Aryloxysulphur(IV) Fluorides†

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Aryloxysulphur(IV) fluorides result from the interaction between aryl silyl ethers and sulphur tetrafluoride and its derivatives. The derivatives prepared [$ArOSF_3$ (Ar = Ph; *o*-, *m*-, *p*-Tol; *o*-, *m*-, *p*-FC_6H_4; *m*-, *p*-ClC_6H_4), $(ArO)_2SF_2$ (Ar = Ph; *m*-, *p*-Tol; *m*-, *p*-FC_6H_4; *m*-, *p*-ClC_6H_4; *p*-$CF_3C_6H_4$; *p*-$O_2NC_6H_4$), $(ArO)_3SF$ (Ar = Ph or C_6F_5), $(PhO)_4S$, $(C_6H_4O_2)_2S$, $ArOSF_2CF_3$ (Ar = Ph or C_6F_5), $ArOSF_2C_3F_7$ (Ar = *p*-$CF_3C_6H_4$ or *p*-$O_2NC_6H_4$)] have been examined spectroscopically and in all cases the structures appear to be based on trigonal bipyramidal arrangements about the sulphur with the lone-pair equatorial and fluorines apical.

THE preparation of phenoxysulphur(IV) fluorides has been briefly described previously.[1] We now give further details of these compounds together with preparations of some other aryloxysulphur(IV) fluorides.

TABLE 1

Products of the reactions between silyl ethers and sulphur tetrafluoride

Ar	Reactants		Yield			
	$ArOSiMe_3$ mmol	SF_4 mmol	Me_3SiF mmol	Product		*M* and analyses found/calc.
(*a*) Reactions with SF_4						
Ph	11	13	9	$PhOSF_3$ (1)	M.p. 293 K	C 40·1/39·6; H 3·0/2·8; F 29·5/31·3; S 16·6/17·6
Ph	11	5	9	$(PhO)_2SF_2$ (2)	M.p. 293 K	C 56·1/56·2; H 4·0/3·9; F 14·7/14·8; S 12·3/12·5
Ph	6	2	5	$(PhO)_2SF_2 + (PhO)_3SF$(?) (3)		See text
Ph	8	3	3	$(PhO)_4S$ (4)	Solid	C 71·4/71·3; H 5·1/5·1; S 7·9/7·8
o-Tol	12	16	12	*o*-$TolOSF_3$ (5)	Liq.	N.m.r. evidence only
m-Tol	15·5	17	16	*m*-$TolOSF_3$ (6)	Liq.	*M* 196/196
m-Tol	17	9	17	(*m*-$TolO)_2SF_2$ (7)	Solid	*M* 262/262; C 59·2/59·1; H 5·1/4·9; S 11·1/11·2
p-Tol	16	18	16	*p*-$TolOSF_3$ (8)	Liq.	*M* 196/196 disproportionates to SF_4 + (*p*-$TolO)_2SF_2$
p-Tol	20	11	20	(*p*-$TolO)_2SF_2$ (9)	Solid	C 59·1/59·1; H 5·1/4·2; F 13·4/13·3; S 11·2/11·2
o-FC_6H_4	16·5	20	16	*o*-$FC_6H_4OSF_3$ (10)	Liq.	*M* 200/200
m-FC_6H_4	16	21	16	*m*-$FC_6H_4OSF_3$ (11)	Liq.	*M* 200/200
m-FC_6H_4	20	11	20	(*m*-$FC_6H_4O)_2SF_2$ (12)	Liq.	C 48·9/49·3; H 2·6/2·7; F 26·1/26·0; S 10·8/11·0
p-FC_6H_4	17	21	17	*p*-$FC_6H_4OSF_3$ (13)	Liq.	*M* 200/200
p-FC_6H_4	18	11	11	(*p*-$FC_6H_4O)_2SF_2$ (14)	Liq.	C 49·8/49·3; H 2·8/2·7; F 25·8/26·0; S 10·8/11·0
m-ClC_6H_4	15	18	14	*m*-$ClC_6H_4OSF_3$ (15)	Liq.	*M* 216/216
m-ClC_6H_4	17	10	17	(*m*-$ClC_6H_4O)_2SF_2$ (16)	Solid	C 44·3/44·3; H 2·5/2·5; Cl 22·0/21·8; F 11·9/11·7; S 9·6/9·8
p-ClC_6H_4	13·5	16	13	*p*-$ClC_6H_4OSF_3$ (17)	Liq.	*M* 216/216
p-ClC_6H_4	18	10	18	(*p*-$ClC_6H_4O)_2SF_2$ (18)	Solid	C 44·4/44·3; H 2·6/2·5; Cl 22·1/21·8; F 12·0/11·7; S 9·7/9·8
p-$CF_3C_6H_4$	17	20	18	(*p*-$CF_3C_6H_4O)_2SF_2$ (19)	Solid	C 42·2/42·9; H 2·1/2·1; F 38·3/38·4; S 8·2/8·2
p-$O_2NC_6H_4$	14	25	12	(*p*-$O_2NC_6H_4O)_2SF_2$ (20)	Solid	C 42·1/41·6; H 2·5/2·3; F 11·3/11·0; N 4·0/4·1; S 9·3/9·2
C_6F_5	16	24	16	$(C_5F_5O)_3SF$ (21)	Solid	C 35·6/36·0; F 50·4/50·6; S 5·5/5·3
o-C_6H_4	18	50	35	(*o*-$C_6H_4O_2)_2S$ (22)	Solid	*M* 248/248; C 57·8/58·1; H 3·4/3·2; S 12·8/12·9
(*b*) Reactions with CF_3SF_3						
		CF_3SF_3 mmol				
Ph	11	12	10	$PhOSF_2CF_3$ (23)	Liq.	Spectroscopic evidence only
C_6F_5	14	16	14	$C_6F_5OSF_2CF_3$ (24)	Liq.	*M* 322/322
(*c*) Reactions with $(CF_3)_2CFSF_3$						
		$(CF_3)_2CFSF_3$ mmol				
p-$CF_3C_6H_4$	10	15	4	*p*-$CF_3C_6H_4OSF_2CF(CF_3)_2$ (25)	Liq.	*M* 400/400
p-$O_2NC_6H_4$	12	14	11	*p*-$O_2NC_6H_4OSF_2CF(CF_3)_2$ (26)	Liq.	*M* 377/377; C 28·8/38·6; H 1·1/1·1; F 45·1/45·4; N 3·6/3·7; S 8·4/8·5

Sulphur tetrafluoride is known to have a structure of approximately C_{2v} symmetry based on a trigonal bipyramid with the lone-pair occupying an equatorial position[2] and substituted derivatives of SF_4 have structures derived from this with the less-electronegative substituents occupying the equatorial positions[3] as

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† No reprints available.

[1] J. I. Darragh and D. W. A. Sharp, *Angew. Chem. Internat. Edn.*, 1970, **9**, 73.

[2] H. L. Roberts, *Quart. Rev.*, 1961, **15**, 30.

[3] *E.g.* W. A. Sheppard, *J. Amer. Chem. Soc.*, 1962, **84**, 3058; G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 1903; D. T. Sauer and J. M. Shreeve, *Chem. Comm.*, 1970, 1679; S. P. von Halasz and O. Glemser, *Chem. Ber.*, 1970, **103**, 594.

have the diaryldialkoxysulphuranes and related derivatives of known structure.[4] These structures are comparable with those adopted by phosphorus pentafluoride and most of its substituted derivatives although it is known that biscatecholatofluorophosphorane, (o-$C_6H_4O_2)_2PF$, has a structure in which the co-ordination arrangement is intermediate between a trigonal bipyramid and a tetragonal pyramid.[5]

Aryloxytrimethylsilanes, $ArOSiMe_3$, react readily with sulphur tetrafluoride to give products which depend upon the nature of the aryl group and upon the relative amounts of reactants (Table 1). In some reactions the products have been identified by full analysis but in other cases they are too unstable to allow satisfactory analysis and characterization is based on spectroscopic studies using mass spectroscopic and/or n.m.r. methods. The parent ion is generally observed in the mass spectrum (Table 1 and supplementary data *) although disproportionation or hydrolysis occurs for some derivatives. The ^{19}F n.m.r. spectra (Table 2) of the aryloxysulphur(IV) trifluorides all show a doublet and a triplet (relative intensities 2 : 1) corresponding to the axial and equatorial fluorines. The ^{19}F spectra of the bis(aryloxy)sulphur difluorides show a single signal at a shift corresponding to the axial fluorines of the trifluorides. The n.m.r. spectra are discussed in more detail later.

An excess or equimolar quantities of sulphur tetrafluoride react with aryloxytrimethylsilanes to give aryloxysulphur(IV) trifluorides $ArOSF_3$ (Ar = Ph, o-Tol, m-Tol, p-Tol, o-FC_6H_4, m-FC_6H_4, p-FC_6H_4, m-ClC_6H_4, and p-ClC_6H_4). No identifiable o-ClC_6H_4 derivatives could be isolated and even although excess of sulphur tetrafluoride was used for Ar = p-$CF_3C_6H_4$ and p-$O_2NC_6H_4$ only bis(aryloxy)sulphur(IV) difluorides were isolated. Other than o-$FC_6H_4OSF_3$, o-$TolOSF_3$, and o-$ClC_6H_4OSF_3$ all the aryloxysulphur(IV) trifluorides slowly disproportionate at room temperature to give bis(aryloxy)sulphur(IV) difluorides and sulphur tetrafluoride; the

TABLE 2

N.m.r. data for aryloxysulphur(IV) fluorides

All shifts in p.p.m., δF relative to CCl_3F, δH relative to Me_4Si, coupling constants in Hz. Spectra recorded on neat samples or on CCl_4 solutions unless otherwise stated

(a) $ArOSF_3$ compounds

			δF_a	δF_e	JF_a–F_e		δH (Aromatic)
(1)	$PhOSF_3$	298	−79·1	−30·5	67·7		−6·55(m)
(5)	o-$TolOSF_3$	298	−76·2	−31·2	45		−6·8(m) δCH_3 −1·95
(6)	m-$TolOSF_3$	298	−78·8	−31·3	76		−7·0(m) δCH_3 −2·1
(8)	p-$TolOSF_3$	298	−78·6	−30·3	72		−6·9(b.s) δCH_3 −1·95
(10)	o-$FC_6H_4OSF_3$	298	−77·4	−31·4	77	δCF + 128	−7·3(m)
(11)	m-$FC_6H_4OSF_3$	237	−82·0	−30·3	76	δCF + 107·7	−7·38 (m)
(13)	p-$FC_6H_4OSF_3$	253	−78·8	−30·1	75	δCF + 111	−7·16(q)
(15)	m-$ClC_6H_4OSF_3$	253	−79·2	−31·0	74		−7·3(m)
(17)	p-$ClC_6H_4OSF_3$	253	−79·0	−30·5	75		−7·25(q)

(b) $(ArO)_2SF_2$ compounds (all recorded at 310 K in CCl_4)

		δF		δH
(2)	$(PhO)_2SF_2$	−67·4		−6·42(b.s)
(7)	(m-$TolO)_2SF_2$	−67·7		−7·01(b.s) CH_3 −1·96
(9)	(p-$TolO)_2SF_2$	−66·3		−6·9(b.s.) CH_3 −2·1
(12)	(m-$FC_6H_4O)_2SF_2$	−69·2	δCF + 108·7	−7·3(m)
(14)	(p-$FC_6H_4O)_2SF_2$	−69·0	δCF + 112	−7·4(q)
(16)	(m-$ClC_6H_4O)_2SF_2$	−70·0		−7·38(m)
(18)	(p-$ClC_6H_4O)_2SF_2$	−71·2		−7·28(q)
(19)	(p-$CF_3C_6H_4O)_2SF_2$	−72·0	δCF_3 + 62	−7·4(q)

(c) $(ArO)_3SF$

(3)	$(PhO)_3SF$	δSF −70·8				δCH −6·6
(21)	$(C_6F_5O)_3SF$	δSF −67·4	$\delta CF(o)$ +152	$\delta CF(m)$ +162·4	$\delta CF(p)$ +155·2	

(d) Fully substituted derivatives

		δH(Aromatic)
(4)	$(PhO)_4S$	δH −6·82(b.s.) in CD_3CN
(22)	$(C_6H_4O_2)_2S$	δH −6·95(b.s.)

(e) Derivatives of perfluoroalkylsulphur trifluorides

(23)	$PhOSF_2CF_3$	δSF_2 −35 δCF +68·5 δH −6·7(b.s.) JSF_2CF_3 24
(24)	$C_6F_5OSF_2CF_3$	δSF_2 −37·5 δCF_3 +67·5 $\delta CF(o)$ +152·1 $\delta CF(m)$ +162·8 $\delta CF(p)$ +155·7 JSF_2CF_3 24 JCF_3SOCF_2 6
(25)	p-$CF_3C_6H_4OSF_2C_3F_7$	δSF_2 −44·4 δCF_3 +68·8 δCF +152·1 $\delta CF_3C_6H_4$ +61·8 JSF_2CF 28 JSF_2CCF_3 12 JCF_3CF 6 δCH −7·56
(26)	p-$O_2NC_6H_4OSF_2C_3F_7$	δSF_2 −42·4 δCF_3 +69·2 δCF +151·8 JCF_3CF 6 δCH −7·93(q)

q = A_2B_2 quartet; m = multiplet; b.s. broad singlet.

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* Full data for all compounds have been deposited with the National Lending Library SUP No. 21214 (11 pp., 1 microfiche). See note about Supplementary Publications in Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[4] *E.g.* N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, 1969, **91**, 5749; I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, 1972, **94**, 5010; A. Kálmán, K. Sasvari, and I. Kapovits, *Acta Cryst.*, 1973, **B29**, 355.

[5] A. Wunderlich, D. Mootz, R. Schmutzler, and M. Wieber, *Z. Naturforsch.*, 1974, **29b**, 32.

rate of this reaction increases markedly with temperature. The lack of observation of monosubstituted derivatives for some aryloxides may be due either to rapid disproportionation or to increased reactivity of fluorines after the initial monosubstitution.

The detailed n.m.r. data for the aryloxysulphur trifluorides are given in Table 2. Fine structure due to fluorine–fluorine coupling is not observed for $ArOSF_3$ (Ar = m-FC_6H_4, p-FC_6H_4, m-ClC_6H_4, and p-ClC_6H_4) at room temperature but is seen at lower temperatures. Signals due to the distinct axial and equatorial fluorines are observed at room temperature and the behaviour is comparable to that of SF_4 over the temperature range **195**—**215** K.[6] Over the temperature range **243**—**333** K, m-$FC_6H_4OSF_3$ exhibits the complete range of exchange behaviour of SF_4, showing a broad singlet at **333** K, a broad singlet plus two broad peaks at **313** K, and a doublet and a triplet at the fields of the two latter peaks at **243** K. A study of the coalescence temperature as a function of concentration and solvent (Table 3) shows that it depends upon the concentration but is apparently independent of the dielectric constant of the solvent. These results are again similar to those of sulphur tetrafluoride and suggest an intermolecular mechanism for the exchange process.

TABLE 3

Coalescence temperatures

Dilution solvent	CCl_4	CH_3CN	CCl_3F
0	243 K		
20%	263—265 K	263—265 K	263—265 K
50%	293 K	293 K	293 K

The mass spectra of all the $ArOSF_3$ derivatives show a parent ion, M^+, except for phenoxysulphur trifluoride in which this peak is missing. All the derivatives except for $PhOSF_3$ show metastables corresponding to cleavage of the S–O bonds of the molecule to form ArO^+ species; SF_3^+ species are also observed in relatively high abundance. The cleavage of the S–O bond is similar to that observed in aryloxy-derivatives of thionyl tetrafluoride.[7]

On controlled hydrolysis, the aryloxysulphur trifluorides (except the o-tolyl derivative) give aryl fluorosulphinates, ROS(O)F. Phenyl fluorosulphinate has been previously prepared[8] by fluorination of phenyl chlorosulphinate, PhOS(O)Cl, with sodium fluoride in acetonitrile and other aryl fluorosulphinates have been prepared in the present work by the same method. Characterisation was by mass spectrometry and n.m.r. spectroscopy (Table 4 and Supplementary publication *).

Sulphur tetrafluoride reacts with aryloxytrimethylsilanes in a 1 : 2 molar ratio to give bis(aryloxy)sulphur difluorides, $(RO)_2SF_2$ (R = Ph, m-Tol, p-Tol, m-FC_6H_4, p-FC_6H_4, m-ClC_6H_4, p-ClC_6H_4). When R = p-$CF_3C_6H_4$ and p-$O_2NC_6H_4$, $(RO)_2SF_2$ derivatives are formed even although sulphur tetrafluoride is in excess. The n.m.r. data of these derivatives are given in Table 2 [except for $(p$-$O_2NC_6H_4O)_2SF_2$ which was not sufficiently soluble in any of the solvents tried to allow the recording of a spectrum]. In each case the ^{19}F resonance appears as a broad signal which suggests that fluorine-exchange occurs at room temperature; the fluorophenyl derivatives give much sharper signals on cooling to **243** K. The chemical shifts of the single sulphur–fluorine signals are close to those of the axial fluorines of the aryloxysulphur trifluorides which is consistent with the proposed geometry. As the compounds are solids, mass spectra of the completely unhydrolysed materials could not be obtained but the recorded spectra were characteristic of hydrolysis products $(RO)_2SO$ and in each case parent ions were observed. Deliberate hydrolysis of the difluorides also gives $(RO)_2SO$ as hydrolysis products.

TABLE 4

M and n.m.r. data for compounds $XC_6H_4OS(O)F$

	M	δ(SF)/p.p.m.	δ(CF)/p.p.m.
PhOS(O)F		−62·5	
m-$CH_3C_6H_4OS(O)F$	174	−64·1	
p-$CH_3C_6H_4OS(O)F$	174	−66·0	
o-$FC_6H_4OS(O)F$	178	−59·7	+129·5
m-$FC_6H_4OS(O)F$	178	−65·8	+104·0
p-$FC_6H_4OS(O)F$	178	−62·4	+108·8
m-$ClC_6H_4OS(O)F$	194	−64·1	
p-$ClC_6H_4OS(O)F$	194	−64·5	

Reaction of phenoxytrimethylsilane with sulphur tetrafluoride in a 2·5 to 1 ratio gives a mixture of $(PhO)_2SF_2$ and a new compound which appears to be trisphenoxysulphur(IV) fluoride although the derivative could not be obtained pure even by use of other ratios of reactants. Surprisingly, pentafluorophenoxytrimethylsilane reacts with an excess of sulphur tetrafluoride to give tris(pentafluorophenoxy)sulphur(IV) fluoride; this was confirmed by analysis. The ^{19}F n.m.r. spectra of both these derivatives give single signals in the region associated with axial fluorines in trigonal-bipyramidal derivatives although it must be pointed out that other geometries might give resonances at comparable energies. The multiple substitution in the case of the pentafluorophenoxy-derivative may arise either as a result of the reactivity of the initial substituted product or as a result of disproportionation of the initial product to give a stable product and sulphur tetrafluoride.

Complete substitution of fluorine in sulphur tetrafluoride is effected by excess of phenoxytrimethylsilane or of bis(trimethylsilyl)catecholate. The solid products were both characterised by analysis, but no information could be deduced as to their geometries from the spectroscopic measurements. Tetrakisphenoxysulphur(IV) was too unstable to give a meaningful mass spectrum but the mass spectrum of biscatecholatosulphur(IV) suggested a monomeric species. Bis(perfluoropinacolato)-sulphur(IV) has been previously prepared from sodium perfluoropinacolate and sulphur tetrachloride.[9]

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* Same footnote as on page 219.

[6] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084; F. A. Cotton, J. W. George, and J. S. Waugh, *J. Chem. Phys.*, 1958, **28**, 994.

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[8] H. A. Pacini and A. E. Pavlath, *J. Chem. Soc.*, **1965**, 5741.

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Substitution of aryloxy-groups into perfluoroalkylsulphur trifluorides, R_FSF_3 [$R_F = CF_3$ or $(CF_3)_2CF$] can be effected in specific cases and $PhOSF_2CF_3$, $C_6F_5OSF_2CF_3$, p-$CF_3C_6H_4OSF_2C_3F_7$, and p-$O_2NC_6H_4$-$OSF_2C_3F_7$ have been isolated. In all cases the spectra are in accord with both residual sulphur–fluorines being in axial positions as has been found for dialkylamino-derivatives of perfluoroalkylsulphur trifluorides.[10]

All the substituted derivatives of sulphur tetrafluoride prepared in the present work have strong bands in their i.r. spectra between 950 and 600 cm^{-1} (supplementary data). By analogy with previous work these are assigned to S–F vibrational modes but vibrations of the aromatic groups also occur in this region and the bands are not particularly characteristic.

Attempts have been made[11] to prepare alkoxy-derivatives of sulphur(IV) fluorides but these were unsuccessful and, if formed, the derivatives break down immediately although 2-fluoro-2,2-dinitroethoxysulphur trifluoride is known[12] and the presence of the electron-withdrawing groups apparently stabilises the molecule. The greater stability of aryloxysulphur(IV) fluorides over the alkoxy-derivatives is comparable with that observed for the related phosphorus derivatives.[13]

EXPERIMENTAL

Materials were handled by standard vacuum-line procedures. I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Solutions (<0.05M) for i.r. measurements were made up in dry carbon tetrachloride using a Lintott inert-atmosphere box. N.m.r. spectra were recorded, generally at 310 K, on a Perkin-Elmer R10 spectrometer. Mass spectra were recorded on an A.E.I. M.S.12 spectrometer using an accelerating voltage of 70 eV and a source temperature of 350—390 K. Analyses are by Bernhardt.

Sulphur tetrafluoride was purchased from P.C.R. and was redistilled from dry sodium fluoride. Silyl ethers were prepared by refluxing the appropriate phenol with chlorotrimethylsilane overnight;[14] the silyl ethers were distilled at atmospheric pressure. The preparation of phenylene-1,2-dioxybis(trimethylsilane) required a refluxing period of 5 days.

Reactions were carried out in flamed-out Pyrex tubes fitted with Teflon stopcocks as described for the preparation of aryloxy-derivatives of thionyl tetrafluoride.[7] The relative amounts of reactants and products are given in the Tables.

Hydrolysis of aryloxysulphur trifluorides gave fluorosulphinates $XC_6H_4OS(O)F$ characterised by the appearance of parent ions in their mass spectra. The identical fluorosulphinates were also prepared by fluorination of arylchlorosulphinates with sodium fluoride in acetonitrile.[8]

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