trans-Chlorotetrafluoro(trifluoromethyl)sulphur and its Reactions with Olefins and Acetylenes †

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trans-$S(CF_3)ClF_4$ has been prepared by the reaction between $S(CF_3)F_3$ and Cl_2 in the presence of caesium fluoride. Its properties and addition reactions with olefins and acetylenes to give the compounds RCH_2CH_2Cl, $RCH_2CH(Cl)Me$, RCF_2CF_2Cl, $RCF(CF_3)CF_2Cl$, $RCF_2CF(Cl)CF_3$, RCH_2CF_2Cl, $RCF(H)CF_2Cl$, RCF_2CFCl_2, $R(CF_2CFCl)_2Cl$, and $RCH=CHCl$ [R = *trans*-$S(CF_3)F_4$] are described.

PREVIOUSLY[1] brief details of the preparation of *trans*-chlorotetrafluoro(trifluoromethyl)sulphur $S(CF_3)ClF_4$, (I), were reported and in the present paper further details of this compound are given together with a description of its reactions with olefins.

RESULTS AND DISCUSSION

Chlorine reacts with trifluoro(trifluoromethyl)sulphur $S(CF_3)F_3$ in the presence of caesium fluoride to give the compound *trans*-$S(CF_3)ClF_4$, (I). All four fluorine atoms attached to sulphur are equivalent, as would be expected for the *trans*-derivative. Disubstituted derivatives of sulphur hexafluoride could have either a *cis*- or a *trans*-configuration (it has very recently been shown that derivatives $R_fSF_4R_f'$ can be formed as a mixture of isomers [2]), but no trace of a *cis*-isomer of $S(CF_3)ClF_4$ was detected in the present work. Present evidence on the formation of chloropentafluorosulphur $SClF_5$, from sulphur tetrafluoride and chlorine in the presence of caesium fluoride, is in favour of attack of chlorine on an intermediate square-pyramidal[3,4] SF_5^- anion. In formation of (I), $S(CF_3)F_4^-$ can be postulated as an intermediate and attack on $S(CF_3)F_4^-$ with *trans*-arrangement of CF_3 and the lone pair would seem logical.

Chlorotetrafluoro(trifluoromethyl)sulphur is similar in its properties to chloropentafluorosulphur. Hydrolysis of (I) by water is slow but the compound decomposes in the presence of mercury when set aside (the reaction is accelerated by light) to give CF_3Cl, SF_4, and the products of the reaction between sulphur tetrafluoride and the container. Compound (I) remains unchanged on photolysis in Pyrex, but in quartz apparatus, which apparently allows the passage of radiation of higher energy, there is some decomposition to CF_3Cl and SF_4. Spectroscopic properties of compound (I) are considered below along with those of other $S(CF_3)F_4X$ derivatives.

Compound (I) reacted in Pyrex apparatus with olefins and acetylenes, when u.v. irradiated, to give products which were generally the result of addition of *trans*-$S(CF_3)F_4$ and Cl across the multiple C–C bond (Table 1). In some of the reactions, small yields of the dichlorine adduct of the olefin and a common compound, possibly $CF_3SF_4SF_4CF_3$, were formed. When the reaction was carried out in quartz apparatus, the major reaction was decomposition of (I) to CF_3Cl and SF_4. There were no reactions at room temperature between compound (I) and olefins or acetylenes in the dark. The reactions between (I) and ethylene or propylene gave only olefin adducts as products. The reactions appeared to reach an equilibrium, *e.g.* equation (1), as the yields of product

$$S(CF_3)ClF_4 + H_2C{=}CH_2 \rightleftharpoons F_4(CF_3)SCH_2CH_2Cl \quad (1)$$

reached a maximum after *ca.* 15 h irradiation, but further product was formed if that initially prepared was removed. The product of the reaction with propylene, $F_4(CF_3)SCH_2CH(Cl)Me$ (III), is analogous[5] to that formed in the corresponding reaction with SF_5Cl and corresponds to radical attack on the CH_2 group. Compound (I) reacted with equimolar quantities of tetrafluoroethylene to give the 1 : 1 adduct $F_4(CF_3)SCF_2CF_2Cl$, (IV), together with traces of $CF_3SF_4SF_4CF_3$ and $ClCF_2CF_2Cl$. With higher ratios of C_2F_4, telomerisation was marked and compound $F_4(CF_3)S(CF_2)_4Cl$, (V), could be separated from the mixture and identified spectroscopically; $CF_3SF_4SF_4CF_3$ was not identified from the latter reaction. Hexafluoropropene reacted with (I) to give the compounds $F_4(CF_3)SCF(CF_3)CF_2Cl$, (VI), and $F_4(CF_3)SCF_2CF(Cl)CF_3$, (VII), in a 97 : 3 ratio (products identified spectroscopically). The compound $SClF_5$ reacts with $CF_2{=}CFCF_3$ to give approximately equal quantities of the two possible adducts.[6,7]

Reactions between $CH_2{=}CF_2$ or $CFH{=}CF_2$ and (I) gave the 1 : 1 adducts $F_4(CF_3)SCH_2CF_2Cl$, (VIII), and $F_4(CF_3)SCF(H)CF_2Cl$, (IX), respectively, corresponding to the favoured position for radical attack on the olefins and to products formed by reactions between $SClF_5$ and the olefins.[6] Reaction between equimolar quantities of (I) and $CF_2{=}CFCl$ gave both the 1 : 1 adduct $F_4(CF_3)SCF_2CFCl_2$, (X), and two isomers $F_4(CF_3)SCF_2CF(Cl)CF_2CFCl_2$, (XIa), and $F_4(CF_3)SCF_2CF(Cl)CF(Cl)CF_2Cl$, (XIb), of the 1 : 2 adduct. Compound (I)

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† No reprints available.

[1] J. I. Darragh and D. W. A. Sharp, *Chem. Comm.*, 1969, 864.

[2] T. Abe and J. M. Shreeve, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 465.

[3] C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1964, **86**, 357; C. J. W. Fraser, D. W. A. Sharp, G. Webb, and J. M. Winfield, *J.C.S. Dalton*, 1972, 2226.

[4] F. L. Drillinger and J. E. Griffiths, *Spectrochim. Acta*, 1971, **A27**, 1793; K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 1972, **11**, 1679.

[5] J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 1961, 2066.

[6] J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 1961, 2070.

[7] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1963, 1083.

reacts with acetylene to give $\mathrm{F_4(CF_3)SCH{=}CHCl}$, (XII). The *trans*-product is also formed in photochemical or thermal addition of $\mathrm{SClF_5}$ to acetylene.[5,8]

TABLE 1

Products from reactions between compound (I) and olefins and acetylenes

Amount of acetylene/olefin mmol	Amount of (I) mmol	Reaction time h	Products mmol, % yield	B.p. (t/°C)	Vapour pressure mmHg		M	Analyses (%) C	H	F	S	Cl
$\mathrm{CH_2{=}CH_2}$		20	$\mathrm{F_4(CF_3)SCH_2CH_2Cl}$ (II)	109—110	17·9	Found	252	14·8	1·7	55·2	13·5	14·6
(4·02)	3·85		(2·02, 52,)			Calc.	240	15·0	1·7	55·3	13·3	14·7
$\mathrm{MeCH{=}CH_2}$		20	$\mathrm{F_4(CF_3)SCH_2CH(Cl)Me}$ (III)	122—123	9·7	Found	254	19·1	2·4	52·1	12·5	14·0
(3·98)	3·74		(2·20, 59)			Calc.	254	18·9	2·4	52·2	12·6	13·9
$\mathrm{CF_2{=}CF_2}$		20	$\mathrm{F_4(CF_3)SCF_2CF_2Cl}$ (IV)*	124—126	12·9	Found	336	11·7		66·6	10·1	11·2
(3·62)	3·78		(3·06, 85)			Calc.	312	11·5		66·9	10·2	11·3
$\mathrm{CF_2{=}CF_2}$		20	$\mathrm{F_4(CF_3)S(CF_2CF_2)_{\mathit{n}}Cl}$									
(14·05)	6·60		$n = 1$ (trace) $n = 2$ (75%) (V) $n > 2$ (25%)									
$\mathrm{CF_3CF{=}CF_2}$		82	$\mathrm{F_4(CF_3)SCF(CF_3)CF_2Cl}$ (VI)*									
(5·71)	5·84		(2·51, 44)	116—117	9·8		Pure sample of $\mathrm{F_4(CF_3)SC_3F_6Cl}$ not obtained for analysis.					
			$\mathrm{F_4(CF_3)SCF_2CF(Cl)CF_3}$									
			(0·1, 1)									
$\mathrm{CF_2{=}CH_2}$		98	$\mathrm{F_4(CF_3)SCH_2CF_2Cl}$ (VIII)*	86—88	20·3	Found	278	12·8	0·6	61·6	11·8	12·7
(5·31)	5·57		(3·04, 57)			Calc.	276	13·0	0·7	61·8	11·6	12·8
$\mathrm{CF_2{=}CFH}$		120	$\mathrm{F_4(CF_3)SCFHCF_2Cl}$ (IX)†	85—86	43·2	Found	308	12·0	0·5	64·1	11·1	11·5
(5·36)	5·40		(2·52, 47)			Calc.	294	12·2	0·4	64·5	10·9	12·0
$\mathrm{CF_2{=}CFCl}$		120	$\mathrm{F_4(CF_3)SCF_2CFCl_2}$ (X)†	99—100	27·0	Found	328	11·1		57·7	10·1	20·8
(5·67)	5·72		(1·28, 23)			Calc.	329	11·0		57·8	9·8	21·3
			$\mathrm{F_4(CF_3)S(CF_2CFCl)_2Cl}$ (XI)	164—166	3·2	Found	444	13·5		55·2	7·3	23·7
			(0·87, 15)			Calc.	445	13·5		55·5	7·2	23·8
$\mathrm{HC{\equiv}CH}$		34	$\mathrm{F_4(CF_3)SCH{=}CHCl}$ (XII)†	98—99	31·2	Found	246	15·4	0·9	55·3	13·9	14·4
(3·69)	3·76		(2·30, 62)			Calc.	238	15·1	0·9	55·8	13·5	14·9

Molecular weights were determined by vapour density.

* $\mathrm{CF_3SF_4SF_4CF_3}$ and the 1,2-dichloroalkane were also formed. † $\mathrm{CF_3SF_4SF_4CF_3}$ was also formed.

The reactions between compound (I) and olefins are thus very similar to those previously described for $\mathrm{SClF_5}$, which have been studied in detail and are considered to involve an $\mathrm{SF_5^{\cdot}}$ chain [equations (2)—(7)].[9]

$$\mathrm{SClF_5 \xrightarrow{h\nu} SF_5^{\cdot} + Cl} \tag{2}$$

$$\mathrm{SF_5^{\cdot} + E \longrightarrow SF_5E^{\cdot}} \quad (\mathrm{E} = \text{olefin}) \tag{3}$$

$$\mathrm{Cl^{\cdot} + E \longrightarrow ClE^{\cdot}} \tag{4}$$

$$\mathrm{SF_5E^{\cdot} + SClF_5 \longrightarrow SF_5ECl + SF_5^{\cdot}} \tag{5}$$

$$\mathrm{ClE^{\cdot} + SClF_5 \longrightarrow ClECl + SF_5^{\cdot}} \tag{6}$$

$$\mathrm{SF_5^{\cdot} + SF_5^{\cdot} \longrightarrow S_2F_{10}} \tag{7}$$

Double addition of $\mathrm{SF_5^{\cdot}}$ to an olefin to form $\mathrm{F_5SESF_5}$ has not been detected in these systems. It would seem by analogy, therefore, that the reactions between compound (I) and olefins are best considered as involving $\mathrm{F_4(CF_3)S^{\cdot}}$ and $\mathrm{Cl^{\cdot}}$ radicals.

The major product of the reaction between compound (I) and $\mathrm{CF_3CF{=}CF_2}$ is not that which would normally be formed by free radical attack on this olefin.[7] $\mathrm{CF_3CF{=}CF_2}$ is particularly susceptible to nucleophilic attack but the $\mathrm{SF_5^{\cdot}}$ radical is considered a relatively poor nucleophile and the $\mathrm{S(CF_3)F_4^{\cdot}}$ radical is apparently even less nucleophilic. The $\mathrm{Cl^{\cdot}}$ radical is thought to be an electrophile[10] so that compound (I) gives rise to two relatively poor nucleophiles. The telomerisation reactions observed with $\mathrm{CF_2{=}CF_2}$ and $\mathrm{CF_2{=}CFCl}$ can easily be accommodated in terms of radical reactions, *e.g.* equations (8)—(14).

$$\mathrm{S(CF_3)ClF_4 \xrightarrow{u.v.} S(CF_3)F_4^{\cdot} + Cl^{\cdot}} \tag{8}$$

$$\mathrm{S(CF_3)F_4^{\cdot} + CF_2{=}CFCl \longrightarrow F_4(CF_3)SCF_2CFCl^{\cdot}} \tag{9}$$

$$\mathrm{F_4(CF_3)SCF_2CFCl^{\cdot} + S(CF_3)ClF_4 \longrightarrow F_4(CF_3)SCF_2CFCl_2 + S(CF_3)F_4^{\cdot}} \tag{10}$$

$$\mathrm{F_4(CF_3)SCF_2CFCl^{\cdot} + CF_2{=}CFCl \longrightarrow F_4(CF_3)SCF_2CFClCF_2CFCl^{\cdot}} \tag{11}$$

$$\mathrm{F_4(CF_3)SCF_2CFClCF_2CFCl^{\cdot} + S(CF_3)ClF_4 \longrightarrow F_4(CF_3)SCF_2CFClCF_2CFCl_2 + S(CF_3)F_4^{\cdot}} \tag{12}$$

$$\mathrm{Cl^{\cdot} + CF_2{=}CFCl \longrightarrow ClCF_2CFCl^{\cdot}} \tag{13}$$

$$\mathrm{F_4(CF_3)SCF_2CFCl^{\cdot} + ClCF_2CFCl^{\cdot} \longrightarrow F_4(CF_3)SCF_2CFClCFClCF_2Cl} \tag{14}$$

In all cases the products contain only the *trans*-$\mathrm{S(CF_3)F_4R}$ group so that the $\mathrm{S(CF_3)F_4^{\cdot}}$ radical, if present

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[8] F. W. Hoover and D. D. Coffman, *J. Org. Chem.*, 1964, **29**, 3567.

[9] H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Trans. Faraday Soc.*, 1969, **65**, 2103; *Chem. Comm.*, 1970, 253; R. E. Banks, R. N. Haszeldine, and W. D. Morton, *J. Chem. Soc.* (*C*), 1969, 1947.

[10] E. S. Gould, ' Mechanism and Structure in Organic Chemistry,' Holt, Reinhart, and Winston, New York, 1959.

as a distinct entity, must have considerable configurational stability in square-pyramidal geometry. The configurational stability of this radical must, in fact, be similar to that of the $S(CF_3)F_4^-$ anion. E.p.r. studies on radicals such as $S(CF_3O)F_4^{\bullet}$, which give *cis*-derivatives on further reaction, suggest that the CF_3O group and unpaired electron are relatively *cis*[11] in these radicals.

All the compounds prepared in the present work gave fairly complex ^{19}F n.m.r. spectra (Table 2) which could however be readily interpreted by first order analysis. That all of the species $S(CF_3)F_4R$ are in the *trans*-configuration was established by the observation of a single signal for the SF_4 group and by the observed coupling to CF_3 and R; it is known that *cis*-SF_4XY derivatives give A_2B_2 type spectra for the SF_4 groups.[12]

TABLE 2

^{19}F N.m.r. data for $S(CF_3)F_4R$ compounds

Compound	δ(CF_3S)	δ(SF_4)	δ(CF_3)	δ(CF_2)	δ(CF)	$J_{CF_3SF_4}$		
(I)	+67·3	−101·9				24·0		
(II)	+64·6	−41·0				27·1	$J_{SF_4CH_2}$ 9·4	
(III)	+65·1	−41·9				24·8	$J_{SF_4CH_2}$ 9·6	J_{CH_3CH} 6·0
(IV)	+66·1	−22·4		(i) +94·4 (ii) +70·0		22·6	$J_{SF_4CF_2}$ 16·9 $J_{CF_2CF_2}$ <1·0	$J_{SF_4CCF_2}$ 13·2
(V) [a]	+66·0	−23·2		(i) +94·0 (ii) +121·0 (iii) +119·9 (iv) +69·5		22·8		
(VI) [a]	+67·5	−35·3	+71·2	+78·1	+142·3	23·1	$J_{SF_4CCF_3}$ 10·2 J_{SF_4CF} *ca.* 0·0	$J_{SF_4CCF_2}$ 15·3 J_{CF_3CF} 6·6
(VIII)	+64·7	−47·1		+68·2		24·5	$J_{SF_4CH_2}$ 7·3 $J_{CH_2CF_2}$ 4·1	$J_{SF_4CCF_2}$ 12·7
(IX)	+65·0	−30·1		+66·0	+161·5	23·7	J_{SF_4CH} 4·8 J_{SF_4CF} *ca.* 0·0 J_{CFH} 43·7	$J_{SF_4CCF_2}$ 12·3 J_{CFCF_2} 14·7
(X)	+64·9	−25·0		+87·6	+74·0	23·4	$J_{SF_4CF_2}$ 17·2 J_{CF_2CF} 7·9	J_{SF_4CCF} 11·9
$F_4(CF_3)SCF_2CFClCF_2CFCl_2$ (XIa) [a]	+68·5	−26·9		(i) +88·0 (iii) +126·7	(ii) +93·5 (iv) +70·9	22·4		
$F_4(CF_3)SCF_2CFClCFClCF_2Cl$ (XIb) [a]	+68·8	−25·0		(i) +89·9 (iv) +70·1	(ii) +91·3 (iii) +111·8	24·0		
(XII)	+65·7	−42·9				22·7	J_{SF_4CH} 3·0 J_{CHCH} 12·6	J_{SF_4CCH} *ca.* 0·0
(XIII) [a]	+65·5	−33·3				22·6		

Chemical shifts/p.p.m. with respect to external CCl_3F. Carbon atoms marked from the sulphur.

[a] Not all possible coupling constants were measured because of complexity of the spectrum.

The CF_3 groups showed very little variation in chemical shift with the *trans*-substituent, all of the signals lying within the range +64·6 to +68·8 p.p.m. (with respect to external CCl_3F). The SF_4 chemical shift was, however, very sensitive to the substituents. For *trans*-CF_3 and -CF_2– the chemical shift of compounds studied in the present work lay in the range $-(24 \pm 3)$ p.p.m. which includes previously studied compounds[13] [except for *trans*-$S(CF_3)_2F_4$ which has a shift[2] of −18·6 p.p.m.]. There are fewer examples of other types of *trans*-substituents but CF_3 and CH_2 or CH give SF_4 chemical shifts in the range −40 to −50 p.p.m. whilst CF_3 and $CF(CF_3)$ or CFH have intermediate shifts in the region −30 to −40 p.p.m. Chemical shifts of the SF_4 group of RSF_4R derivatives follow a similar trend and chlorine is more strongly deshielding than fluorine.[14] The CF_3 signal of the $S(CF_3)F_4R$ derivatives appeared as a quintet due to coupling with four equivalent equatorial fluorine atoms but further coupling to substituents on R was not observed.

TABLE 3

^1H N.m.r. data for $S(CF_3)F_4R$ compounds

Compound	δ(CH_3)	δ(CH_2)	δ(CH)
(II)		+4·02 +4·10	
(III)	+1·94	*a*	*a*
(VIII)		+4·38	
(IX)			+5·13
(XII)			(i) +7·84 (ii) +6·64

Chemical shifts/p.p.m. with respect to external Me_4Si.

[a] Spectrum was too complex for analysis.

I.r. spectra of the *trans*-$S(CF_3)F_4R$ derivatives contained a series of strong bands (Table 4). Assignments

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[11] J. R. Morton and K. F. Preston, *Chem. Phys. Letters*, 1973, **18**, 98.

[12] See, for example, S. M. Williamson, *Progr. Inorg. Chem.*, 1966, **7**, 39.

[13] M. T. Rogers and J. D. Graham, *J. Amer. Chem. Soc.*, 1962, **84**, 3667.

[14] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1963, **59**, 620; M. G. Barlow, R. R. Dean, and J. Lee, *ibid.*, 1969, **65**, 321; C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, jun., *Inorg. Chem.*, 1962, **1**, 215.

for these were made by comparison with the spectra of $S(CF_3)F_5$ and other derivatives of sulphur hexafluoride.[15] The strongest bands in the spectra of all the substances studied occurred near 1 250 and 800—900 cm^{-1}, followed in intensity by bands near 1 150 and 650—680 cm^{-1}. The SF_4 out-of-plane deformation mode occurring between 550 and 650 cm^{-1} and CF_3 symmetric deformation between 740 and 780 cm^{-1} were sometimes very intense but were sometimes of only medium intensity so that, with, for example, C–F modes also occurring in these regions, definite assignments were not always possible. Positive identification of the S–Cl stretch in compound (I) could not be made; the corresponding mode of $SClF_5$ occurs [14] at 402 cm^{-1}.

TABLE 4

Characteristic i.r. bands of $S(CF_3)F_4R$ derivatives

Compound	$\nu(CF_3)$ asym	$\nu(CF_3)$ sym	$\nu(SF_4)$ asym	$\nu(SF_4)$ sym	$\delta(SF_4)$ out-of-plane	$\delta(CF_3)$ sym
$S(CF_3)F_5$	1 256	1 168	902	691	612	755
(I)	1 250	1 155	860	678	643	785
(II)	1 249	1 150	812	657	603	743
(III)	1 247	1 135	804	639	602	744
(IV)	1 259	1 156	855	664	570	780
(V)	1 255	1 153	851	666	*a*	778
(VI)	1 257	1 154	852	678	572	*a*
(VIII)	1 251	1 151	889	655	610	746
(IX)	1 258	1 155	891	658	573	761
(X)	1 256	1 152	887	651	570	*a*
(XI)	1 258	1 156	850	657	*a*	*a*
(XII)	1 261	1 156	890	654	602	782
(XIII)	1 256	1 168	902	692	612	*a*

[a] Not identified.

Mass spectra were recorded for all the compounds prepared in this work and full data are to be found in Supplementary Publication No. SUP 20813 (12 pp.).* Molecular ions were not observed for any of the compounds even when the ionising beam was reduced from 70 to 12 eV (below this there was no ionisation). $S(CF_3)F_4(NF_2)$ does not give a molecular ion [16] and only a weak molecular ion is observed in the mass spectrum of $SClF_5$,[17] whilst most SF_5–R derivatives (R = halogenocarbon residue) do not show molecular ions.[18] All the spectra showed considerable abundances of the ions $S(CF_3)F_2^+$ (*m*/*e* 139), SF_3^+ (89), SF_2^+ (70), CF_3^+ (69) (the most intense peak), and SF^+ (51), although SF_4^+ was not observed in any of the spectra. The $S(CF_3)F_4R$ derivatives, other than $F_4(CF_3)SCF(CF_3)CF_2Cl$ and $F_4(CF_3)SCF_2CFCl_2$, all gave reasonably high abundances of R^+. Apart from the observation of CF_2Cl^+ in the spectrum of $F_4(CF_3)SCF_2CFCl_2$ (probably resulting from a rearrangement process), all the observed spectra are in complete accord with the structures postulated for the adducts.

In some of the reactions between compound (I) and olefins, in addition to the readily identified adducts resulting from addition of (I) across the multiple bond and adducts resulting from addition of Cl_2 across this bond, a constant further product was identified. The latter compound (XIII) was also formed in very small yield by irradiation of a mixture of (I) and hydrogen in quartz apparatus. By analogy with reactions of $SClF_5$,[9] compound (XIII) would be expected to be $CF_3SF_4SF_4CF_3$, but it is formed in too small yield to allow complete characterisation. The compound is a clear liquid, indefinitely stable in air. It gave rise to two signals in the ^{19}F n.m.r. spectrum and no proton signal (Tables 2 and 3). The quintet (*J* 22·6 Hz) at +65·5 p.p.m. is characteristic of a *trans*-$S(CF_3)F_4$ group and no coupling would be expected with the further substituent of this group. The other signal was a very complex multiplet. The i.r. spectrum showed all of the bands associated with $S(CF_3)F_4$ groups (Table 4). The compound could not be obtained sufficiently pure to give a reliable mass spectrum. All these results are consistent with the formulation of (XIII) as *trans*-$CF_3SF_4SF_4CF_3$. A substance of this formula has been described [19] previously from electrochemical fluorination of *S*-methylthioglycollyl chloride, $MeSCH_2COCl$, but the physical properties of the two substances are different and the CF_3 signal of this latter substance is a triplet rather than a quintet.

EXPERIMENTAL

Materials were handled in a Pyrex vacuum system using standard techniques. Irradiation was carried out in Pyrex or quartz vessels with a Hanovia 12277 medium-pressure mercury-arc lamp. I.r. spectra (Table 4) were recorded in the gas phase or in carbon tetrachloride and dioxan solutions over the range 4 000—250 cm^{-1} with a Perkin-Elmer 457 spectrophotometer. ^{19}F and ^1H N.m.r. spectra (Tables 2 and 3) were recorded, generally on neat liquid samples, with a Perkin-Elmer R10 spectrometer operating at 60 or 56·4 MHz. Mass spectra were recorded on A.E.I. MS 12 and MS 902 mass spectrometers. Analyses were by Bernhardt; molecular weights were determined by vapour-density methods.

Chlorotetrafluoro(trifluoromethyl)sulphur, (I).—Trifluoro(trifluoromethyl)sulphur, $S(CF_3)F_3$, was prepared from bis(trifluoromethyl)disulphide (Peninsular Chem. Research) and silver(II) fluoride.[20] Excess of dried caesium fluoride (American Potash Co. or B.D.H.) and $S(CF_3)F_3$ and Cl_2 (1 : 2) were allowed to warm to room temperature over 3 h in a metal vessel (75 cm^3). Cl_2, SiF_4, and CCl_3F were removed at 77 K and compound (I) (b.p. −15 °C at atmospheric pressure) containing a trace of $CF_3S(O)F$ was collected at 153 K. N.m.r. spectra are given in Tables 2 and 3, and the most intense and characteristic peaks in the i.r. spectrum are listed in Table 4. The mass spectrum

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue.

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was recorded and high-resolution measurements made on the following ions characteristic of compound (I): *m/e* 145, $S^{37}ClF_4^+$ (Found: 144·93155. Calc.: 144·93158); *m/e* 139, $S(CF_3)F_2^+$ (Found: 138·96156. Calc.: 138·96408); and *m/e* 101, $S(CF_3)^+$ (Found: 101·96625. Calc.: 101·96728).

Compound (I), sealed in a glass ampoule with mercury, when exposed to bright sunlight gave a scum on the mercury and CF_3Cl, SOF_2, SF_4 (trace), and SiF_4 (all identified by i.r. spectroscopy) after 5 h. The compound and mercury in a metal bomb gave CF_3Cl and SF_4, together with some unreacted (I), after 4 days. U.v. irradiation of compound (I) in Pyrex apparatus gave unchanged starting material; in quartz apparatus CF_3Cl, SF_4, and unchanged (I) (86%) were obtained. U.v. irradiation of compound (I) (4·48 mmol) and H_2 (in excess) in Pyrex apparatus gave no reaction; in quartz apparatus CF_3Cl, SiF_4, HCl, SOF_2, (I) (90%), together with traces of $CF_3SF_4SF_4CF_3$ (i.r. and n.m.r.), were obtained.

Quantities used for the addition of compound (I) to olefins and acetylenes are given in Table 1; reactions were carried out at room temperature and approximately at atmospheric pressure in Pyrex apparatus and n.m.r. (Tables 2 and 3), i.r. (Table 4), and mass-spectral data were recorded for the products. Mass measurement was carried out for ions in the mass spectrum of $F_4(CF_3)SCH_2CH_2Cl$: for *m/e* 164, $CF_3SCH_2CH_2{}^{35}Cl^+$ (Found: 163·967156. Calc.: 163·967431); *m/e* 133, $SF_2CH_2CH_2{}^{35}Cl^+$ (Found: 132·969203. Calc.: 132·969029); *m/e* 95, $SCH_2CH_2{}^{35}Cl^+$ (Found: 94·972777. Calc.: 94·972225); *m/e* 63, $CH_2CH_2{}^{35}Cl^+$ (Found: 63·000460. Calc.: 63·000152); and CFS (Found: 62·970388. Calc.: 62·970475). Dichlorine adducts of olefins were identified by spectroscopic methods.

We thank the S.R.C. (mass spectrometer) and the Ministry of Defence for support.

[3/944 *Received*, 10*th May*, 1973]