F_2^+$ or $C_3HF_3^+$; 83, 2, $SCHF_2^+$; 82, 14, CF_2S^+ or CF_2CFH^+; 76, 2, SC_2FH or $C_3H_2F_2^+$; 75, 3, SC_2F^+ or $C_3HF_2^+$; 69, 100, CF_3^+; 64, 6, $SCFH^+$; 63, 14, CFS^+ or $CFHCF^+$; 51, 22, SF^+; 50, 1, CF_2^+; 45, 40, SCH^+; 32, 2, CFH^+ or S^+; 31, 5, CF^+.

(16) $CF_3S(CF_2CFH)_4SCF_3$

530, 1, $CF_3S(CF_2CFH)_4SCF_3^+$ (M^+); 511, 1, $(M-F)^+$; 429, 3, $(M-CF_3S)^+$; 409, <1, $(M-CF_3S,HF)^+$; 397, 3, $CF_3S(CF_2CFH)_3CF_2^+$; 391, 3, $(M-CF_3S,2F)^+$; 379, 2, $CF_3S(CF_2CFH)_3CFH^+$; 347, 1, $CF_3S(CF_2CFH)_3^+$; 315, <1, $CF_3S(CF_2CFH)_2CF_2^+$; 309, 1, $CF_3S(CF_2CFH)_2(CH{=}CF)^+$; 297, 2, $CF_3S(CF_2CFH)_2CFH^+$; 277, 1, $CF_3S(CF_2CFH)(CF{=}CF)CFH^+$; 265, 2, $CF_3S(CF_2CFH)_2^+$; 259, 2, $CF_3S(CF_2CFH)(CH{=}CF)CFH^+$; 245, 1, $CF_3S(CF_2CFH)(CF{=}CF)^+$; 233, 4, $CF_3S(CF_2CFH)CF_2^+$; 227, 2, $CF_3S(CF_2CFH)(CH{=}CF)^+$; 213, 3, $CF_3SCF_2(CF{=}CF)^+$; 195, 3, $CF_3SCF_2(CH{=}CF)^+$; 183, 12, $CF_3S(CF_2CFH)^+$; 177, 7, $C_4H_2F_5S^+$ or $C_5H_3F_6^+$; 164, 2, $CF_3S(CFHCF)^+$; 163, 5, $CF_3SCF{=}CF^+$; 151, 20, $CF_3SCF_2^+$; 145, 7, $CF_3S(CF{=}CH)^+$; 133, 68, CF_3SCFH^+; 132, 3, CF_3SCF^+ or $CF_2CFHCF_2^+$; 131, 4, $CF_2CFCF_2^+$; 114, 11, $C_2HF_3S^+$ or $C_3H_2F_4^+$; 113, 28, $C_2F_3S^+$ or $C_3HF_4^+$; 107, 3, $SC_3HF_2^+$ or $C_4H_2F_3^+$; 101, 9, CF_3S^+; 100, 2, $CF_2CF_2^+$; 95, 28, SCF_2CH^+ or $CFHCF_2CH^+$; 94, 2, $SC_2F_2^+$ or $C_3HF_3^+$; 93, 2, $C_3F_3^+$; 83, 2, CF_2HS^+; 82, 27, CF_2S^+ or CF_2CFH^+; 76, 3, $SCFCH^+$ or $C_3H_2F_2^+$; 75, 5, SC_2F^+ or $C_3HF_2^+$; 69, 100, CF_3^+; 64, 16.5, $SCFH^+$; 63, 22, CFS^+ or $CFHCF^+$; 51, 22, SF^+; 50, 4, CF_2^+; 45, 55, CHS^+; 44, 8, CS^+; 32, 5, CFH^+ or S^+; 31, 17, CF^+.

Table 1.17 (cont.)

(17) $\underline{CF_3S(CF_2CFH)_5SCF_3}$:
+(18) $\underline{CF_3S(CF_2CFH)_6SCF_3}$:
+(19) $\underline{CF_3S(CF_2CFH)_7SCF_3}$:

776, <1, $CF_3S(CF_2CFH)_7SCF_3^+$ (M_1^+); 757, <1, $(M_1-F)^+$; 694, 1, $CF_3S(CF_2CFH)_6SCF_3^+$; 675, 2, $CF_3S(CF_2CFH)_7^+$; 655, <1, $CF_3S(CF_2CFH)_6(CF=CF)^+$; 643, 2, $CF_3S(CF_2CFH)_6CF_2^+$; 637, <1, $CF_3S(CF_2CFH)_6(CH=CF)^+$; 625, <1, $CF_3S(CF_2CFH)_6CFH^+$; 623, <1, $CF_3S(CF_2CFH)_5(CF=CF)CF_2^+$; 612, 1, $CF_3S(CF_2CFH)_5SCF_3^+$; 605, <1, $CF_3S(CF_2CFH)_5(CF=CH)CF_2^+$; 593, 1, $CF_3S(CF_2CFH)_6^+$ 573, <1, $CF_3S(CF_2CFH)_5(CF=CF)^+$; 561, <1, $CF_3S(CF_2CFH)_5CF_2^+$; 555, <1, $CF_3S(CF_2CFH)_5(CH=CF)^+$; 541, <1, $CF_3S(CF_2CFH)_4(CF=CF)CF_2^+$; 523, <1, $CF_3S(CF_2CFH)_4(CH=CF)CF_2^+$; 511, <1, $CF_3S(CF_2CFH)_5^+$; 491, <1, $CF_3S(CF_2CFH)_4(CF=CF)^+$; 479, <1, $CF_3S(CF_2CFH)_4CF_2^+$; 473, 1, $CF_3S(CF_2CFH)_4(CH=CF)^+$; 459, <1, $CF_3S(CF_2CFH)_3(CF=CF)CF_2^+$; 441, <1, $CF_3S(CF_2CFH)_3(CH=CF)CF_2^+$; 429, <1, $CF_3S(CF_2CFH)_4^+$; 423, <1, $CF_3S(CF_2CFH)_3(CH=CF)CFH^+$; 409, <1, $CF_3S(CF_2CFH)_3(CF=CF)^+$; 397, <1, $CF_3S(CF_2CFH)_3CF_2^+$; 391, <1, $CF_3S(CF_2CFH)_3(CF=CH)^+$; 347, <1, $CF_3S(CF_2CFH)_3^+$; 315, <1, $CF_3S(CF_2CFH)_2CF_2^+$; 309, <1, $CF_3S(CF_2CFH)_2(CH=CF)^+$; 295, 1, $CF_3S(CF_2CFH)(CF=CF)CF_2^+$; 277, <1, $CF_3S(CF_2CFH)(CF=CF)CFH^+$; 265, 1, $CF_3S(CF_2CFH)_2^+$; 259, <1, $CF_3S(CF_2CFH)(CH=CF)CFH^+$; 245, 2, $CF_3S(CF_2CFH)(CF=CF)^+$; 233, 7, $CF_3S(CF_2CFH)CF_2^+$; 227, 2, $CF_3S(CF_2CFH)(CH=CF)^+$; 213, 3, $CF_3SCF_2(CF=CF)^+$; 195, 3, $CF_3SCF_2(CH=CF)^+$; 183, 15, $CF_3S(CF_2CFH)^+$; 177, 2.5, $C_4H_2F_5S^+$ or $C_5H_3F_6^+$; 164, 1.5, $CF_3S(CFHCF)^+$; 163, 5, $CF_3SCF=CF^+$; 151, 19, $CF_3SCF_2^+$; 145, 9, $CF_3S(CF=CH)^+$; 133, 100, CF_3SCFH^+; 131, 5, $CF_2CFCF_2^+$; 114, 1, $C_2HF_3S^+$ or $C_3H_2F_4^+$; 113, 20, $C_2F_3S^+$ or $C_3HF_4^+$; 107, 1, $SC_3HF_2^+$ or $C_4H_2F_3^+$; 101, 4, CF_3S^+; 100, 1, $CF_2CF_2^+$; 95, 22, SCF_2CH^+ or $CFHCF_2CH^+$; 94, <1, $SC_2F_2^+$ or $C_3HF_3^+$; 93, <1, $C_3F_3^+$; 83, 1, CF_2HS^+; 82, 11, CF_2S^+ or CF_2CFH^+; 75, 2, SC_2F^+ or $C_3HF_2^+$; 69, 49, CF_3^+; 64, 2, $SCFH^+$; 63, 6, CFS^+ or $CFHCF^+$; 51, 13, SF^+; 50, 14, CF_2^+; 45, 2, CHS^+; 44, 2, CS^+; 32, 2, CFH^+ or S^+; 31, 3, CF^+.

Table 1.17 (cont.)

(20) $\underline{\overline{\mathrm{CF_2CFClCF_2CFClS}}}$:

264, 22, $\overline{\mathrm{CF_2CFClCF_2CFClS}}^+$ ($\mathrm{M^+}$); 245, 3, $\mathrm{(M-F)^+}$; 232, 2, $\mathrm{CF_2CFClCF_2CFCl^+}$; 229, 61, $\mathrm{(M-Cl)^+}$; 213, 1, $\mathrm{C_4F_5Cl_2^+}$; 182, 25, $\mathrm{CFClCF_2CFCl^+}$; 163, 3, $\mathrm{C_3F_3Cl_2^+}$; 148, 5, $\mathrm{S(CF_2CFCl)^+}$; 147, 85.5, $\mathrm{C_3F_4Cl^+}$; 144, 1.5, $\mathrm{C_3F_4S^+}$; 143, 1.5, $\mathrm{C_4F_5^+}$; 131, 54.5, $\mathrm{C_3F_5^+}$; 125, 5, $\mathrm{C_3F_3S^+}$; 116, 32, $\mathrm{CF_2CFCl^+}$; 113, 33, $\mathrm{C_2F_3S^+}$; 112, 3, $\mathrm{C_3F_4^+}$; 110, 2, $\mathrm{C_2FClS^+}$; 109, 4, $\mathrm{C_3F_2Cl^+}$; 106, 2, $\mathrm{C_3F_2S^+}$; 98, 26, $\mathrm{CFClS^+}$; 97, 2.5, $\mathrm{C_2F_2Cl^+}$; 94, 8, $\mathrm{C_2F_2S^+}$; 93, 15, $\mathrm{C_3F_3^+}$; 85, 31, $\mathrm{CF_2Cl^+}$; 82, 7, $\mathrm{CF_2S^+}$; 81, 11, $\mathrm{C_2F_3^+}$; 79, 27, $\mathrm{CClS^+}$; 74, 5, $\mathrm{C_3F_2^+}$; 69, 62, $\mathrm{CF_3^+}$; 66, 8.5, $\mathrm{CFCl^+}$; 63, 100, $\mathrm{CFS^+}$; 56, 1, $\mathrm{C_2S^+}$; 50, 5, $\mathrm{CF_2^+}$; 47, 6, $\mathrm{CCl^+}$; 44, 7, $\mathrm{SC^+}$; 35, 4, $\mathrm{Cl^+}$; 32, 4, $\mathrm{S^+}$; 31, 39, $\mathrm{CF^+}$.

(21) $\underline{\mathrm{CF_3SCF_2CFClCF_3}}$:

286, 2, $\mathrm{CF_3SCF_2CFClCF_3^+}$; 251, < 1, $\mathrm{CF_3SCF_2CFCF_3^+}$; 217, < 1, $\mathrm{CF_3SCF_2CFCl^+}$; 185, 28, $\mathrm{CF_2CFClCF_3^+}$; 182, 2, $\mathrm{CF_3SCF_2CF^+}$; 166, 1.5, $\mathrm{CF_3CFClCF^+}$; 163, <1, $\mathrm{CF_3SCFCF^+}$; 151, 37, $\mathrm{CF_3SCF_2^+}$; 147, 8, $\mathrm{CF_3CCl{=}CF^+}$; 135, 22, $\mathrm{CF_3CFCl}$; 132, 15, $\mathrm{CF_3SCF^+}$; 131, 55, $\mathrm{C_3F_5^+}$; 116, 4, $\mathrm{CF_2CFCl^+}$; 113, 4, $\mathrm{C_2F_3S^+}$; 101, 6.5, $\mathrm{CF_3S^+}$; 100, 29, $\mathrm{CF_3CF^+}$; 98, 3, $\mathrm{SCFCl^+}$; 85, 4, $\mathrm{CF_2Cl^+}$; 82, 1, $\mathrm{CF_2S^+}$; 81, 1, $\mathrm{CF_2CF^+}$; 79, 3.5, $\mathrm{SCCl^+}$; 69, 100, $\mathrm{CF_3^+}$; 66, 1, $\mathrm{CFCl^+}$; 63, 12, $\mathrm{CFS^+}$; 44, 1, $\mathrm{SC^+}$; 31, 5, $\mathrm{CF^+}$.

(22) $\underline{\mathrm{CF_3SCF_2CFClSCF_3}}$:

318, 1, $\mathrm{CF_3SCF_2CFClSCF_3^+}$; 280, 2, $\mathrm{CF_3SCFCClSCF_3^+}$; 249, 1, $\mathrm{CF_3S(CF_2CFCl)S^+}$; 217, <1, $\mathrm{CF_3S(CF_2CFCl)^+}$; 182, 1, $\mathrm{CF_3S(CF_2CF)^+}$; 167, 2, $\mathrm{CF_3SCFCl^+}$; 151, 80.5, $\mathrm{CF_3SCF_2^+}$; 132, 44, $\mathrm{CF_3SCF^+}$; 116, 2, $\mathrm{CF_2CFCl^+}$; 113, 3, $\mathrm{C_2F_3S^+}$; 101, 30, $\mathrm{CF_3S^+}$; 81, 1, $\mathrm{CF_2CF^+}$; 69, 100, $\mathrm{CF_3^+}$; 63, 7.5, $\mathrm{CFS^+}$; 31, 3, $\mathrm{CF^+}$.

Table 1.17 (cont.)

(23) $\underline{CF_3S(CF_2CFCl)_2SCF_3}$:

434, <1, $CF_3S(CF_2CFCl)_2SCF_3^+$; 333, <1, $CF_3S(CF_2CFCl)_2^+$; 283, <1, $CF_3S(CF_2CFCl)CFCl^+$; 229, 3, $CF_3S(CF{=}CCl)CF_2^+$; 217, 1, $CF_3S(CF_2CFCl)^+$; 197, 1, $(CF_2CFCl)(CF_2CF)^+$; 167, <1, CF_3SCFCl^+; 163, 1, $CF_3SCF{=}CF^+$ or $CFCl(CFClCF)^+$; 151, 51, $CF_3SCF_2^+$; 147, 14, $(CF_2CFCl)CF^+$; 129, 4, $S(CF_2CCl)^+$; 125, 2, $SC_3F_3^+$ or $C_3FCl_2^+$; 116, 5, CF_2CFCl^+; 113, 9, $S(CF_2CF)^+$; 101, 2, CF_3S^+; 94, 1, $CClCCl^+$; 93, 9.5, $C_3F_3^+$; 85, 27, CF_2Cl^+ ; 82, 7, CF_2S^+; 81, 2, CF_2CF^+; 79, 5, $SCCl^+$; 69, 100, CF_3^+; 63, 30, CFS^+; 50, 2, CF_2^+; 44, 2, SC^+; 32, 3, S^+; 31, 8, CF^+.

(24) $\underline{CF_3S(CF_2CFCl)_3SCF_3}$:

550, 1, $CF_3S(CF_2CFCl)_3SCF_3^+$ (M^+); 449, 1, $CF_3S(CF_2CFCl)_3^+$; 399, <1, $CF_3S(CF_2CFCl)_2CFCl^+$; 379, 2, $(M{-}CF_3S,Cl_2)^+$; 361, 1, $(M{-}\ CF_3SCF_2,F_2)^+$; 345, 1, $(M{-}CF_3SCF_2,ClF)^+$; 333, 2, $CF_3S(CF_2CFCl)_2^+$; 283, <1, $CF_3S(CF_2CFCl)CFCl^+$; 267, <1, $CF_3S(CF_2CFCl)CF_2^+$; 245, 3, $CF_3S(CF{=}CCl)CFCl^+$; 229, 3, $CF_3S(CF{=}CCl)CF_2^+$; 217, 3, $CF_3S(CF_2CFCl)^+$; 213, 1.5, $CF_3SC_3F_4^+$; 197, 2, $(CF_2CFCl)CFCF_2^+$; 179, 2, $CF_3S(CF{=}CCl)^+$; 175, 1, $SC_4F_5^+$; 167, 1, CF_3SCFCl^+; 163, 4, $CF_3SCF{=}CF^+$ or $C_3F_3Cl_2^+$; 162, 1, $C_4F_6^+$; 159, 1, $C_4F_4Cl^+$; 153, 10, $SC_4F_2Cl^+$; 151, 86.5, $CF_3SCF_2^+$; 147, 15, $(CF_2CFCl)CF^+$; 143, 3, $C_4F_5^+$; 137, 6, $SC_4F_3^+$; 131, 22, $C_3F_5^+$; 129, 4, $S(CF_2CCl)^+$; 125, 2, $SC_3F_3^+$; 124, 2, $C_4F_4^+$; 116, 7, CF_2CFCl^+; 113, 7, $SC_2F_3^+$; 112, 3, $C_3F_4^+$; 110, 2, $S(CF{=}CCl)^+$; 109, 2, $C_3F_2Cl^+$; 105, 1, $C_4F_3^+$; 101, 3, CF_3S^+; 94, <1, $C_2Cl_2^+$; 93, 7, $C_3F_3^+$; 85, 22, CF_2Cl^+; 82, 6, CF_2S^+; 81, 1.5, CF_2CF^+; 79, 4, $SCCl^+$; 74, 2, $C_3F_2^+$; 69, 100, CF_3^+; 66, 1, $CFCl^+$; 63, 26, CFS^+; 55, 2.5, C_3F^+; 50, 3, CF_2^+; 44, 3, SC^+; 35, 1, Cl^+; 32, 3, S^+; 31, 5, CF^+.

Table 1.17 (cont.)

(25) $\underline{CF_3S(CF_2CFCl)_4SCF_3}$:
666, <1, $CF_3S(CF_2CFCl)_4SCF_3^+$ ($M^{+\cdot}$); 565, <1, $(M-CF_3S)^+$; 515, <1, $(M-CF_3SCF_2)^+$; 495, 1, $(M-CF_3S,Cl_2)^+$; 449, <1, $CF_3S(CF_2CFCl)_3^+$; 399, <1, $CF_3S(CF_2CFCl)_2CFCl^+$; 364, 1, $CF_3S(CF_2CFCl)_2CF^+$; 347, 1, $SC_8F_6Cl_3^+$; 333, 1, $CF_3S(CF_2CFCl)_2^+$; 295, 1, $CF_3S(CF_2CFCl)(CF{=}CCl)^+$; 283, <1, $CF_3S(CF_2CFCl)CFCl^+$; 267, <1, $CF_3S(CF_2CFCl)CF_2^+$; 263, 1, $CF_3SCF_2CF{=}CFCF_2^+$; 245, 2, $CF_3S(CF{=}CCl)CFCl^+$; 241, 1, $SC_5F_6Cl^+$ or $C_5F_4Cl_3^+$; 231, 1, $C_5F_9^+$; 229, 2, $CF_3S(CF{=}CCl)CF_2^+$; 217, 3.5, $CF_3S(CF_2CFCl)^+$; 213, 2, $CF_3SC_3F_4^+$; 197, 2, $C_4F_6Cl^+$; 193, 2, $C_5F_7^+$; 179, 2, $CF_3S(CF{=}CCl)^+$; 178, 2, $C_4F_5Cl^+$; 175, 1, $SC_4F_5^+$; 174, 1, $C_5F_6^+$; 167, 2, CF_3SCFCl^+; 163, 5, $CF_3SCF{=}CF^+$ or $C_3F_3Cl_2^+$; 162, 1, $C_4F_6^+$; 151, 99, $CF_3SCF_2^+$; 147, 16, $(CF_2CFCl)CF^+$; 144, 2, $SC_3F_4^+$ or $C_3F_2Cl_2^+$; 143, 2, $C_4F_5^+$; 132, 8, $CFClCFCl^+$ or CF_3SCF^+; 131, 21, $C_3F_5^+$; 129, 4, $S(CF_2CCl)^+$; 125, 2, $SC_3F_3^+$; 124, 1, $C_4F_4^+$; 116, 8, CF_2CFCl^+; 113, 7, $SC_2F_3^+$; 112, 1, $C_3F_4^+$; 110, <1, $S(CF{=}CCl)^+$; 109, 2, $C_3F_2Cl^+$; 101, 3, CF_3S^+; 97, 2, $C_2F_2Cl^+$; 94, 1, $CCl{=}CCl^+$; 93, 6, $C_3F_3^+$; 85, 24, CF_2Cl^+; . 82, 6, CF_2S^+; 81, 2, CF_2CF^+; 79, 4, $SCCl^+$; 69, 100, CF_3^+; 66, 1, $CFCl^+$; 63, 26, CFS^+; 50, 1.5, CF_2^+; 35, 1, Cl^+; 32, 2, S^+; 31, 5, CF^+ .

(27) $\underline{CF_3SCCl_2CCl_2SCF_3}$:
331, 2, $CF_3SCClCCl_2SCF_3^+$; 296, 6, $CF_3SCCl{=}CClSCF_3$; 265, 2, $CF_3SCCl_2CCl_2^+$; 230, 40, $CF_3SC_2Cl_3^+$; 227, 21, $CF_3SCCl{=}CClS^+$; 195, 7, $CF_3SC_2Cl_2^+$; 183, 87, $CF_3SCCl_2^+$; 164, 50, $CCl_2CCl_2^+$; 161, 58, $SCCl{=}CCl_2^+$; 160, 1.5, $CF_3SC{\equiv}CCl^+$; 129, 35, $CF_2SCCl^+ + CCl{=}CCl_2^+$; 126, 57.5, $S{=}C{=}CCl_2^+$; 101, 2, CF_3S^+; 94, 41, $C_2Cl_2^+$; 91, 56, SC_2Cl^+; 82, 16, CCl_2^+ & CF_2S^+; 79, 80, $SCCl^+$; 69, 100, CF_3^+; 63, 11, CFS^+; 59, 40, C_2Cl^+; 50, 16, CF_2^+; 47, 55, CCl^+; 35, 18, Cl^{35+}; 32, 32, S^+; 31, 15, CF^+;

(28) $\underline{CF_3SCCl{=}CCl_2}$:
230, 36, $CF_3SCCl{=}CCl_2^+$; 195, 7, $CF_3SC_2Cl_2^+$; 161, 54, $C_2Cl_3S^+$; 160, 2, $C_3F_3ClS^+$ 129, 100, CF_2SCCl^+ or $CCl{=}CCl_2^+$; 126, 36, $S{=}C{=}CCl_2^+$; 94, 60, $C_2Cl_2^+$; 91, 28, SC_2Cl^+; 82, 14, CCl_2^+ and CF_2S^+; 79, 28, $SCCl^+$; 69, 42, CF_3^+; 63, 7, CF_2S ; 59, 20, C_2Cl^+; 50, 2, CF_2^+; 47, 48, CCl^+; 35, 16, Cl^{35+}; 32, 8, S^+; 31, 3, CF^+.

Table 1.17 (cont.)

(29) $\underline{CF_3SCCl_2CCl_3}$:
300, 2, $CF_3SCCl_2CCl_3^+$; 265, 2, $CF_3SCCl_2CCl_2^+$; 230, 41, $CF_3SC_2Cl_3^+$; 199, 49, $CCl_2CCl_3^+$; 195, 8, $CF_3SC_2Cl_2^+$; 183, 96, $CF_3SCCl_2^+$; 164, 56, $CCl_2{=}CCl_2^+$; 161, 64, $SCCl{=}CCl_2^+$; 160, 5, $CF_3SC{\equiv}CCl^+$; 129, 33, CF_2SCCl^+ and $CCl{=}CCl_2^+$; 126, 63, $S{=}C{=}CCl_2^+$; 117, 51, CCl_3^+; 101, 2, CF_3S^+; 94, 46, $C_2Cl_2^+$; 91, 57, SC_2Cl^+; 82, 17, CCl_2^+ & CF_2S^+; 79, 79, $SCCl^+$; 69, 100, CF_3^+; 63, 10, CFS^+; 59, 44, C_2Cl^+; 50, 17.5, CF_2^+; 47, 57, CCl^+; 35, 22, Cl^{35+}; 32, 35, S^+; 31, 17, CF^+

Table 1.19 : Metastable transitions obtained for Bis(trifluoromethylthio)-alkanes and -fluoroalkanes. (M^+ represents the molecular ion)

m_1	Transition			m_2	m^*	
					calc.	found
	$\underline{CF_3SCH_2CH_2SCF_3}$					
230	M^+	$\longrightarrow CF_3SCH_2CH_2S^+$	$+\ CF_3^\bullet$	161	112.6	112.7
230	M^+	$\longrightarrow CF_3SCH_2CH_2^+$	$+\ CF_3S^\bullet$	129	72.3	72.3
115	$CF_3SCH_2^+$	$\longrightarrow CFS^+$	$+\ CF_2H_2$	63	34.5	34.5
129	or $\{CF_3SCH_2CH_2^+$	$\longrightarrow CH_3S^+$	$+\ CF_2{=}CFH$	47	17.1	17.1
60	$SCH_2CH_2^+$	$\longrightarrow S^+$	$+\ CH_2{=}CH_2$	32	17.1	
	$\underline{CF_3SCH(CH_3)CF_2SCF_3}$					
244	M^+	$\longrightarrow C_4F_3H_6S_2^+$	$+\ CF_3^\bullet$	175	125.5	125.5
143	$CF_3SC_3H_6^+$	$\longrightarrow CF_2SC_3H_5^+$	$+\ HF$	123	105.8	105.9
143	$CF_3SC_3H_6^+$	$\longrightarrow CF_3SCH_2^+$	$+\ CH_2{=}CH_2$	115	92.3	92.3
244	M^+	$\longrightarrow C_4F_3H_6S^+$	$+\ CF_3S^\bullet$	142	82.6	82.6
129	$CF_3SCHCH_3^+$	$\longrightarrow CF_2SH^+$	$+\ CH_2{=}CHF$	83	53.3	53.3
101	or $\{CF_3S^+$	$\longrightarrow CFS^+$	$+\ F_2$	63	39.3	39.1
41	$C_3H_5^+$	$\longrightarrow C_3H_4^+$	$+\ H^\bullet$	40	39.0	
115	or $\{CF_3SCH_2^+$	$\longrightarrow CFS^+$	$+\ CH_2F_2$	63	34.5	34.6
61	CH_3CHS^+	$\longrightarrow CH_2S^+$	$+\ {:}CH_2$	46	34.7	
129	or $\{CF_3SCHCH_3^+$	$\longrightarrow CH_3S^+$	$+\ {:}CHCF_3$	47	17.1	17.2
60	$SC_2H_4^+$	$\longrightarrow S^+$	$+\ CH_2{=}CH_2$	32	17.1	
60	$SC_2H_4^+$	$\longrightarrow C_2H_2^+$	$+\ H_2S$	26	11.4	11.5

Table 1.19 (cont.).

m_1	Transition	m_2	m^* calc.	m^* found
	$CF_3S(CF_2CF_2)_2SCF_3$			
402	$M^+ \longrightarrow CF_3S(CF_2)_4S^+ + CF_3^\bullet$	333	275.8	275.9
383	$C_6F_{13}S_2^+ \longrightarrow C_5F_{11}S^+ + CF_2{=}S$	301	236.6	236.6
181	$C_4F_7^+ \longrightarrow C_3F_5^+ + {:}CF_2$	131	94.8	94.9
	$CF_3SCF(CF_3)CF_2SCF_3$			
352	$M^+ \longrightarrow C_4F_9S_2^+ + CF_3^\bullet$	283	227.5	227.6
333	$C_5F_{11}S_2^+ \longrightarrow C_4F_7S_2^+ + CF_4$	245	180.3	180.3
352	$M^+ \longrightarrow C_4F_9S^+ + CF_3S^\bullet$	251	179.0	179.1
245	$C_4F_7S_2^+ \longrightarrow C_3F_5S^+ + CF_2{=}S$	163	108.4	108.5
213	$C_4F_7S^+ \longrightarrow C_2F_5S^+ + C_2F_2$	151	107.0	107.0
	$CF_3S[CF(CF_3)CF_2]_2SCF_3$			
502	$M^+ \longrightarrow C_7F_{15}S_2^+ + CF_3^\bullet$	433	373.3	373.4
433	$C_7F_{15}S_2^+ \longrightarrow C_6F_{11}S_2^+ + CF_4$	345	274.9	274.9
401	or $C_7F_{15}S^+ \longrightarrow C_6F_{12}S^+ + CF_3^\bullet$	332	274.9	
401	$C_7F_{15}S^+ \longrightarrow C_6F_{11}S^+ + CF_4$	313	244.0	244.0
231	$C_5F_9^+ \longrightarrow C_4F_7^+ + {:}CF_2$	181	141.8	141.8
181	$C_4F_7^+ \longrightarrow C_3F_5^+ + {:}CF_2$	131	94.8	94.8
	$CF_3SCF_2CH_2SCF_3$			
247	$C_4F_7H_2S_2^+ \longrightarrow C_4F_6HS_2^+ + HF$	227	208.8	208.8
165	$CF_3SC_2F_2H_2^+ \longrightarrow C_3F_4HS^+ + HF$	145	127.5	127.4
247	$C_4F_7H_2S_2^+ \longrightarrow C_3F_5H_2S^+ + CF_2{=}S$	165	110.3	110.2
266	$M^+ \longrightarrow C_3F_5H_2S^+ + CF_3S^\bullet$	165	102.4	102.4
165	$CF_3SC_2F_2H_2^+ \longrightarrow C_2FH_2S^+ + CF_4$	77	35.9	35.9
266	$M^+ \longrightarrow C_2F_2H_2S^+ + CF_3SCF_3$	96	34.6	34.5
163	or $CF_3SC_2F_2^+ \longrightarrow C_2FS^+ + CF_4$	75	34.5	
115	or $CF_3SCH_2^+ \longrightarrow CFS^+ + CH_2F_2$	63	34.5	
	$CF_3S(CH_2CF_2)_2SCF_3$			
330	$M^+ \longrightarrow C_6F_9H_3S_2^+ + HF$	310	291.0	291.0

Table 1.19 (cont.).

m_1	Transition			m_2	m^*	
					calc.	found.
		$CF_3S(CH_2CF_2)_2SCF_3$ (cont.)				
311	$C_6F_9H_4S_2^+$	$\longrightarrow C_6F_8H_3S_2^+$	$+ HF$	291	272.3	272.3
330	$M^{+\cdot}$	$\longrightarrow C_5F_7H_4S_2^+$	$+ CF_3^\cdot$	261	206.6	206.6
229	$C_5F_7H_4S^+$	$\longrightarrow C_5F_6H_3S^+$	$+ HF$	209	190.7	190.7
330	$M^{+\cdot}$	$\longrightarrow C_5F_7H_4S^+$	$+ CF_3S^\cdot$	229	159.0	159.0
310	$C_6F_9H_3S_2^+$	$\longrightarrow C_5F_6H_3S^+$	$+ CF_3S^\cdot$	209	140.9	141.0
165	$CF_3SC_2F_2H_2^+$	$\longrightarrow C_3F_4HS^+$	$+ HF$	145	127.3	127.3
310	$C_6F_9H_3S_2^+$	$\longrightarrow C_4F_6HS^+$	$+ CF_3SCH_2^\cdot$	195	122.7	122.7
141	$C_4F_3H_4S^+$	$\longrightarrow C_4F_2H_3S^+$	$+ HF$	121	103.8	103.9
261	$C_5F_7H_4S_2^+$	$\longrightarrow C_4F_4H_3S^+$	$+ CF_3SH$	159	96.8	96.8
229	$CF_3SC_4F_4H_4^+$	$\longrightarrow C_4F_3H_4S^+$	$+ CF_4$	141	86.8	86.8
115	$CF_3SCH_2^+$	$\longrightarrow CFS^+$	$+ CH_2F_2$	63	34.5	34.5
		$CF_3S(CH_2CF_2)_3SCF_3$				
375	$C_8F_{11}H_6S_2^+$	$\longrightarrow C_8F_{10}H_5S_2^+$	$+ HF$	355	336.1	336.0
374	$C_8F_{11}H_5S_2^+$	$\longrightarrow C_8F_{10}H_4S_2^+$	$+ HF$	354	335.1	335.1
355	$C_8F_{10}H_5S_2^+$	$\longrightarrow C_8F_9H_4S_2^+$	$+ HF$	335	316.1	316.1
374	$C_8F_{11}H_5S_2^+$	$\longrightarrow C_7F_8H_5S_2^+$	$+ CF_3^\cdot$	305	248.7	248.7
279	$CF_3SC_5F_6H_4^+$	$\longrightarrow C_6F_8H_3S^+$	$+ HF$	259	240.4	240.5
273	$C_7F_8H_5S^+$	$\longrightarrow C_7F_7H_4S^+$	$+ HF$	253	234.4	234.4
374	or $\{C_8F_{11}H_5S_2^+$	$\longrightarrow C_7F_7H_4S^+$	$+ CF_3S^\cdot + HF$	253	171.1	171.2
209	$C_5F_6H_3S^+$	$\longrightarrow C_5F_5H_2S^+$	$+ HF$	189	171.1	
259	$C_6F_8H_3S^+$	$\longrightarrow C_4F_6HS^+$	$+ CH_2{=}CF_2$	195	146.8	146.7
165	$CF_3SC_2F_2H_2^+$	$\longrightarrow C_3F_2HS^+$	$+ HF$	145	127.5	127.4
127	or $\{C_3F_3H_2S^+$	$\longrightarrow C_3F_2HS^+$	$+ HF$	107	89.9	89.9
	$C_4F_4H_3^+$	$\longrightarrow C_4F_3H_2^+$	$+ HF$			
115	$CF_3SCH_2^+$	$\longrightarrow CFS^+$	$+ CH_2F_2$	63	34.5	34.5
		$CF_3S(CH_2CF_2)_4SCF_3$				
419	$C_{10}F_{12}H_7S_2^+$	$\longrightarrow C_{10}F_{11}H_6S_2^+$	$+ HF$	399	379.9	379.9
357	$C_9F_{11}H_8S^+$	$\longrightarrow C_9F_{10}H_7S^+$	$+ HF$	337	318.1	318.1
418	$C_{10}F_{12}H_6S_2^+$	$\longrightarrow C_9F_9H_6S^+$	$+ CF_3S^\cdot$	317	240.4	240.5

Table 1.19 (cont.).

$\underline{m}_1$	Transition			$\underline{m}_2$	$\underline{m}^*$ calc.	$\underline{m}^*$ found
	$\underline{CF_3S(CH_2CF_2)_4SCF_3}$ (cont.)					
279	or $C_6F_9H_4S^+$	$\longrightarrow C_6F_8H_3S^+$	+ HF	259	240.4	240.5
273	$C_7F_8H_5S^+$	$\longrightarrow C_7F_7H_4S^+$	+ HF	253	234.4	234.4
293	$CF_3SC_6F_6H_6^{\dot{+}}$	$\longrightarrow C_6F_8H_3S^+$	+ CH_3F	259	229.0	229.1
223	$C_6F_6H_5S^+$	$\longrightarrow C_6F_5H_4S^+$	+ HF	203	184.8	184.8
209	$C_5F_6H_3S^+$	$\longrightarrow C_5F_5H_2S^+$	+ HF	189	171.1	171.2
165	$CF_3SC_2F_2H_2^{\dot{+}}$	$\longrightarrow C_3F_4HS^+$	+ HF	145	127.5	127.4
127	or $C_3F_3H_2S^+$ $C_4F_4H_3^+$	$\longrightarrow C_3F_2HS^+$ $\longrightarrow C_4F_3H_2^+$	+ HF + HF	107	89.9	89.9
115	$CF_3SCH_2^+$	$\longrightarrow CFS^+$	+ CH_2F_2	63	34.5	34.5
	$\underline{CF_3S(CH_2CF_2)_5SCF_3}$					
522	M^+	$\longrightarrow C_{12}F_{15}H_9S_2^+$	+ HF	502	482.7	482.7
522	M^+	$\longrightarrow C_{11}F_{13}H_{10}S_2^+$	+ $CF_3^{\cdot}$	453	393.1	393.1
387	$C_{10}F_{12}H_7S^{\dot{+}}$	$\longrightarrow C_{10}F_{11}H_6S^+$	+ HF	367	348.1	348.1
522	$M^{\dot{+}}$	$\longrightarrow C_{11}F_{13}H_{10}S^+$	+ $CF_3S^{\cdot}$	421	339.6	339.6
273	$C_7F_8H_5S^+$	$\longrightarrow C_6F_7H_2S^+$	+ CH_3F	239	209.0	209.0
407	$C_{10}F_{13}H_8S^{\dot{+}}$	$\longrightarrow C_6F_9H_4S^+$	+ $C_4F_4H_4$	279	190.8	190.8
179	$CF_3SC_3F_2H_4^{\dot{+}}$	$\longrightarrow C_4F_4H_3S^+$	+ HF	159	141.2	141.2
165	$CF_3SC_2F_2H_2^{\dot{+}}$	$\longrightarrow C_3F_4HS^+$	+ HF	145	127.5	127.5
127	or $C_3F_3H_2S^+$ $C_4F_4H_3^+$	$\longrightarrow C_3F_2HS^+$ $\longrightarrow C_4F_3H_2^+$	+ HF + HF	107	89.9	89.9
109	$C_4F_3H_4^+$	$\longrightarrow C_4F_2H_3^+$	+ HF	89	72.6	72.6
115	$CF_3SCH_2^+$	$\longrightarrow CFS^+$	+ CF_2H_2	63	34.5	34.5
	$\underline{CF_3S(CH_2CF_2)_6SCF_3}$					
387	$C_{10}F_{12}H_7S^{\dot{+}}$	$\longrightarrow C_{10}F_{11}H_6S^+$	+ HF	367	348.1	348.1
273	$C_7F_8H_5S^+$	$\longrightarrow C_6F_7H_2S^+$	+ CH_3F	239	209.0	209.0
407	$C_{10}F_{13}H_8S^+$	$\longrightarrow C_6F_9H_4S^+$	+ $C_4F_4H_4$	279	190.8	190.8
179	$CF_3SC_3F_2H_4^{\dot{+}}$	$\longrightarrow C_4F_4H_3S^+$	+ HF	159	141.2	141.2
165	$CF_3SC_2F_2H_2^+$	$\longrightarrow C_3F_4HS^+$	+ HF	145	127.5	127.5
109	$C_4F_3H_4^+$	$\longrightarrow C_4F_2H_3^+$	+ HF	89	72.6	72.6

Table 1.12 (cont.).

m_1	Transition				m_2	m^* calc.	m^* found
	$CF_3S(CH_2CF_2)_6SCF_3$ (cont.)						
115	$CF_3SCH_2^+$		CFS^+	$+ CH_2F_2$	63	34.5	34.5
	$CF_3SCF_2CFHSCF_3$						
284	M^+	$\longrightarrow$	$C_3F_6HS_2^+$	$+ CF_3^\bullet$	215	162.8	162.8
177	$C_3F_4HS_2^+$	$\longrightarrow$	$C_3F_3S_2^+$	+ HF	157	139.3	139.3
183	$CF_3SC_2F_3H^+$	$\longrightarrow$	$C_2F_4HS^+$	$+ :CF_2$	133	96.7	96.7
195	$C_3F_5S_2^+$	$\longrightarrow$	$C_2F_2S_2^+$	$+ CF_3^\bullet$	126	81.4	81.4
163	$C_3F_5S^+$	$\longrightarrow$	$C_2F_3S^+$	$+ :CF_2$	113	78.4	78.4
157	$C_3F_3S_2^+$	$\longrightarrow$	$C_2FS_2^+$	$+ :CF_2$	107	72.9	72.9
101	or CF_3S^+	$\longrightarrow$	S^+	$+ CF_3^\bullet$	32	10.1	10.1
95	$C_2F_2HS^+$	$\longrightarrow$	CF^+	$+ CFH{=}S$	31	10.1	
	$CF_3S(CF_2CFH)_2SCF_3$						
366	M^+	$\longrightarrow$	$C_6F_{11}HS_2^+$	+ HF	346	327.1	327.1
366	M^+	$\longrightarrow$	$C_5F_9H_2S_2^+$	$+ CF_3^\bullet$	297	241.0	241.0
366	M^+	$\longrightarrow$	$C_5F_9H_2S^+$	$+ CF_3S^\bullet$	265	191.8	191.9
297	$C_5F_9H_2S_2^+$	$\longrightarrow$	$C_4F_5H_2S_2^+$	$+ CF_4$	209	147.0	147.1
177	$C_4F_5H_2S^+$	$\longrightarrow$	$C_4F_4HS^+$	+ HF	157	139.3	139.3
265	or $CF_3SC_4F_6H_2^+$	$\longrightarrow$	$C_3F_6HS^+$	$+ CFH{=}CF_2$	183	126.4	126.3
195	$C_4F_6HS^+$	$\longrightarrow$	$C_4F_4HS^+$	$+ F_2$	157	126.4	
265	$CF_3SC_4F_6H_2^+$	$\longrightarrow$	$C_4F_5H_2S^+$	$+ CF_4$	177	118.2	118.2
183	$CF_3SC_2F_3H^+$	$\longrightarrow$	$C_2F_4HS^+$	$+ :CF_2$	133	96.7	96.7
366	M^+	$\longrightarrow$	$CF_3SC_2F_3H^+$	$+ CF_3SC_2F_3H^\bullet$	183	91.2	91.2
95	$C_2F_2HS^+$	$\longrightarrow$	$C_2F_2H^+$	+ S	63	41.7	41.7
	$CF_3S(CF_2CFH)_3SCF_3$						
448	M^+	$\longrightarrow$	$C_8F_{14}H_2S_2^+$	+ HF	428	408.9	408.8
379	$C_7F_{12}H_3S_2^+$	$\longrightarrow$	$C_7F_{11}H_2S_2^+$	+ HF	359	340.1	340.2
448	M^+	$\longrightarrow$	$C_7F_{12}H_3S_2^+$	$+ CF_3^\bullet$	379	320.6	320.7
315	$CF_3SC_5F_8H_2^+$	$\longrightarrow$	$C_6F_{10}HS^+$	+ HF	295	276.3	276.3
309	$C_7F_{10}H_3S^+$	$\longrightarrow$	$C_7F_9H_2S^+$	+ HF	289	270.3	270.4
259	$C_6F_8H_3S^+$	$\longrightarrow$	$C_6F_7H_2S^+$	+ HF	239	220.6	220.6

Table 1.19 (cont.).

m_1			Transition			m_2	m^*	
							calc.	found
			$CF_3S(CF_2CFH)_3SCF_3$ (cont.)					
177	or	$C_4F_5H_2S^+$	$\longrightarrow$	$C_4F_4HS^+$	+ HF	157	139.1	139.1
		$C_5F_6H_3^+$	$\longrightarrow$	$C_5F_5H_2^+$	+ HF			
265	or	$CF_3SC_4F_6H_2^+$	$\longrightarrow$	$C_3F_6HS^+$	+ $CFH{=}CF_2$	183	126.4	126.3
195		$C_4F_6HS^+$	$\longrightarrow$	$C_4F_4HS^+$	+ F_2	157	126.4	
265		$CF_3SC_4F_6H_2^+$	$\longrightarrow$	$C_4F_5H_2S^+$	+ CF_4	177	118.2	118.2
183		$CF_3SC_2F_3H^+$	$\longrightarrow$	$C_2F_4HS^+$	+ $:CF_2$	133	96.7	96.7
233		$CF_3SC_3F_5H^+$	$\longrightarrow$	$C_3F_4HS^+$	+ CF_4	145	90.2	90.2
145		$C_3F_4HS^+$	$\longrightarrow$	$C_2F_2HS^+$	+ $:CF_2$	95	62.2	62.2
			$CF_3S(CF_2CFH)_4SCF_3$					
530		M^+	$\longrightarrow$	$C_9F_{15}H_4S^+$	+ $CF_3S^\bullet$	429	347.3	347.3
429		$C_9F_{15}H_4S^+$	$\longrightarrow$	$C_9F_{14}H_3S^+$	+ HF	409	389.8	389.8
397		$CF_3SC_7F_{11}H_3^+$	$\longrightarrow$	$C_7F_{10}H_3S^+$	+ CF_4	309	240.5	240.6
315		$CF_3SC_5F_8H_2^+$	$\longrightarrow$	$C_6F_{10}HS^+$	+ HF	295	276.3	276.3
265		$CF_3SC_4F_6H_2^+$	$\longrightarrow$	$C_3F_6HS^+$	+ $CFH{=}CF_2$	183	126.4	126.3
183		$C_3F_6HS^+$	$\longrightarrow$	$C_2F_4HS^+$	+ $:CF_2$	133	96.7	96.7
295	or	$C_6F_{10}HS^+$	$\longrightarrow$	$C_3F_5S^+$	+ $CF_2HCF{=}CF_2$	163	90.7	90.7
233		$C_4F_7HS^+$	$\longrightarrow$	$C_3F_3HS^+$	+ CF_4	145	90.6	
163		$C_3F_5S^+$	$\longrightarrow$	$C_2F_3S^+$	+ $:CF_2$	113	78.5	78.5
			$CF_3S(CF_2CFH)_nSCF_3$ n = 5,6,7					
675		$CF_3SC_{14}F_{21}H_7^+$	$\longrightarrow$	$C_{15}F_{23}H_6S^+$	+ HF	655	635.4	635.4
511		$CF_3SC_{10}F_{15}H_5^+$	$\longrightarrow$	$C_{10}F_{13}H_5S^+$	+ F_2	473	437.9	437.9
612		$M^+_{(n\ =\ 5)}$	$\longrightarrow$	$C_{11}F_{18}H_5S^+$	+ $CF_3S^\bullet$	511	426.6	426.6
315		$CF_3SC_5F_8H_2^+$	$\longrightarrow$	$C_6F_{10}HS^+$	+ HF	295	276.3	276.3
233		$CF_3SC_3F_5H^+$	$\longrightarrow$	$C_4F_7S^+$	+ HF	213	194.7	194.7
133		CF_3SCFH^+	$\longrightarrow$	$C_2F_2HS^+$	+ F_2	95	68.0	68.0
			$\overline{CF_2CFClCF_2CFClS}$					
264		M^+	$\longrightarrow$	$C_4F_6ClS^+$	+ Cl	229	198.6	198.6
179		$C_3F_4ClS^+$	$\longrightarrow$	$C_3F_4Cl^+$	+ S	147	120.7	120.7
182		$C_3F_4Cl_2^+$	$\longrightarrow$	$C_3F_4Cl^+$	+ Cl	147	118.7	118.7

Table 1.19 (cont.).

m_1	Transition	m_2	m^* calc.	m^* found
	$CF_3SCF_2CFClSCF_3$			
318	$M^+ \longrightarrow C_3F_6ClS^+ + CF_3S^\bullet$	217	148.1	148.1
179	$C_3F_5ClS^+ \longrightarrow C_2F_4S^+ + :CFCl$	132	97.5	97.5
318	$M^+ \quad CF_3SCFCl^+ + CF_3SCF_2^\bullet$	167	87.7	87.6
	$CF_3S(CF_2CFCl)_2SCF_3$			
434	$M^+ \longrightarrow C_5F_9Cl_2S_2^+ + CF_3^\bullet$	365	307.0	307.0
279	$C_5F_8ClS^+ \longrightarrow C_4F_5S^+ + CF_3Cl$	175	109.8	109.8
295	or $\{ C_5F_7Cl_2S^+ \longrightarrow C_2F_4ClS^+ + C_3F_3Cl$	167	94.4	94.5
229	$C_4F_6ClS^+ \longrightarrow C_3F_4Cl^+ + CF =S$	147	94.4	
	$CF_3S(CF_2CFCl)_4SCF_3$			
279	$C_5F_8ClS^+ \longrightarrow C_4F_5S^+ + CF_3Cl$	175	109.8	109.8
151	$CF_3SCF_2^+ \longrightarrow CFS^+ + CF_4$	63	26.3	26.3
	$CF_3SCCl=CCl_2$			
230	$M^+ \longrightarrow C_2Cl_3S^+ + CF_3^\bullet$	161	112.7	112.7
161	$C_2Cl_3S^+ \longrightarrow C_2Cl_3^+ + S$	129	103.4	103.4
129	$C_2F_2ClS^+ \longrightarrow C_2ClS^+ + F_2$	91	64.2	64.3
	$CF_3SCCl_2CCl_2SCF_3$			
161	$C_2Cl_3S^+ \longrightarrow C_2Cl_3^+ + S$	129	103.4	103.4
129	$C_2F_2ClS^+ \longrightarrow C_2ClS^+ + F_2$	91	64.2	64.3
101	$CF_3S^+ \longrightarrow CFS^+ + F_2$	63	39.3	39.2
183	$CF_3SCCl_2^+ \longrightarrow CCl_2^+ + CF_3S^\bullet$	82	36.7	36.7
	$CF_3SCCl_2CCl_3$			
161	$C_2Cl_3S^+ \longrightarrow C_2Cl_3^+ + S$	129	103.4	103.4
199	$CCl_3CCl_2^+ \longrightarrow CCl_3^+ + :CCl_2$	117	68.8	68.8
129	$C_2F_2ClS^+ \longrightarrow C_2ClS^+ + F_2$	91	64.2	64.3

whilst the molecular ions of the perfluoroparaffins are either zero or vanishingly small (200) as shown in Table 1.20.

Perfluoroparaffin	Relative Abundance of Molecular Ion (%)
CF_4	0
C_2F_6	0.15
C_3F_8	0
C_4F_{10}	0
C_5F_{12}	0.03
C_6F_{14}	0.05
C_7F_{16}	0
C_9F_{20}	0

Table 1.20

Cullen has shown that the C-S bonds are strongest when the molecule is asymmetrical (74), ie when CF_3-S and CH_3-S are both present to give CF_3SCH_3, compared to CF_3SCF_3 and CH_3SCH_3 where the molecule is symmetric. This effect would explain the greater intensity of the molecular ions of the bis(trifluoromethylthio)alkanes compared to the -fluoroalkanes.

The mass spectrum of $CF_3SCH_2CH_2SCF_3$ is listed in Table 1.17. No (1). Table 1.19. lists all the metastable transition observed in the mass spectrum of $CF_3SCH_2CH_2SCF_3$. In this table , as in all the other tables of metastable transition given, m^* refers to the metastable peak observed in the mass spectrum and arising from decomposition of the parent ion m_1 to the daughter m_2. The symmetry of the molecular ion of $CF_3SCH_2CH_2SCF_3$ allows localisation of the charge on either sulphur atoms, if, as is most likely, it is assumed that the ionisation step is removal of an electron from a sulphur lone pair, $CF_3SCH_2CH_2SCF_3 + e \longrightarrow CF_3SCH_2CH_2\overset{+}{S}CF_3 + 2e$ β cleavage, giving rise to the same products if it originates from either sulphur, would appear to be the most important fragmentation process here thus :-

$$CF_3SCH_2CH_2\overset{+}{\dot{S}}CF_3 \longrightarrow CF_3S\dot{C}H_2 + \underset{m/e\ 115}{CH_2{=}\overset{+}{S}{-}CF_3} \qquad 1.$$

since m/e 115 is the base peak. It is worth noting however, that the abundance of an ion in the mass spectrum will depend, not only on the rate of reaction producing this ion but also on the rate of decomposition of the product ion. Hence the correlation between major fragment and major fragmentation pathway is not rigorous since it may well be that the major fragmentation pathway gives rise to an ion which is sufficiently unstable not to be detected in the quantities in which it is formed. However, since it is thought that stability of products plays a part in determining fragmentation pathways (194), this anomaly is not very common.

α cleavage with charge retention on sulphur represents another mode of breakdown for the molecular ion of $CF_3SCH_2CH_2SCF_3$, but two possibilities exist :-

$$CF_3SCH_2CH_2\overset{+\cdot}{S}CF_3 \begin{array}{l} \nearrow CF_3SCH_2CH_2S^{+} + CF_3^{\cdot} \qquad 2. \\ \searrow CF_3SCH_2CH_2^{\cdot} + {}^{+}SCF_3 \qquad 3. \end{array}$$

A metastable peak for process 2 is observed at m/e 112.7. Process 3 is highly unfavoured due to the instability of CF_3S^+ as found by Cullen (74). This is perhaps reflected in the very low abundances of the CF_3S^+ ion found, not only in the mass spectrum of $CF_3SCH_2CH_2SCF_3$, but in the mass spectra of all the bis(trifluoromethylthio)alkanes and -fluoroalkanes and of CF_3SSCF_3 and CF_3SCH_3 (74). α cleavage with charge retention on carbon, the M-14N-5 series in Table 1.14, found for the aliphatic thioethers (199) can also take place in two ways; viz. processes 4 and 5.

$$CF_3SCH_2CH_2\overset{+\cdot}{S}CF_3 \begin{array}{l} \nearrow CF_3SCH_2CH_2S^{\cdot} + \underset{\underline{m/e\ 69}}{CF_3^{+}} \qquad 4. \\ \searrow \underset{\underline{m/e\ 129}}{CF_3SCH_2CH_2^{+}} + CF_3S^{\cdot} \qquad 5. \end{array}$$

In the aliphatic thioethers, α cleavage usually occurs with loss of the larger aliphatic fragment (199). If this is the case here, 5 should be the favoured pathway. The large abundance of both m/e 69 (65%) and m/e 129 (72%) would seem to argue that both processes, 4 and 5, occur. However, there is a metastable peak at m/e 72.3 which confirms that process 5 is a major fragmentation pathway whilst the peak at m/e 69 need not arise from the molecular ion but may arise from other ion fragments or even by rearrangement (200).

Sequential loss of CH_2 units in saturated hydrocarbons is well known (195) as is sequential loss of CF_2 fragments in perfluorocarbons (200). Thus, the ion at m/e 129 may lose CH_2 units

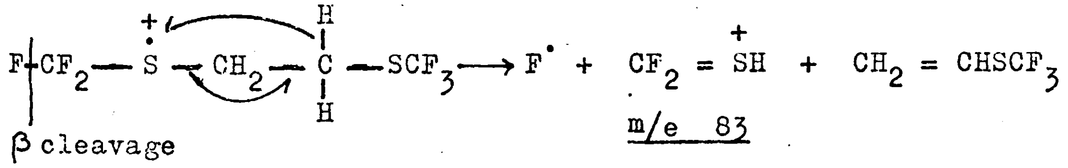
$$\underset{m/e\ 129}{CF_3SCH_2\overset{\curvearrowright}{C}H_2^+} \longrightarrow \underset{m/e\ 115}{CF_3SCH_2^+} + :CH_2 \qquad 6.$$

$$\downarrow$$

$$\underset{m/e\ 101}{CF_3S^+} + :CH_2 \qquad 7.$$

although there is no direct evidence in the form of metastable peaks.

The other fragmentation mode quoted for aliphatic thioethers (199), viz. α, β cleavage with hydrogen rearrangement, is also found here, but is not nearly so important a fragmentation mode as β cleavage or α cleavage with charge retention on carbon, thus:-

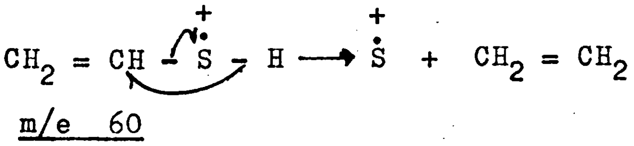


$$F\,|\,CF_2-\overset{+\bullet}{S}-CH_2-\overset{H}{\underset{H}{C}}-SCF_3 \longrightarrow F^\bullet + \underset{m/e\ 83}{CF_2=\overset{+}{S}H} + CH_2=CHSCF_3 \qquad 8.$$

β cleavage

The low abundances of the ion at m/e 83 and that derived from it, $CFHS^+$ at m/e 64, show that this fragmentation mode, although observed, is not relatively important.

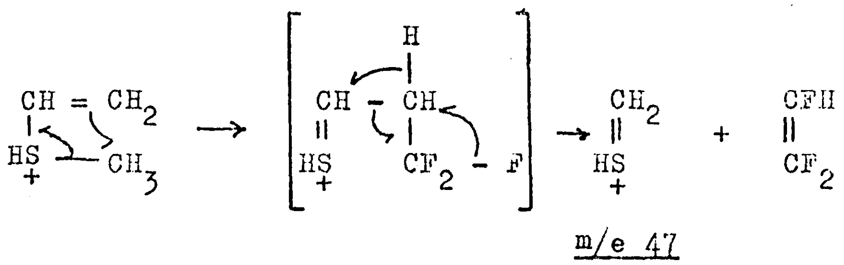
The metastable peak at m/e 17.1 can arise in one of two ways:-



$$\underset{m/e\ 60}{CH_2=CH-\overset{+\bullet}{S}-H} \longrightarrow \overset{+\bullet}{S} + CH_2=CH_2 \qquad 9.$$

$$\underset{m/e\ 129}{CF_3SCH_2CH_2^+} \longrightarrow \underset{m/e\ 47}{CH_3S^+} + C_2F_3H \qquad 10.$$

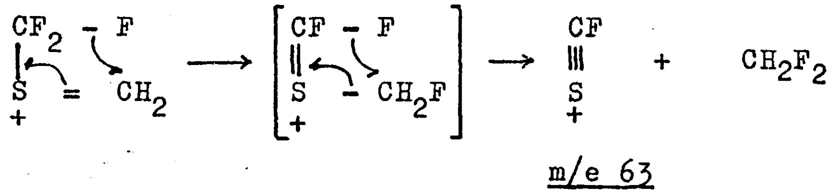
The most feasible mechanism by which 10 can proceed is through a four-centre transition state:-



10'.

Process 10 accounts for the anomalously high abundance of the CH_3S^+ ion at m/e 47, although both fragmentations may be occurring. It should be noted, however, that many of the most prominent peaks in the mass spectra of organic compounds are derived from ions which possess no unpaired electrons (196). Those odd-electron ions which are present in high abundance are usually formed by particularly favourable fragmentation paths. Process 9 is an odd-electron decomposition and if this is a decomposition pathway giving rise to the metastable peak at m/e 17.1, it must be a favourable pathway.

One mode of decomposition of the ion $CF_3SCH_2^+$ is suggested by the observation of a metastable peak at m/e 34.5 which is thought to arise from the metastable transition $CF_3SCH_2^+ \rightarrow CFS^+ + CH_2F_2$. A proposed mechanism for this is again through a four-centre transition state:-



11.

with elimination of the neutral difluoromethane.

To discuss the analysis of the mass spectra of all the other bis(trifluoromethylthio)alkanes and - fluoroalkanes in such detail would be very space-consuming. Instead, Table 1.21 summarises five of the decomposition processes for the molecular ion $CF_3S(R)_nSCF_3$ by listing the m/e values of the product ions. (A lack of space precludes the formulae being listed and reference should be made to the appropriate mass spectrum in Table 1.17). Although for some of the molecular ions, some of the fragmentation processes are confirmed by the observation of metastable peaks, it should be noted that the product ions may also arise

Table 1.21 : Fragmentation process in the mass spectra of $CF_3S(R)_nSCF_3$

Mass Spectrum No.	R	n	Process 1	Process 2	Process 3	Process 4	Process 5
(1)	CH_2CH_2	1	161* (101)	129* 69	115	(83)	
(2)	$CH(CH_3)CH_2$	1	175* (101)	143* 69	129 115	(83)	(212)
(3)	CF_2CF_2	2	333* (101)	301 69	151	(101)	(370)
(5)	$CF(CF_3)CF_2$	1	283* (101)	251* 69	201 151	(101)	
(6)		2	433* (101)	401 69	151	(101)	
(7)	CH_2CF_2	1	(101)	165* 69	115 (151)	83 (101)	
(8)		2	261*	229* 69	115 (151)		
(9)		3	(325) (101)	(293) 69	115 151	(83) (101)	
(10)		4	389 (101)	357 69	115 151	(83) (101)	
(11)		5	453* (101)	421* 69	115	(101)	
(12)		6	517 (101)	(485) 69	115	(101)	
(13)	$CFHCF_2$	1	215* (101)	183 69	151 133	83 (101)	
(14)		2	297* (101)	265* 69	151 133	(83) (101)	
(15)		3	379* 101	347 69	151 133	(83) 101	
(16)		4	101	429* 69	151 133	83 101	
(17)	(a)	5		511*			
(18)		6		593	151 133	(83) 101	
(19)		7		675			
(22)	CF_2CFCl	1	(249) 101	217* 69	167* 151	101	
(23)		2	365* (101)	333 69	(167) 151	(101)	
(24)		3	101	449 69	167 151	101	
(25)		4	101	565 69	167 151	101	(117)
(27)	CCl_2CCl_2	1	101	(265) 69	183		

(a) Since the mass spectrum is of a mixture, only process 2 gives meaningful figures.

Key

Process 1 α cleavage with charge retention at sulphur

(a) $CF_3\overset{+\bullet}{S}(R)_nSCF_3 \longrightarrow \overset{\bullet}{C}F_3 + {}^{\bullet}\overset{+}{S}(R)_nSCF_3$

(b) $\longrightarrow CF_3\overset{+}{S}{}^{\bullet} + (R)_nSCF_3$

Process 2 α cleavage with charge retention at carbon

for $(R)_n$ = C(AB) C(XY); (a) $CF_3\overset{+}{S}C(AB)C(XY)SCF_3 \longrightarrow \overset{+}{C}F_3 + \overset{\bullet}{S}C(AB)C(XY)SCF_3$

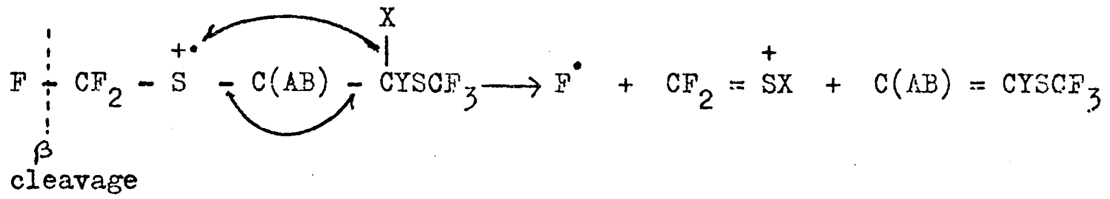
(b) $\longrightarrow CF_3\overset{\bullet}{S} + \overset{+}{C}(AB)C(XY)SCF_3$

Process 3   β cleavage

for $(R)_n$ = C(AB)C(XY) $CF_3SC(AB)C(XY)\overset{+}{\dot{S}}CF_3 \longrightarrow CF_3SC(AB)^{\bullet} + C(XY) = \overset{+}{S}CF_3$

Process 4 α, β cleavage with rearrangement of A, B, X or Y

for $(R)_n$ = C(AB)C(XY)



$$F - CF_2 - \overset{+\bullet}{S} - C(AB) - CX YSCF_3 \longrightarrow F^{\bullet} + CF_2 = \overset{+}{S}X + C(AB) = CYSCF_3$$

β cleavage

Process 5   Expulsion of sulphur with recombination of fragments

$$\left[CF_3S(R)_nSCF_3\right]^+ \longrightarrow \left[CF_3(R)_nSCF_3\right]^+ + S^{\bullet}$$

* observation of a metastable peak in the mass spectrum confirms the process (Table 1.19 gives details)

( ) ion observed in very small relative abundance.

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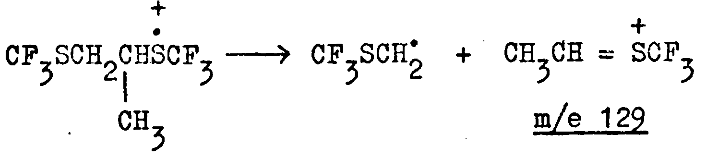
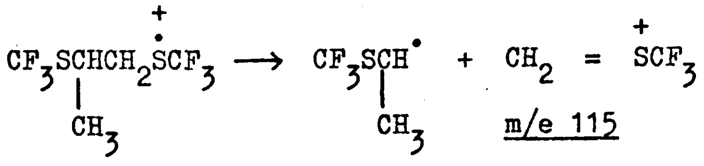
from other pathways. Conversely, although some of the fragmentation processes are not confirmed by the observation of metastable peaks, this does not necessarily imply that the "product ions" do not arise from these processes.

The mass spectrum of $CF_3SCH(CH_3)CH_2SCF_3$ is given in Table 1.17, No. (2) and the metastable transitions are listed in Table 1.19. This mass spectrum has as its base peak the ion at m/e 129 which probably arises mainly from β cleavage of the molecular ion:-



$$CF_3SCH_2CH(CH_3)\overset{+}{\dot{S}}CF_3 \longrightarrow CF_3SCH_2^{\bullet} + \underset{m/e\ 129}{\underline{CH_3CH = \overset{+}{S}CF_3}} \qquad 12.$$

Since the molecule is not symmetrical as in the previous case, β cleavage may originate from the positive charge being localised on the other sulphur to give:-

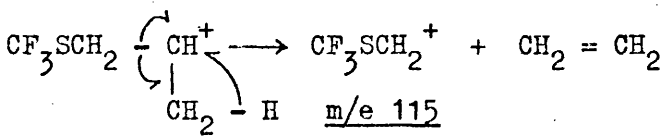


$$CF_3\overset{+}{\dot{S}}CH(CH_3)CH_2SCF_3 \longrightarrow CF_3SCH^{\bullet}(CH_3) + \underset{m/e\ 115}{\underline{CH_2 = \overset{+}{S}CF_3}} \qquad 13.$$

The relative amounts of the ions at m/e 129 and m/e 115 is <u>ca</u>. 5:2, suggesting that process 12 is favoured over process 13. However, this assumes that the decomposition of both product ions is unimportant or that the rates of the decomposition are similar and such assumptions are not valid. So whether the positive charge is localised on sulphur (a) or sulphur (b) cannot be determined from the ratio of the ions at m/e 129 and m/e 115.

$$CF_3\underset{(a)}{S}CH_2CH(CH_3)\underset{(b)}{S}CF_3$$

The observation of a metastable peak at m/e 92.3 is attributed to the fragmentation mode

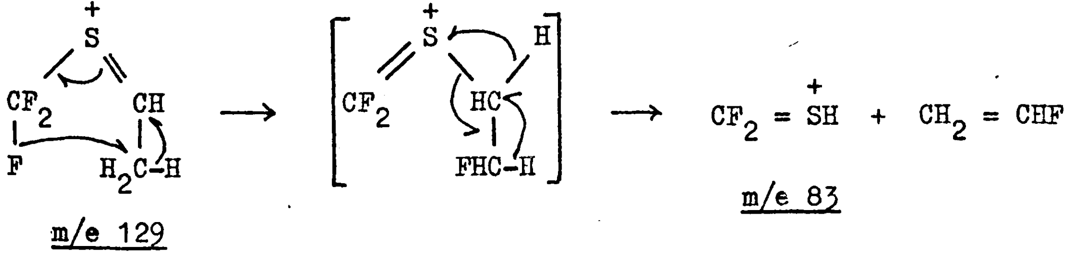


$$CF_3SCH_2-\underset{CH_2-H}{\overset{+}{CH}} \longrightarrow \underset{m/e\ 115}{CF_3SCH_2^+} + CH_2=CH_2$$

14.

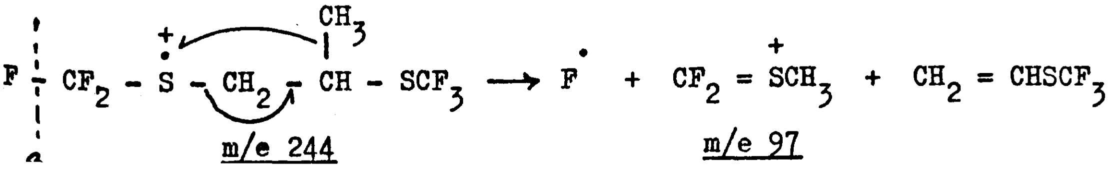
The significance of this is two-fold. Firstly, not all the ions at m/e 115 arise from β cleavage of the molecular ion since this metastable peak proves another mode of formation. Secondly, although the ion at m/e 143 may be either $CF_3SCH(CH_3)CH_2^+$ or $CF_3SCH_2\overset{+}{C}HCH_3$, arising from ∝ cleavage of the molecular ion with retention of charge on carbon, the latter structure is proved to exist by process 14, thus supporting ∝ cleavage from $CF_3SCH_2CH(CH_3)\overset{+\bullet}{S}CF_3$; i.e. with localisation of charge on sulphur (a). ∝ cleavage from $CF_3\overset{+\bullet}{S}CH_2CH(CH_3)SCF_3$ is unsubstantiated.

The metastable peak at m/e 53.3 is due to loss of C_2H_3F from $CF_3SCHCH_3^+$ thus:-



15.

The peak at m/e 83 however, is less than 1% abundant, therefore this does not represent a major breakdown pathway for the ion $CF_3SCHCH_3^+$. The peak at m/e 83 may also be derived from the molecular ion by ∝, β cleavage with hydrogen rearrangement as described for $CF_3SCH_2CH_2SCF_3$, though, in this case, there is a possibility of CH_3 transfer by the same method thus:-



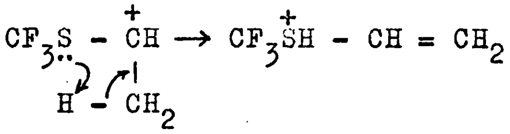
$$\underset{m/e\ 244}{F-CF_2-\overset{+\bullet}{S}-CH_2-\overset{CH_3}{CH}-SCF_3} \longrightarrow F^{\bullet} + \underset{m/e\ 97}{CF_2=\overset{+}{S}CH_3} + CH_2=CHSCF_3$$

16.

However, no ion is found at m/e 97.

The metastable peak at m/e 39.1 is probably due to loss of H$^{\cdot}$ from $CH_3\overset{+}{C}=CH_2$, although this gives rise to an odd-electron species $[CH_2=C-CH_2]^{+\cdot}$, since loss of F_2 from CF_3S^+ is not observed in the mass spectra of any of the other bis(trifluoromethylthio)alkanes and -fluoroalkanes.

Again, there is a high abundance (43%) of the ion CH_3S^+ at m/e 47. This is probably formed and accounts for the metastable peak at m/e 17.1 by a process similar to 10' above from the rearranged ion at m/e 129, i.e.

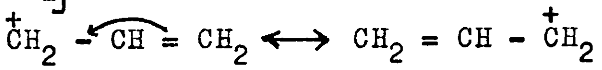


$$\begin{array}{l} CF_3\ddot{S}-\overset{+}{C}H \\ \quad H-CH_2 \end{array} \rightarrow CF_3\overset{+}{S}H-CH=CH_2$$

17.

with decomposition as before.

A further mode of fragmentation observed in aliphatic sulphides is observed here to a small extent. This is the expulsion of the heteroatom, with or without hydrogen, followed by recombination of the alkyl portions (201), e.g., $CH_3SCH=CH_2$ gives rise to an $(M-S)^+$ ion, 3.6%, an $(M-SH)^+$ ion, 95.1%, and an $(M-SH_3)^+$ ion, 10.7%. This is only important when the resultant ion can be stabilised e.g. the $[CH_2-CH=CH_2]^+$ ion from $(M-SH)^+$ can be resonance stabilised:-

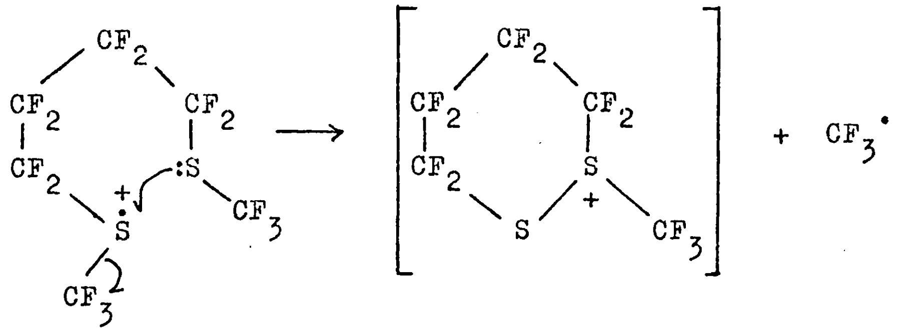


$$\overset{+}{C}H_2-CH=CH_2 \longleftrightarrow CH_2=CH-\overset{+}{C}H_2$$

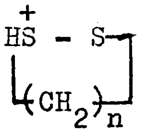
In the present case, an ion at m/e 212 (less than 1%) probably results from loss of S from the molecular ion with recombination of the fragments.

The mass spectrum of $CF_3S(CF_2CF_2)_2SCF_3$, Table 1.17 No. (3), has a vanishingly small molecular ion with respect to the base peak, m/e 69 CF_3^+, but this is probably due to the very high abundance of the CF_3^+ ion. The only other peak of any great relative abundance is $CF_3SCF_2^+$ (20%). Table 1.19 lists the metastable transitions observed in the mass spectrum of $CF_3S(CF_2CF_2)_2SCF_3$.

It is possible that ∝ cleavage with charge retention at sulphur, for which a metastable peak at m/e 275.9 is observed, may proceed through the cyclic compound:-



18.

though the stability of this relative to the open chain compound is doubtful due to the positive charge being located on the sulphur with both the electron-withdrawing CF_3 and CF_2 groups attached. Cyclic compounds of the type  $\overset{+}{H}S - S\underbrace{}_{(CH_2)_n}$ are postulated in the decomposition of dithioethers (195).

Whether the ion at m/e 301, $CF_3S(CF_2)_4^+$, is derived from the molecular ion by loss of $CF_3S^{\bullet}$ or from $CF_3S(CF_2CF_2)_2S^+$ by loss of sulphur cannot be determined since no metastable peaks are observed for either process. Both should be possible. Once the ion $CF_3S(CF_2)_4^+$ is formed, decomposition may occur by sequential loss of CF_2 groups:-

$$\underset{\underline{m/e\ 301}}{CF_3S(CF_2)_4^+} \longrightarrow :CF_2 + \underset{\underline{m/e\ 251}}{CF_3S(CF_2)_3^+} \longrightarrow :CF_2 + \underset{\underline{m/e\ 201}}{CF_3S(CF_2)_2^+}$$

$$\longrightarrow :CF_2 + \underset{\underline{m/e\ 151}}{CF_3SCF_2^+}$$

$$\longrightarrow :CF_2 + \underset{\underline{m/e\ 101}}{CF_3S^+}$$

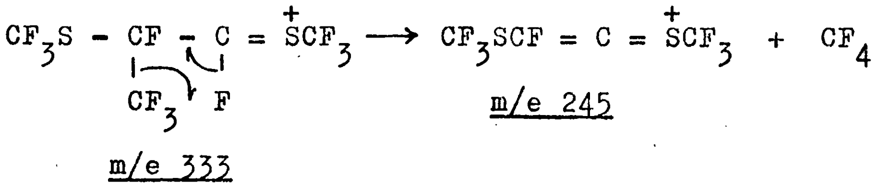
19.

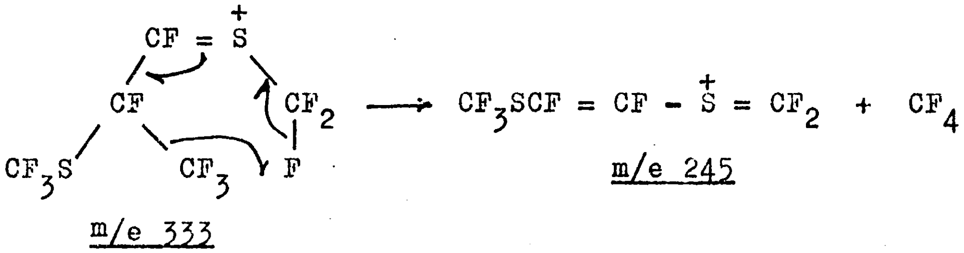
although there are no metastable peaks to support this pathway.

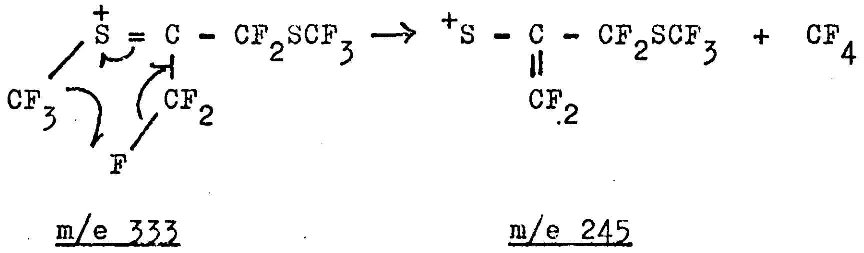
The mass spectra of $CF_3S\left[CF(CF_3)CF_2\right]_nSCF_3$, n = 1 and 2, are given in Table 1.17 Nos. (5) and (6) respectively whilst the metastable transitions are listed in Table 1.19. The molecular ions are of low abundance due to the dominating $\overset{+}{CF_3}$ ion. The mass spectra compare well with the mass spectra of $CF_3SCF_2CF_3$ and $CF_3SCF_2CF_2CF_3$ (51).

α cleavage with charge retention on sulphur is shown by a metastable peak at m/e 227.6 to be a mode of decomposition for $CF_3SCF(CF_3)CF_2SCF_3$, though which of the two F_3C-S bonds cleave is not known.

The metastable peak at 180.3 is due to loss of CF_4 from the ion at m/e 333, $(M-F)^+$, though how this is effected is not known. There are a number of possibilities, especially since the structure of the $(M-F)^+$ ion is not known though it probably arises from cleavage of a C-F bond.

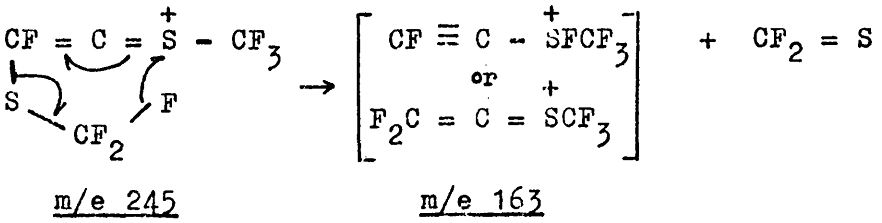

20.


21.

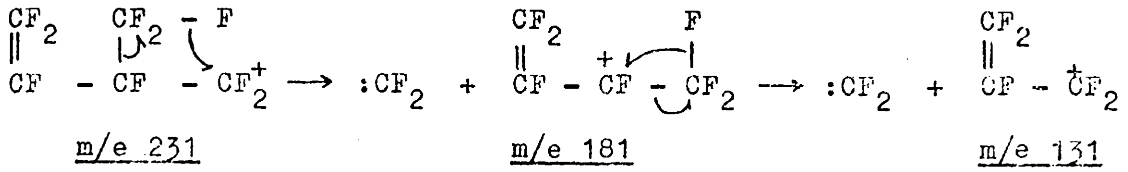

22.

Process 22 seems unlikely and choosing between 20 and 21 is trivial since rearrangements within the product ions can interconvert them.

The metastable peak at m/e 108.5 can arise from the decomposition of the ion at m/e 245, a possible mechanism for which is


23.

The mass spectrum of CF_3S CF(CF_3)CF_2 $_2SCF_3$ contains metastable peaks at m/e 141.8 and at m/e 94.8 which arise from loss of CF_2 groups from $C_5F_9^+$ and $C_4F_7^+$ respectively. There are several mechanisms possible for these transitions and one example is:-



$$\underset{m/e\ 231}{\overset{CF_2}{\overset{\|}{CF}} - \overset{CF_2 - F}{\overset{|}{CF}} - CF_2^+} \longrightarrow :CF_2 + \underset{m/e\ 181}{\overset{CF_2}{\overset{\|}{CF}} - \overset{+}{CF} - \overset{F}{\overset{|}{CF_2}}} \longrightarrow :CF_2 + \underset{m/e\ 131}{\overset{CF_2}{\overset{\|}{CF}} - \overset{+}{C}F_2}$$

24.

Several methods can be formulated whereby the ion $CF_3S\left[CF(CF_3)CF_2\right]_2^+$ loses CF_4 to account for the metastable peak at m/e 244.0, but determination of which one is responsible is not possible. Also, which of the two transitions listed in Table 1.19, viz. 433 345 and 401 313, gives rise to the metastable peak at m/e 274.9 cannot be determined.

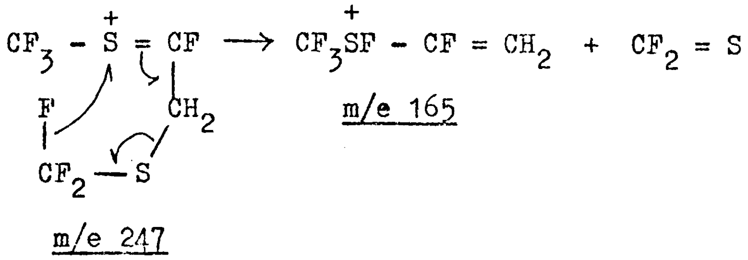
The ^{19}F n.m.r. spectrum suggests that the structure of the molecule is $CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3$ and this is substantiated by the mass spectrum thus:- there is no ion at m/e 201, if there was a $CF_3SCF(CF_3) - CF_2$ fragment in the molecule, then β cleavage would give rise to $CF_3SCF(CF_3)^+$, m/e 201, as already seen in the mass spectrum of $CF_3SCF(CF_3)CF_2SCF_3$. β cleavage, already shown to be an important fragmentation process in the previous bis(trifluoromethylthio)alkanes and -fluoroalkanes and in aliphatic sulphides (199), does give rise to a peak at m/e 151, $CF_3SCF_2^+$, which is the third largest peak (10%) in the spectrum:-

$$CF_3\overset{+}{\dot{S}} - CF_2 - CF(CF_3)CF(CF_3)CF_2SCF_3 \longrightarrow \underset{m/e\ 151}{CF_3\overset{+}{S} = CF_2} + {}^{\bullet}CF(CF_3)CF(CF_3)CF_2SCF_3$$

25.

The mass spectra of the series of compounds $CF_3S(CH_2CF_2)_nSCF_3$, n = 1-6, are given in Table 1.17 Nos. (7)-(12). The metastable transitions are listed in Table 1.19. In all but the n = 1 compound, where the base peak is m/e 69, CF_3^+, the base peak is found to be m/e 115, $CF_3SCH_2^+$. All the compounds show a reasonably strong molecular ion.

The peak at m/e 165, produced by α fission with charge retention at sulphur, may also arise from decomposition of the ion at m/e 247, as is shown by a metastable peak at m/e 110.2:-



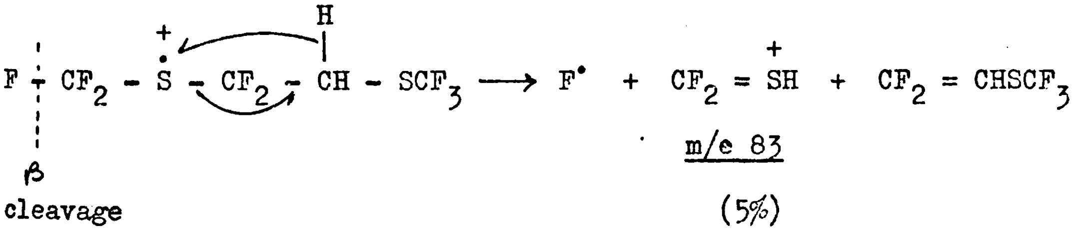
26.

Breakdown of the ion at m/e 165 to eventually give the CF_3SF^+ and SF^+ ions explains the otherwise anomalous peaks at m/e 120, $CF_3\overset{+}{S}F$, and m/e 51, SF^+, both less than 1% abundant.

Charge localisation on sulphur (a) is more favourable than on sulphur (b) and α cleavage

$$\underset{(a)}{CF_3S}CH_2CF_2\underset{(b)}{S}CF_3$$

therefore probably occurs at the H_2C-S (a) bond. However, charge localisation at sulphur (b) must occur to some extent since α, β cleavage with hydrogen rearrangement is a mode of fragmentation:-



27.

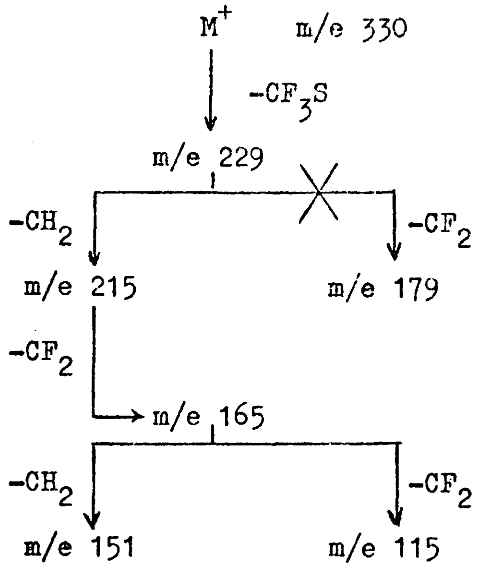
The metastable peak at m/e 34.5 is probably due to the process,

$$\underset{m/e\ 115}{CF_3\overset{+}{S}=CH_2} \longrightarrow \underset{m/e\ 63}{CFS^+} + CF_2H_2 \qquad 28.$$

since this is found in the $CF_3SCH_2CH_2SCF_3$ mass spectrum as well as the mass spectra of all the $CF_3S(CH_2CF_2)_nSCF_3$, n = 2-6, compounds.

n = 2 β fission to give $CF_3SCH_2^+$, m/e 115, 100%, is an important fragmentation mode of the molecular ion and this would argue again charge localisation on the sulphur with an adjacent CH_2 group rather than an adjacent CF_2 group.

α cleavage with charge retention at carbon is supported by the metastable peak at m/e 159.0. If sequential loss of CF_2 and CH_2 groups is then postulated thus:-



29.

a suggestion of the isomeric structures of $CF_3S(CH_2CF_2)_2SCF_3$ is obtained. The n = 2 compound has three possible structures, viz.

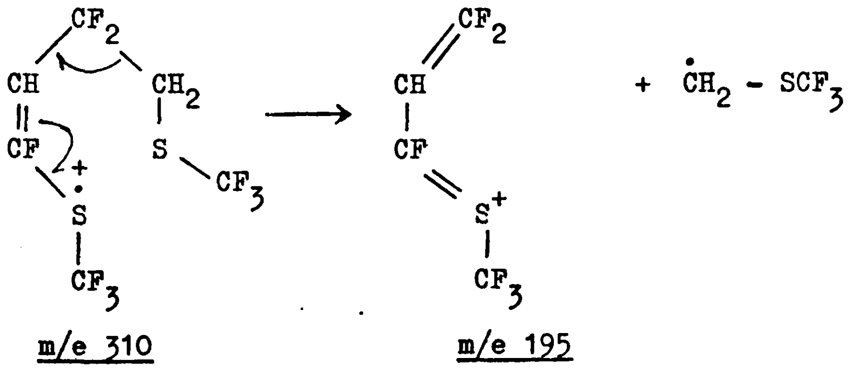
$CF_3SCH_2CF_2CF_2CH_2SCF_3$
VIII (a)

$CF_3SCH_2CF_2CH_2CF_2SCF_3$
VIII (b)

$CF_3SCF_2CH_2CH_2CF_2SCF_3$
VIII (c)

Lack of a peak at m/e 179, which is necessary for structure VIII (c) for this mode of breakdown, and of a peak due to $CH_2CH_2^+$, m/e 28 when peaks due to $CF_2CF_2^+$, m/e 100, and $CH_2CF_2^+$, m/e 64, are observed, tends to eliminate structure VIII (c). Scheme 29 can be accounted for by VIII (a) and VIII (b) and further proof of these structures comes from observation of peaks at m/e 115, $CF_3SCH_2^+$, m/e 64 $CH_2CF_2^+$, structure VIII (a), and m/e 151, $CF_3SCF_2^+$, m/e 100, $CF_2CF_2^+$, structure VIII (b).

The mechanism for the metastable transition giving rise to the metastable peak at m/e 122.7 is suggested to be,



30.

This mechanism is suggested by the very great stability of the products.

The ion at m/e 195 can be resonance stabilised whilst the radical $CF_3SCH_2^{\bullet}$ is similar to $RSCH_2^{\bullet}$, formed by $H^{\bullet}$ abstraction from $RSCH_3$ by a $CF_3^{\bullet}$ radical, which was found to be stable (202) and did not decompose.

The ion at m/e 51, SF^+, is probably formed by a rearrangement process similar to that found in the mass spectrum of the n = 1 compound although no metastable peak confirming this is observed.

<u>n = 3</u> There are three possible structures for the n = 3 compound:-

$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2SCF_3$

IX (a)

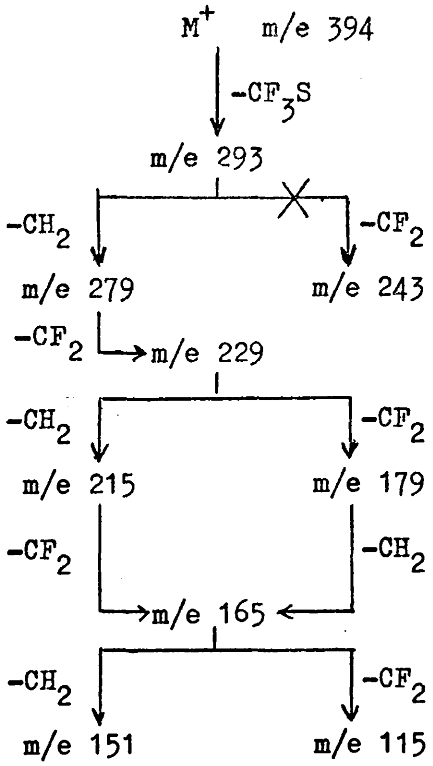
$CF_3SCH_2CF_2CH_2CF_2CF_2CH_2SCF_3$

IX (b)

$CF_3SCF_2CH_2CH_2CF_2CH_2CF_2SCF_3$

IX (c)

The isomeric structures are suggested by the nature of the ions arising from the postulated decomposition pathway:-

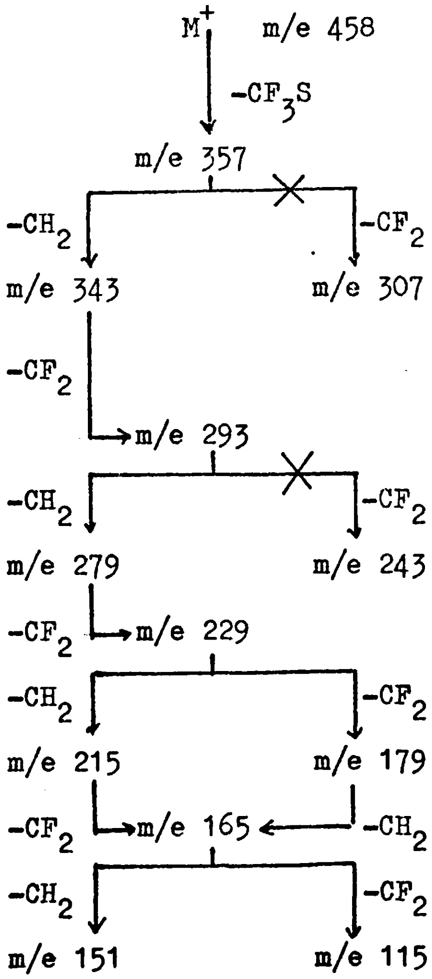


31.

Lack of an ion at m/e 243 and an ion at m/e 28, $CH_2CH_2^+$, tends to rule out structure IX (c). Structures IX (a) and IX (b) are confirmed by this scheme and by the presence of ions at m/e 115, $CF_3SCH_2^+$, m/e 64, $CF_2CH_2^+$, for structure IX (a), and at m/e 151, $CF_3SCF_2^+$ and m/e 100, $CF_2CF_2^+$, for structure IX (b). A similar mechanism to 31 but originating from $(M - HF)^+$, m/e 374, supports this argument.

The metastable peaks at m/e 171.2 and 89.9 can each arise from two processes and it is not possible to differentiate between them. It is worth noting that the transition m/e 374 → m/e 253 is probably loss of $CF_3S^{\bullet}$ and HF although loss of <u>ca.</u> CF_3SH and $F^{\bullet}$ is possible. Until recently, the presence of a metastable peak for the transition $m_1 \rightarrow m_2$ has been regarded as evidence that the neutral atoms of mass $(m_1 - m_2)$ are ejected in a one-step process as a single entity. Usually this is correct, but consecutive loss of <u>two</u> entities, perhaps in a concerted process, can happen, e.g. consecutive loss of two $HC \equiv CH$ molecules from $C_7H_7^+$ gives rise to a metastable peak at m/e 16.8 in the mass spectrum of toluene (195).

<u>n = 4</u> α cleavage with charge retention at carbon followed by possible sequential loss of CH_2 and CF_2 units establishes the structures X (a), X (b) and X (c) thus:-



32.

Structure X (a) is suggested by peaks at m/e 215 and 151

direction of
group loss
$\longrightarrow$
$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2SCF_3$

X (a)

Structure X (b) is suggested by peaks at m/e 215, 115, 223, 203.

direction of
group loss
$\longrightarrow$
$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2SCF_3$

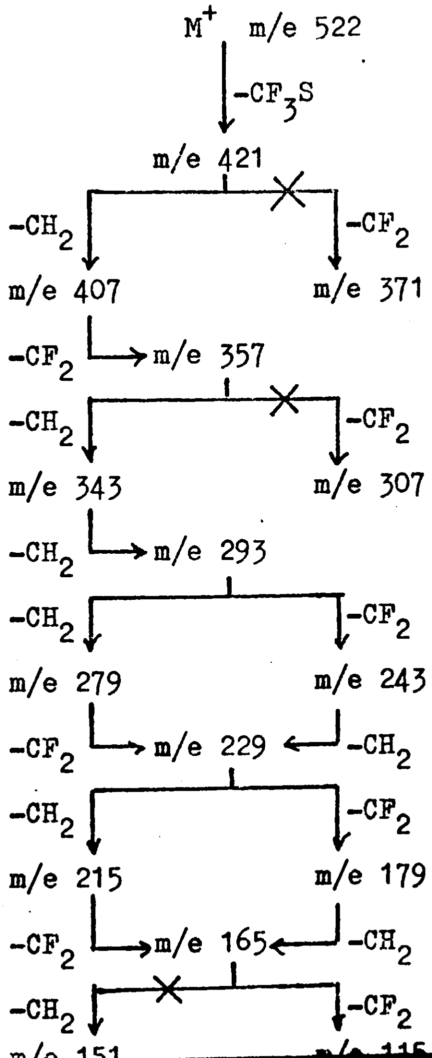
X (b)

Structure X (c) is suggested by peaks at m/e 179, 115

direction of group loss
$\longrightarrow$ $\longleftarrow$
$CF_3SCH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2SCF_3$

X (c)

n = 5 β cleavage to give $CF_3SCH_2^+$ is an important process. α cleavage with charge retention at carbon is evidenced by a metastable peak at m/e 339.6. If sequential loss of CH_2 and CF_2 groups is then postulated, a suggestion of the structures forming the n = 5 compound is obtained:-



Only structures XI (a) and XI (b) "fit" this scheme

direction of group loss →

$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2SCF_3$

XI (a)

The ion at m/e 215 can only come from XI (a) and not from XI (b)

→ direction of group loss ←

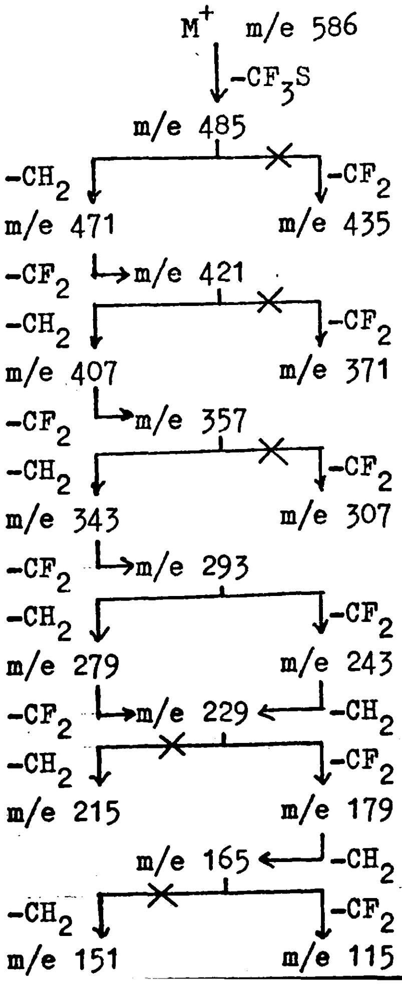
$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2SCF_3$

XI (b)

The ions at m/e 243 and 179 cannot arise from XI (a) but only from XI (b).

The metastable peak at m/e 190.8 shows that there is loss of $C_4F_4H_4$ from $CF_3S(CH_2CF_2)_4CH_2^+$, m/e 407. Whether this is simultaneous loss of two $CH_2 = CF_2$ groups or just the loss of one group, such as $CH_2F - CF = CF - CH_2F$, is not certain.

<u>n = 6</u> β cleavage to give $CF_3SCH_2^+$, m/e 115, again appears to be important, but, as before, α cleavage with charge retention at carbon and possible subsequent sequential breakdown of the ion formed gives a suggestion of the isomers composing the n = 6 compound thus:-



The structures which fit this sequence are

$\longrightarrow$ direction of group loss

$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2SCF_3$

XII (a)

confirmation of this structure is from the observation of the ion at m/e 279 which cannot arise from XII (b)

$\longrightarrow$ direction of loss of groups $\longleftarrow$

$CF_3SCH_2CF_2CH_2CF_2CH_2CF_2CF_2CH_2CF_2CH_2CF_2CH_2SCF_3$

XII (b)

The ion at m/e 243 helps to confirm XII (b) since it cannot arise from XII (a).

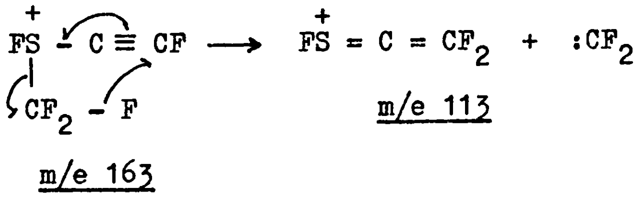
In all the compounds $CF_3S(CF_2CH_2)_nSCF_3$, n = 1-6, there is an ubiquitous loss of HF with metastable peaks appearing in the mass spectra as proof. Loss of HF is well substantiated in the literature e.g. in the fluoroethylenes (203).

Loss of HF is also observed in the mass spectra of $CF_3S(CF_2CFH)_nSCF_3$ n = 1-7. The mass spectra are given in Table 1.17 Nos. (13)-(19). All these compounds show molecular ions though they are not nearly so intense as in the $CF_3S(CF_2CH_2)_nSCF_3$ series, presumably a consequence of the increasing fluorine content of the series.

<u>n = 1</u> In this mass spectrum, the base peak is at m/e 45, CHS^+; this is not the base peak in the rest of the series and presumably, therefore, there is a particularly favourable fragmentation pathway for its formation here.

The metastable transitions for the n=1-7 compounds are listed in Table 1.19.

A mechanism for the metastable transition m/e 163 → m/e 113 is suggested to be,

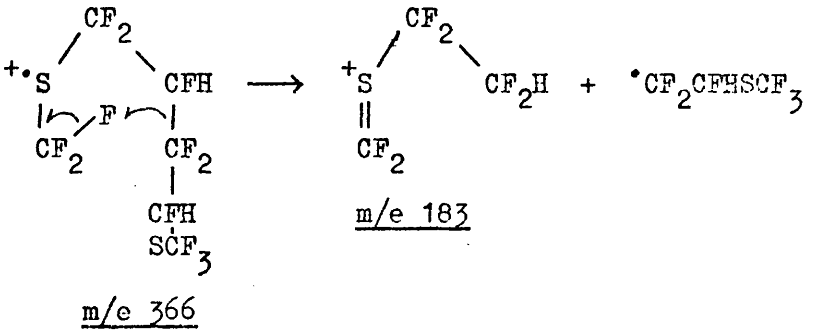


$$\underset{\text{m/e 163}}{\overset{+}{F}S(CF_2F)-C\equiv CF} \longrightarrow \underset{\text{m/e 113}}{\overset{+}{F}S=C=CF_2} + :CF_2 \qquad 35.$$

since decomposition of the ion at m/e 113 would account for the SF^+ ion found to the extent of 30% at m/e 51.

The metastable peak observed at m/e 10.1 is probably due to the transition m/e 95 → m/e 31 rather than the decomposition of CF_3S^+ as this latter is not observed in any other mass spectrum

n = 2 Most of the metastable transition listed require no further comments, but that with a metastable peak at m/e 91.2 is somewhat unusual, since it represents a γ-cleavage of the molecular ion not observed in the other compounds examined. A mechanism by which γ-cleavage may occur may be postulated as:-



36.

There are three possible structures for the n = 2 compound viz.

$CF_3SCFHCF_2CFHCF_2SCF_3$

XIV (a)

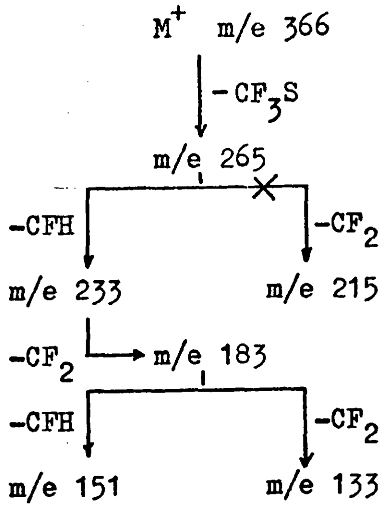
$CF_3SCFHCF_2CF_2CFHSCF_3$

XIV (b)

$CF_3SCF_2CFHCFHCF_2SCF_3$

XIV (c)

By postulating sequential loss of CF_2 and CFH units, originating from α cleavage with charge retention at carbon thus:-



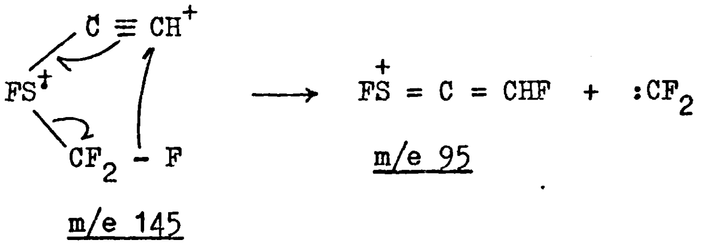
37.

it can be seen that although XIV (a) and XIV (b) can account for this sequence; XIV (c) is eliminated by the lack of an ion at m/e 215.

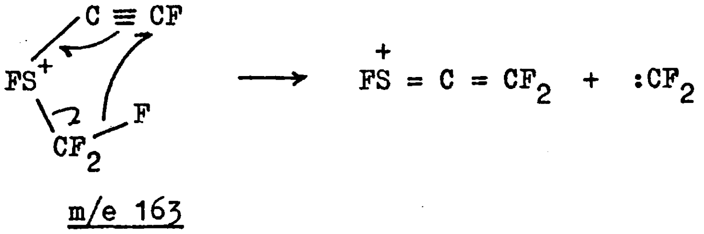
This is in agreement with the ^{19}F n.m.r. data.

It should also be noted that it is not possible to distinguish between the two processes giving rise to the metastable peak at m/e 126.3. However, loss of F_2 is very unusual and the metastable peak at m/e 126.3 probably arises from decomposition of the ion at m/e 265. For the compounds n = 3-7, no information about the structures of the isomers can be obtained from the mass spectra by the method used for the n = 2 compound and the $CF_3S(CF_2CH_2)_nSCF_3$ series of compounds since there are no "missing" ions which allow elimination of certain structures. Also, in the n = 5, 6, 7 compounds, the mass spectrum of a mixture of all three was run and the percentages quoted have no "absolute" meaning.

In all these mass spectra, a peak at m/e 51, due to the SF^+ ion, is observed in considerable abundance and is obviously due to some rearrangement process as observed in several previous examples although in the n = 3 and n = 4 compounds these are metastable peaks at m/e 62.2 and m/e 78.5 respectively showing how precursors of the SF^+ ion may be formed thus:-



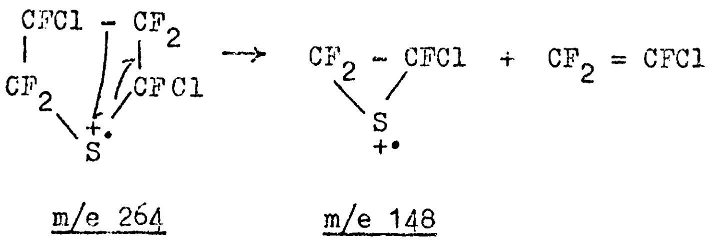
38.



39.

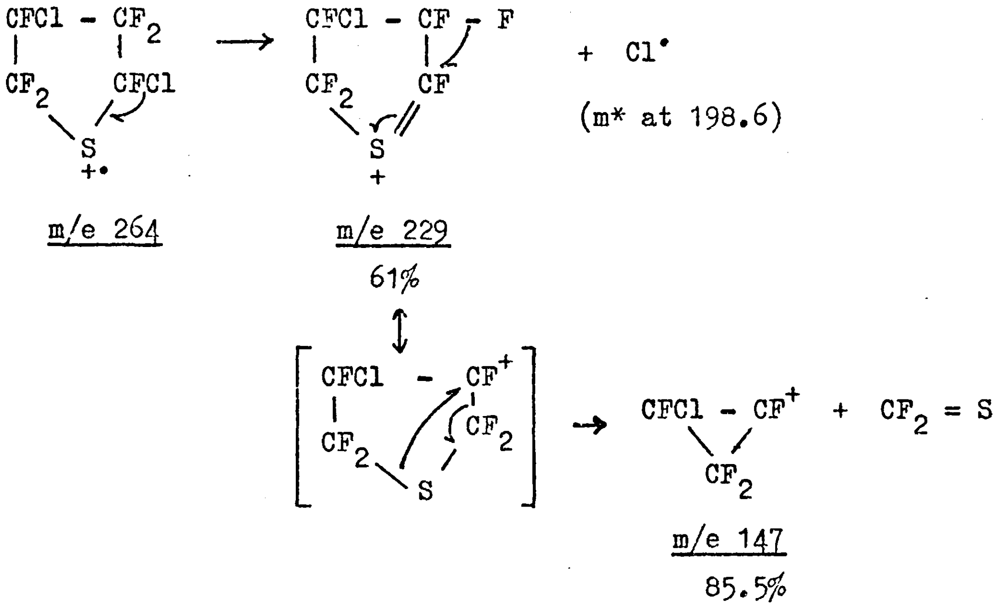
The mass spectra of $\overline{CF_2CFClCF_2CFClS}$, $CF_3SCF_2CFClCF_3$ and $CF_3S(CF_2CFCl)_nSCF_3$, n = 1-4, are listed in Table 1.17 Nos. (20)-(25).

Table 1.19 lists the metastable transitions observed in the mass spectra. The fragmentation of aliphatic cyclic thioethers is well known (195) and it is found that ring size influences the decomposition pattern. The breakdown of $\overline{CF_2CFClCF_2CFClS}$ is not similar to that found for the cyclic thioethers. One mode of decomposition found in cyclic thioethers however, may be occurring here:-



40.

although there is no substantiation for this. Next to the base peak, m/e 63, CFS^+, the most abundant ion is at m/e 147 85.5%, $C_3F_4Cl^+$. The following mechanism is suggested for its formation



41.

42.

There is however no support for the latter part of this mechanism save the high abundance of the ion m/e 147.

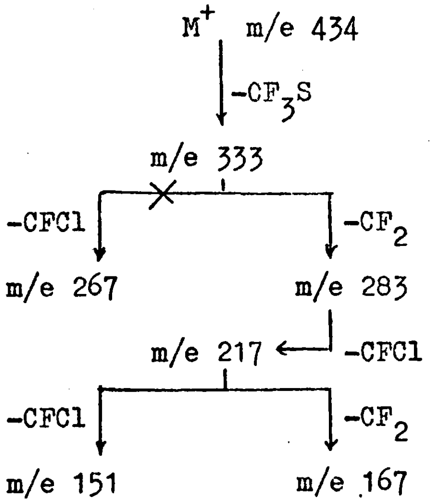
There are no metastable transitions observed in the mass spectrum of $CF_3SCF_2CFClCF_3$. The structure is deduced as $CF_3SCF_2CFClCF_3$ from the ion at m/e 151 $CF_3SCF_2^+$ and lack of an ion at m/e 167 CF_3SCFCl^+; and from the ion at m/e 135, CF_3CFCl^+, and lack of an ion at m/e 119, $CF_3CF_2^+$. Rapp et al. (204) base their identification of the reaction product from the $CH_3CH_2SH/CF_2 = CFCl$ reaction as $CH_3CH_2SCF_2CFClH$, rather than the isomer $CH_3CH_2SCFClCF_2H$, on the observation of the ion $CH_3CH_2SCF_2^+$ and lack of the ion $CH_3CH_2SCFCl^+$ in the mass spectrum.

β cleavage and α cleavage with charge retention at carbon and loss of $CF_3S^•$ are both fragmentation modes.

The metastable transitions observed in the mass spectrum of

$CF_3SCF_2CFClSCF_3$ are listed in Table 1.19. β cleavage to give $CF_3SCF_2^+$, m/e 151 (80.5%), rather than CF_3SCFCl^+, m/e 167 (2%), would seem to be favoured according to the relative relative abundances of the ions, but it may well be that the ion CF_3SCFCl^+ is relatively unstable. As in all the $CF_3S(CF_2CFCl)_nSCF_3$, n = 1-4, compounds, the base peak is m/e 69, CF_3^+.

n = 2 The metastable transitions are listed in Table 1.19. The structures of the isomers composing the n = 2 compound are suggested by postulating the sequential loss of CF_2 and CFCl groups from the ion originating from α cleavage of the molecular ion with charge retention at carbon thus:-



43.

This sequence can be accounted for by structures XXIII (a) and XXIII (b) only since lack of an ion at m/e 267 eliminates structure XXIII (c)

direction of group loss $\longrightarrow$

$CF_3SCF_2CFClCF_2CFClSCF_3$

XXIII (a)

direction of group loss $\longrightarrow$ $\longleftarrow$

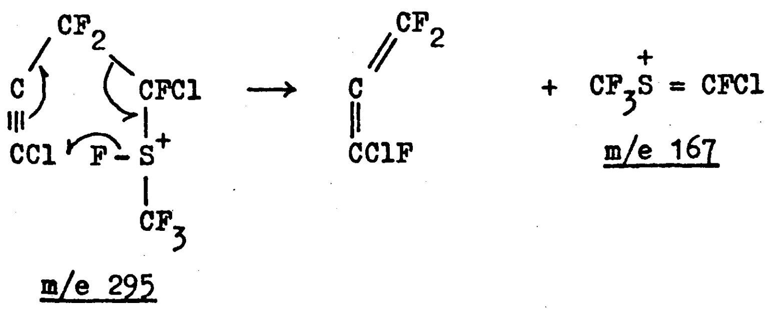
$CF_3SCF_2CFClCFClCF_2SCF_3$

XXIII (b)

$CF_3SCFClCF_2CF_2CFClSCF_3$

XXIII (c)

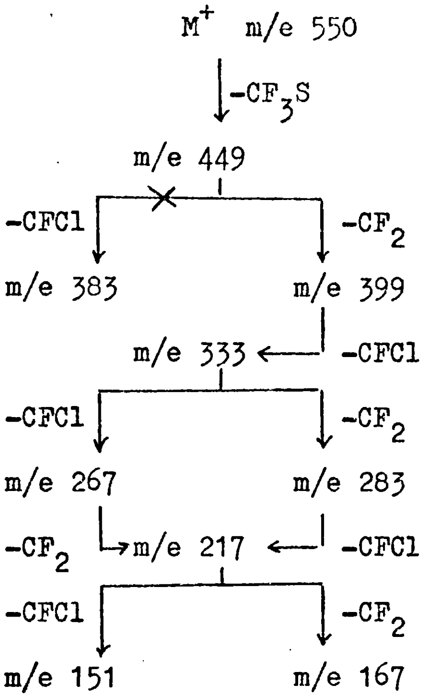
Whether the metastable peak at m/e 94.5 arises from the transition m/e 295 → m/e 167 or m/e 229 → m/e 147 cannot be determined. The former may take place thus:-



44.

with the stability of the $CF_3\overset{+}{S} = CFCl$ ion perhaps determining the mode of breakdown.

n = 3 Again, by postulating α cleavage with charge retention at carbon followed by sequential loss of CF_2 and CFCl groups, a suggestion as to the possible isomeric structure of which the n = 3 compound is composed may be obtained:-



45.

Only XXIV (a) and XXIV (b) of the three possible structures can account for this pathway, XXIV (c) being eliminated by the lack of an ion at m/e 383

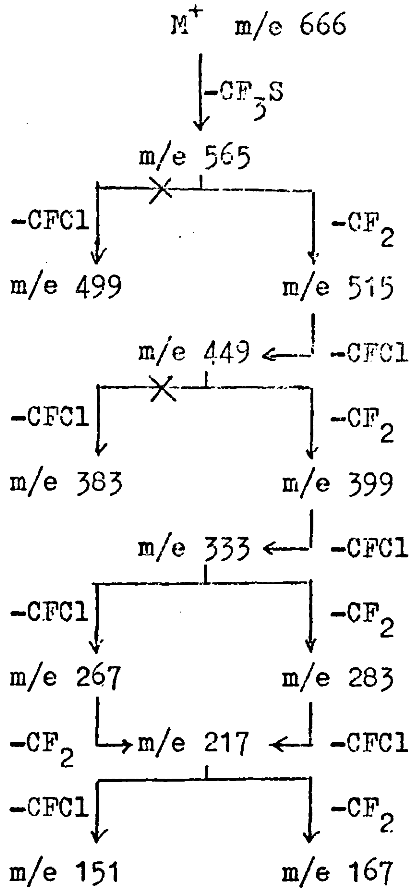
direction of
group loss
$\overrightarrow{}$
$CF_3SCF_2CFClCF_2CFClCF_2CFClSCF_3$ XXIV (a)

direction of group loss
$\overrightarrow{}$ $\overleftarrow{}$
$CF_3SCF_2CFClCF_2CFClCFClCF_2SCF_3$ XXIV (b)

$CF_3SCFClCF_2CF_2CFClCF_2CFClSCF_3$ XXIV (c)

In the absence of metastable peaks, it is difficult to comment on unusual fragmentation pathways, so suffice it to say that β cleavage is very probably also occurring here and would give rise to peaks at m/e 151, $CF_3SCF_2^+$, and at m/e 167, CF_3SCFCl^+.

n = 4 The metastable peaks observed in the mass spectrum of $CF_3S(CF_2CFCl)_4SCF_3$ are listed in Table 1.19. The structure of the isomers composing the n = 4 compound are suggested by a process similar to that used above:-



46.

There are three possible structures which can account for this scheme viz:-

direction of group loss →

$CF_3SCF_2CFClCF_2CFClCF_2CFClCF_2CFClSCF_3$ XXV (a)

direction of group loss → ←

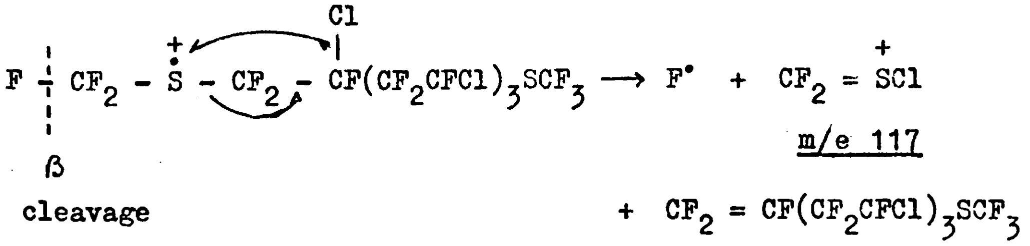
$CF_3SCF_2CFClCF_2CFClCF_2CFClCFClCF_2SCF_3$ XXV (b)

direction of group loss → ←

$CF_3SCF_2CFClCF_2CFClCFClCF_2CFClCF_2SCF_3$ XXV (c)

Peaks at m/e 79, $SCCl^+$, and m/e 167, CF_3SCFCl^+, confirm XXV (a) while the peak at m/e 267 confirms XXV (c). XXV (b) accounts for this sequence equally well, but there are no unique ions for this isomer.

α, β cleavage with chlorine rearrangement is observed:-



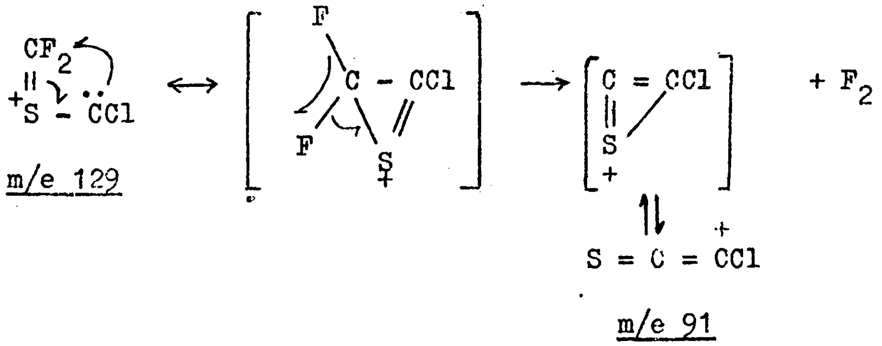
47.

Decomposition of the ion at m/e 117 may account for the otherwise anomalous ion at m/e 85, CF_2Cl^+, 24%, which is not only found here but also in the $CF_3S(CF_2CFCl)_nSCF_3$, n = 2,3 compounds.

The mass spectra of the compounds $CF_3SCCl_2CCl_2SCF_3$, $CF_3SCCl = CCl_2$, and $CF_3SCCl_2CCl_3$ are given in Table 1.17, Nos. (27)-(29) and the metastable transitions are listed in Table 1.19.

For $CF_3SCCl_2CCl_2SCF_3$, no molecular ion is observed although a molecular ion is observed in the mass spectra of the other two compounds. α cleavage with charge retention on carbon and β cleavage are both fragmentation modes.

The metastable peak at m/e 64.3, also observed in the mass spectra of the other two compounds, is calculated to be due to the transition m/e 129 ⟶ m/e 91. A tentative mechanism is postulated to be:-

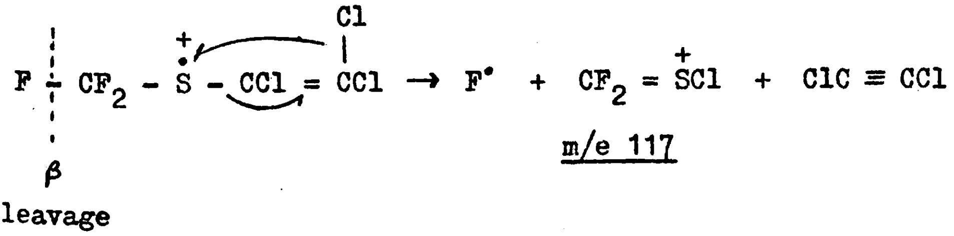


48.

β cleavage does not appear to be a possible mode of decomposition for $CF_3SCCl = CCl_2$ and the ion $(CF_3S - CCl)^{+\bullet}$ is not observed.

A metastable peak at m/e 112.7 shows that α cleavage of the $CF_3 - S$ bond with charge retention at sulphur is a mode of fragmentation. Also important is α cleavage with charge retention at carbon to give a high abundance of m/e 129, $CCl_2 = CCl^+$, 100%. However, some of the ion current may be carried by $CF_2 = \overset{+}{S}CCl$ also m/e 129.

A less important mode of fragmentation is α,β cleavage with chlorine rearrangement:-



The ion at m/e 117 is less than 1% abundant.

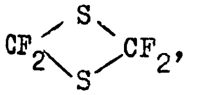
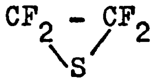
β cleavage of $CF_3SCCl_2CCl_3$ is an important fragmentation process, judging by the very high abundance of the product ion, m/e 195, $CF_3SCCl_2^+$. 96%. α cleavage is also reasonably important, taking place with charge retention at carbon and loss of CF_3S to give an ion at m/e 199, $CCl_3CCl_2^+$, 49%.

B. Some Reactions of Bis(trifluoromethylthio)alkanes and -fluoroalkanes with Iodine Pentafluoride and Chlorine Monofluoride.

Reaction of 1,2-bis(trifluoromethylthio)ethane with Iodine Pentafluoride

The room temperature reaction does not proceed to completion under the conditions used and unreacted $CF_3SCH_2CH_2SCF_3$ and IF_5 are recovered from the reaction mixture. The more volatile materials are CF_4, CF_3I and SiF_4. The SiF_4 is presumably derived from reaction of HF with the glass vacuum line since HF is a more logical product of this reaction in a metal bomb. The formation of CF_4 and CF_3I indicates that the CF_3-S bond is cleaved. Cullen (74) has shown that in an asymmetric sulphide such as CF_3SCH_3, there is very little difference in the two C-S bond energies:-

	bond energy (kcals./mole)	
	$CH_3 - S$	$CF_3 - S$
$CH_3 - S - CF_3$	99.0	96.5

Therefore one would expect evidence of volatile CF_3S compounds e.g. CF_3SF_3 or CF_3SF_5, from cleavage of the $S - CH_2$ bond but such compounds are not found, although IF_5 is known to oxidise tetrafluorodithietane , to CF_3SF_3 (27). The HF is almost certainly formed by fluorination of the hydrocarbon part of the molecule; the driving force for the reaction probably being the high bond energy [136 kcals./mole (183)], though how many hydrogens are exchanged for fluorine in one molecule of $CF_3SCH_2CH_2SCF_3$ cannot be determined. The solid products were not investigated further, although a polymer such as $\left(SC_2H_xF_{4-x}\right)_n$ may be formed, possibly with deposition of sulphur, since no alkenes or alkanes are found. A polymer of this type is known, viz. $\left(SCF_2CF_2\right)_n$ (94) originating from the $CF_3S^{\bullet}$ initiated polymerisation of tetrafluorothiirane, 

Reaction of 1,2-bis(trifluoromethylthio)ethane with Chlorine Monofluoride

The reaction of $CF_3SCH_2CH_2SCF_3$ with ClF at room temperature in a 1:4 ratio does not give the expected $CF_3SF_2CH_2CH_2SF_2CF_3$. Instead, only ~30% of the

$CF_3SCH_2CH_2SCF_3$ is used up, being converted to $CF_3SCHClCH_2SCF_3$ (trace; identified by the mass spectrum, Table 1.22, with the metastable transitions listed in Table 1.23), $CF_3SCCl_2CH_2SCF_3$, (identified by the mass spectrum

<u>Table 1.22</u>: Mass spectrum of $CF_3SCHClCH_2SCF_3$ (m/e value, relative abundance, ion, respectively; ions quoted for ^{35}Cl isotope only)

264, 6, M^+; 229, 10, $(M-Cl)^+$; 195, 1, $C_3H_3F_3ClS_2^+$; 163, 9, $C_3H_3F_3ClS^+$; 160, 2, $C_3H_3F_3S_2^+$; 159, 2, $C_4H_2F_3S_2^+$; 149, 9, CF_3SCHCl^+; 128, 9, $C_3H_3F_3S^+$; 127, 3, $C_3H_2F_3S^+$; 115, 58, $CF_3SCH_2^+$; 101, 15, CF_3S^+; 94, 3, $C_2H_3ClS^+$; 93, 3, $C_2H_2ClS^+$; 91, 10, C_2ClS^+ and $C_2H_3S_2^+$; 90, 3, $C_2H_2S_2^+$; 82, 11, CF_2S^+; 77, 9, $C_2H_2FS^+$; 69, 100, CF_3^+; 63, 36, CFS^+; 62, 20, $C_2H_3Cl^+$; 61, 13. $C_2H_2Cl^+$; 60, 1, C_2HCl^+; 59, 17, $C_2H_3S^+$; 58, 16, $C_2H_2S^+$; 57, 5, C_2HS^+; 50, 9, CF_2^+; 47, 88, CCl^+, 35, 23, Cl^+; 32, 19, S^+; 31, 19, CF^+, 27, 45, $C_2H_3^+$; 26, 51, $C_2H_2^+$.

<u>Table 1.23</u>: Metastable transitions observed in the mass spectra of $CF_3SCHClCH_2SCF_3$ and $CF_3SCCl_2CH_2SCF_3$.

m_1	Transition	m_2	m^* calc.	m^* found
	$CF_3SCHClCH_2SCF_3$			
264	$M^+ \longrightarrow C_4H_3F_6S_2^+ + Cl^\bullet$	229	198.6	198.6
115	$CF_3SCH_2^+ \longrightarrow CFS^+ + CF_2H_2$	63	34.5	34.5
	$CF_3SCCl_2CH_2SCF_3$			
298	$M^+ \longrightarrow C_3H_2F_3ClS_2^+ + CF_3Cl$	194	126.4	126.5
298	$M^+ \longrightarrow C_3H_2F_3ClS^+ + CF_3SCl$	162	88.1	88.2
115	$CF_3SCH_2^+ \longrightarrow CFS^+ + CF_2H_2$	63	34.5	34.5

<u>Table 1.24</u>: Mass spectrum of $CF_3SCCl_2CH_2SCF_3$ (m/e value, relative abundance, ion, respectively; ions quoted for ^{35}Cl isotope only).

298, 8, M^+; 263, 8, $(M-Cl)^+$; 261, 3, $C_4F_6ClS_2^+$; 229, 46, $C_3H_2F_3Cl_2S_2^+$; 228, 26, $C_3HF_3Cl_2S_2^+$ and $C_4H_2F_6S_2^+$; 226, 3, $C_4F_6S_2^+$; 197, 3, $C_3H_2F_3Cl_2S^+$; 196, 4, $C_3HF_3Cl_2S^+$; 195, 4, $C_3F_3Cl_2S^+$; 194, 6, $C_3H_2F_3ClS_2^+$; 192, 4, $C_3F_3ClS_2^+$; 177, 3, $C_3HF_2Cl_2S^+$; 176, 2, $C_3F_2Cl_2S^+$; 162, 10, $C_3H_2F_3ClS^+$; 161, 8, $C_3HF_3ClS^+$; 159, 4, $C_3H_2F_3S_2^+$; 157, 4, $C_3F_3S_2^+$; 127, 67, $C_3H_2F_3S^+$; 125, 59, $C_3F_3S^+$; 115, 54, $CF_3SCH_2^+$; 114, 14, $C_2HF_3S^+$ and CCl_2S^+; 101, 4, CF_3S^+; 92, 9, C_2HClS^+; 91, 10, C_2ClS^+; 82, 38, CCl_2^+ and CF_2S^+; 79, 39, $CClS^+$; 77, 3, $C_2H_2FS^+$; 69, 100, CF_3^+; 63, 8, CFS^+; 60, 6, C_2HCl^+; 59, 12, C_2Cl^+; 58, 8, $C_2H_2S^+$; 56, 2, C_2S^+; 50, 5, CF_2^+; 47, 85, CCl^+; 46, 10, CH_2S^+; 45, 3, CHS^+; 44, 16, CS^+; 32 2, S^+; 31, 1, CF^+; 26, 11, $C_2H_2^+$.

in Table 1.24, with metastable transitions listed in Table 1.23 and a S(VI) compound (trace). The nature of this last compound is not known but the ^{19}F n.m.r. spectrum shows two signals: one at $\delta = -101.4$ p.p.m. and one at $\delta = +115.7$ p.p.m. (w.r.t. CCl_3F ext.). The former signal is indicative of *trans*-R_fSF_4Cl. [*Cf.* *trans*-CF_3SF_4Cl, $\delta_{SF_4} = -102.1$ p.p.m. (205)], and is split into a doublet with $J = 12$ Hz. The latter signal is too weak for coupling to be observed, but the chemical shift is indicative of $-SF_4-C\underline{F}Cl-CX_3$ (206). The coupling $J_{S\underline{F}_4C\underline{F}Cl}$ in $SF_5CFClCF_2Cl$ is 11.0 Hz. (206) and on this basis the compound may be *trans*-$ClSF_4CFClCCl_3$ or of similar type.

The dichloro-bis(trifluoromethylthio)ethane is thought to be the 1,1-dichloro compound, $CF_3SCCl_2CH_2SCF_3$ rather than the 1,2-dichloro compound $CF_3SCHClCHClSCF_3$ from both the mass and the ^1H n.m.r. spectra. The mass spectrum shows the ions CCl_2^+, m/e 82, and $SCCl_2^+$, m/e 114, (identified as being present from the Cl^{37} isotopes), and the ^1H n.m.r. spectrum shows a signal, $\delta = 3.44$ p.p.m., indicative of CH_2 rather than CH. (207). The ^{19}F n.m.r. spectrum of $CF_3SCCl_2CH_2SCF_3$ has the chemical shifts $\delta\, C\underline{F}_3SCH_2 = +40.8$ p.p.m., $\delta\, C\underline{F}_3SCCl_2 = +43.6$ p.p.m. The i.r. spectrum is very similar to that of $CF_3SCH_2CH_2SCF_3$ except for the appearance of a strong broad band at 804 cm^{-1} and assigned to ν(C-Cl) (208). The reaction involves a considerable amount of the breakdown products CF_4 and CF_3Cl. The SiF_4 found presumably comes from reaction of HF with the glass vacuum line, the HF being formed as a result of chlorine substitution into the alkyl part of the molecule. Formation of HF as a product of ClF reaction is well known e.g.

		Reference
1.	$(SO_2F)_2NH \xrightarrow{ClF} (SO_2F)_2NCl + HF$	209
2.	$R_fOH \xrightarrow{ClF} R_fOCl + HF$, $R_f = (CF_3)_3C$ etc.	210
3.	$CF_3OOH \xrightarrow{ClF} CF_3OOCl + HF$	211

The HF found here, as well as the HCl found, may also result from hydrolysis of unreacted ClF. A trace of chlorine is also observed as a product, as would be expected from an oxidation reaction involving ClF.

The mass spectra of $CF_3SCH_2CHClSCF_3$ and $CF_3SCH_2CCl_2SCF_3$ show fragmentation patterns which can be interpreted as βcleavage and α cleavage with subsequent breakdown in a similar manner to that already discussed in Section A.

Reaction of 1,2-Bis(trifluoromethylthio)hexafluoropropane with Chlorine Monofluoride

The reaction of $CF_3SCF(CF_3)CF_2SCF_3$ with ClF also does not give the expected product $CF_3SF_2CF(CF_3)CF_2SF_2CF_3$. Instead, a whole variety of products is obtained. The more volatile are CF_4, CF_3Cl, SiF_4 (trace), Cl_2, CF_3SF_5 and CF_3SF_4Cl. These last two products alone suggest that oxidative cleavage of the C - S bond takes place. The remainder of the products form two fractions which could not be separated further; viz. a fraction which passes a -22^o trap but stops at -45^o and a fraction which passes a -45^o trap but stops at -80^o. Table 1.25 lists the ^{19}F n.m.r. chemical shifts found, with a tentative identification of the compounds giving rise to them. Table 1.26 lists the coupling constants observed and these are assigned with regard to the proposed structures of the compounds. In some cases, a full analysis is not possible due to the complexity of the signals. Reference (180) was particularly useful in the assigning of chemical shifts.

The sulphur (VI) compounds all seemed to have a trans structure about the sulphur.

From the mass spectra, support for some of the compounds is found :- m/e 236, M^+ for $(CF_3)_2CFSCl$; m/e 286, M^+ for both $CF_3SCF_2CFClCF_3$ and $CF_3SCF(CF_3)CF_2Cl$; m/e 239, $(CF_3)_2CFSF_2^+$, m/e 220, $(CF_3)_2CFSF^+$, and m/e 67, SCl^+, support the structure $(CF_3)_2CFSF_4Cl$. All the S(VI) compounds receive support from m/e 108, SF_4^+; m/e 89, SF_3^+; m/e 70, SF_2^+; and m/e 51, SF^+; m/e 139, $CF_3SF_2^+$; and m/e 120, CF_3SF^+; lend support to

Compound	δSF_4	δCF_3S	δCF_3	δCF_2	δCF
$(CF_3)_2CFSF_4Cl$	−122.0		+74.7		+156.9
$CF_3SF_4CF_2CFClCF_3$	− 22.9	+68.1	+76.1	+86.9	+143.9
$CF_3CFClCF_2SF_4Cl$	−124.4		+77.4	+105.6	+147.6
$CF_3SCF_2CFClCF_3$ (a)		+39.0	+75.1	+78.4	+141.6
$CF_3SCF(CF_3)CF_2Cl$ (a)		+37.6	+71.9	+63.3	+165.7
$(CF_3)_2CFSCl$			+76.8		+167.1
$CF_3CFClCF_2SCl$			+80.0	+79.1 and +79.8	+138.8
$(CF_3)_2CFCl$			+82.2		+145.8
$CF_3(CF_2Cl)CFSCl$			+73.0	+67.9	+152.7

(a) agrees with published spectrum (142)

Table 1.25 : Chemical shifts (p.p.m. w.r.t. ext. CCl_3F)

$(CF_3)_2CFSF_4Cl$	$J_{C\underline{F}S\underline{F}_4} = 4.5$; $J_{C\underline{F}_3CS\underline{F}_4} = 12.4$; $J_{C\underline{F}_3C\underline{F}} = 5.6$
$CF_3SF_4CF_2CFClCF_3$	$J_{C\underline{F}_3S\underline{F}_4} = 23.0$
$CF_3CFClCF_2SF_4Cl$	$J_{C\underline{F}_2S\underline{F}_4} = 23.6$; $J_{C\underline{F}CS\underline{F}_4} = 11.4$; $J_{C\underline{F}_3CCS\underline{F}_4} = 5.6$
$CF_3SCF_2CFClCF_3$	$J_{C\underline{F}_3SC\underline{F}_2} = 10.2$; $J_{C\underline{F}_3SCC\underline{F}} = 4.8$; $J_{C\underline{F}_3SCCC\underline{F}_3} \sim 0$;
	$J_{C\underline{F}_3C\underline{F}} = 10.1$; $J_{C\underline{F}_3CC\underline{F}_2} = 10.1$; $J_{C\underline{F}_2C\underline{F}} = 14.7$
$(CF_3)_2CFSCl$	$J_{C\underline{F}_3C\underline{F}} = 10.2$
$CF_3CFClCF_2{}^{*}SCl$	$J_{C\underline{F}\underline{F}^1} = 39.6$; $J_{C\underline{F}C\underline{F}} = 10.4$; $J_{C\underline{F}^1C\underline{F}} = 11.3$;
	$J_{C\underline{F}C\underline{F}_3} = 7.2$; $J_{C\underline{F}^1C\underline{F}_3} = 6.0$; $J_{C\underline{F}ClC\underline{F}_3} = 10.8$
$(CF_3)_2CFCl$	$J_{C\underline{F}_3C\underline{F}} = 6.2$
$CF_2Cl(CF_3)CFSCl$	$J_{C\underline{F}_3CC\underline{F}_2} = 9.0$; $J_{C\underline{F}C\underline{F}_2} = 9.0$; $J_{C\underline{F}_3C\underline{F}} = 16.9$

* denotes non-equivalence

Table 126 : Coupling constants (Hz.)

Table 1.27

Compound	$\nu_{asym}(SF_4)$	$\nu_{sym}(SF_4)$
S(VI)	865	682
CF_3SF_4Cl	860	678
CF_3SF_5	903	692
SF_5Cl	909	707

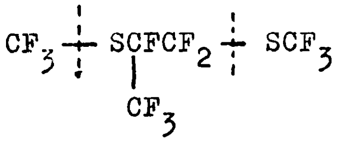
(all the bands are very strong absorptions)

$CF_3SF_4CF_2CFClCF_3$. The i.r. spectra of the two fractions also tend to support the S(VI) compounds:- the SF_4 asymmetric and symmetric stretching frequencies observed are given in Table 1.27, together with those of CF_3SF_4Cl (212), CF_3SF_5 (213) and SF_5Cl (213).

From the nature of the products, bond cleavage appears to be indiscriminate save to say that only C-S bonds are cleaved. Bond cleavage by ClF has been previously reported for $R_fN = SF_2$ (214, 215):-

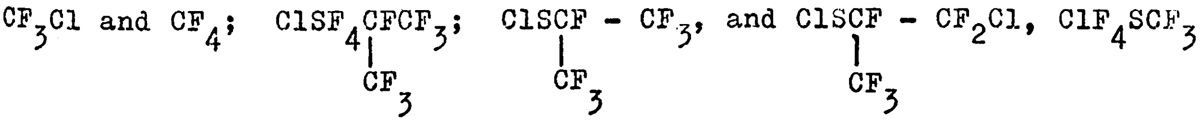
$$R_fN = SF_2 + ClF(excess) \longrightarrow RNCl_2 + SF_4$$

The products found in the $CF_3SCF(CF_3)CF_2SCF_3$/ClF reaction can be rationalised thus:-

(1) cleavage thus 

$CF_3 \vdots S\underset{\underset{CF_3}{|}}{C}FCF_2 \vdots SCF_3$

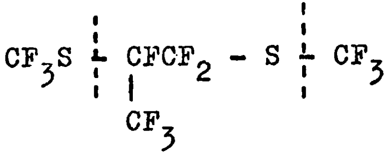
with addition of ClF accounts for



CF_3Cl and CF_4; $ClSF_4\underset{\underset{CF_3}{|}}{C}FCF_3$; $ClS\underset{\underset{CF_3}{|}}{C}F - CF_3$, and $ClS\underset{\underset{CF_3}{|}}{C}F - CF_2Cl$, ClF_4SCF_3

and F_5SCF_3.

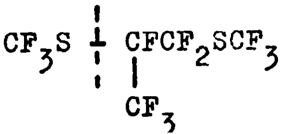
(2) cleavage thus



$CF_3S \vdots \underset{\underset{CF_3}{|}}{C}FCF_2 - S \vdots CF_3$

and addition of ClF accounts for CF_3SF_4Cl, and CF_3SF_5, $CF_3CFClCF_2SF_4Cl$ and $CF_3CFClCF_2SCl$; $ClCF_3$ and CF_4.

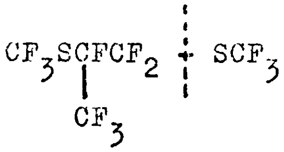
(3) cleavage thus



$CF_3S \vdots \underset{\underset{CF_3}{|}}{C}FCF_2SCF_3$

and addition of ClF accounts for CF_3SF_4Cl, CF_3SF_5, $CF_3CFClCF_2SF_4CF_3$, and $CF_3CFClCF_2SCF_3$.

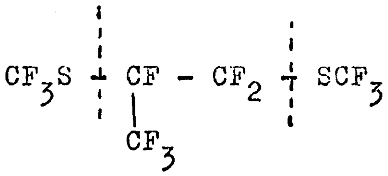
(4) cleavage thus



$$CF_3S\underset{\substack{|\\ CF_3}}{C}FCF_2 \;\vdots\; SCF_3$$

and addition of ClF accounts for $CF_3S\underset{\substack{|\\ CF_3}}{C}FCF_2Cl$, ClF_4SCF_3 and F_5SCF_3.

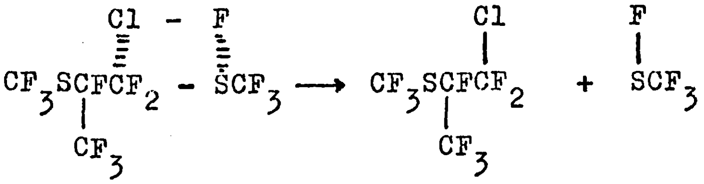
(5) cleavage thus



$$CF_3S \;\vdots\; \underset{\substack{|\\ CF_3}}{CF} - CF_2 \;\vdots\; SCF_3$$

and addition of ClF accounts for CF_3SF_4Cl and CF_3SF_5, $Cl\underset{\substack{|\\ CF_3}}{C}F - CF_3$ and CF_3SF_4Cl, CF_3SF_5.

Although these bond breaking and ClF addition processes are represented above as individual processes, there is probably a concerted mechanism taking place. No excess ClF is found in the reaction, nor is any unreacted $CF_3SCF(CF_3)CF_2SCF_3$ observed. This would explain the formation of S(II) compounds when oxidation would be expected to take place, i.e. there is insufficient ClF in the reaction mixture used. For example, consider process (4) above in more detail. A mechanism such as



$$CF_3S\underset{\substack{|\\ CF_3}}{C}F\overset{\substack{Cl\\ \vdots}}{C}F_2 - \overset{\substack{F\\ \vdots}}{S}CF_3 \longrightarrow CF_3S\underset{\substack{|\\ CF_3}}{C}F\overset{\substack{Cl\\ |}}{C}F_2 + \overset{\substack{F\\ |}}{S}CF_3$$

with ClF addition to CF_3SF thus

$$CF_3SF + 2ClF \longrightarrow CF_3SF_3 + Cl_2 \qquad (a)$$

$$CF_3SF_3 \left[\begin{array}{l} ClF \longrightarrow CF_3SF_4Cl \qquad (b) \\ 2ClF \longrightarrow CF_3SF_5 + Cl_2 \qquad (a) \end{array} \right.$$

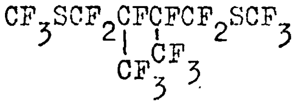
Both methods of addition of ClF (a) and (b) are well documented e.g.

(a) $CF_3SCF_2CF_3 \xrightarrow{ClF} CF_3SF_2CF_2CF_3 + Cl_2$ Ref.(51)

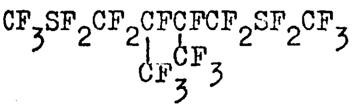
(b) $SO_2 + ClF \longrightarrow SO_2ClF$ Ref.(107)

$CF_3SCF(CF_3)CF_2Cl$ remains as S(II) due to insufficient ClF.

Reaction of 1,4-Bis(trifluoromethylthio)2,3-bis(trifluoromethyl)hexafluorobutane with Chlorine Monofluoride.



Reaction of $CF_3SCF_2\underset{CF_3}{CF}\underset{CF_3}{CF}CF_2SCF_3$ with ClF proceeds, other than slight breakdown to give trace amounts of HCl, SiF_4 (from hydrolysis), CF_4, CF_3Cl, SF_4 and SOF_2, smoothly to give 75% conversion to the bis-S(IV) compound,



$CF_3SF_2CF_2\underset{CF_3}{CF}\underset{CF_3}{CF}CF_2SF_2CF_3$ and chlorine. The compound is identified by mass, i.r. and ^1H and ^{19}F n.m.r. spectra and by elemental analysis. As far as is known, this is the first compound of this type, i.e. containing two S(IV) SF_2 groups in the perfluorocarbon chain, although $R_f^1SF_2R_f^2$ compounds are previously reported (38, 51-53, 73).

The compound is stable in air for short periods but there is slight decomposition at its boiling point (288-290° at 760 mm. Hg).

The i.r. spectrum is listed in Table 1.28 together with that of $CF_3SF_2CF_2CF_2CF_3$, quoted for comparison (51). The spectra compare very well, the band at ~675 cm^{-1} being assigned by Shreeve to a S-F stretching mode. It should be noted that this band is absent in the i.r spectrum of $CF_3S\left[CF_2CF(CF_3)\right]_2SCF_3$.

The mass spectrum is given in Table 1.29, with the metastable transition listed in Table 1.30. As in this work, molecular ions were not observed in the mass spectra of the $R_fSF_2R_f$ compounds (51) although $R_fSF_2^+$ ions were characteristic. Here, $CF_3SF_2^+$ is observed at m/e 139 (4%) and $C_6F_{13}SF_2^+$ at m/e 389 (less than 1%). Many of the ions listed in Table 1.29 are less than 1% abundant while there are no very intense ions other than CF_3^+, 100%. This is suggested to be due to the very high abundance of the m/e 69 CF_3^+ ion, which may be formed easily by rearrangement processes as well as normal breakdown processes (200), an effect which is observed in the mass spectra of $R_fSF_2R_f$ (51)

The ^{19}F n.m.r. chemical shifts and the coupling constants which could be

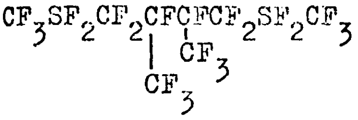
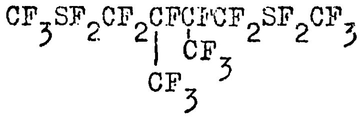
$CF_3SF_2CF_2CF_2CF_3$ (47)	1343(m), 1280(vs), 1260(vs), 1230(s-vs), 1158(s), 1112(s-vs), 1080(w-m), 1045(w), 905(w-m), 842(m), 760(w-m), 697(m), 675(s), 505(w), 482(w-m).
 $CF_3SF_2CF_2\underset{CF_3}{\underset{\vert}{C}}F\underset{CF_3}{\underset{\vert}{C}}FCF_2SF_2CF_3$ (this work)	1322(w), 1278(vs), 1255(vs), 1227(vs), 1201(s), 1163(m), 1143(m), 1129(m), 1101(vs), 1026(w), 1014(m), 934(w), 899(m), 855(m), 842(m), 809(s), 785(m), 752(s), 681(s), 649(s), 619(s).

Table 1.28: I.r. Spectrum of  $CF_3SF_2CF_2\underset{CF_3}{\underset{|}{C}}F\underset{CF_3}{\underset{|}{C}}FCF_2SF_2CF_3$

401*, $C_7F_{15}S^+$; 389*, $C_6F_{13}SF_2^+$; 370*, $C_6F_{14}S^+$; 351, 1, $C_6F_{13}S^+$; 332*, $C_6F_{12}S^+$; 313*, $C_6F_{11}S^+$; 301*, $C_5F_{11}S^+$; 281*, $C_6F_{11}^+$; 263, 1, $C_5F_9S^+$; 251*, $C_4F_9S^+$; 250*, $C_5F_{10}^+$; 232*, $C_4F_8S^+$; 231, 2, $C_5F_9^+$; 225*, $C_5F_7S^+$; 213*, $C_4F_7S^+$; 212*, $C_5F_8^+$; 201, 1, $CF_3SF_2CF{=}CF^+$ and $CF_3SF{-}CF{=}CF_2^+$; 182, 1, $C_3F_6S^+$; 181, 7, $C_4F_7^+$; 175*, $C_4F_5S^+$; 169*, $C_3F_7^+$; 163*, $C_3F_5S^+$; 162*, $C_4F_6^+$; 151, 1, $C_2F_5S^+$; 150, 8, $C_3F_6^+$; 144*, $C_3F_4S^+$; 143*, $C_4F_5^+$; 139, 4, $CF_3SF_2^+$; 132*, $C_2F_4S^+$; 131, 3, $C_3F_5^+$; 124*, $C_4F_4^+$; 120, 4, CF_4S^+; 113, 2, $C_2F_3S^+$; 112, 1, $C_3F_4^+$; 101, 6, CF_3S^+; 100, 10, $C_2F_4^+$; 93, 5, $C_3F_3^+$; 82, 3, CF_2S^+; 81, 2, $C_2F_3^+$; 70, 10, SF_2^+; 69, 100, CF_3^+; 63, 5, CFS^+; 51, 7, SF^+; 50, 51, CF_2^+; 44, 3, CS^+; 32, 5, S^+; 31, 12, CF^+.

Table 1.29: Mass Spectrum of $CF_3SF_2CF_2CF(CF_3)CF(CF_3)CF_2SF_2CF_3$

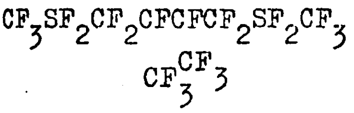
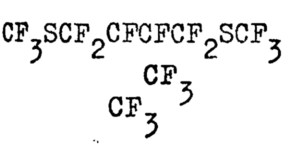
(m/e, relative abundance, ion respectively)

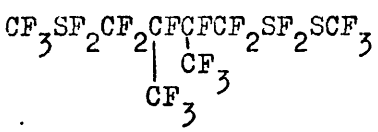
* denotes important ions of less than 1% abundance.

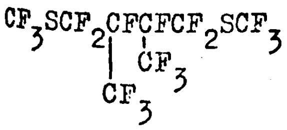
Table 1.30: Metastable transitions observed in the mass spectrum of

$CF_3SF_2CF_2CF(CF_3)CF(CF_3)CF_2SF_2CF_3$

m_1	Transition	m_2	m^*	
			calc.	found
231	$C_5F_9^+ \longrightarrow C_4F_7^+ + :CF_2$	181	141.9	141.9
101	$CF_3S^+ \longrightarrow CF_2S^+ + F^\bullet$	82	66.6	66.7
69	$CF_3^+ \longrightarrow CF_2^+ + F^\bullet$	50	36.2	36.2
131	or $C_3F_5^+ \longrightarrow CF_3^+ + FC{\equiv}CF$	69	36.3	

Compound	δCF_3S	δCF_3	δCF_2	δCF	δSF_2	Coupling Constants(Hz).	Ref.
$CF_3SF_2CF_2CF_2CF_3$	+55.6	+81.2	+97.1		+11.2	$J_{C\underline{F}_3S\underline{F}_2} = 20.1$ $J_{C\underline{F}_3SF_2C\underline{F}_2} = 7.3$	(47)
$CF_3SF_2CF_2CF_3$	+55.8	+80.2	+100.7		+13.0	$J_{C\underline{F}_3S\underline{F}_2} = 19.5$ $J_{C\underline{F}_3SF_2C\underline{F}_2} = 7.0$	(47)
$CF_3SF_2CF(CF_3)_2$	+61.7	+75.4		+170	+16	$J_{S\underline{F}_2C\underline{F}_3} = 19.0$	(55)
 $CF_3SF_2CF_2\underset{CF_3}{C}F\underset{CF_3}{C}FCF_2SF_2CF_3$	+55.8	+69.3	+80.8 +87.7	+169.8	+9.5 +13.1	$J_{S\underline{F}\underline{F}'} = 113.0$ $J_{C\underline{F}\underline{F}'} = 191.8$ $J_{C\underline{F}_3S\underline{F}_2} = 20.3$ $J_{C\underline{F}_3SF_2C\underline{F}_2} = 7.9$	this work
 $CF_3SCF_2\underset{CF_3}{C}F\underset{CF_3}{C}FCF_2SCF_3$	+36.4	+69.1	+71.5 +73.7	+164.7	-	$J_{C\underline{F}_3SC\underline{F}_2} = 10.3$	this work

<u>Table 1.31</u>: ^{19}F n.m.r. parameters for  $CF_3SF_2CF_2\underset{CF_3}{C}F\underset{CF_3}{C}FCF_2SF_2SCF_3$ and related compounds.

measured are listed in Table 1.31, together with the ^{19}F n.m.r. data for some related compounds for comparison. Both the SF_2 fluorines and the CF_2 fluorines show magnetic non-equivalence, and both signals are analysed as AB spectra (69) to extract the parameters listed. Similar non-equivalence is exhibited by $CF_3SF_2CF_2CF_3$ (108) and it will be remembered that magnetic non-equivalence is exhibited by the fluorines of the CF_2 group in  $CF_3SCF_2\underset{CF_3}{C}F\underset{CF_3}{C}FCF_2SCF_3$ as discussed in Section A. A "preferred rotamer" concept is proposed for the non-equivalence found in $CF_3SF_2CF_3CF_3$ (108), with the bulky sulphur lone pair "locking" the molecule into the rotamer shown in Fig. 1-10.

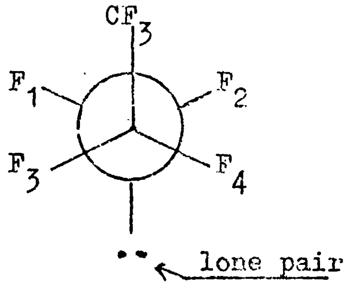
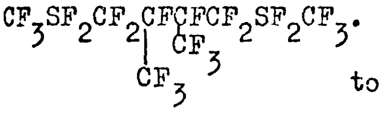
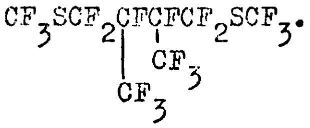


Fig. 1-10

a similar concept may or may not explain the magnetic non-equivalence in  $CF_3SF_2CF_2CF(CF_3)CF(CF_3)CF_2SF_2CF_3$. Restricted rotation about the central C-C bond due to the 2 bulky $-CF_3$ groups would also tend to make the CF_2 fluorines non-equivalent as is found for  $CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3$.

There is a whole chemistry of this compound to be investigated and one wonders whether it will parallel that of the $R_fSF_2R_f$ already investigated, e.g. controlled hydrolysis to give the sulphoxides $R_fS(O)R_f$ (51, 54) which can then be reacted with ClF to give $R_fS(O)F_2R_f$ (108). Further reaction of these compounds with NH_3 is found to give $(R_f)_2S(O){=}NH$ compounds (216).

It should also be possible to prepare further bis [S(IV)] derivatives by the action of ClF on some of the compounds described in Section A if the correct compounds and conditions are chosen.

C. Some Reactions of Bis(trifluoromethylthio)alkanes and -fluoroalkanes with Chlorine.

The reaction of $CF_3SCH_2CH_2SCF_3$ with chlorine gives $CF_3SCH_2CHClSCF_3$ and HCl in poor yield. The $CF_3SCH_2CHClSCF_3$ is identified by its mass spectrum (Section B Table 1.22). The ^{19}F n.m.r. spectrum gives the chemical shifts $\delta_{CF_3SCH_2} = +39.5$ p.p.m. and $\delta_{CF_3SCHCl} = +38.4$ p.p.m. (w.r.t. ext. CCl_3F). The ^1H n.m.r. spectrum is analysed as an ABX system (69) to give the parameters $\delta_X = +5.17$ p.p.m., $\delta_B = +3.37$ p.p.m., $\delta_A = +3.26$ p.p.m., $J_{AB} = 7.7$ Hz., $J_{AX} = 7.4$ Hz., $J_{BX} = 5.4$ Hz.,

The reaction of $CF_3SCH(CH_3)CH_2SCF_3$ with chlorine gives $CF_3SCH_2CCl(CH_3)SCF_3$ in very poor yield such that identification is based on the mass spectrum

Table 1.32: Mass Spectrum of $CF_3SCCl(CH_3)CH_2SCF_3$ (m/e, relative abundance, ion respectively).

278, *, M^+; 263, *, $(M-CH_3)^+$; 243, *, $(M-Cl)^+$; 209, *, $C_4H_5F_3ClS_2^+$; 177: 1, $C_4H_5F_3ClS^+$; 176, 1, $C_4H_4Cl^+$; 162, 2, $C_3H_2F_3ClS^+$; 141, *, $C_4H_4F_3S^+$; 139, *, $C_4H_2F_3S^+$; 128, 5, $C_3H_3F_3S^+$; 115, 3, $CF_3SCH_2^+$; 114, 8, CF_3SCH^+; 113, 4, $C_2F_3S^+$; 101, 10, CF_3S^+; 94, *, $C_2H_3ClS^+$; 82, 18, CF_2S^+; 77, 3, $C_2H_2FS^+$; 76, 2, C_2HFS^+ and $C_3H_5Cl^+$; 75, 2, $C_3H_4Cl^+$ and C_2FS^+; 74, 1, $C_3H_5S^+$; 72, 1, $C_3H_4S^+$; 69, 100, CF_3^+; 63, 13, CFS^+; 62, 13, CH_3CCl^+; 59, 1, $C_2H_3S^+$; 51, 2, SF^+; 50, 6, CF_2^+, 49, 1, CH_2Cl^+; 48, 2, $CHCl^+$; 47, 1, CCl^+; 45, 3, CHS^+; 44, 3, CS^+; 41, 5, $C_3H_5^+$; 39, 4, $C_3H_3^+$; 38, 3, $C_3H_2^+$; 36, 8, HCl^+; 35, 3, Cl^+; 32, 6, S^+, 31, 6, CF^+; 27, 2, CH_3C^+; 26, 1, CH_2C^+.

Table 1.33: Metastable transitions observed in the mass spectrum of $CF_3SCCl(CH_3)CH_2SCF_3$.

m1	Transition	m2	m* calc.	m* found
139	$C_4H_2F_3S^+ \longrightarrow C_2H_2F_3S^+ + C_2$	115	95.2	95.1
209	$C_4H_5F_3ClS_2^+ \longrightarrow C_4H_4F_3S^+ + HCl + S$	141	95.1	

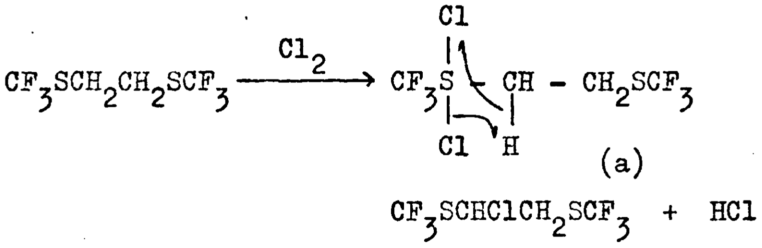
listed in Table 1.32 with the metastable transitions listed in Table 1.33. Peaks such as m/e 49, CH_2Cl^+, m/e 48, $CHCl^+$, m/e 51, SF^+, can easily be formed by rearrangement processes, but the lack of an ion at m/e 129, so prominent (100%) in the mass spectrum of $CF_3SCH_2CH(CH_3)SCF_3$, is really indicative of the structure suggested.

The reaction between $CF_3SCF_2CF(CF_3)SCF_3$ and chlorine does not proceed at all under the conditions employed.

There are three possible mechanisms for the reaction of Cl_2 with the bis(trifluoromethylthio)alkanes, using $CF_3SCH_2CH_2SCF_3$ as an example,

$$\begin{array}{l} CF_3SCH_2CH_2SCF_3 + Cl^{\bullet} \longrightarrow CF_3S\underset{\bullet}{C}HCH_2SCF_3 + HCl \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \big\downarrow Cl_2 \\ \qquad\qquad\qquad\qquad\qquad\quad CF_3SCHClCH_2SCF_3 + Cl^{\bullet} \quad \text{etc.} \end{array} \qquad (i)$$

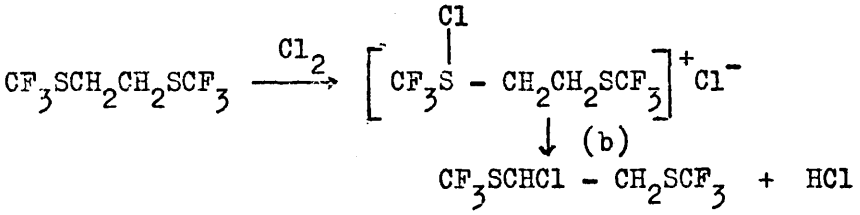
However, in the absence of a free radical initiator or U.V. light, this free radical process seems unlikely, especially as the chlorine radical is an electrophilic species (101) and the electron-withdrawing effect of the CF_3S group would make attack by $Cl^\bullet$ more difficult. What eliminates this mechanism, however, is the experimental conditions observed in the reaction between Cl_2 and $CF_3SCH(CH_3)CH_2SCF_3$. Here after reaction, the system was cooled to -80° and chlorine removed under static vacuum. If mechanism (i) were operating, then HCl would be formed during reaction and would be removed with chlorine at -80°. HCl was not in fact observed until the system was warmed to room temperature, a fact not compatible with mechanism (i)



$$CF_3SCH_2CH_2SCF_3 \xrightarrow{Cl_2} CF_3\overset{Cl}{\underset{Cl}{S}}-\underset{H}{C}H-CH_2SCF_3 \quad (a)$$

$$CF_3SCHClCH_2SCF_3 + HCl$$

(ii)



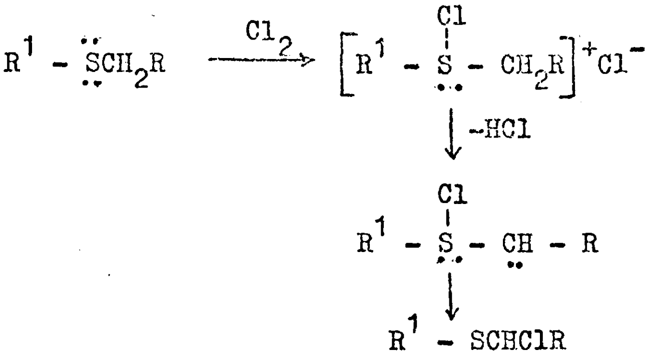
$$CF_3SCH_2CH_2SCF_3 \xrightarrow{Cl_2} \left[CF_3\overset{Cl}{S}-CH_2CH_2SCF_3\right]^+Cl^-$$

$$\downarrow (b)$$

$$CF_3SCHCl-CH_2SCF_3 + HCl$$

(iii)

Both (ii) and (iii) would explain the observed facts. Thus, both structure (a) and (b) would be stable in the presence of Cl_2 but would immediately decompose on removal of Cl_2. However, with $CF_3SCF(CF_3)CF_2SCF_3$, if (a) or (b) were formed, there would be no elimination of HCl possible. (b) would simply revert to starting material on removal of Cl_2 (217), but (a), if formed, would have no reason to revert to starting material. That reaction does not take place place can be explained thus: mechanism (iii) is preferred and hence does not give a product with $CF_3SCF(CF_3)CF_2SCF_3$ or mechanism (ii) operates, but only with the hydrocarbon derivatives and not with $CF_3SCF(CF_3)CF_2SCF_3$ due to the lone pair on sulphur being partially delocalised by the electronegative fluorocarbon groups and not therefore being available for bonding to chlorine. However, what suggests that (iii) is the correct mechanism is the precedent established by Bohme et al. (218) for alkyl sulphides:-



$$R^1 - \underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}CH_2R \xrightarrow{Cl_2} \left[R^1 - \underset{\cdot\cdot}{\overset{Cl}{S}} - CH_2R\right]^+Cl^- \xrightarrow{-HCl} R^1 - \underset{\cdot\cdot}{\overset{Cl}{S}} - \underset{\cdot\cdot}{CH} - R \longrightarrow R^1 - SCHClR$$

Perhaps under suitable conditions, oxidative chlorination of the bis-(trifluoromethylthio)alkanes and -fluoroalkanes may proceed to give the S(IV) dichlorides. Oxidative chlorination has been established for mustard gas:-

$$(ClCH_2CH_2)_2S \xrightarrow[(CCl_4)]{Cl_2} (ClCH_2CH_2)_2SCl_2$$

with no immediate elimination of HCl and chlorination of the αcarbon (113) as is found here and with $CF_3SCFHCF_2H$ which gives $CF_3SCFClCF_2Cl$ on reaction with chlorine (142).

EXPERIMENTAL

A. Reactions of Bistrifluoromethyldisulphide with Olefins

Reagents were obtained from the sources indicated in Table 1.34. Commercial bistrifluoromethyldisulphide was purified by distillation through traps held at -78°, -95° and -196°, the pure material being collected in the -95° trap.

Table 1.34 also lists the infrared and n.m.r. spectra references for both starting materials and those products identified by these techniques.

Table 1.34

Compound	Source	I.R.	N.M.R.
CF_3SSCF_3	Peninsular Chemresearch. Inc.	(176)	(186)
$CH_2 = CH_2$	Matheson Co.	(219)	
$CH_3CH = CH_2$	Matheson Co.	(219)	
$CF_2 = CF_2$	Peninsular Chemresearch Inc.	(220)	
$CF_3CF = CF_2$	Peninsular Chemresearch Inc.	(220)	
$CH_2 = CF_2$	Peninsular Chemresearch Inc.	(220)	
$CFH = CF_2$	Peninsular Chemresearch Inc.	(220)	
$CFCl = CF_2$	Peninsular Chemresearch Inc.	(220)	
$CCl_2 = CCl_2$	B.D.H.	(221)	
$CF_3SCH_2CH_2SCF_3$		(23)	(23)
$CF_3SCF(CF_3)CF_2SCF_3$			(142)

In general, the olefin and the bistrifluoromethyldisulphide were condensed together at -196° into a Pyrex reaction flask, of diameter 40 mm., capacity ca. 120 ml. and fitted with a "Rotaflo" Teflon stop-cock, such that at room temperature both reactants were in the vapour phase and the total pressure inside the flask was approximately one atmosphere. The flask and contents were exposed to ultra-violet light from a Hanovia 12277 Medium Pressure Mercury Arc Lamp until no more liquid product was seen to collect at the bottom of the reaction flask. For the reaction between CF_3SSCF_3 and

$CCl_2 = CCl_2$, the bottom of the flask was covered with black paper to ensure that any reaction taking place under the influence of the ultra-violet light would do so in the gas phase - $CCl_2 = CCl_2$ was found to have a comparatively low vapour pressure, <u>ca.</u> 13 mm. Hg. at the reaction temperature and was therefore mainly present as a liquid in the reaction flask. This was done so that a direct comparison between the reactions of CF_3SSCF_3 with $CCl_2 = CCl_2$ and the other olefins could be made without interference from

<u>Table 1.35</u>: Reaction of CF_3SSCF_3 with olefins

CF_3SSCF_3 (mmoles)	Olefin (mmoles)	Reaction Time (hrs.)	% age conversion of olefin	Products
5.51	$CH_2 = CH_2$ 5.69	44	48.8	$CF_3SCH_2CH_2SCF_3$
6.06	$CH_3CH = CH_2$ 5.91	20	59.9	$CF_3SCH(CH_3)CH_2SCF_3$
4.27	$CF_2 = CF_2$ 4.53	16	100	$CF_3S(CF_2CF_2)_nSCF_3$ n = 2, and v. large
5.73	$CF_2 = CF_2$ 1.13	16	100	$CF_3S(CF_2CF_2)_nSCF_3$ n = 2 and v. large
5.32	$CF_3CF = CF_2$ 6.56	184	48.5	$CF_3S\left[CF(CF_3)CF_2\right]_nSCF_3$ n = 1,2
5.82	$CH_2 = CF_2$ 5.92	26	100	$CF_3S(CH_2CF_2)_nSCF_3$ n = 1-6
5.78	$CFH = CF_2$ 6.24	28	100	$CF_3S(CFHCF_2)_nSCF_3$ n = 1-7
4.80	$CFH = CF_2$ 10.61	28	100	$CF_3S(CFHCF_2)_nSCF_3$ n = 1-7, > 7
5.87	$CF_2 = CFCl$ 6.08	24	100	$\overline{CFClCF_2CFClCF_2S}$ $CF_3SCF_2CFClCF_3$ $CF_3S(CF_2CFCl)_nSCF_3$ n = 1-4, > 4
6.66	$CF_2 = CFCl$ 1.32	24	100	$\overline{CFClCF_2CFClCF_2S}$ $CF_3SCF_2CFClCF_3$ $CF_3S(CF_2CFCl)_nSCF_3$ n = 1-4

Table 1.35 (cont'd)

	$CCl_2 = CCl_2$	500	13.6	$CF_3SCCl_2CCl_2SCF_3$ $CF_3SCCl = CCl_2$ $CF_3SCCl_2CCl_3$
6.40	5.71			

Table 1.36

Compound	n	B.P. (°C)	Vapour Pressure (mm. Hg.)	M.W. Found(a)	M.W. Calc.
$CF_3SCH_2CH_2SCF_3$		110-111(b)	16.18	230	230
$CF_3SCH(CH_3)CH_2SCF_3$		117-118	17.05	244	244
$CF_3S(CF_2CF_2)_2SCF_3$		127-129	5.25	402	402
$CF_3S\left[CF(CF_3)CF_2\right]_nSCF_3$	1	96-98(c)	45.26	352	352
	2	153.155(d)	0.64	502	502
$CF_3S(CH_2CF_2)_nSCF_3$	1	116-117	14.79	266	266
	2	166-167	0.21	330	330
	3	grease	-	394	394
	4	grease	-	458	458
	5	grease	-	522	522
	6	grease	-	586	586
$CF_3S(CFHCF_2)_nSCF_3$	1	89-91	51.77	284	284
	2	115-117	8.53	366	366
	3	162-164	0.09	448	448
	4	262-264	-	530	530
	5	grease	-	612	612
	6	grease	-	694	694
	7	grease	-	776	776
$\overline{CFClCF_2CFClCF_2S}$				264	264
$CF_3SCF_2CFClCF_3$		94-99	mixture	286	286
$CF_3S(CF_2CFCl)_nSCF_3$	1			318	318
	2	158-159	0.46	434	434
	3	196-198	-	550	550
	4	grease	-	666	666
$CF_3SCCl_2CCl_2SCF_3$		168-170	-	-	-
$CF_3SCCl = CCl_2$		137-138	9.83	230	230
$CF_3SCCl_2CCl_3$		-	-	300	300

(a) Molecular weight determined by mass spectrometry

(b) B.P. 110°C published (23)

(c) B.P. 100°C published (142)

(d) B.P. 156-159 °C published (140)

any liquid phase reaction in the former case. After reaction, the products volatile under static vacuum were fractionated by trap-to-trap distillation. The material involatile under static vacuum but volatile under dynamic vacuum was removed from the reaction flask by pumping through a trap held at -196°. Any remaining involatile material was removed as a diethyl ether solution. The ultra-violet induced reactions of CF_3SSCF_3 with olefins and the products from these reactions are summarised in Table 1.35. The boiling points, vapour pressures and molecular weights of the products are summarised in Table 1.36.

The reaction between CF_3SSCF_3 and $CH_2 = CH_2$ was also carried out in a metal bomb in the dark:- Ethylene (0.069 moles) and bistrifluoromethyldisulphide (0.070 moles) were packed into a 75 ml. monel Hoke bomb and kept at 100° for seven days. Fractionation of the contents of the bomb gave unreacted ethylene and bistrifluoromethyldisulphide (-196°) and $CF_3SCH_2CH_2SCF_3$ (-65°/0.53 mmoles).

The results of elemental analyses performed on several of the products are:-

		%C	%H	%F	%S
$CF_3SCH(CH_3)CH_2SCF_3$	Found	24.8	2.5	46.6	26.2
	Calc.	24.6	2.5	46.7	26.3
$CF_3SCF(CF_3)CF_2SCF_3$	Found	17.0		65.0	18.0
	Calc.	17.0		64.8	18.2
$CF\ S\left[CF(CF_3)CF_2\right]_2SCF_3$	Found	19.2		68.3	12.7
	Calc.	19.1		68.2	12.7

B. Reactions of Iodine Pentafluoride and Chlorine Monofluoride with Bis(trifluoromethylthio)alkanes and -fluoroalkanes

Tables 1.34 and 1.37 list the i.r. and n.m.r. spectra references for both starting materials and those products identified by these techniques.

IF_5 (Matheson Co.) was purified of iodine over mercury while the ClF (Ozark Mahoning) was used direct from the cylinder.

General Reaction Procedure

A weighted amount of the bis(trifluoromethylthio)alkane was condensed

Table 1.37

Compound	I.R.	N.M.R.
IF_5	(222)	
CF_3I	(223)	
CF_4	(224)	
SiF_4	(220)	
CF_3Cl	(220)	
HCl	(225)	
CF_3SF_5	(159)	(226)
CF_3SF_4Cl	(158)	(205)
$CF_3SCF_2CFClCF_3$		(142)
$CF_3SCF(CF_3)CF_2Cl$		(142)
SF_4	(227)	
SOF_2	(228)	

(-196°) into a 75 ml. monel Hoke bomb fitted with a monel Hoke valve. IF_5 was added using the Pyrex vacuum line while a metal vacuum line, illustrated in the General Experimental Section, was employed to add the ClF. Both reagents were used in an approximate 4:1 excess. The bomb was allowed to slowly warm from -196° to -78°, kept at -78° for 24 hours and allowed to slowly warm to room temperature. The products of the reaction were examined by standard vacuum line techniques in the pyrex vacuum line.

$CF_3SCH_2CH_2SCF_3/IF_5$ Reaction

$CF_3SCH_2CH_2SCF_3$ (1.86 mmoles) and excess IF_5 were reacted as above. The volatile products were CF_3I, CF_4, $CF_3SCH_2CH_2SCF_3$ and IF_5 with unidentified solid products left in the bomb. A little SiF_4 was also obtained, presumably from a hydrolysis reaction in the Pyrex vacuum line.

$CF_3SCH_2CH_2SCF_3/ClF$ Reaction

$CF_3SCH_2CH_2SCF_3$ (4.70 mmoles) and ClF (approx. 20 mmoles) were allowed to react as described above. The material which distilled from the bomb at -78° consisted of HCl, CF_4, and CF_3Cl. This mixture also contained a greenish yellow compound, which did not appear in the i.r. spectrum and was presumably chlorine, and SiF_4, which was presumably due to a hydrolysis reaction in the Pyrex vacuum line. The material remaining in the bomb distilled at -45° and consisted of approximately 70% unreacted $CF_3SCH_2CH_2SCF_3$, $CF_3SCCl_2CH_2SCF_3$ [M found (mass spec.), 298; M calc., 298], $CF_3SCHClCH_2SCF_3$ [M found (mass spec.), 264; M calc., 264] and a compound which gave ^{19}F n.m.r. signals at δ = -101.5 p.p.m. (doublet) and δ = +115.7 p.p.m. The latter two compounds were present in trace quantities.

$CF_3SCF(CF_3)CF_2SCF_3$/ ClF Reaction

$CF_3SCF(CF_3)CF_2SCF_3$ (4.50 mmoles) and ClF (approx. 20 mmoles) were allowed to react as described above. The contents of the bomb were then fractionated to give CF_4, CF_3Cl, a greenish yellow compound which was presumably chlorine and SiF_4, presumably from a hydrolysis reaction with the Pyrex vacuum line (-196°); $CF_3SCF_2CFClCF_3$, $CF_3SCF(CF_3)CF_2Cl$, $(CF_3)_2CFSCl$ [M found (mass. spec.), 236; M calc., 236], $CF_3CFClCF_2SCl$, $CF_2Cl(CF_3)CFSCl$, $(CF_3)_2CFCl$, and *trans*-$(CF_3)_2CFSF_4Cl$ (-80°); and $CF_3SCF_2CFClCF_3$, $CF_3SCF(CF_3)CF_2Cl$ [M found (mass spec.), 286; M calc. 286], $(CF_3)_2CFSCl$, $CF_2Cl(CF_3)CFSCl$, *trans*-$(CF_3)_2CFSF_4Cl$, *trans*-$CF_3CFClCF_2SF_4Cl$, and $CF_3CFClCF_2SF_4CF_3$ (-45°).

$CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3$/ClF Reaction

$CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3$ (6.51 mmoles) and ClF (approx. 28 mmoles) were allowed to react as described above. The contents (trace) of the bomb volatile under static vacuum consisted of CF_4, CF_3Cl, SF_4, HCl, SiF_4 and SOF_2, the last three compounds presumably from a hydrolysis reaction in the Pyrex vacuum line. The material remaining in the bomb was removed under dynamic vacuum and was found to be a mixture, almost wholly separable by atmospheric distillation, of unreacted $CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3$ (ca. 25%) and the bis-sulphur(IV) compound $CF_3SF_2CF_2CF(CF_3)CF(CF_3)CF_2SF_2CF_3$ [ca. 75%; Found: C, 16.5; F, 72.5; S, 10.9%. Calc.: C, 16.6; F, 72.3; S, 11.1%; b.p., 288-290° at 760 mm. Hg.; v.p. not detected].

C. Reactions of Chlorine with Bis(trifluoromethylthio)alkanes and -fluoroalkanes

General Reaction Procedure

Commercial chlorine (Matheson Co.) was purified by slow fractionation through traps held at -78°, -126° and -196°, the pure material being collected in the -126° trap. The bis(trifluoromethylthio)alkanes or -fluoroalkanes and excess chlorine were condensed (-196°) into the reaction vessel, a ca. 20 ml. flask fitted with a West Glass 0.4 mm. Teflon stop-cock. The mixture was allowed to warm to room temperature and vigorously shaken for two days. The reaction products were examined by conventional vacuum line techniques.

$CF_3SCH_2CH_2SCF_3/Cl_2$ Reaction

$CF_3SCH_2CH_2SCF_3$ (1.27 mmoles) and Cl_2 (20.22 mmoles) were allowed to react as described above. The contents of the flask were then fractionated to give Cl_2 and HCl, identified by its i.r. spectrum (225), (-196°); unreacted $CF_3SCH_2CH_2SCF_3$ (ca. 80%) and $CF_3SCHClCH_2SCF_3$ (ca. 20%) (-65°). Slow fractionation of the -65° trap contents through a trap held at -45° isolated sufficient pure $CF_3SCHClCH_2SCF_3$ for a mass spectrum [M found (mass spec.), 264; M calc., 264].

$CF_3SCH(CH_3)CH_2SCF_3/Cl_2$ Reaction

$CF_3SCH(CH_3)CH_2SCF_3$ (1.11 mmoles) and Cl_2 (18.67 mmoles) were allowed to react as described. Cl_2 was then removed from the reaction flask by pumping on it at -78°. No trace of HCl was detected in the volatile material. The flask and remaining material were allowed to warm to room temperature whereupon HCl, identified by its i.r. spectrum (225) was evolved. Slow fractionation of the remaining material gave a mixture of $CF_3SCH(CH_3)CH_2SCF_3$ and $CF_3SCCl(CH_3)CH_2SCF_3$ (-196°) and a trace of $CF_3SCCl(CH_3)CH_2SCF_3$ [M found (mass spec.), 278; M calc., 278], (-22°).

$CF_3SCF(CF_3)CF_2SCF_3/Cl_2$ Reaction

$CF_3SCF(CF_3)CF_2SCF_3$ (0.60 mmoles) and Cl_2 (39.92 mmoles) did not react under the conditions described above.

CHAPTER II

REACTIONS OF TRIFLUOROMETHYLSULPHUR(VI) CHLORIDE TETRAFLUORIDE

INTRODUCTION

Trans-trifluoromethylsulphur(VI) chloride tetrafluoride, *trans*-CF_3SF_4Cl, was first prepared in 1969 by the combined action of Cl_2 and CsF on CF_3SF_3 (205, 212). The *trans* structure about the sulphur was established by the infrared and ^{19}F n.m.r. spectra (212). The *cis* compound was not detected in this preparation; *trans*-CF_3SF_4Cl will therefore be referred to as CF_3SF_4Cl, with the understanding that the *trans* isomer is indicated.

The aim of the work described in this chapter was to determine to what extent, if any, the chemistry of CF_3SF_4Cl parallels that of SF_5Cl.

SF_5Cl was first isolated and characterised as a minor constituent in the products of the reaction of fluorine with sulphur dichloride (229). Preparatively, two reactions are of value,

$$SF_4 + ClF \xrightarrow{380^\circ} SF_5Cl \qquad (230)$$

$$SF_4 + CsF + Cl_2 \xrightarrow{110^\circ} SF_5Cl + CsCl \qquad (231)$$

The chemistry of SF_5Cl is well reviewed (3, 5, 11, 137). The ability of SF_5Cl to give the $SF_5^\bullet$ radical is an important feature of its chemistry. With olefins, either under the influence of u.v. irradiation or thermally, SF_5Cl adds across the unsaturated linkage (127, 128, 136, 137, 159, 160),

$$SF_5Cl + {>}C = C{<} \xrightarrow[\text{or } \Delta]{\text{u.v.}} SF_5 - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - Cl$$

or, in some cases, polymerisation can take place to give $SF_5(C - C)_nCl$, n = 1, 2, 3, etc. With acetylenes, a similar reaction takes place (127, 232).

$$SF_5Cl + -C \equiv C- \xrightarrow[\text{or } \Delta]{\text{u.v.}} SF_5 - \underset{|}{C} = CCl$$

with H_2, SF_5Cl gives S_2F_{10} (146),

$$2SF_5Cl + H_2 \xrightarrow{\text{u.v.}} S_2F_{10} + 2HCl$$

With O_2, SF_5Cl gives the oxide and peroxide (233, 234)

$$SF_5Cl \quad + \quad O_2 \xrightarrow{u.v.} SF_5OSF_5 \quad + \quad SF_5OOSF_5$$

with N_2F_4, SF_5Cl gives SF_5NF_2 (235) and with $(CF_3)_2NCl$, SF_5Cl gives $(CF_3)_2NSF_5$ (236).

In Section A of this chapter, the reactions of CF_3SF_4Cl with olefins is investigated and it is found that the main products are trans-bis(haloalkylsulphur(VI) tetrafluorides and so reference is made to the many reviews on this class of compounds (3-5, 7, 9, 11-14).

The direction of radical addition to olefins has been discussed in Chapter I and, therefore, when discussing the reactions of CF_3SF_4Cl with olefins, reference is made to the discussion in Chapter I for the olefin concerned.

The second part of this chapter describes the examination of a series of miscellaneous reactions of CF_3SF_4Cl, carried out to see what interesting derivatives could be made for future investigation, again using those of SF_5Cl as a model.

SUMMARY OF REACTIONS

A. Reaction with Unsaturated Hydrocarbons and Fluorocarbons(*)

1 $CF_3SF_4Cl + CH_2 = CH_2 \xrightarrow{u.v.} CF_3SF_4CH_2CH_2Cl$

1(a) $CF_3SF_4CH_2CH_2Cl + KOH/H_2O/EtOH \longrightarrow CF_3H + CF_3SF_4CH = CH_2$ + solid products

2 $CF_3SF_4Cl + CH_2 = CHCH_3 \xrightarrow{u.v.} CF_3SF_4CH_2CHClCH_3$

3 $CF_3SF_4Cl(1) + CF_2 = CF_2(1) \xrightarrow{u.v.} CF_3SF_4CF_2CF_2Cl + CF_3SF_4SF_4CF_3$
$+ CF_2ClCF_2Cl$

3(a) $CF_3SF_4Cl(1) + CF_2 = CF_2(2) \xrightarrow{u.v.} CF_3SF_4(CF_2CF_2)_nCl,$ $n = 1,2,3$ etc.

4 $CF_3SF_4Cl + CF_2 = CFCF_3 \xrightarrow{u.v.} CF_3SF_4CF(CF_3)CF_2Cl + CF_3SF_4SF_4CF_3$
$+ CF_2ClCFClCF_3$

5 $CF_3SF_4Cl + CH_2 = CF_2 \xrightarrow{u.v.} CF_3SF_4CH_2CF_2Cl + CF_3SF_4SF_4CF_3$
$+ CF_2ClCH_2Cl$

6 $CF_3SF_4Cl + CFH = CF_2 \xrightarrow{u.v.} CF_3SF_4CFHCF_2Cl + CF_3SF_4SF_4CF_3$ (trace)

7 $CF_3SF_4Cl + CF_2 = CFCl \xrightarrow{u.v.} CF_3SF_4(CF_2CFCl)_nCl,$ $n = 1,2$
$+ CF_3SF_4SF_4CF_3$ (trace)

8 $CF_3SF_4Cl + HC \equiv CH \xrightarrow{u.v.} CF_3SF_4CH = CHCl + CF_3SF_4SF_4CF_3$ (trace)

(*) All the S(VI) compounds have a trans structure about sulphur.

B. Miscellaneous Reactions

9 $CF_3SF_4Cl + Hg \longrightarrow CF_3Cl + SF_4 + Hg(Cl)_x$ $x = 1,2$

10 CF_3SF_4Cl (a) $\xrightarrow[\text{pyrex}]{u.v.}$ no reaction

(b) $\xrightarrow[\text{quartz}]{u.v.} CF_3SF_4Cl + CF_3Cl + SF_4$

11 $CF_3SF_4Cl + H_2$ (a) $\xrightarrow[\text{pyrex}]{u.v.}$ no reaction

(b) $\xrightarrow[\text{quartz}]{u.v.} CF_3Cl, SiF_4, SOF_2, HCl, CF_3SF_4Cl,$
$CF_3SF_4SF_4CF_3$

12 $CF_3SF_4Cl + O_2$ (a) $\xrightarrow[\text{pyrex}]{\text{u.v.}}$ no reaction

(b) $\xrightarrow[\text{quartz}]{\text{u.v.}} CF_3SF_4Cl$ + (trace) COF_2, CF_4, SiF_4, SOF_2, HCl

13 $CF_3SF_4Cl + CF_3SSCF_3$ (a) $\xrightarrow[\text{pyrex}]{\text{u.v.}} CF_3Cl$, SiF_4, SOF_2, CF_3SCF_3, CF_3SCl, CF_3SSCF_3, CF_3SF_4Cl

(b) $\xrightarrow[\text{quartz}]{\text{u.v.}} CF_3Cl$, SiF_4, SOF_2, CF_3SCF_3, CF_3SCl, CF_3SSCF_3, CF_3SF_4Cl

14 $SF_5Cl + CF_3SSCF_3$ (a) $\xrightarrow[\text{pyrex}]{\text{u.v.}}$ no reaction

(b) $\xrightarrow[\text{quartz}]{\text{u.v.}} SF_5Cl$, SF_6, SOF_2, CF_3SSCF_3, CF_3SCF_3, CF_3SCl

RESULTS

All the evidence points to CF_3SF_4Cl adding to unsaturated carbon-carbon linkage by a free-radical mechanism identical to that observed in the similar additions of SF_5Cl (127, 128, 136, 137, 159, 160, 232). The reactions of CF_3SF_4Cl with olefins/acetylene do not take place in the dark, but under the influence of u.v. irradiation, CF_3SF_4Cl adds to the carbon-carbon multiple bonds by a mechanism which apparently involves homolytic cleavage of the S-Cl bond to give $CF_3SF_4^\bullet$ and $Cl^\bullet$ radicals. In some cases, the addition reaction is accompanied by what appears to be dimerisation of $CF_3SF_4^\bullet$ radicals to form $CF_3SF_4SF_4CF_3$ with the $Cl^\bullet$ radicals being taken up by the olefin to give the 1,2-dichloro compound.

In some of these cases, just a trace of $CF_3SF_4SF_4CF_3$ is found and the 1,2-dichloro compound is not detected. Roberts has postulated the reaction mechanism (127) for the reaction of SF_5Cl with olefins,e.g. with $CH_2 = CH_2$

$$SF_5Cl \xrightarrow{h\nu} SF_5^\bullet + Cl^\bullet$$

$$SF_5^\bullet + CH_2 = CH_2 \longrightarrow SF_5CH_2CH_2^\bullet$$

$$SF_5CH_2CH_2^\bullet + SF_5Cl \longrightarrow SF_5CH_2CH_2Cl + SF_5^\bullet$$

$$Cl^\bullet + CH_2 = CH_2 \longrightarrow ClCH_2CH_2^\bullet$$

$$ClCH_2CH_2^\bullet + SF_5Cl \longrightarrow ClCH_2CH_2Cl + SF_5^\bullet$$

and this has been confirmed by kinetic work by Tedder et al. (128) who also showed that the addition step was reversible and that the termination step for that system was $2SF_5^{\bullet} \longrightarrow S_2F_{10}$

This scheme would fit the observations here as the reaction of CF_3SF_4Cl with an olefin seems to reach the equilibrium

$$CF_3SF_4Cl \;+\; C(AB) = C(XY) \longrightarrow CF_3SF_4C(AB)C(XY)Cl$$

for ethylene and propylene where no $CF_3SF_4SF_4CF_3$ is detected. $CF_3SF_4SF_4CF_3$, whose characterisation is discussed later, is detected by the observation of the chemical shifts at -33.3 p.p.m. and +65.5 p.p.m. in the ^{19}F n.m.r. spectrum of the neat liquid products. By comparing the SF_4 signals in various mixtures of $CF_3SF_4SF_4CF_3$ and $CF_3SF_4CF(CF_3)CF_2Cl$, the limit for detection of $CF_3SF_4SF_4CF_3$ is estimated as 5 parts per 1000, i.e. $CF_3SF_4SF_4CF_3$ can be present to the extent of less than 0.5% of the neat liquid product and not be detected by this method. The reaction is crudely monitored by observing the level of liquid at the bottom of the reaction flask. This reaches a maximum after <u>ca</u>. 15 hours irradiation and does not increase no matter for how much longer irradiation is continued. If the products are removed, however, and the unreacted starting materials re-irradiated, then more liquid is seen to form at the bottom of the reaction flask and this again reaches a maximum level.

In the other reactions examined, $CF_3SF_4SF_4CF_3$ is formed and this type of equilibrium is not observed although reaction was stopped before completion, by removing the reagents from the u.v. source, except in the reaction with $CF_2 = CF_2$ where all the CF_3SF_4Cl and $CF_2 = CF_2$ is consumed.

If the reactions between CF_3SF_4Cl and olefins/acetylene are performed using quartz instead of Pyrex vessels, very little addition of CF_3SF_4Cl to olefin occurs but decomposition of CF_3SF_4Cl to CF_3Cl and SF_4 is the main process.

The fact that products of the type $CF_3\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}}Cl$ or $CF_3 - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - CF_3$ are not found suggests two mechanisms:-

$$CF_3SF_4Cl \xrightarrow{h\nu} CF_3SF_4^{\bullet} \;+\; Cl^{\bullet};\quad Cl^{\bullet} \;+\; CF_3SF_4Cl \longrightarrow Cl - CF_3 \;+\; SF_4Cl^{\bullet}$$

$$SF_4Cl^{\bullet} \longrightarrow SF_4 \;+\; Cl^{\bullet} \qquad 1.$$

or an intramolecular process with elimination of CF_3Cl from the same molecule, perhaps by u.v. catalysed rearrangement to the <u>cis</u> CF_3SF_4Cl followed by CF_3Cl elimination, 2.

Which of 1. and 2., operates is difficult to say, but for 1. one would expect perhaps

$$\begin{array}{l} Cl^{\bullet} + \gt C = C\lt \longrightarrow Cl - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}}{}^{\bullet} + CF_3 - SF_4Cl \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad ClC\overset{|}{\underset{|}{}} - \overset{|}{\underset{|}{C}}CF_3 + SF_4Cl \end{array}$$

and this is not found.

With a 1:1 ratio of CF_3SF_4Cl to olefin/acetylene, telomerisation is not observed except in the case of $CF_2 = CFCl$, but when the ratio is increased to 1:2 for tetrafluoroethylene telomerisation is very marked.

The reaction with ethylene and propylene give only $CF_3SF_4CH_2CH_2Cl$ and $CF_3SF_4CH_2CHClCH_3$, the latter formed by radical attack at the CH_2 group as expected from previous results. In both cases, the ^1H n.m.r. spectra are very complex.

The n.m.r. of $SF_5CH_2CH_2Cl$ and $SF_5CH_2CHClCH_3$ have been analysed as $AB_4XX'YY'$ and AB_4P_3XYZ spin systems respectively (190).

The reaction with $CF_2 = CF_2$ to give the 1:1 adduct with CF_2ClCF_2Cl and $CF_3SF_4SF_4CF_3$ is unambiguous and requires no further comment.

The reaction with $CF_2 = CFCF_3$ gives $CF_3SF_4CF(CF_3)CF_2Cl$ and $CF_3SF_4CF_2CFClCF_3$ in the ratio of 97%:3%.

$CF_3SF_4CF_2CFClCF_3$ is produced by the reaction of $CF_3SCF(CF_3)CF_2SCF_3$ with ClF, as described in Chapter I. Comparison of the ^{19}F n.m.r. spectra characterises the 3% product as $CF_3SF_4CF_2CFClCF_3$ and the 97% product is therefore $CF_3SF_4CF(CF_3)CF_2Cl$, a structure which is supported by the ^{19}F n.m.r. spectrum. Previous free radical additions to $CF_2 = CFCF_3$ (see Chapter I) occur preferentially at the CF_2 group. The major product from the CF_3SF_4Cl reaction is therefore the unfavoured one. SF_5Cl reacts with $CF_2 = CFCF_3$ to give 50% of each of the two products (136) and, according to Haszeldine (144), this is due to the poor nucleophilic character of the $SF_5^{\bullet}$ radical since $CF_2 = CFCF_3$ is particularly susceptible to nucleophilic attack. Nucleophilic character is dependent on the number of electron-releasing substituents or on the power of the electron-releasing substituents. The $CF_3SF_4^{\bullet}$ radical should therefore be less nucleophilic than the $SF_5^{\bullet}$ radical. The chlorine atom is thought to be an electrophilic species (101), hence CF_3SF_4Cl gives rise to two poor nucleophiles. Therefore one would expect the reaction of CF_3SF_4Cl with $CF_2 = CFCF_3$ to be very inefficient as far as producing a $CF_3SF_4Cl/CF_2 = CFCF_3$ adduct is concerned but the termination steps

$$CF_3SF_4^{\bullet} + CF_3SF_4^{\bullet} \longrightarrow CF_3SF_4SF_4CF_3$$

$$CF_2Cl\dot{C}FCF_3 + CF_3SF_4Cl \longrightarrow CF_2ClCFClCF_3 + CF_3SF_4^{\bullet}$$

to be relatively fast. This is borne out by experiment since large amounts, relative to the other olefin/acetylene reactions, of $CF_3SF_4SF_4CF_3$ and $CF_2ClCFClCF_3$ are found while the reaction to produce the 1:1 adduct is extremely slow.

The reaction with $CH_2 = CF_2$ and $CFH = CF_2$ both proceed to give the 1:1 adducts $CF_3SF_4CH_2CF_2Cl$ and $CF_3SF_4CFHCF_2Cl$ respectively, i.e. the adducts formed by addition of the $CF_3SF_4^{\bullet}$ radical to the favoured end of the olefin in each case. No trace of $CF_3SF_4CF_2CFHCl$ is found although previous studies on radical addition to $CF_2 = CFH$ (Chapter I) have shown that addition to the unfavoured end of this olefin usually occurs, albeit to a small extent. The $CH_2 = CF_2$ gives $CF_3SF_4SF_4CF_3$ and $ClCH_2CF_2Cl$ in reasonable amounts but the $CF_2 = CFH$ reaction gives a trace of $CF_3SF_4SF_4CF_3$ only.

The reaction with $CF_2 = CFCl$ gives both a 1:1 adduct, $CF_3SF_4CF_2CFCl_2$, and a 1:2 adduct which consists of the two isomers $CF_3SF_4CF_2CFClCF_2CFCl_2$ and $CF_3SF_4CF_2CFClCFClCF_2Cl$; both of these isomers would appear to be formed by addition of the $CF_3SF_4^{\bullet}$ radical to the favoured end of the $CF_2 = CFCl$ molecule, i.e. at the CF_2 end (see Chapter I), thus

$$CF_3SF_4Cl \xrightarrow{u.v.} CF_3SF_4^{\bullet} + Cl^{\bullet}$$

$$CF_3SF_4^{\bullet} + CF_2 = CFCl \longrightarrow CF_3SF_4CF_2CFCl^{\bullet}$$

$$CF_3SF_4CF_2CFCl^{\bullet} + CF_3SF_4Cl \longrightarrow CF_3SF_4CF_2CFCl_2 + CF_3SF_4^{\bullet}$$

$$CF_3SF_4CF_2CFCl^{\bullet} + CF_2 = CFCl \longrightarrow CF_3SF_4CF_2CFClCF_2CFCl^{\bullet}$$

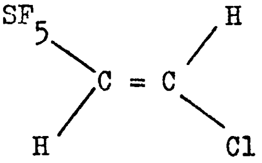
$CF_3SF_4CF_2CFClCF_2CFCl^{\bullet} + CF_3SF_4Cl \longrightarrow CF_3SF_4CF_2CFClCF_2CFCl_2 + CF\ SF_4^{\bullet}$

$Cl^{\bullet} + CF_2 = CFCl \longrightarrow ClCF_2CFCl^{\bullet}$

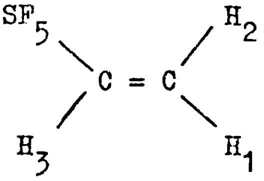
$CF_3SF_4CF_2CFCl^{\bullet} + ClCF_2CFCl^{\bullet} \longrightarrow CF_3SF_4CF_2CFClCFClCF_2Cl$

SF_5Cl adds to $HC \equiv CH$ thermally (232) to give the trans-$SF_5CH{=}CHCl$,.

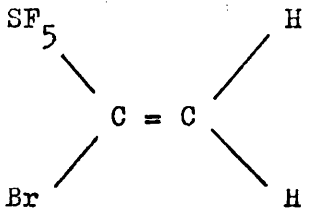
i.e.



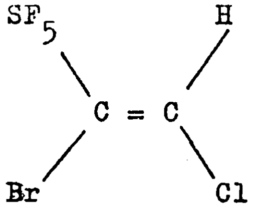
the structure being established by the proton n.m.r. spectrum. It has been established that the basal fluorines in SF_5 couple to protons in the trans position but not to protons in the cis position by examination of the ^{19}F and ^{1}H n.m.r. spectra of $SF_5CH = CH_2$ (190).



Coupling is observed between the basal fluorines and H_1 and H_3, but not H_2. Thus $SF_5CH = CHCl$ was established as trans because of the lack of trans HF coupling. Similar systems have been examined (232)e.g.,



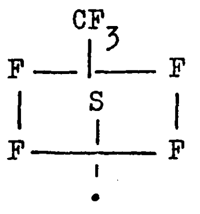
and



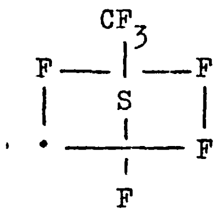
CF_3SF_4Cl reacts with $HC \equiv CH$ to give $CF_3SF_4CH = CHCl$, the structure being identified as having Cl and CF_3SF_4 groups trans to each other by the ^{1}H n.m.r. spectrum which is analysed as an AB system (69) with coupling between the B (i.e. geminal) proton and the SF_4 group and no coupling between the A (cis vicinal) proton and the SF_4 group. $\delta_A = 7.84$ p.p.m. and $\delta_B = 6.64$ p.p.m. (w.r.t. external TMS) and $J_{AB} = 12.6$ Hz., $J_{SF_4CH_3} = 3.0$ Hz., $J_{SF_4CCH_3} = 0.0$ Hz.

Treatment of $SF_5CH_2CH_2Cl$ with ethanolic potassium hydroxide removes HCl to give $SF_5CH = CH_2$ (127). A similar treatment of $CF_3SF_4CH_2CH_2Cl$ proves too drastic and the compound is almost completely decomposed. However, a small amount of $CF_3SF_4CH = CH_2$, identified on the basis of the i.r. spectrum, is isolated.

Steric factors indicate that in di-substituted derivatives of SF_6 SF_4A_2, trans substitution of the A groups is preferred. However, most SF_4A_2 compounds have a cis octahedral environment (237-239) although the perfluoroalkyl derivatives, $(R_f)_2SF_4$ (12), $CF_3SF_4NF_2$ (235), and CF_3SF_4Cl all favour trans substitution. The ultra-violet induced reactions of CF_3SF_4Cl with olefins give only the trans isomers in all cases, suggesting the reactions are stereospecific. If, as is thought, the reaction proceeds by initial homolytic cleavage of the S - Cl bond to give the $CF_3SF_4^{\bullet}$ and $Cl^{\bullet}$ radicals, then the unpaired electron in $CF_3SF_4^{\bullet}$ must remain in the trans position and rearrangements such as



(a)



(b)

must be slow with respect to addition to olefin or do not occur at all, since (b) would give rise to cis derivatives. There is a tendency for lone pairs to occupy positions which minimise their interactions with other electron pairs (240), e.g. in ICl_4^- and BrF_4^- (241), the lone pairs occupy the axial position so that the molecules both have a square planar geometry. It is also thought that $CF_3SF_4^-$ prefers the lone pair in the trans position of distorted octahedron (212). Although the odd electron in the $CF_3SF_4^{\bullet}$ radical may not occupy the same amount of space as the lone pair in $CF_3SF_4^-$, arguments such as these which determine the position of a lone pair must apply to $CF_3SF_4^{\bullet}$ in order to explain the stereospecific addition of CF_3SF_4Cl to olefins unless the addition reaction is so fast that rearrangement of the $CF_3SF_4^{\bullet}$ radical does not take place.

Infrared spectra of the trans-disubstituted SF_6 derivatives

The common feature of all the molecular studies in this work is the presence of the CF_3SF_4-group and the observed infrared absorption bands which can be directly related to vibrational modes within this group will be discussed first. Of the simple molecules for which a complete or nearly complete vibrational assignment is possible, CF_3SF_5 provides the best model with which to compare the molecules studied.

CF_3SF_5 can be considered to be a derivative of SF_6. It has been argued (241) that under conditions of a low or zero barrier to internal rotation of the CF_3 group against the SF_5 framework, the vibrational spectrum of CF_3SF_5 might reasonably be expected to obey selection rules for a molecule of C_{4v} symmetry, as opposed to O_h symmetry for SF_6. If, on the other hand, the barrier height in CF_3SF_5 were high, the effective point group would be Cs or possibly lower (241). Griffiths (213) has carried out a detailed study of the i.r. and Raman spectra of CF_3SF_5 from which he concludes that the barrier to internal rotation in CF_3SF_5 is very low and that the spectra are best interpreted by the molecule possessing C_{4v} rather than Cs symmetry.

In the infrared spectrum of CF_3SF_5 (213), two bands, at 902 and 692 cm^{-1}, are assigned to SF_4 square stretching vibrations, the former being the asymmetric and the latter being the symmetric stretching vibration. There are also two SF_4 deformation vibrations in the infrared spectrum, at 612 and 425 cm^{-1}. The infra red spectrum also shows four bands at 1256, 1168, 755, and 558 cm^{-1} assigned to CF_3 asymmetric stretch, CF_3 symmetric stretch, CF_3 symmetric deformation and CF_3 asymmetric deformation respectively. Of all these bands, the most intense are at 1256, 1168, 902, 755, 692, and 612 cm^{-1} with the two bands at 558 and 425 cm^{-1} being not nearly so strong. Darragh (212) has examined the i.r. spectrum of CF_3SF_4Cl and assigned the following vibrations:- 1250 cm^{-1}, $\nu(CF_3)$asym; 1155 cm^{-1}, $\nu(CF_3)$sym; 860 cm^{-1}, $\nu(SF_4$ square)asym; 785 cm^{-1}, $\delta(CF_3)$sym; 678 cm^{-1}, $\nu(SF_4$ square)sym. An examination of the i.r. spectrum of SF_5Cl (241) has identified $\nu(SF_4$ square)asym

Compound	νCF_3 asym	νCF_3 sym	νSF_4 asym	νSF_4 sym	δSF_4 out of plane	δCF_3 sym
CF_3SF_5 (213)	1256	1168	902	691	612	755
CF_3SF_4Cl (212)	1250	1155	860	678	643	785
$CF_3SF_4CH_2CH_2Cl$	1249	1150	812	657	603	743
$CF_3SF_4CH = CH_2$	1247	1156	820	655	581	740
$CF_3SF_4CH_2CH(CH_3)Cl$	1247	1135	804	639	602	744
$CF_3SF_4CF_2CF_2Cl$	1259	1156	855	664	570	780
$CF_3SF_4(CF_2CF_2)_2Cl$	1255	1153	851	666	(a)	778
$CF_3SF_4CF(CF_3)CF_2Cl$	1257	1154	852	678	572	(a)
$CF_3SF_4CH_2CF_2Cl$	1251	1151	889	655	610	746
$CF_3SF_4CFHCF_2Cl$	1258	1155	891	658	573	761
$CF_3SF_4CF_2CFCl_2$	1256	1152	887	651	570	(a)
$CF_3SF_4(CF_2CFCl)_2Cl$	1258	1156	850	657	(a)	(a)
$CF_3SF_4CH = CHCl$	1261	1156	890	654	602	782

Table 2.1: CF_3 and SF_4 stretching and bending frequencies

(a) not identified

at 909 cm^{-1}; $\nu(SF_4$ square)sym at 707 cm^{-1} with SF_4 square deformation at 602 cm^{-1} and 441 cm^{-1}. A study has been made of the i.r. spectra of some derivatives of sulphur hexafluoride (242) and the conclusion that the most intense bands should occur in the region 850-920 cm^{-1}, due to S - F stretching modes, and in the region of 600 cm^{-1}, due to S - F deformation modes, was reached. Bands in these two regions were found to dominate the spectra of these SF_5- compounds and were easily assigned. However, difficulty was found in assigning the $\nu(SF_4$ square)sym vibration at or near 700 cm^{-1} since it lay in a region where other vibrations also gave rise to absorption.

Table 2.1 lists the frequency assignments for the CF_3 and SF_4 stretching and bending vibration of the trans-di-substituted SF_6 derivatives. Those of

CF_3SF_5 and CF_3SF_4Cl are included for comparison.

The bands assigned to $\nu(CF_3)$asym, around 1250 cm^{-1}, and $\nu(SF_4)$asym, around 800-900 cm^{-1}, are the strongest bands in all the spectra studied. This is also the case with CF_3SF_5 (213) and CF_3SF_4Cl (212). Thus, assignments of these bands is relatively simple.

The next most intense bands are those assigned to $\nu(CF_3)$sym, $\nu(SF_4)$sym and $\delta(SF_4)$ out-of-plane vibrations. The last one varies from medium to strong in intensity in different derivatives and where there are several bands in the region, as is the case with the fluorocarbon residues, assignment is difficult and at best must be regarded as tentative. The same applies to the bands assigned to $\delta(CF_3)$sym where in some cases, this band could not be identified unequivocably due to other bands in the region. However, even in the compounds where CF_3SF_4 is attached to a fluorocarbon residue, the bands assigned to $\nu(CF_3)$asym and $\nu(SF_4)$asym dominate the i.r. spectra, though not nearly to the same extent as they do in the compounds with CF_3SF_4 bound to a hydrocarbon residue.

Other Characteristic Bands

1. -C=C- stretching: the olefinic -C=C- stretching frequency occurs at 1596 cm^{-1} in $CF_3SF_4CH = CH_2$ and at 1572 cm^{-1} in $CF_3SF_4CH = CHCl$. These values compare very well with 1640 cm^{-1} for $SF_5CH = CH_2$ and 1615 cm^{-1} for $SF_5CH = CHCl$ (242) and are in the normal range of such frequencies (208).

2. C-H vibrations: C-H stretching vibrations are observed at 2979 cm^{-1} for $CF_3SF_4CH_2CH_2Cl$, 3100, 3054 and 3021 cm^{-1} for $CF_3SF_4CH = CH_2$, 2982, 2940 and 2884 cm^{-1} for $CF_3SF_4CH_2CHClCH_3$, 3008 and 2970 cm^{-1} for $CF_3SF_4CH_2CF_2Cl$, 3019 cm^{-1} for $CF_3SF_4CFHCF_2Cl$ and 3082 cm^{-1} for $CF_3SF_4CH = CHCl$ while C - H deformation vibrations are observed at 1442 cm^{-1} for $CF_3SF_4CH_2CH_2Cl$, 1439 and 1389 cm^{-1} for $CF_3SF_4CH = CH_2$, 1459 and 1381 cm^{-1} for $CF_3SF_4CH_2CHClCH_3$, 1418 and 1384 cm^{-1} for $CF_3SF_4CH_2CF_2Cl$, 1421 cm^{-1} for $CF_3SF_4CFHCF_2Cl$ and 1401, 1385 cm^{-1} for $CF_3SF_4CH = CHCl$. The C - H stretching vibrations are all weak absorptions while the C - H deformations vary between weak and medium in intensity. This

is partly due to the very strong CF_3 and SF_4 stretching vibrations

Other Bands

It is difficult to obtain other reliable diagnostic bands for these molecules as C-C, C-S, C-Cl, and C-F stretching modes all appear over a wide range of frequencies (124,189) and therefore cannot be assigned with any certainty. The detailed spectra, therefore, although useful for characterisation of the compounds, cannot be used to obtain further structural information.

Mass spectra of the trans-di-substituted SF_6 derivatives.

The mass spectra are listed in Table 2.2 whilst the mass measured peaks in the mass spectrum of $CF_3SF_4CH_2CH_2Cl$ are given in Table 2.3. No molecular ions are found in the mass spectra of any of the compounds, even when the ionising beam is reduced from 70eV to 12eV. Below 12eV there is no ionisation. Neither of the similar compounds, CF_3SF_4Cl (212) and $CF_3SF_4NF_2$ (183), show molecular ions in their mass spectra. The positive ion mass spectrum of SF_5Cl (244) shows a very weak molecular ion. The most probable ionisation process is postulated as loss of a Cl atom from the molecular ion since few ions containing sulphur, fluorine and chlorine are formed and these are generally of low abundance. The mass spectra of seven RSF_5 derivatives, where R is a halocarbon residue, have been recorded (245) and in only two of these, viz. $SF_5CHBrCH_2CHBrCH_2F$ and $SF_5CHFCF_2C_2H_5$, are molecular ions observed. It is worth noting, however, that both the above investigations were made using a Bendix time-of-flight mass spectrometer whereas the present work was carried out on a single-focussing mass spectrometer (A.E.I.MS12). Since one of the main advantages of a time-of-flight mass spectrometer is its ability to record very short-lived ions (139), its use in the above two studies is perhaps the reason that molecular ions were observed for some of the compounds. The implication is that molecular ions for such compounds are very short-lived and, in some cases, too short-lived for detection by a time-of-flight mass spectrometer.

(continued on page 149).

Table 2.2

(1) $CF_3SF_4CH_2CH_2Cl$:

164, 2, $C(F_3)SCH_2CH_2Cl^{35+}$, 139, 3, $CF_3SF_2^+$, 135, 2, $SF_2CH_2CH_2Cl^{37+}$, 133 6, $SF_2CH_2CH_2Cl^{35+}$, 117, 2, $SF_3CH_2CH_2^+$, 115, 4.5, $C_2H_2F_3S$, 97, 3, $SF_2C_2H_3^+$ and $SCH_2CH_2Cl^{37+}$, 95, 1.5, $SCH_2CH_2Cl^{35+}$, 89, 15, SF_3^+, 70, 9, SF_2^+, 69, 40, CF_3^+, 65, 31, CH_2SF^+ and $CH_2CH_2Cl^{37+}$, 64, 10.5, $CHSF^+$ and $C_2H_3Cl^{35+}$, 63, 86, CFS^+; $C_2H_2Cl^{37+}$ and $CH_2CH_2Cl^{35+}$, 62, 24, $C_2H_3Cl^{35+}$, 61, 4.5, $C_2H_2Cl^{35+}$, 60, 2, $SC_2H_4^+$, 59, 2, $SC_2H_3^+$, 58, 2, $SC_2H_2^+$, 57, 4, SC_2H^+, 56, 3.5, SC_2^+, 51, 4.5, SF^+ and CH_2Cl^{37+}, 50, 2, $CHCl^{37+}$ and CF_2^+, 49, 5, CCl^{37+} and CH_2Cl^{35+}, 48, 1, $CHCl^{35+}$, 47, 11, CCl^{35+}, 46, 3, CH_2S^+, 45, 4, CHS^+, 44, 4, CS^+, 36, 1.5, HCl^{35+}, 33, 1, CH_2F^+, 32, 5, S^+ or CFH^+, 31, 1, CF^+, 28, 22, $C_2H_4^+$, 27, 100, $C_2H_3^+$, 26, 11, $C_2H_2^+$, 25, 1, C_2H^+.

(2) $CF_3SF_4CH_2CH(CH_3)Cl$:

153, 0.5, $SF_3CH_2CHCl^{37+}$, 151, 1.5, $SF_3CH_2CHCl^{35+}$, 147, 3, $C_3H_3F_4S^+$, 144, 3, $C_3F_4S^+$, 143, 15, $C(F_3)SCH_2CHCH_3^+$, 139, 3, $CF_3SF_2^+$, 129, 8, $SF_3C_3H_3^+$, 123, 1, $C(F_2)SC_3H_5^+$, 115, 2, $C_2H_2F_3S^+$, 111, 1, $SF_2C_3H_5^+$, 89, 7, SF_3^+, 84, 1, $SF_2CH_2^+$, 83, 1, SF_2CH^+, 79, 11, $C_3H_6Cl^{37+}$, 78, 8, $C_3H_5Cl^{37+}$, 77, 30, $C_3H_6Cl^{35+}$, 76, 18, $C_3H_5Cl^{35+}$, 75, 2, C_2FS^+ or $C_3H_4Cl^{35+}$, 70, 4, SF_2^+, 69, 44.5, CF_3^+, 65, 5, $SFCH_2^+$, 64, 1, $SFCH^+$ and $C_2H_3Cl^{37+}$, 63, 4, CFS^+ and $C_2H_2Cl^{37+}$, 62, 2, $C_2H_3Cl^{35+}$, 61, 13, $C_2H_2Cl^{35+}$, 59, 1, $SC_2H_3^+$, 57, 2, SC_2H^+, 56, 4, SC_2^+, 51, 3.5, CH_2Cl^{37+} and SF^+, 50, 2, CF_2^+, 49, 6, CCl^{37+} and CH_2Cl^{35+}, 47, 5, CCl^{35+}, 46, 6, SCH_2^+, 42, 7, $CH_3CHCH_2^+$, 41, 100, $C_3H_5^+$, 40, 5, $C_3H_4^+$, 39, 27, $C_3H_3^+$, 38, 3, $C_3H_2^+$, 32, 1.5, S^+, 31, 4, CF^+, 29, 4, $CH_3CH_2^+$, 28, 6, $C_2H_4^+$, 27, 11, $C_2H_3^+$, 26, 2, $C_2H_2^+$.

Table 2.2 (cont.)

(3) $CF_3SF_4CF_2CF_2Cl$:

151, 2, $C_2F_5S^+$, 139, 14.5, $CF_3SF_2^+$, 137, 1, $CF_2CF_2Cl^{37+}$, 135, 3.5, $CF_2CF_2Cl^{35+}$, 100, 13, $CF_2CF_2^+$, 89, 17, SF_3^+, 87, 5, CF_2Cl^{37+}, 85, 15, CF_2Cl^{35+};70,8,SF_2^+, 69, 100, CF_3^+, 63, 3, CFS^+, 51, 4, SF^+, 50, 4, CF_2^+, 31, 7, CF^+.

(4) $CF_3SF_4CF(CF_3)CF_2Cl$:

239, 4, $CF_3SF_2CFCF_3^+$, 163, 1, $C_3F_5S^+$ and $C_3F_3Cl^{35+}$, 150, 2, $C_3F_6^+$, 139, 2, $CF_3SF_2^+$, 131, 4, $C_3F_5^+$, 100, 3, CF_3CF^+, 89, 25, SF_3^+, 87, 2, CF_2Cl^{37+}, 85, 6, CF_2Cl^{35+}, 82, 4, CF_2S^+, 81, 20, CF_2CF^+, 70, 9, SF_2^+, 69, 100, CF_3^+, 66, 4, $CFCl^{35+}$, 63, 5, CFS^+, 51, 11, SF^+, 50, 5, CF_2^+, 49, 5, CCl^{37+}, 47, 15, CCl^{35+}, 44, 3, CS^+, 32, 4, S^+, 31, 8.5, CF^+.

(6) $CF_3SF_4CH_2CF_2Cl$:

184, 17, $C(F_3)SFCH_2CF_2^+$, 183, 22, $C_3H_2F_4SCl^{37+}$ and $C(F_3)SFCHCF_2^+$, 181, 2, $C_3H_2F_4SCl^{35+}$, 165, 40.5, $C(F_3)SCH_2CF_2^+$, 145, 2, $C(F_3)SCH{=}CF^+$, 139, 1, $CF_3SF_2^+$, 134, 11, $C_2H_2F_4S^+$, 133, 2, $C(F_3)SFCH^+$, 115, 58, $C(F_3)SCH_2^+$, 114, 13, $C(F_3)SCH^+$, 101, 4, $CH_2CF_2Cl^{37+}$ and CF_3S^+, 100, 2, $CHCF_2Cl^{37+}$, 99, 17, CCF_2Cl^{37+} and $CH_2CF_2Cl^{35+}$, 98, 7, $CHCF_2Cl^{35+}$, 97, 5, CCF_2Cl^{35+}, 96, 4, $SCH_2CF_2^+$, 95, 18, $C_2F_2HS^+$, 89, 6, SF_3^+, 87, 27, CF_2Cl^{37+}, 85, 86, CF_2Cl^{35+}, 83, 9, SF_2CH^+, 82, 8, CF_2S^+ and CH_2CFCl^{37+}, 81, 8, $CHCFCl^{37+}$, 80, 5, CH_2CFCl^{35+}, 79, 34, $CHCFCl^{35+}$, 77, 7, SCH_2CF^+, 70, 7, SF_2^+, 69, 100, CF_3^+, 68, 2, $CFCl^{37+}$, 66, 5.5, $CFCl^{35+}$, 64, 2, $SFCH^+$, 63, 23, CFS^+, 51, 21, CH_2Cl^{37+} and SF^+, 50, 18, $CHCl^{37+}$ and CF_2^+, 49, 50, CH_2Cl^{35+} and CCl^{37+}, 48, 17, $CHCl^{35+}$, 47, 7, CCl^{35+}, 46, 9, SCH_2^+, 45, 26, SCH^+, 44, 20, CS^+, 35, 3, Cl^{35+}, 32, 7, S^+, 31, 27, CF^+.

Table 2.2 (cont.)

(7) $CF_3SF_4CFHCF_2Cl$:

220, 1, $C(F_3)SCFHCF_2Cl^{37+}$ and $CF_3SF_2CFCF_2^+$, 218, 4, $C(F_3)SCFHCF_2Cl^{35+}$, 189, 2, $SF_2CFHCF_2Cl^{37+}$, 187, 6, $SF_2CFHCF_2Cl^{35+}$, 171, 24, $CF_3SF_2CFH^+$, 139, 11, $CF_3SF_2^+$, 133, 10, $C(F_3)SCFH^+$, 120, 1, CF_3SF^+, 119, 12, $CFHCF_2Cl^{37+}$, 117, 33, $CFHCF_2Cl^{35+}$, 102, 4, SF_2CFH^+, 101, 11, $C(F_3)S^+$, 100, 1, $C_2F_2HCl^{37+}$ 98, 2, $C_2F_2HCl^{35+}$, 95, 2, $C_2F_2HS^+$, 91, 1, $SC{\equiv}CCl^{35+}$, 89, 3, SF_3^+, 87, 4, CF_2Cl^{37+}, 85, 12, CF_2Cl^{37+}, 83, 2, SF_2CH^+, 82, 12, CFS^+, 70, 15, SF_2^+, 69, 100, $CFHCl^{37+}$ and CF_3^+, 68, 3.5, $CFCl^{37+}$, 67, 25, $CFHCl^{35+}$, 66, 12, $CFCl^{35+}$, 64, 4, $SFCH^+$, 63, 5, CFS^+, 51, 15, SF^+, 50, 4, $CHCl^{37+}$ and CF_2^+, 48, 6, $CHCl^{35+}$, 47, 1, CCl^{35+}, 45, 7, SCH^+, 32, 3, CFH^+ and S^+, 31, 10, CF^+.

(8) $CF_3SF_4CF_2CFCl_2$:

151, 3, $C_2F_5S^+$, 139, 15, $CF_3SF_2^+$, 101, 1, $CFCl_2^{35+}$ and CF_3S^+, 89, 17.5, SF_3^+, 87, 5, CF_2Cl^{37+}, 85, 15, CF_2Cl^{35+}, 82, 1, CF_2S^+ and CCl_2^{35+}, 81, 2, CF_2CF^+, 70,8, SF_2^+, 69, 100, CF_3^+, 51, .4, SF^+, 50, 3, CF_2^+, 31, 7, CF^+.

Table 2.2 (cont.)

(9) $\underline{CF_3SF_4CF_2CFClCF_2CFCl_2}$ and

(10) $\underline{CF_3SF_4CF_2CFClCFClCF_2Cl}$:

267, 2, $C_4F_6Cl_3^{35+}$, 182, 1, $C_3F_4Cl_2^{35+}$ and $C_3F_6S^+$, 181, 1, $C_3F_4Cl^{37}S^+$ and $C_3F_2Cl_2^{35}Cl^{37+}$, 179, 1, $C_3F_4Cl^{35}S^+$ and $C_3F_2Cl_3^{35+}$, 167, 1, $C_3F_3Cl_2^{37+}$ and $SFCF_2CFCl^{35+}$, 165, 1, $C_3F_3Cl^{35}Cl^{37+}$, 163, 2, $C_3F_3Cl_2^{35+}$ and $C_3F_5S^+$, 155, 8, $C_4F_2Cl^{37}S^+$, 153, 25, $C_4F_2Cl^{35}S^+$, 151, 39, $C_2F_5S^+$, 149, 2, $C_3F_4Cl^{37+}$, 147, 6.5, $C_3F_4Cl^{35+}$, 141, 2, $C_3F_2Cl^{35}S^+$, 139, 35, $CF_3SF_2^+$, 137, 14.5, $C_4F_3S^+$, 134, 2, $C_2F_2Cl^{35}Cl^{37+}$, 132, 2.5, $C_2F_2Cl_2^{35+}$, 131, 5, $C_3F_5^+$ and $C_2F_2Cl^{37}S^+$, 129, 3, $C_2F_2Cl^{35}S^+$, 120, 1, CF_3SF^+, 118, 9, CF_2CFCl^{37+}, 116, 26, CF_2CFCl^{35+}, 113, 4, $C_2F_3S^+$, 109, 1.5, $C_3F_2Cl^{35+}$, 105, 4, $C_4F_3^+$ and $CFCl_2^{37+}$, 103, 39, $CFCl^{35}Cl^{37+}$, 101, 60, CF_3S^+ and $CFCl_2^{35+}$, 99, $C_2F_2Cl^{37+}$, 97, 3.5, $C_2F_2Cl^{35+}$, 94, 1, $C_2F_2S^+$, 93, 3.5, $C_3F_3^+$, 89, 22, SF_3^+, 87, 17, CF_2Cl^{37+}, 85, 52, CF_2Cl^{35+}, 82, 4.5, CF_2S^+, 78, 1, C_2FCl^{35+}, 74, 1, $C_3F_2^+$, 70, 11, SF_2^+, 69, 100, CF_3^+, 68, 4, $CFCl^{37+}$, 66, 12.5, $CFCl^{35+}$, 63, 10.5, CFS^+, 62, 1, $C_2F_2^+$, 56, 2, C_2S^+, 51, 7, SF^+, 50, 5, CF_2^+, 49, 2, CCl^{37+}, 47, 6, CCl^{35+}, 44, 4, CS^+, 43, 3, C_2F^+, 35, 2, Cl^{35+}, 32, 9, S^+, 31, 17, CF^+.

(11) $\underline{CF_3SF_4CH{=}CHCl}$:

164, 9, $C(F_3)SCH{=}CHCl^{37+}$, 162, 26, $C(F_3)SCH{=}CHCl^{35+}$, 139, 12, $CF_3SF_2^+$, 127, 4, $C(F_3)SCH{=}CH^+$, 125, 1, $C_3F_3S^+$, 120, 3, CF_3SF^+, 115, 4, $SF_3CH{=}CH^+$, 101, 2, CF_3S^+, 95, 10, $SCH{=}CHCl^{37+}$, 93, 26, $SCH{=}CHCl^{35+}$ and $SC{\equiv}CCl^{37+}$, 92, 2.5, $SCH{=}CCl^{35+}$, 91, 1, $SC{\equiv}CCl^{35+}$, 89, 18, SF_3^+, 82, 4, CF_2S^+, 77, 4, $SFCH{=}CH^+$, 76, 2, $CFSCH^+$, 70, 19, SF_2^+, 69, 100, CF_3^+, 64, 1, $SFCH^+$, 63, 6, $C_2H_2Cl^{37+}$ and CFS^+, 61, 4, C_2Cl^{37+} and $C_2H_2Cl^{35+}$, 60, 2, C_2HCl^{35+}, 59, 1, C_2Cl^{35+}, 58, 22, $SC_2H_2^+$, 57, 13, SC_2H^+, 56, 1, SC_2^+, 51, 5, SF^+, 50, 4, $CHCl^{37+}$ and CF_2^+, 48, 3, $CHCl^{35+}$, 47, 1, CCl^{35+}, 45, 9, SCH^+, 32, 4, S^+, 31, 6, CF^+.

In the present work, therefore, it is hardly surprising that no molecular ions are observed, even at low ionisation. energies.

The formation of negative ions plays a major part in the fragmentation of SF_5Cl and SF_6 in the mass spectrometer (244) and it is probable that such processes occur with the CF_3SF_4X derivatives examined here.

No metastable peaks are observed in any of the mass spectra. Analysis of the spectra, therefore, is based solely on the ions observed and on analogous systems.

All the spectra show considerable abundances of the ions SF_3^+, m/e 89; SF_2^+, m/e 70; and SF^+, m/e 51; but none show a peak at m/e 108, SF_4^+. All the spectra show a peak at m/e 139 which has been formulated as $CF_3SF_2^+$ in the mass spectra of $CF_3SF_4NF_2$ (183) and CF_3SF_4Cl (212).

R-S bond cleavage of $R\text{-}SF_4CF_3$ may occur in two ways,

$$(R\text{-}SF_4CF_3)^{+\cdot} \begin{array}{l} \nearrow R^+ + {}^{\cdot}SF_4CF_3 \qquad \text{(i)} \\ \searrow R^{\cdot} + (SF_4CF_3)^+ \qquad \text{(ii)} \end{array}$$

By pathway (ii), an ion at m/e 177, $CF_3SF_4^+$, should be produced, but no such ion is observed in any of the mass spectra examined here or in the mass spectra of CF_3SF_4Cl (212) and $CF_3SF_4NF_2$ (183). It is possible that $CF_3SF_4^+$ may decompose to $CF_3SF_2^+$ with loss of F_2. Pathway (i) is suggested by the reasonably high abundances of the ions R^+ in all the mass spectra except those of $CF_3SF_4CF(CF_3)CF_2Cl$ and $CF_3SF_4CF_2CFCl_2$:- m/e 63, $ClCH_2CH_2^+$; m/e 77, $CH_3CHClCH_2^+$; m/e 135, $ClCF_2CF_2^+$; m/e 99, $ClCF_2CH_2^+$; m/e 119, $ClCF_2CFH^+$; m/e 267, $C_4F_6Cl_3^+$; and m/e 61, $ClC_2H_2^+$. For $CF_3SF_4CF_2CFCl_2$, R^+ should occur at m/e 151 and a small peak at m/e 153 suggests $Cl^{37}Cl^{35}CFCF_2^+$. That scheme (ii) occurs as well as scheme (i) is suggested by analogy with $SF_5\text{-}X$ compounds where large abundances of m/e 127, SF_5^+, ions are found due to S-X cleavage for X = NF_2 (183), NH_2 (246), $N{=}SF_2{=}NSF_5$ (247), NCl_2 (248), Cl and F (244), $CHClCH_2F$, $CHBrCH_2CHBrCH_2F$, $CHBrCH_2F$, $CH_2CHFCH{=}CH_2$ and $CHFCF_2C_2H_5$ (245).

Loss of HCl from the R^+ ion perhaps gives rise to the base peaks for $CF_3SF_4CH_2CH_2Cl$ and $CF_3SF_4CH_2CHClCH_3$:-

Table 2.3 : Mass Measured Peaks in Mass Spectrum of $CF_3SF_4CH_2CH_2Cl$

m/e	Calcd. Exact Mass	Found Exact Mass	Ion*
164	163.967431	163.967156	$CF_3SCH_2CH_2Cl^+$
133	132.969029	132.969203	$SF_2CH_2CH_2Cl^+$
95	94.972225	94.972777	$SCH_2CH_2Cl^+$
63	1) 63.000152	63.000460	$CH_2CH_2Cl^+$
	2) 62.970475	62.970388	CFS^+
	3) 62.996804	62.981712	$C^{13}C^{12}F_2$

* refers to Cl^{35} isotope.

$$ClCH_2CH_2^+ \qquad CH_2{=}CH^+ + HCl$$
$$CH_3CHClCH_2^+ \qquad C_3H_5^+ \quad + HCl$$

In all the other mass spectra, the base peak is m/e 69, CF_3^+.

That schemes (i) and (ii) are not the only fragmentation pathways is evidenced by the observation of the ions RSF_2^+, at m/e 133 for $ClCH_2CH_2SF_4CF_3$ and at m/e 187 for $ClCF_2CFHSF_4CF_3$; SF_2CXY, with X = Y = H, at m/e 84 for $CF_3SF_4CH_2CHClCH_3$, with X =F and Y = H, at m/e 102 for $CF_3SF_4CFHCF_2Cl$, with X = Y = F, at m/e 120 for $CF_3SF_4(CF_2CFCl)_2Cl$; SFCXY, with X = Y = H, at m/e 65 for $CF_3SF_4CH_2CH_2Cl$ and $CF_3SF_4CH_2CHClCH_3$, with X = H and Y = F, at m/e 83 for $CF_3SF_4CFHCF_2Cl$, with X = Y = F, at m/e 101 for $CF_3SF_4(CF_2CFCl)_nCl$, n = 1,2, with X = H and Y = =CH, at m/e 77 for $CF_3SF_4CH{=}CHCl$.

There are several unique species which bear mention. The ion at m/e 164 in the mass spectrum of $CF_3SF_4CH_2CH_2Cl$ can have several formulations, $(FC{\equiv}SF_2CH_2CH_2Cl)^+$, $(F_2C{=}SFCH_2CH_2Cl)^+$ and $(F_3C{-}SCH_2CH_2Cl)^+$ with no clue as to which is correct. In the mass spectrum of $CF_3SF_4CF(CF_3)CF_2Cl$, the ion at m/e 239 can have several formulations but that given, $(CF_3SF_2CFCF_3)^+$, is compatible with the main structure deduced from the ^{19}F n.m.r spectrum. The ion at m/e 85 in the mass spectrum of $CF_3SF_4CF_2CFCl_2$ is probably CF_2Cl^+ and must arise from some rearrangement process since the ^{19}F n.m.r.

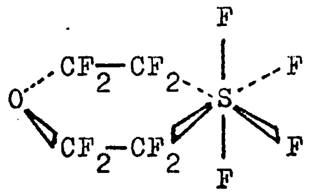
spectrum establishes the structure as $CF_3SF_4CF_2CFCl_2$.

N.m.r spectra of the trans-di-substituted SF_6 derivatives.

^{19}F n.m.r. spectra.

All the derivatives give complicated ^{19}F n.m.r. spectra, but most of these are readily interpreted by a first order analysis. The ^{19}F chemical shifts are listed in Table 2.4 together with those of CF_3SF_4Cl (205) and the coupling constants are listed in Table 2.5.

That the two substituents are trans to one another is proved, not only by the quintet fine structure of the CF_3 group, but by the fact that only one signal for the SF_4 group is observed whereas a cis di-substituted derivative would give rise to two signals for the SF_4 group, probably of an A_2B_2 nature. The compound $\overline{SF_4CF_2CF_2OCF_2CF_2}$ affords an excellent example of the latter case since the cyclic nature of the perfluoroalkyl group forces a cis configuration about the sulphur atom :-



The ^{19}F n.m.r. spectrum (68) of this compound shows two sets of triplets for the two non-equivalent pairs of fluorines in the SF_4 group (δ= -44.4p.p.m. and δ= -16.2p.p.m. relative to CCl_3F). In contrast, the trans di-substituted derivatives $(C_2F_5)_2SF_4$ and $(C_3F_7)_2SF_4$ each show only one resonance, at -25.4p.p.m. and -27.5p.p.m. (relative to CCl_3F) respectively, for the SF_4 group (68). Single resonances for the $\overset{*}{S}F_4$ groups in the ^{19}F n.m.r. spectra (249) of the trans derivatives $CF_3^*SF_4CF_2CF_3$, $CF_3^*SF_4CF_2CO_2CH_3$ and $CF_3^*SF_4CF_2SF_5$ are also found; at -21.1, -21.1 and -25.3p.p.m. respectively.

An examination of the chemical shifts of the CF_3 groups shows that there is very little variation as the substituents in the trans position are varied. The chemical shifts all lie within the range +64.6 to +68.8 p.p.m. (with respect to external CCl_3F). This compares very well with

Compound	δCF_3S	δSF_4	δCF_3	δCF_2	δCF
CF_3SF_4Cl	+67.3	-101.9			
$CF_3SF_4CH_2CH_2Cl$	+64.6	- 41.0			
$CF_3SF_4CH_2CHClCH_3$	+65.1	- 41.9			
$CF_3SF_4\underset{i}{CF_2}\underset{ii}{CF_2}Cl$	+66.1	- 22.4		i + 94.4 ii + 70.0	
$CF_3SF_4\underset{i}{CF_2}\underset{ii}{CF_2}\underset{iii}{CF_2}\underset{iv}{CF_2}Cl$	+66.0	- 23.2		i + 94.0 ii +121.0 iii +119.9 iv + 69.5	
$CF_3SF_4CF(CF_3)CF_2Cl$	+67.5	- 35.3	+71.2	+ 78.1	+142.3
$CF_3SF_4CH_2CF_2Cl$	+64.7	- 47.1		+ 68.2	
$CF_3SF_4CFHCF_2Cl$	+65.0	- 30.1		+ 66.0	+161.5
$CF_3SF_4CF_2CFCl_2$	+64.9	- 25.0		+ 87.6	+ 74.0
$CF_3SF_4\underset{i}{CF_2}\underset{ii}{CFCl}\underset{iii}{CF_2}\underset{iv}{CFCl_2}$	+68.5	- 26.9		i + 88.0 iii +126.7	ii + 93.5 iv + 70.9
$CF_3SF_4\underset{i}{CF_2}\underset{ii}{CFCl}\underset{iii}{CFCl}\underset{iv}{CF_2}Cl$	+68.8	- 25.0		i + 89.9 iv + 70.1	ii + 91.3 iii +111.8
$CF_3SF_4CH{=}CHCl$	+65.7	- 42.9			

Table 2.4 : ^{19}F n.m.r. chemical shifts (in p.p.m. relative to external CCl_3F) of the CF_3SF_4X derivatives.

other $C\underline{F}_3SF_4$ chemical shifts found, e.g. $C\underline{F}_3SF_4CF_2CF_3$, +67.2p.p.m.; $C\underline{F}_3SF_4CF_2CO_2CH_3$, +65.9p.p.m.; and $C\underline{F}_3SF_4CF_2SF_5$, +66.7p.p.m. (249).

On the other hand, however, the SF_4 chemical shift is a very sensitive indicator of the nature of the substituent species. For trans CF_3 and CF_2 substituents, the chemical shift lies in the range $-(24\pm3)$p.p.m. according to the compounds examined in the present work. Similar compounds containing the $CF_3SF_4CF_2$ group (249) have their SF_4 chemical shifts within this range. Also in this range is the chemical shift of the SF_4 group of $CF_3SF_4CF_2CFClCF_3$; i.e. the isomer formed to the lesser extent in the $CF_3SF_4Cl/CF_2{=}CFCF_3$ reaction.

It is more difficult to generalise about the other compounds since there is a lack of examples with which to do so. However, the compounds

Compound	$J_{C\underline{F}_3S\underline{F}_4}$	$J_{S\underline{F}_4C\underline{H}_2}$	$J_{C\underline{H}_2C\underline{H}_2}$				
CF_3SF_4Cl	24.0						
$CF_3SF_4CH_2CH_2Cl$	27.1	9.4	(a)				
			$J_{C\underline{H}_3C\underline{H}}$		$J_{C\underline{H}_2C\underline{H}}$		
$CF_3SF_4CH_2CHClCH_3$	24.8	9.6	6.0		(a)		
			$J_{S\underline{F}_4CC\underline{F}_2}$		$J_{C\underline{H}_2C\underline{F}_2}$		
$CF_3SF_4CH_2CF_2Cl$	24.5	7.3	12.7		4.1		
		$J_{S\underline{F}_4C\underline{F}_2}$			$J_{C\underline{F}_2C\underline{F}_2}$		
$CF_3SF_4CF_2CF_2Cl$	22.6	16.9	13.2		<1.0		
$CF_3SF_4(CF_2CF_2)_2Cl$(b)	22.8						
				$J_{S\underline{F}_4CC\underline{F}}$	$J_{C\underline{F}_2C\underline{F}}$		
$CF_3SF_4CF_2CFCl_2$	23.4	17.2		11.9	7.9		
		$J_{S\underline{F}_4CC\underline{F}_3}$		$J_{S\underline{F}_4C\underline{F}}$		$J_{C\underline{F}_3C\underline{F}}$	$J_{C\underline{F}_3CC\underline{F}_2}$
$CF_3SF_4CF(CF_3)CF_2Cl$	23.1	10.2	15.3	~0.0	(a)	6.6	(a)
		$J_{S\underline{F}_4C\underline{H}}$				$J_{C\underline{F}\underline{H}}$	
$CF_3SF_4CFHCF_2Cl$	23.7	4.8	12.3	~0.0	14.7	43.7	
			$J_{S\underline{F}_4CC\underline{H}}$		$J_{C\underline{H}C\underline{H}}$		
$CF_3SF_4CH{=}CHCl$	22.7	3.0	~0.0		12.6		
$CF_3SF_4(CF_2CFCl)_2Cl$ (b)	22.4 24.0						

(a) not measured due to complexity of spectrum
(b) these spectra were too complex for any other coupling constants to be calculated.

Table 2.5 : Coupling constants (Hz.).

with $CF_3SF_4CH_2$ and $CF_3SF_4CH=$ show the SF_4 chemical shifts in the -40 to -50 p.p.m. region while the CF_3SF_4CFX, X = CF_3 and H, compounds have the SF_4 chemical shift in the -30 to -40 p.p.m. region.

This trend is also observed in SF_5- derivatives (190,206). That these two trends are the same is shown by Table 2.6. A lack of data precludes making the table more comprehensive. Table 2.6 is constructed by subtracting the SF_4 chemical shift of SF_5Cl (250) from the SF_4 chemical shifts of SF_5X compounds (190,206) and comparing the results with the difference in SF_4 chemical shifts between CF_3SF_4Cl (212) and the CF_3SF_4X compounds (this work). The results show several things. Firstly, the shielding of the SF_4 group by the substituent X is independent of

X	$\delta SF_4(SF_5X) - \delta SF_4(SF_5Cl)$	$\delta SF_4(CF_3SF_4X) - \delta SF_4(CF_3SF_4Cl)$
CH_2CH_2Cl	60.9	60.9
$CH_2CHClCH_3$	60.3	60.0
CF_2CFCl_2	75.7	76.9
$CFHCF_2Cl$	71.5	71.8

Table 2.6

the nature of the group in the trans position, i.e. F and CF_3. (This bears out the observation that the CF_3 chemical shift is almost constant in all the compounds examined). It follows, therefore, that the shielding effects of X and the group trans to it are additive in influencing the SF_4 chemical shift. Thus the difference in the SF_4 chemical shifts between CF_3SF_4X and SF_5X represents the difference in the shielding effects of CF_3 and F for these compounds and should be a constant. That this is the case is shown by Table 2.7.

X	$(CF_3SF_4X - SF_5X)\delta SF_4$
Cl	23.3
CH_2CH_2Cl	23.3
$CH_2CHClCH_3$	23.0
$CFHCF_2Cl$	23.6
CF_2CFCl_2	24.5

Table 2.7

Secondly, the shielding of the SF_4 by X in Table 2.6 follows the sequence $CH_2 > CFH > CF_2$, which is the reverse order of the electronegativities for these groups (206), i.e. increasing the electronegativity of X decreases the shielding of SF_4 by X. Such a trend is well documented (69, 184, 251).

The chemical shifts of the other fluorine containing groups in the compounds, viz., CF_3 CF_2 and CF are assigned by comparison with analogous systems (38,124,140,142,186,206,249) and from a consideration of the spin - spin coupling constants.

In all the ^{19}F n.m.r. spectra of these compounds, the CF_3 (of the CF_3SF_4 group) resonance appears as a 1 : 4 : 6 : 4 : 1 quintet due to coupling with the SF_4 group and with no further coupling detectable. It has been found for the compounds SF_5X (206) that increasing the electronegativity of the part of the group X which is directly bonded to sulphur increases the magnitude of the axialSF - equatorialSF$_{(4)}$ coupling. This trend was observed for the series $CH_2 < CHF < CF_2$ but there was no obvious trend for the series CHF, CBrF, CClF, CF_2. In contrast, Dyer and Lee found (251) that for compounds of the type $CF_2QCHFCl$, increasing the electronegativity of Q (where Q is substituents $SiMe_3$, $SiCl_3$, PMe_2, PH_2, OMe, SMe and Cl) decreases the geminal F - F coupling. It is this latter trend which appears to be followed for the CF_3SF_4 derivatives with the CH_2, CFH and CF_2 groups bonded to sulphur. As the electronegativity increases $CH_2 < CFH < CF_2$, the coupling $J_{C\underline{F}_3S\underline{F}_4}$ decreases, although the differences are not very marked.

Since the octahedral arrangement of groups about sulphur should reduce "through-space" coupling for groups trans to one another, it is hardly surprising that no further coupling of the CF_3 group, other than with the SF_4 group, is observed. Further coupling would have to be of a "through-bond" nature and would have to take place through four bonds."Through-bond" coupling through three bonds is found to be only 5Hz. for SF(axial) - CF_2 coupling in SF_5CF_2 compounds (206,249). It is known that "through-bond" coupling when the fluorine nuclei are separated by more than three bonds is small or zero (189).

The fine structure of the SF_4 signals was useful in structure elucidation in almost all the compounds.

Fig. 2.1 shows the SF_4 resonance found in the ^{19}F n.m.r. spectra of both $CF_3SF_4CH_2CH_2Cl$ and $CF_3SF_4CH_2CHClCH_3$. The signal is described by a quartet (from CF_3 coupling) of triplets (from CH_2 coupling). $J_{S\underline{F}_4C\underline{H}_2}$ is of the same order as that already found for SF_5CH_2 compounds (152,190).

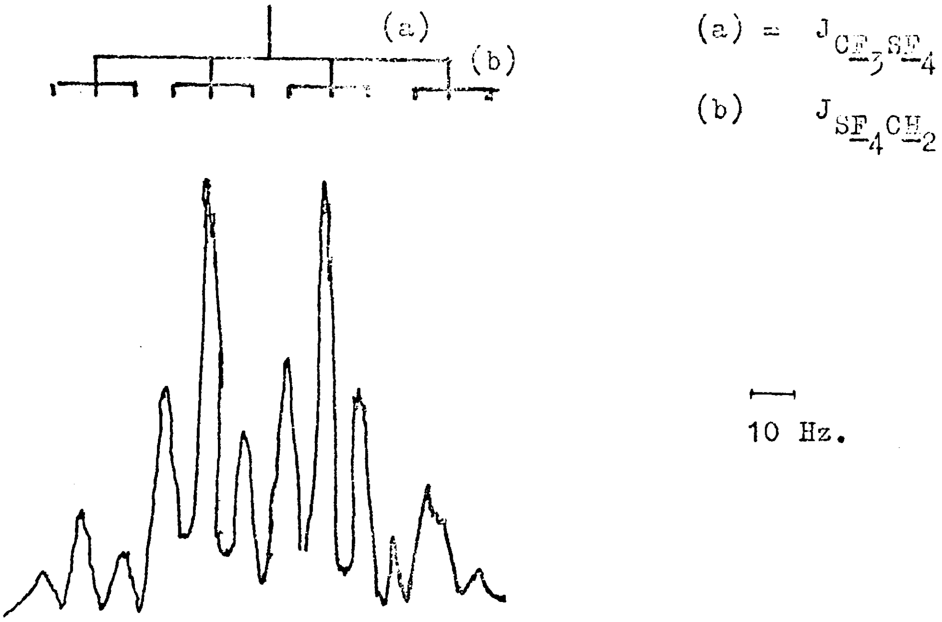


Fig. 2.1 : SF_4 resonance of $CF_3SF_4CH_2CH_2Cl$ and $CF_3SF_4CH_2CHClCH_3$

The SF_4 resonance of $CF_3SF_4CF_2CF_2Cl$ is more complex being a quartet (from CF_3 coupling) of triplets (from α CF_2 coupling) of triplets (from β CF_2 coupling). The $C\underline{F}_2S$ and $C\underline{F}_2Cl$ signals are both quintets from coupling with SF_4 but $J_{C\underline{F}_2C\underline{F}_2}$ is less than 1.0Hz. This latter almost zero coupling is a phenomenon which is not uncommon (184,188) in fluorocarbon compounds and is explained by there being a lack of "through-space" coupling so that the coupling has to occur through three bonds.

There is very little or no observed coupling between the CF and SF_4 fluorines of $CF_3SF_4CF(CF_3)CF_2Cl$, a situation which exists in other $SC\underline{F}X$ compounds where X ≠ F, e.g. $CF_3SF_4CFHCF_2Cl$ (this work), SF_5CFHCF_2Br, SF_5CFHCF_2Cl, SF_5CFHCF_2OMe (206) and $(CF_3)_2SF_3$ (38). The SF_4 signal in $CF_3SF_4CF_2CFClCF_3$ is much more complicated and could not be analysed. Also very complicated are the CF, CF_2, and CF_3 signals in the ^{19}F n.m.r. spectrum of $CF_3SF_4CF(CF_3)CF_2Cl$

The SF_4 resonance of $CF_3SF_4CH_2CF_2Cl$ is best described as a quartet (from CF_3 coupling) of triplets (from CH_2 coupling) of triplets (from CF_2 coupling).

Fig. 2.2 shows the observed SF_4 resonance of $CF_3SF_4CFHCF_2Cl$ with

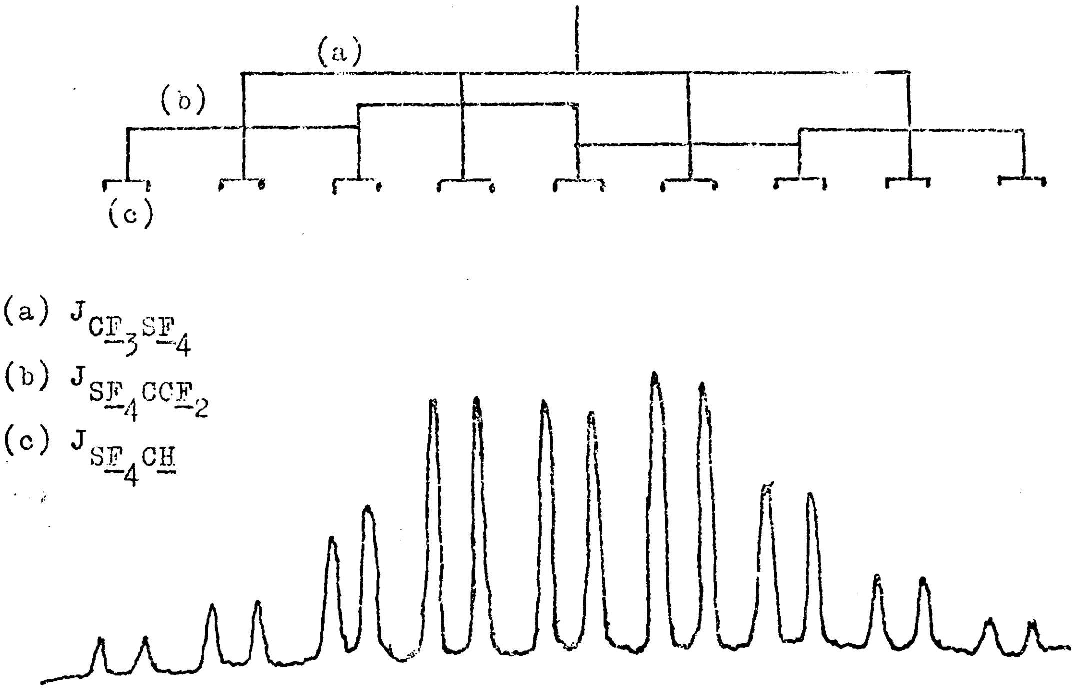


Fig. 2.2 : SF_4 resonance of $CF_3SF_4CFHCF_2Cl$

the analysis of the coupling which is first order. There is again no coupling between the fluorines of the $S\underline{F}_4$ and CF groups. The expected spectrum should have 4 x 3 x 2 (from CF_3, CF_2 and CH coupling respectively) = 24 lines but only 18 are observed. This is because $J_{C\underline{F}_3S\underline{F}_4}$ is approximately twice the value of $J_{S\underline{F}_4CC\underline{F}_2}$ and there is subsequent "doubling up" of six of the lines. The fine structure of the CF signal supports this analysis since it occurs as a well-defined doublet (from geminal C$\underline{H}$ coupling) of triplets (from C$\underline{F}_2$ coupling).

Fig. 2.3 shows the observed SF_4 resonance of $CF_3SF_4CF_2CFCl_2$ together with the analysis which is first order. There is no overlap of lines such as is found in the SF_4 resonance of $CF_3SF_4CFHCF_2Cl$ and the predicted 4 x 3 x 2 (from CF_3, CF_2 and CF coupling respectively) = 24 lines are all observed.

^{1}H n.m.r. Spectra.

The ^{1}H n.m.r. chemical shifts are listed in Table 2.8 while the coupling constants, as far as they could be determined, are listed in

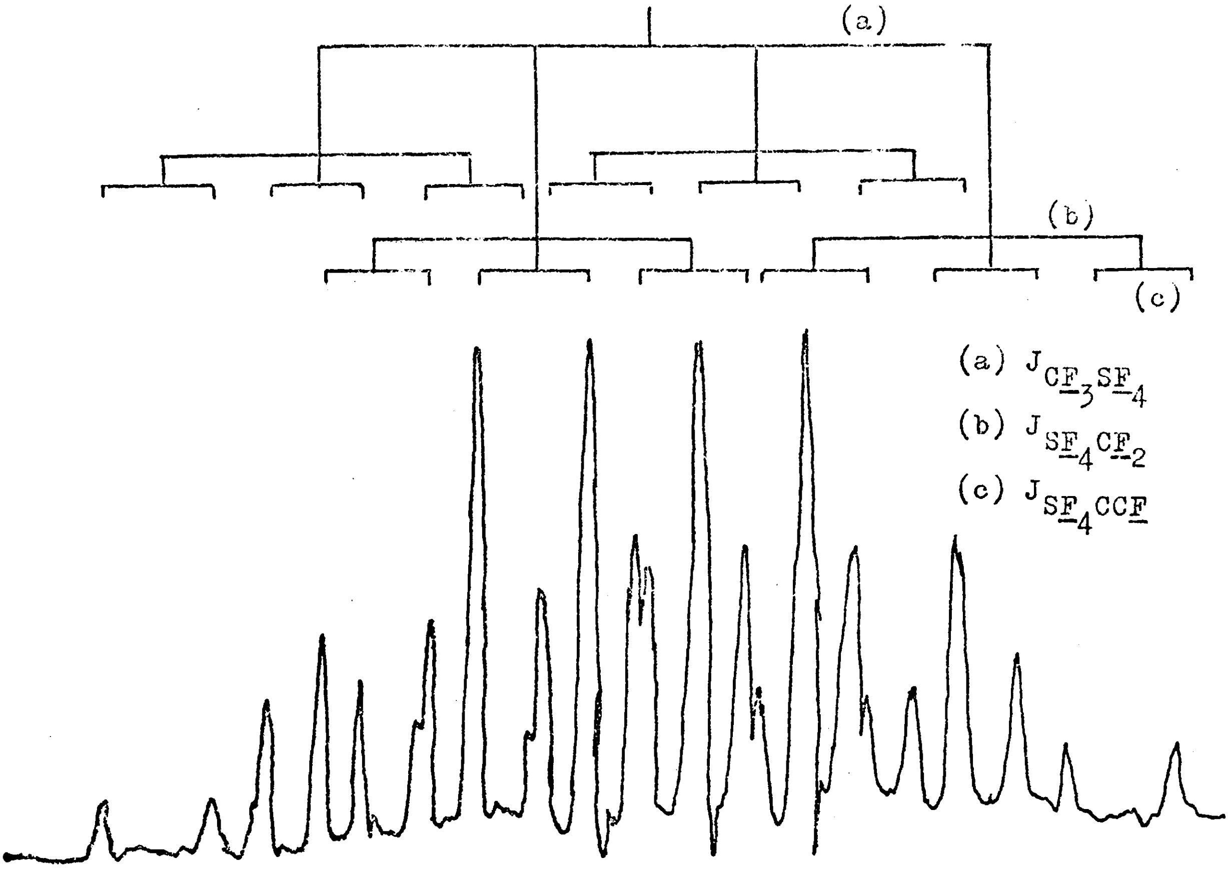


Fig. 2.3 : SF_4 resonance of $CF_3SF_4CF_2CFCl_2$

Compound	δ CH_3–	δ CH_2–	δ CH
$CF_3SF_4CH_2CH_2Cl$		+4.02 +4.10	
$CF_3SF_4CH_2CHClCH_3$	+1.94	(a)	(a)
$CF_3SF_4CH_2CF_2Cl$		+4.38	
$CF_3SF_4CFHCF_2Cl$			+5.13
CF SF CH=CHCl (i)(ii)			(i) +7.84 (ii) +6.64

(a) spectrum too complex for analysis

Table 2.8 : ^1H n.m.r. chemical shifts w.r.t. ext. $(CH_3)_4Si$.

Table 2.5. Tentative chemical shifts are postulated for the CH_2 groups in CF SF CH CH Cl, but a complete analysis is necessary for accurate parameters to be determined. The case of $CF_3SF_4CH_2CHClCH_3$ is similar

although the CH_3 chemical shift and $J_{C\underline{H}_3C\underline{H}}$ are accurately determined since they are first order and simple.

The characterisation of $CF_3SF_4CH{=}CHCl$, trans about the double bond, has already been discussed.

The ^1H n.m.r. spectrum of $CF_3SF_4CH_2CF_2Cl$ is a well-defined quintet of triplets and the coupling constants derived from it agree with the same parameters derived from the ^{19}F n.m.r. spectrum.

The ^1H n.m.r. spectrum of $CF_3SF_4CFHCF_2Cl$ is quite complicated although still first order. It consists of two separate resonances, due to geminal $C\underline{F}$ coupling, each of which is composed of 15 lines as is expected from a quintet (from SF_4 coupling) of triplets (from CF_2 coupling). Again, the coupling constants derived from the ^1H n.m.r. spectrum agree with the same coupling constants derived from the ^{19}F n.m.r. spectrum.

Characterisation of $CF_3SF_4SF_4CF_3$.

In three of the CF_3SF_4Cl/olefin reactions, the 1,2-dichloroalkane is detected; CF_2ClCF_2Cl from the $CF_2{=}CF_2$ reaction is identified by its ^{19}F n.m.r. spectrum (201); $CF_2ClCFClCF_3$, from the $CF_2{=}CFCF_3$ reaction, is identified by its ^{19}F n.m.r. spectrum, $\delta CF_3 = +78.5$ p.p.m., $\delta CF_2 =$ 82.1 p.p.m., CF = +134 p.p.m., assignments being made by comparison with the ^{19}F n.m.r. spectra of similar compounds (186); CF_2ClCH_2Cl, from the $CF_2{=}CH_2$ reaction, is identified by its ^{19}F n.m.r. spectrum, $\delta CF_2 = +59.8$p.p.m. and by its ^1H n.m.r. spectrum, $\delta CH_2 = +3.64$ p.p.m. with $J_{C\underline{F}_2C\underline{H}_2} = 6.1$ Hz., assignments being made by comparison with similar systems (130,201).

These three reactions also produced reasonable quantities of a "common" compound, ca. X, which gives rise to two signals in the ^{19}F n.m.r. spectrum (but none in the ^1H n.m.r. spectrum), viz. a quintet, J = 22.6 Hz., at +65.5 p.p.m. and a signal, whose fine structure is illustrated in Fig. 2.4, at -33.3 p.p.m.. The fine structure of this

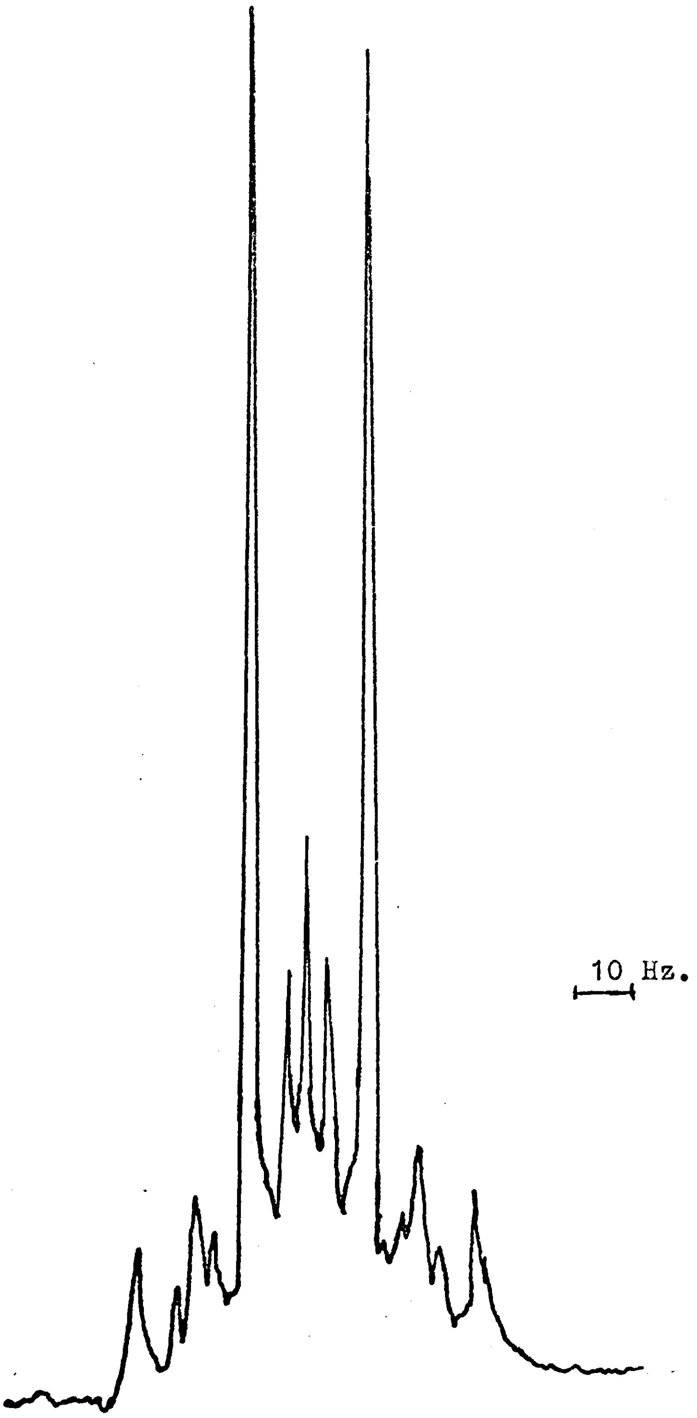


Fig. 2.4 : -33.3 p.p.m. signal in the ^{19}F n.m.r. spectrum of compound X.

signal is quite unique and serves to indicate whether X is present as a reaction product. By employing the presence of the signal at -33.3 p.p.m. in the ^{19}F n.m.r. spectrum as a means of identification, X is also found to be present, in trace amounts, in the products from the reactions of CF_3SF_4Cl with $CFH{=}CF_2$, $CF_2{=}CFCl$ and $HC{\equiv}CH$, although no $CFHClCF_2Cl$, $CF_2ClCFCl_2$ or $CHCl{=}CHCl$ (or $CHCl_2CHCl_2$) is found in these reactions. (Since X is only present in trace amounts, the 1,2-dichloro- compounds may be present but in such small quantities as to miss detection).

Attempts to characterise X were hindered by the fact that it could not be produced in reasonable quantities except in the $CF_3SF_4Cl/CF_2{=}CFCF_3$ reaction. This was the one reaction, however, from which pure material could not be isolated.

As already mentioned, X gives two signals in the ^{19}F n.m.r spectrum. The chemical shift at +65.5 p.p.m. is typical of CF_3 bonded to a S(VI) fluoride. The quintet structure implies coupling to four magnetically equivalent nuclei. Thus, the suggestion is of CF_3 bonded to SF_4 and the chemical shift of the other signal in the ^{19}F n.m.r. spectrum could certainly be due to a S(VI) SF_4 group (see Table 2.4). Also, it has been shown earlier that there is no coupling of the CF_3 group with any group in the <u>trans</u> position of a S(VI) fluoride such as those examined in this work. Hence the lack of fine structure, other than the quintet structure, of the CF_3 signal suggests that X contains a <u>trans</u>-CF_3SF_4- group.

Support for this deduction comes from the infrared spectrum of X where bands assigned to CF_3 and SF_4 vibrations are dominant. These are listed in Table 2.9, together with those of S_2F_{10} (254) and CF_3SF_5 (213).

The signal at -33.3 p.p.m. in the ^{19}F n.m.r. spectrum is very complex and suggests that some sort of second order coupling is taking place. However, there are no other signals, apart from that due to the CF_3 group, in the ^{19}F n.m.r spectrum. A structure for X which would be compatible with these seemingly irreconcilable facts is suggested,

S_2F_{10}	X	CF_3SF_5	Assignment
	1256	1256	$\nu(CF_3)_{asym}$
	1153	1168	$\nu(CF_3)_{sym}$
826	888	902	$\nu(SF_4)_{asym}$
684	653	692	$\nu(SF_4)_{sym}$
571	572	612	$\delta(SF_4)_{out\ of\ plane}$

(all bands are very strong and in cm^{-1})

Table 2.9

therefore to be $CF_3SF_4SF_4CF_3$. This is supported by the observation that the fine structure of the -33.3 p.p.m. signal is somewhat similar to the ^{19}F n.m.r. spectrum of S_2F_{10} (255), bearing in mind that there is the axial-SF signal mixed up with the SF_4 signal. It was suggested earlier that if the chlorine in CF_3SF_4Cl is substituted by some group A, there is a change in the chemical shift of the SF_4 group which is dependent only on the electronegativity difference between Cl and A. To illustrate this, a parallel was drawn with SF_5Cl and it was shown that the "amount of shift" in the SF_4 chemical shift induced by a given A for both SF_5Cl and CF_3SF_4Cl substitutions was the same. Suppose then that A is $-SF_4-R$, and the nature of R is immaterial since there is no interaction across the SF_4 plane, and a similar computation is made. For S_2F_{10}, i.e. R = F, the chemical shift of the SF_4 group lies in the range -51.5 to -56.5 p.p.m. (204), a more accurate determination not being possible, therefore $\delta SF_4(S_2F_{10}) - \delta SF_4(SF_5Cl)$ lies in the range 67.7 to 73.7 (since the SF_4 signal of SF_5Cl is at -125.2 p.p.m. Reference 199). For $CF_3SF_4SF_4CF_3$ i.e. R = CF_3, $\delta SF_4(CF_3SF_4SF_4CF_3) - \delta SF_4(CF_3SF_4Cl) = 68.6$.

This analogy with S_2F_{10} is reinforced when it is recalled that S_2F_{10} is a product of the free radical reaction of SF_5Cl with olefins (127 128,136,137,159,160).

The final piece of evidence for $CF_3SF_4SF_4CF_3$ comes from the reaction between H_2 and CF_3SF_4Cl under the influence of u.v. light (described in Section B) where HCl and what is thought to be $CF_3SF_4SF_4CF_3$ are produced. This compound has the same ^{19}F n.m.r. spectrum as the $CF_3SF_4SF_4CF_3$ described here.

Electrochemical fluorination of S-methylthioglycollic acid is reported (205) to give $CF_3SF_4SF_4CF_3$ but the ^{19}F n.m.r. spectrum is open to question and seems more representative of a cis di-substituted SF_6 derivative. This compound is reported to have a b.p. of 88° whilst the compound suggested here to be $CF_3SF_4SF_4CF_3$ has a b.p. of 116-118°. $CF_3SF_4SF_4CF_3$ produced in this work is a clear liquid and appears to be indefinitely stable in air.

B. Miscellaneous Reactions of CF_3SF_4Cl

Reaction with Mercury.

Darragh has shown that when CF_3SF_4Cl is left in contact with mercury in bright sunlight (212) there is decomposition to give CF_3Cl, SOF_2, SF_4 and SiF_4. These same products are observed here when the reaction is performed in the dark. The SOF_2 and SiF_4 probably arise from hydrolysis of the SF_4 on contact with the glass vacuum line. Thus, mercury catalyses the decomposition of CF_3SF_4Cl to CF_3Cl and SF_4, in the presence or absence of near u.v./visible light. Whether this is a mercury or mercury chloride surface reaction is in some doubt. The apparent mode of decomposition of CF_3SF_4Cl is analogous to that observed in the thermal decomposition of perfluoroalkyl derivatives of SF_6 (65). The reactions are postulated as proceeding via a free radical mechanism,

$$R_fSF_5 \xrightarrow[500^\circ]{400^\circ-} R_fF + R_f{-}R_f + SF_4$$

$$(R_f)_2SF_4 \longrightarrow R_f{-}R_f + SF_4$$

The reactions studied in Section A have shown that the S-Cl bond in CF_3SF_4Cl is susceptible to ready cleavage. It may be therefore that a free radical mechanism similar to that found in the pyrolysis of $(R_f)_2SF_4$ and R_fSF_5 compounds may be operating in this breakdown of CF_3SF_4Cl, with the initiation step being the homolytic cleavage of the S-Cl bond induced by mercury. This would give the $CF_3SF_4^{\bullet}$ radical. Loss of SF_4 would give the $CF_3^{\bullet}$ radical which could propagate the reaction thus :-

$$CF_3^{\bullet} + CF_3SF_4Cl \longrightarrow CF_3Cl + CF_3SF_4^{\bullet} \quad \text{etc.}$$

A mechanism such as this would account for the specificity of the products observed. Indiscriminate cleavage of CF_3-S and S-Cl bonds would produce e.g. CF_3CF_3 which is not found. Another, though perhaps more unlikely, mode of decomposition would be insertion of Hg (or Hg/Cl) into the S-Cl bond to give CF_3SF_4-Hg-Cl followed by elimination of SF_4, leaving CF_3HgCl. Decomposition of CF_3HgCl to CF_3Cl and Hg would again account for the specificity of products. The only substantiation of this unlikely scheme is found in the reaction of <u>trans</u>-stilbenebis(triphenylphosphine)platinum(0 with SF_5Cl (257). The product, $PtCl(SF_5)(PPh_3)_2$, arises from insertion of Pt(0) into the S-Cl bond of SF_5Cl.

However, support for the free radical mechanism comes from the u.v. induced decomposition of CF_3SF_4Cl. When CF_3SF_4Cl is irradiated with u.v. light in quartz (but not in Pyrex), decomposition to CF_3Cl and SF_4 occurs. Again, there are only two products observed. No Cl_2 or CF_3CF_3 is found, arguing a specific mode of decomposition. The free radical mechanism outlined above would fulfill these conditions.

Reaction with H_2.

There is no reaction in a Pyrex reaction vessel. In quartz, u.v. irradiation of a CF_3SF_4Cl/H_2 mixture produces some HCl and some $CF_3SF_4SF_4CF_3$ (with a trans configuration about both sulphur atoms). There is also some decomposition of CF_3SF_4Cl to CF_3Cl and SF_4, but no more than is found with irradiation of CF_3SF_4Cl by itself. The yield, ca. 10% (based on CF_3SF_4Cl consumed) is disappointingly low, but, perhaps instead of a static system, a flow system similar to that used to prepare S_2F_{10} (146) by u.v. irradiation of an SF_5Cl/H_2 mixture and removal of the HCl product by "scrubbing" would improve the yield of $CF_3SF_4SF_4CF_3$.

Reaction with O_2.

There is no reaction between CF_3SF_4Cl and O_2 under the conditions used. It is felt that if a flow system similar to that used for SF_5OOSF_5 production (234) is employed, the peroxide $CF_3SF_4OOSF_4CF_3$ should be produced.

Reactions with CF_3SSCF_3.

The reaction of SF_5Cl with CF_3SSCF_3, as well as that of CF_3SF_4Cl with CF_3SSCF_3, under the influence of u.v. light was investigated since there is no published record of it in the literature. Tattershall and Cady (91) have examined the reaction between CF_3SSCF_3 and S_2F_{10} under the action of u.v. light. They argued that since both compounds are known to give free radicals - $CF_3S^{\bullet}$ from CF_3SSCF_3 (20) and $SF_5^{\bullet}$ from S_2F_{10} (9) - under the action of u.v. light, radical combination should occur to give SF_5SCF_3, the first direct S(VI) - S(II) linkage. However, the only products they recovered were SF_6 and SF_4 from S_2F_{10} decomposition and CF_3SCF_3 from CF_3SSCF_3 decomposition. The present study was made to see whether the compounds SF_5SCF_3 and $CF_3SF_4SCF_3$ could be isolated. As in the case of the S_2F_{10}/CF_3SSCF_3 reaction, decomposition products are observed; CF_3Cl, SF_4 and CF_3SCF_3 from the CF_3SF_4Cl/CF_3SSCF_3 reaction and SF_4 and SF_6 from the SF_5Cl/CF_3SSCF_3 reaction. One hopeful sign is the observation of CF_3SCl in both reactions. This must come from

(i) radical combination of $CF_3S^{\bullet}$ and $Cl^{\bullet}$

or (ii) $Cl^{\bullet}$ radical attack at CF_3SSCF_3

or (iii) $CF_3S^{\bullet}$ radical attack at RCl, R = CF_3SF_4 and SF_5.

If reaction (i) occurs, then radical combination of $CF_3S^{\bullet}$ with either $SF_5^{\bullet}$ or $CF_3SF_4^{\bullet}$ is a possibility and by repeating the reactions on a much larger scale, the desired products may be detected. If (ii) or (iii) is the reaction giving rise to CF_3SCl, then it is highly unlikely that the desired products will be formed by this method.

EXPERIMENTAL.

A. Reactions of CF_3SF_4Cl with Olefins and Acetylene.

Tables 1.34 and 2.10 list the i.r. and n.m.r. references for both the starting materials and those products identified by these techniques.

Table 2.10

Compound	Source	I.R.	N.M.R.
CF_3SF_4Cl	$CF_3SF_3/Cl_2/CsF$(212)	(212)	(212)
$HC\equiv CH$	Matheson Co.	(219)	
$ClCF_2CF_2Cl$			(186)
CF_3H		(220)	

The acetylene was purified of the polymerisation inhibitor, acetone, by passage through a trap held at -126° and collected at -196°.

Table 2.11 : Products from CF_3SF_4Cl/olefins and acetylene reactions.

Acetylene /Olefin (mmoles.)	mmoles. of CF_3SF_4Cl	Reaction Time (hrs.)	Products (mmoles, %yield)	Boiling Point °C	Vapour Pressure mm.Hg.
$CH_2=CH_2$ (4.02)	3.85	20	$CF_3SF_4CH_2CH_2Cl$ (2.02, 52)	109-110	17.9
$CH_3CH=CH_2$ (3.98)	3.74	20	$CF_3SF_4CH_2CHClCH_3$ (2.20, 59)	122-123	9.7
$CF_2=CF_2$ (3.62)	3.78	20	$CF_3SF_4CF_2CF_2Cl$** (3.06, 85)	124-126	12.9
$CF_2=CF_2$ (14.05)	6.60	20	$CF_3SF_4(CF_2CF_2)_nCl$ n=1,2,>2. (-, 75)	-	-
$CF_3CF=CF_2$ (5.71)	5.84	82	$CF_3SF_4CF(CF_3)CF_2Cl$** (2.51, 44) (a)	116-117	9.8
$CF_2=CH_2$ (5.31)	5.57	98	$CF_3SF_4CH_2CF_2Cl$** (3.04, 57)	86- 88	20.3
$CF_2=CFH$ (5.36)	5.40	120	$CF_3SF_4CFHCF_2Cl$* (2.52, 47)	85- 86	43.2
$CF_2=CFCl$ (5.67)	5.72	120	$CF_3SF_4CF_2CFCl_2$* (1.28, 23)	99-100	27.0
			$CF_3SF_4(CF_2CFCl)_2Cl$ (0.87, 15)	164-166	3.2
$HC\equiv CH$ (3.69)	3.76	34	$CF_3SF_4CH=CHCl$* (2.30, 62)	98- 99	31.2

** $CF_3SF_4SF_4CF_3$ and the 1,2-dichloroalkane also formed

* $CF_3SF_4SF_4CF_3$ also formed

(a) $CF_3SF_4CF_2CFClCF_3$ is also formed, but only to a very small extent, *ca* 3%

Table 2.12 : Molecular weights (a) and analytical data for the CF_3SF_4X derivatives.

Compound (b)		Molecular Weight	% C	% H	% F	% S	% Cl
$CF_3SF_4CH_2CH_2Cl$	Found	252	14.8	1.7	55.2	13.5	14.6
	Calc.	240	15.0	1.7	55.3	13.3	14.7
$CF_3SF_4CH_2CHClCH_3$	Found	254	19.1	2.4	52.1	12.5	14.0
	Calc.	254	18.9	2.4	52.2	12.6	13.9
$CF_3SF_4CF_2CF_2Cl$	Found	336	11.7	-	66.6	10.1	11.2
	Calc.	312	11.5	-	66.9	10.2	11.3
$CF_3SF_4CH_2CF_2Cl$	Found	278	12.8	0.6	61.6	11.8	12.7
	Calc.	276	13.0	0.7	61.8	11.6	12.8
$CF_3SF_4CFHCF_2Cl$	Found	308	12.0	0.5	64.1	11.1	11.5
	Calc.	294	12.2	0.4	64.5	10.9	12.0
$CF_3SF_4CF_2CFCl_2$	Found	328	11.1	-	57.7	10.1	20.8
	Calc.	329	11.0	-	57.8	9.8	21.3
$CF_3SF_4(CF_2CFCl)_2Cl$	Found	444	13.5	-	55.2	7.3	23.7
	Calc.	445	13.5	-	55.5	7.2	23.8
$CF_3SF_4CH{=}CHCl$	Found	246	15.4	0.9	55.3	13.9	14.4
	Calc.	238	15.1	0.9	55.8	13.5	14.9

(a) Molecular weights were determined by the vapour density method.
(b) A pure sample of $CF_3SF_4CF(CF_3)CF_2Cl$ was not obtained for analysis purposes.

The reaction method employed, viz. irradiation of a mixture of CF_3SF_4Cl and olefin/ acetylene, generally in a 1:1 ratio, was as described in Experimental Section A of Chapter I.

The reactions of CF_3SF_4Cl with olefins and acetylene are summarised in Table 2.11 while Table 2.12 lists the molecular weights and analytical data for the adducts.

$CF_3SF_4CH_2CH_2Cl$/ Ethanolic KOH Reaction.

A sample of 3 ml. $CF_3SF_4CH_2CH_2Cl$ was introduced into a solution of 9.5 g. KOH, 10 ml. H_2O , 30 ml. CH_3CH_2OH. A white solid was immediately deposited. The volatile material was removed and fractionated through traps held at -80°, -100°, and -196°. The -196° trap contained CF_3H while the -100° trap contained a trace of what was thought to be trans $-CF_3SF_4CH{=}CH_2$.

B. Miscellaneous Reactions of CF_3SF_4Cl.

Tables 1.44, 1.46, 2.10 and 2.13 list the i.r. and n.m.r. spectra references for both the starting materials and products identified by these techniques.

Table 2.13

Compound	Source	I.R.	N.M.R.
H_2	B.O.C.		
O_2	B.O.C.		
COF_2		(220)	
CF_3SCF_3			(186)
CF_3SCl			(97)
SF_5Cl	Peninsular Chemresearch Inc.	(213)	
SF_6		(258)	

Reaction with Mercury

CF_3SF_4Cl (6.35 mmoles.), contaminated with a little Cl_2, was condensed (-196°) into a Hoke bomb containing mercury and the mixture allowed to stand at room temperature for 4 days. Fractionation of the volatile contents of the bomb gave CF_3Cl (-196°) and CF_3SF_4Cl (trace) and SF_4 (-126°). SOF_2 was also found (-126°) but no doubt arose from hydrolysis of the SF_4 in the glass vacuum line.

U.V. Irradiation Reactions

All the following reactions were carried out twice, once using a Pyrex reaction vessel and once using a quartz reaction vessel. In every case, the reactants were condensed or pressurised (-196°) into the reaction flask (Pyrex or quartz), allowed to warm to room temperature and irradiated with u.v. light for 24 hours whereupon the products were fractionated through low temperature traps.

u.v. Irradiation of CF_3SF_4Cl

(a) Pyrex CF_3SF_4Cl (5.21 mmoles.) remained unchanged.

(b) Quartz CF_3SF_4Cl (5.21 mmoles.) gave CF_3Cl (-196°), CF_3SF_4Cl (4.50 mmoles -126°) and SF_4 (-80°; static distillation). This represents 13.5% decomposition of CF_3SF_4Cl.

u.v. Irradiation of CF_3SF_4Cl with H_2.

H_2 was dried by passing slowly over 4A molecular sieves and through four -196° traps.

(a) Pyrex CF_3SF_4Cl (4.48 mmoles) and H_2 in excess did not react.

(b) Quartz CF_3SF_4Cl (4.48 mmoles) and H_2 gave CF_3Cl, SiF_4, HCl (-196°) and SOF_2 and CF_3SF_4Cl (ca 90% unchanged) (-126°)

u.v. Irradiation of CF_3SF_4Cl with O_2.

O_2 was dried by passage over 4A molecular sieves and slow distillation through four -126° traps.

(a) Pyrex CF_3SF_4Cl (4.71 mmoles) and O_2(in excess) gave no reaction.

(b) Quartz CF_3SF_4Cl (4.71 mmoles) and O_2 (in excess) gave COF_2, CF_4, HCl, SiF_4, SOF_2 and Cl_2 (-196°) and CF_3SF_4Cl (ca 86% unchanged; -126°).

u.v. Irradiation of CF_3SF_4Cl with CF_3SSCF_3.

CF_3SSCF_3 was purified as described in Experimental Section A, Chapter I

(a) Pyrex CF_3SF_4Cl (4.05 mmoles) and CF_3SSCF_3 (4.23 mmoles) gave CF_3Cl and SiF_4 (-196°), CF_3SF_4Cl, CF_3SSCF_3, SOF_2 and CF_3SCF_3 (-126°), CF_3SF_4Cl and CF_3SSCF_3 (-100°) and CF_3SSCF_3 (-80°).

(b) Quartz CF_3SF_4Cl (4.33 mmoles) and CF_3SSCF_3 (4.52 mmoles) gave CF_3Cl and SiF_4 (-196°), CF_3SF_4Cl, CF_3SSCF_3, CF_3SCF_3, CF_3SCl and SOF_2 (-126°), CF_3SSCF_3, CF_3SF_4Cl and CF_3SCl (-100°) and CF_3SSCF_3 (-80°).

u.v. Irradiation of SF_5Cl with CF_3SSCF_3.

(a) Pyrex SF_5Cl (5.52 mmoles) and CF_3SSCF_3 (5.34 mmoles) gave no reaction.

(b) Quartz SF_5Cl (5.52 mmoles) and CF_3SSCF_3 (5.34 mmoles) gave SF_5Cl, SiF_4, SOF_2, SF_6, and CF_3SSCF_3 (-196°) and CF_3SSCF_3, CF_3SCF_3 and CF_3SCl (-100°).

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