Aryloxy-derivatives of Thionyl Tetrafluoride

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Thionyl tetrafluoride reacts with arylsilyl ethers to give substituted derivatives $ArO\cdot S(:O)F_3$ (Ar = Ph; *o*-, *m*-, *p*-MeC_6H_4; *m*-, *p*-ClC_6H_4; *o*-, *m*-, *p*-FC_6H_4), $(ArO)_2S(:O)F_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$NO_2\cdot C_6H_4$), $(ArO)_3S(:O)F$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, C_6F_5), $(m\text{-}MeC_6H_4O)_4SO$, and $(o\text{-}C_6H_4O_2)_2SO$. Spectroscopic data and modes of thermal and hydrolytic decomposition were studied for most derivatives. The thionyl trifluorides and difluorides appear to have structures based on a trigonal bipyramidal co-ordination about sulphur.

MONOSUBSTITUTED derivatives of thionyl tetrafluoride, *e.g.* $R_2NS(:O)F_3$, have been prepared by the reaction between silylamines and the fluoride.[1] Substitution by silyl ethers is now reported; † the substitution often proceeding to displace more than one fluorine. Relatively stable aryloxy-derivatives of thionyl tetrafluoride are formed in this way although alkoxy-derivatives are unstable. This increased stability of aryloxy-derivatives as compared with alkoxy- is parallel with that observed for derivatives of phosphorus pentafluoride and sulphur tetrafluoride.[2] The formation and some reactions of phenoxythionyl trifluoride were reported [3] after completion of the present work. Where there is overlap there is good agreement between the present results and those for phenoxythionyl trifluoride. Previous attempts to effect substitution of thionyl tetrafluoride by use of phenols have been unsuccessful.[4]

TABLE 1

Products of the reactions between silyl ethers and thionyl tetrafluoride

	δ (p.p.m. from Me_4Si)	$\delta_{F\text{-}eq}$ (p.p.m. from CCl_3F)	$\delta_{F\text{-}ax}$ (p.p.m. from CCl_3F)	$\lvert J_{F\text{-}eq,\,F\text{-}ax}\rvert$ Hz	$\nu_{S=O}$ (cm^{-1} from i.r.)
$PhO\cdot S(:O)F_3$	−7·24	−67·6	−89·1	213·2	1323
p-$MeC_6H_4\cdot O\cdot S(:O)F_3$	−7·19 (Ar–H), −2·32 (CH_3)	−67·2	−88·4	217·5	1324
m-$MeC_6H_4\cdot O\cdot S(:O)F_3$	−7·08 (Ar–H), −2·22 (CH_3)	−67·0	−88·2	213·4	1323
o-$MeC_6H_4\cdot O\cdot S(:O)F_3$	−7·17 (Ar–H), −2·18 (CH_3)	−67·4	−86·4	209·4	Not observed
p-ClC_6H_4 $O\cdot S(:O)F_3$	−7·20	−68·1	−89·7	222·2	1327
m-$ClC_6H_4\cdot O\cdot S(:O)F_3$	−7·28	−68·4	−89·5	219·8	1327
p-$FC_6H_4\cdot O\cdot S(:O)F_3$	−7·08 [δ_{Ar-F} + 112·3 p.p.m.]	−67·4	−88·2	215·4	1331
m-$FC_6H_4\cdot O\cdot S(:O)F_3$	−7·12 [δ_{Ar-F} + 108·2 p.p.m.]	−67·6	−88·9	218·0	1334
o-$FC_6H_4\cdot O\cdot S(:O)F_3$	−7·24 [δ_{Ar-F} + 129·4 p.p.m.]	−69·8	−86·1	218·0	Not observed
$(PhO)_2S(:O)F_2$	−7·13		−89·0		1288
(*p*-$MeC_6H_4\cdot O)_2S(:O)F_2$	−7·14 (Ar–H), −2·32 (CH_3)		−86·0		1284
(*p*-$ClC_6H_4\cdot O)_2S(:O)F_2$	−7·34		−87·1		1294, 1287
(*p*-$NO_2\cdot C_6H_4\cdot O)_2S(:O)F_2$	Insoluble				1283
$(PhO)_3S(:O)F$	Not measured		−68·4		Not identified
(*p*-$MeC_6H_4\cdot O)_3S(:O)F$	Not measured		−67·0		,,
(*p*-$ClC_6H_4\cdot O)_3S(:O)F$	Not measured		−69·9		,,
$(C_6F_5O)_3S(:O)F$	δ_{CF} at +154·0, +157·2, +164·2 p.p.m.		−68·1		,,
(*m*-$MeC_6H_4O)_4SO$	−7·12 (Ar–H), −2·31 (CH_3)		—		,,
(*o*-$C_6H_4O_2)_2SO$	−6·92				,,

TABLE 2

Mass spectra of $ArO\cdot S(:O)F_3$ derivatives (relative intensities)

	$ArOSOF_3^+$	$ArOSOF^+$	SOF_3^+	ArO^+	SOF_2^+	Ar^+	SOF^+	SO^+
$PhO\cdot S(:O)F_3$	5	11	100	63	25	54	36	7
p-$Tol\cdot O\cdot S(:O)F_3$	10	6	44	100	16	3	29	11
m-$Tol\cdot O\cdot S(:O)F_3$	18	21	100	100	12	30	27	9
o-$Tol\cdot O\cdot S(:O)F_3$	19	11	49	100	50	25	3	59
p-$ClC_6H_4\cdot O\cdot S(:O)F_3$ *	1	7	100	66	32	15	11	41
m-$ClC_6H_4\cdot O\cdot S(:O)F_3$ *	15	7	100	18	4	10	13	59
p-$FC_6H_4\cdot O\cdot S(:O)F_3$	8	7	100	78	25	31	60	22
m-$FC_6H_4\cdot O\cdot S(:O)F_3$	7	5	100	19	8	16	17	6
o-$F_6C_6H_4\cdot O\cdot S(:O)F_3$	11	6	100	46	19	21	35	9

* Peaks for ^{35}Cl only.

The aryloxy-derivatives of thionyl tetrafluoride isolated in the present work are listed in Table 1. There is no consistent pattern as to which substituted derivatives may be isolated and many of the derivatives are too unstable to permit analysis and were identified by spectroscopy only. However, n.m.r., i.r. (Table 1), and mass spectroscopic (Table 2) data are all consistent with the formulation shown. The two orthosulphates formed in these reactions are the first examples of these deriva-

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† A preliminary account of this work was given at the Sixth International Fluorine Symposium, Durham, 1971, Abstract C46.

[1] S. P. von Halasz and O. Glemser, *Chem. Ber.*, 1971, **104**, 1256, and references therein.

[2] S. C. Peake and R. Schmutzler, *Chem. Comm.*, 1968, 665; J. I. Darragh and D. W. A. Sharp, *Angew. Chem.*, 1970, **82**, 45.

[3] S. P. von Halasz, O. Glemser, and M. F. Feser, *Chem. Ber.*, 1971, **104**, 1242.

[4] R. Cramer and D. D. Coffmann, *J. Org. Chem.*, 1961, **26**, 4164.

tives. No structural information is available for these compounds which could be polymeric.

Thionyl tetrafluoride has a structure based on a trigonal bipyramid with the oxygen occupying an equatorial position.[5] By analogy with substitution patterns in phosphorus pentafluoride and the published work on thionyl tetrafluoride, substitution would be expected to leave apical fluorines. In accordance with this the aryloxythionyl trifluorides show AB_2 ^{19}F n.m.r. spectra whilst the bis(aryloxy)thionyl difluorides show only one ^{19}F signal which occurs in almost the same position as the signal for the axial fluorines of the trifluorides. The compounds formulated as tris(aryloxy)-thionyl fluorides show only one ^{19}F signal but the chemical shift of these signals would appear to indicate that they are equatorial fluorines. This would be a most unexpected conclusion since only a few examples where the steric effects of bridging groups leave an equatorial fluorine in preference to an axial fluorine in substituted derivatives of trigonal bipyramidal fluorides are known.[6] It is possible that the entire geometry of the molecule has been altered (*e.g.* to a polymer or to a square pyramidal configuration) in these tris(aryloxy)thionyl fluoride derivatives so that conventional distinctions between equatorial and axial fluorines are no longer meaningful. The ^{19}F chemical shift of these derivatives is consistent with an S–F bond and is inconsistent with an ionic fluoride.

The i.r. spectra of these derivatives have many bands but the S–O stretching frequency can be identified for most of the trifluoride derivatives (Table 1). Replacement of the fluorine of thionyl tetrafluoride by less electronegative substituents lowers the S–O stretching frequency, a situation analogous to that found in derivatives of phosphoryl trifluoride[7] and thionyl fluoride.[8] The minor shifts observed with change in substituent of the aryl group also reflect changes in electronic releasing power of the substituents. The S–O stretching bands in the tris(aryloxy)- and tetrakis(aryloxy)-derivatives could not be identified because of the presence of other bands in the region expected for their occurrence. Although it was possible to assign S–F modes in *NN*-dialkylaminothionyl trifluorides definite identification of S–F modes in the aryloxy-derivatives is not possible on account of the presence of large numbers of bands from the aryloxy-groups.

The mass spectra of the aryloxythionyl trifluorides were readily obtained and are recorded in Table 2, the other aryloxy-derivatives do not give satisfactory spectra as they are too involatile for passing into the mass spectrometer in the vapour phase and decompose on direct insertion. The spectra of the aryloxytrifluorides are characteristic; the strongest peaks show the corresponding ^{32}S and ^{34}S peaks. The parent ion occurs in all of the aryloxythionyl trifluoride mass spectra although it is a relatively weak species in the mass spectra of *NN*-dialkylaminothionyl trifluorides[1,9] and thionyl tetrafluoride.[10] The parent ion is particularly intense in the methylsubstituted derivatives.

On heating, and in many cases merely on standing, the aryloxythionyl trifluorides eliminate aryl fluorides and leave sulphuryl fluoride. Decomposition of the more highly substituted thionyl tetrafluoride derivatives yields diaryl sulphates although the other products of this decomposition have not been identified. Hydrolysis generally gives aryloxylsulphuryl fluorides, $ArO{\cdot}SO_2F$.

EXPERIMENTAL

Materials were handled by standard vacuum-line procedures. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer. Solutions (<0·05M) for i.r. measurements were made up in dry carbon tetrachloride using a dry box. N.m.r. spectra were recorded 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.

Thionyl tetrafluoride was prepared from sulphur tetrafluoride, nitrogen(IV) oxide, and oxygen;[11] sulphur tetrafluoride was purchased from Peninsular ChemResearch. Silyl ethers were prepared by refluxing the appropriate phenol with trimethylchlorosilane overnight;[12] the silyl ethers were distilled at atmospheric pressure. The preparation of *o*-phenylene-1,2-dioxybis(trimethylsilane) required a refluxing period of 5 days.

Trimethylphenoxysilane–Thionyl Tetrafluoride.—1 : 1 *Reaction.* The reaction was carried out in a glass tube fitted with a Teflon stopcock. $Me_3Si{\cdot}OPh$ (10·2 mmol) was placed in the tube and $S(:O)F_4$ (11·4 mmol) was condensed in at 77 K. The reactants were set aside at room temperature for 3 h during which time effervescence occurred and the solution turned red. The volatile products were Me_3SiF (10 mmol) (identified by n.m.r.[13] and i.r.[14]) and traces of $S(:O)F_4$ (i.r.)[15] and SO_2F_2 (i.r.).[15] Phenoxythionyl trifluoride, $PhO{\cdot}S(:O)F_3$ (8·4 mmol), is only slightly volatile and was recovered by distillation. *Bisphenoxythionyl difluoride* $(PhO)_2S(:O)F_2$, (1 mmol; n.m.r.) remained with some red liquid as a non-volatile fraction. $PhO{\cdot}S(:O)F_3$ decomposed to SO_2F_2[16] and C_6H_5F[17] (n.m.r.) when set aside at room temperature for 5 days or at 350 K for 30 min. It is hydrolysed to SO_2F_2, C_6H_5F, and $PhOSO_2F$ (δ_F — 36·6 p.p.m.).

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2 : 1 *Reaction.* The reaction was carried out in a two-armed reactor fitted with Teflon stopcocks, the arms being joined by a tube containing a glass sinter. $Me_3Si{\cdot}OPh$ (14 mmol) and $S(:O)F_4$ (7·1 mmol) were placed in the reactor and the reaction was set aside at room temperature for 48 h; the products were Me_3SiF (i.r.;[14] 13·8 mmol) and a trace of SO_2F_2 (i.r.).[15] Removal of volatile materials left $(PhO)_2S(:O)F_2$ contaminated with a red liquid; it was recrystallised from $CCl_2F{\cdot}CClF_2$ at 273 K to give a white solid, m.p. 353 K (decomp.). It appears stable indefinitely at room temperature, and is hydrolysed to $(PhO)_2SO_2$ (mass spec.).

3 : 1 *Reaction.* $Me_3Si{\cdot}OPh$ (12·0 mmol) and $S(:O)F_4$ (4·1 mmol) were allowed to react at room temperature for 30 min. The products were Me_3SiF (i.r.; 11·8 mmol) $(PhO)_2S(:O)F_2$ (n.m.r.) and *trisphenoxythionyl fluoride*, $(PhO)_3S(:O)F$. The latter compound is very unstable and cannot be isolated from the mixture.

4 : 1 *Reaction.* $Me_3Si{\cdot}OPh$ (12·0 mmol) and $S(:O)F_4$ (3·0 mmol) were allowed to react at room temperature for 20 min. The products were Me_3SiF (i.r.;[15] 11·9 mmol) and a dark red liquid. Fractional distillation of the liquid gave only diphenyl sulphate (mass spectrum *m/e* found 250. Calc. for parent ion of diphenyl sulphate *m/e* 250) as an identifiable product.

Detailed experimental procedures (where these differ from the description above) and results are given below.

$PhO{\cdot}SiMe_3$. Conditions as above. Product from 1 : 1 reaction $PhO{\cdot}S(:O)F_3$, too unstable for analysis. Major product from 2 : 1 reaction $(PhO)_2S(:O)F_2$ (Found: C, 53·1; H, 3·7; F, 14·1; S, 11·9. $C_{12}H_{10}F_2O_3S$ requires C, 52·9; H, 3·7; F, 14·0; S, 11·8%). Major product from 3 : 1 reaction $(PhO)_3S(:O)F$, too unstable for analysis.

p-$MeC_6H_4{\cdot}O{\cdot}SiMe_3$. 1 : 1 *Reaction.* *p*-$MeC_6H_4{\cdot}O{\cdot}SiMe_3$ (10·5 mmol) and $S(:O)F_4$ (11·2 mmol) were set aside at room temperature for 3 h. Products were Me_3SiF (10·4 mmol), *p*-$MeC_6H_4{\cdot}O{\cdot}S(:O)F_3$ (9·9 mmol) (Found for p-*tolyloxythionyl trifluoride*: C, 39·8; H, 3·5; F, 26·8; S, 14·9. $C_7H_7F_3O_2S$ requires C, 39·6; H, 3·3; F, 26·9; S, 15·1%) and (*p*-$MeC_6H_4O)_2S(O)F_2$ (n.m.r.). On prolonged heating at 370 K *p*-$MeC_6H_4{\cdot}O{\cdot}S(:O)F_3$ decomposed to *p*-MeC_6H_4F (δ_F = 120·2) and SO_2F_2 (n.m.r.). On exposure to moist air *p*-$MeC_6H_4{\cdot}O{\cdot}S(:O)F_3$ gives SO_2F_2, SiF_4, *p*-$MeC_6H_4{\cdot}O{\cdot}SO_2F$ [Found: *M*, 190 (mass spec.). Calc.: *M*, 190] and solids.

2 : 1 *Reaction.* *p*-$MeC_6H_4{\cdot}O{\cdot}SiMe_3$ (12·2 mmol) and $S(:O)F_4$ (6·1 mmol) were set aside at room temperature for 48 h. Products were Me_3SiF (11·9 mmol) and (*p*-$MeC_6H_4O)_2S(:O)F_2$ (4·9 mmol) [Found for *bis*(p-*tolyloxy*)-*thionyl difluoride*: C, 56·3; H, 4·9; F, 12·9; S, 10·9. $C_{14}H_{14}F_2SO_3$ requires C, 56·0; H, 4·7; F, 12·7; S, 10·7%]. Thermal and hydrolytic decomposition of (*p*-$MeC_6H_4O)_2S(O)F_2$ gave (*p*-$MeC_6H_4O)_2SO_2$ (Found: *M*, 278. Calc.: *M*, 278).

3 : 1 *Reaction.* *p*-$MeC_6H_4OSiMe_3$ (12·6 mmol) and $S(:O)F_4$ (4·3 mmol) were set aside at room temperature for 30 min. Products were Me_3SiF (12·5 mmol) and (*p*-$MeC_6H_4O)_2S(:O)F_2$ and (*p*-$MeC_6H_4O)_3S(:O)F$ (n.m.r.) in approximately equal amounts. The latter compound was too unstable for analysis.

4 : 1 *Reaction.* *p*-$MeC_6H_4{\cdot}O{\cdot}SiMe_3$ (13·2 mmol) and $S(:O)F_4$ (3·4 mmol) were set aside at room temperature for 30 min. Products were Me_3SiF (13·2 mmol), a red viscous oil, and (*p*-$MeC_6H_4O)_2SO_2$ (identified by mass spectroscopy, *m/e* found 278. Calc. for parent ion of bis-*p*-tolylsulphate *m/e* 278).

m-$MeC_6H_4O{\cdot}SiMe_3$. 1 : 1 *Reaction.* *m*-$MeC_6H_4{\cdot}O{\cdot}SiMe_3$ (12·5 mmol) and $S(:O)F_4$ (13·0 mmol) were set aside at room temperature for 3 h. Products were Me_3SiF (12·5 mmol), SO_2F_2 (trace), *m*-$MeC_6H_4{\cdot}O{\cdot}S(:O)F_3$ (8·9 mmol), and (*m*-$MeC_6H_4{\cdot}O)_4SO$ (1·4 mmol) (Found for *tetrakis*-m-*tolylorthosulphate*: C, 69·4; H, 5·7; S, 7·3. $C_{28}H_{28}O_5S$ requires C, 70·6; H, 5·7; S, 6·8%). On standing at room temperature for several days or on heating at 350 K for 15 min *m*-$MeC_6H_4{\cdot}O{\cdot}S(:O)F_3$ decomposed to SO_2F_2, *m*-$CH_3C_6H_4F$ (n.m.r.), and *m*-$MeC_6H_4{\cdot}O{\cdot}SO_2F$ (δ_F − 36·9 p.p.m.) (Found: *M*, 190. Calc.: *M*, 190).

o-$MeC_6H_4{\cdot}O{\cdot}SiMe_3$. 1 : 1 *Reaction.* *o*-$MeC_6H_4{\cdot}O{\cdot}SiMe_3$ (13·9 mmol) and $S(:O)F_4$ (14·0 mmol) were set aside at room temperature for 3 h. Products were Me_3SiF (13·8 mmol), *o*-$MeC_6H_4{\cdot}O{\cdot}S(:O)F_3$ (8·1 mmol), and a yellow viscous liquid. *o*-$MeC_6H_4{\cdot}O{\cdot}S(:O)F_3$ decomposes on standing to a tar and SO_2F_2. On heating to 340 K *o*-MeC_6H_4F, SO_2F_2, and solids are formed; hydrolysis gives *o*-$MeC_6H_4OSO_2F$ (δ_F − 38·5 p.p.m.).

p-$ClC_6H_4{\cdot}O{\cdot}SiMe_3$. 1 : 1 *Reaction.* *p*-$ClC_6H_4{\cdot}O{\cdot}SiMe_3$ (10·5 mmol) and $S(:O)F_4$ (11·0 mmol) were set aside at room temperature for 3 h. Identified products were Me_3SiF (10·4 mmol) and *p*-$ClC_6H_4O{\cdot}S(:O)F_3$ (8·9 mmol) (Found for p-*chlorophenoxythionyl trifluoride*: C, 31·1; H, 1·9; Cl, 15·4; F, 25·3; S, 13·5. $C_6H_4ClF_3O_2S$ requires C, 31·0; H, 1·7; Cl, 15·3; F, 24·5; S, 13·8%). *p*-$ClC_6H_4{\cdot}O{\cdot}S(:O)F_3$ decomposes on prolonged heating at 380 K to give SO_2F_2 and a black tar. *p*-ClC_6H_4F was not identified amongst the products, hydrolysis gave SO_2F_2, SiF_4, and *p*-$ClC_6H_4{\cdot}O{\cdot}SO_2F$ (δ_F −36·8 p.p.m.) [Found: *M* (mass spec.), 210. Calc.: *M*, 210].

2 : 1 *Reaction.* *p*-$ClC_6H_4{\cdot}O{\cdot}SiMe_3$ (12·1 mmol) and $S(:O)F_4$ (6·1 mmol) were set aside at room temperature for 48 h. Identified products were Me_3SiF (12·1 mmol) and (*p*-$ClC_6H_4{\cdot}O)_2S(:O)F_2$ (5·2 mmol) [Found for *bis*(p-*chlorophenoxy*)*thionyl difluoride*: C, 42·4; H, 2·6; Cl, 21·0; F, 11·3; S, 9·2. $C_{12}H_8Cl_2F_2O_3S$ requires C, 42·0; H, 2·4; Cl, 20·8; F, 11·1; S, 9·4%].

3 : 1 *Reaction.* *p*-$ClC_6H_4{\cdot}O{\cdot}SiMe_3$ (11·5 mmol) and $S(:O)F_4$ (5·8 mmol) were shaken together at room temperature for 12 h. Products were Me_3SiF (11·4 mmol), *p*-$ClC_6H_4{\cdot}O{\cdot}S(:O)F_3$, (*p*-$ClC_6H_4{\cdot}O)_2S(:O)F_3$, and (*p*-$ClC_6H_4{\cdot}O)_3S(:O)F$ all identified by n.m.r. spectroscopy and present in approximately equal proportions. Hydrolysis of (*p*-$ClC_6H_4{\cdot}O)_2S(:O)F_2$ gives (*p*-$ClC_6H_4{\cdot}O)_2SO_2$ [Found: *M* (mass spec.), 318. Calc.: *M*, 318].

4 : 1 *Reaction.* *p*-$ClC_6H_4{\cdot}O{\cdot}SiMe_3$ (12 mmol) and $S(:O)F_4$ (1·2 mmol) were set aside at room temperature for 30 min. Products were Me_3SiF (12·2 mmol), (*p*-$ClC_6H_4O)_2S(:O)F_2$, and (*p*-$ClC_6H_4O)_3S(:O)F$ (n.m.r.) in approximately equal proportions. A mixture of *p*-$ClC_6H_4{\cdot}O{\cdot}SiMe_3$ (10·5 mmol) and $S(:O)F_4$ (2·6 mmol) left at room temperature for 30 min gave Me_3SiF (10·5 mmol) and a dark red liquid in which bis-(*p*-chlorophenyl)orthosulphate was identified (Found *m/e* of highest ratio 318, 322. Calc. for $C_{12}H_8{}^{35}Cl_2O_4S$ and $C_{12}H_8{}^{37}Cl_2O_4S$, *m/e* 318, 322).

m-$Cl_6H_4{\cdot}O{\cdot}SiMe_3$. 1 : 1 *Reaction.* *m*-$ClC_6H_4{\cdot}O{\cdot}SiMe_3$ (11·5 mmol) and $S(:O)F_4$ (12·9 mmol) were set aside at room temperature for 3 h. Identified products were Me_3SiF (11·4 mmol) and *m*-$ClC_6H_4{\cdot}O{\cdot}S(:O)F_3$ (9·5 mmol) (Found for m-*chlorophenoxythionyl trifluoride*: C, 31·1; H, 1·7; Cl, 15·2; F, 24·8; S, 13·9. $C_6H_4ClF_3O_2S$ requires C, 31·0; H, 1·7; Cl, 15·3; F, 24·5; S, 13·8%). On heating to 400 K and on hydrolysis *m*-$ClC_6H_4{\cdot}O{\cdot}S(:O)F_3$ gives SO_2F_2, *m*-$ClC_6H_4{\cdot}O{\cdot}SO_2F$ (δ_F −38·8 p.p.m.) [Found: *M* (mass spec.), 210. Calc.: *M*, 210].

o-ClC$_6$H$_4$·O·SiMe$_3$. 1 : 1 *Reaction.* *o*-ClC$_6$H$_4$·O·SiMe$_3$ (9·4 mmol) and S(:O)F$_4$ (10·6 mmol) were set aside at room temperature for 3 h. Identified products were Me$_3$SiF (7·1 mmol), SO$_2$F$_2$, SiF$_4$, and *o*-ClC$_6$H$_4$·O·SO$_2$F (δ_F = −40·4 p.p.m.) [Found: *M* (mass spec.), 210. Calc.: *M*, 210].

p-FC$_6$H$_4$O·SiMe$_3$. 1 : 1 *Reaction.* *p*-FC$_6$H$_4$·O·SiMe$_3$ (11·1 mmol) and S(:O)F$_4$ (11·9 mmol) were set aside at room temperature for 3 h. Identified products were Me$_3$SiF (11·0 mmol) and *p*-FC$_6$H$_4$OS(O)F$_3$ (9·8 mmol) (Found for p-*fluorophenoxythionyl trifluoride*: C, 33·7; H, 2·0; F, 34·8; S, 15·1. C$_6$H$_4$F$_4$O$_2$S requires C, 33·4; H, 1·8; F, 35·2; S, 14·8%). On prolonged heating *p*-FC$_6$H$_4$·O·S(:O)F$_3$ gave SO$_2$F$_2$ as the only identifiable product; hydrolysis gave SO$_2$F$_2$ and *p*-FC$_6$H$_4$·O·SO$_2$F (δ_F = −36·2 p.p.m.) [Found: *M* (mass spec.), 194. Calc.: *M*, 194].

m-FC$_6$H$_4$·O·SiMe$_3$. 1 : 1 *Reaction.* *m*-FC$_6$H$_4$·O·SiMe$_3$ (10·8 mmol) and S(:O)F$_4$ (11·5 mmol) were set aside at room temperature for 3 h. Identified products were Me$_3$SiF (10·4 mmol) and *m*-FC$_6$H$_4$·O·S(:O)F$_3$ (9·5 mmol) (Found for m-*fluorophenoxythionyl trifluoride*: C, 33·5; H, 1·9; F, 35·0; S, 14·6. C$_6$H$_4$F$_2$O$_2$S requires C, 33·4; H, 1·8; F, 35·2; S, 14·8%). Heating (400 K) and hydrolysis gave SO$_2$F$_2$ and *m*-FC$_6$H$_4$·O·SO$_2$F (δ_{S-F} = −37·6 p.p.m., δ_{C-F} = +110·3 p.p.m.) [Found: *M* (mass spec.), 194. Calc.: *M*, 194].

o-FC$_6$H$_4$·O·SiMe$_3$. 1 : 1 *Reaction.* *o*-FC$_6$H$_4$·O·SiMe$_3$ (8·5 mmol) and S(:O)F$_4$ (9·7 mmol) were set aside at room temperature for 3 h. Identified products were Me$_3$SiF (8·1 mmol) and *o*-FC$_6$H$_4$·O·S(:O)F$_3$ (6·5 mmol). *o*-FC$_6$H$_4$·O·S(:O)F$_3$ decomposes with time and did not give a satisfactory analysis. Decomposition and hydrolysis gave SO$_2$F$_2$ and *o*-FC$_6$H$_4$·O·SO$_2$F (δ_{S-F} = −38·8 p.p.m., δ_{C-F} = 127·1 p.p.m.) [Found: *M* (mass spec.), 194. Calc.: *M*, 194].

p-NO$_2$·C$_6$H$_4$·O·SiMe$_3$. 1 : 1 *Reaction.* *p*-NO$_2$·C$_6$H$_4$·O·SiMe$_3$ (7·4 mmol) and S(:O)F$_4$ (8·9 mmol) were set aside at room temperature for 3 h. Identified products were Me$_3$SiF (7·3 mmol), unchanged S(:O)F$_4$ (3·9 mmol), and solid (*p*-NO$_2$C$_6$H$_4$O)$_2$S(:O)F$_2$ (3·1 mmol) (Found for *bis*-p-*nitrophenoxythionyl difluoride*: C, 40·2; H, 2·6; F, 10·5; N, 8·0; S, 8·9. C$_{12}$H$_8$F$_2$N$_2$O$_7$S requires C, 40·0; H, 2·2; F, 10·7; N, 7·9; S, 9·4%). (*p*-NO$_2$·C$_6$H$_4$·O)$_2$S(:O)F$_2$ was only soluble in hydroxylic solvents which induced decomposition to (*p*-NO$_2$C$_6$H$_4$O)$_2$SO$_2$) [Found: *M* (mass spec.), 328. Calc.: *M*, 328].

o-C$_6$H$_4$(OSiMe$_3$)$_2$. 1 : 1 *Reaction.* *o*-C$_6$H$_4$(OSiMe$_3$)$_2$ (11·9 mmol) and S(:O)F$_4$ (14·3 mmol) were set aside at room temperature for 8 days. Identified products were Me$_3$SiF (22·2 mmol), unchanged S(:O)F$_4$ (6·3 mmol) and (*o*-C$_6$H$_4$O$_2$)$_2$S(:O) a colourless solid recrystallised from n-pentane [Found for *bis*(o-*phenylene*)*orthosulphate:* C, 54·6; H, 3·2; S, 11·9. C$_{12}$H$_8$O$_5$S requires C, 54·6; H, 3·0; S, 12·1%]. The highest *m*/*e* ratio peak observed in the mass spectrum is at 248 (*M*, 264) and other peaks occur at 172, 156, 140, and 108.

C$_6$F$_5$·O·SiMe$_3$. 1 : 1 *Reaction.* C$_6$F$_5$·O·SiMe$_3$ (7·1 mmol) and S(:O)F$_4$ (10·0 mmol) were heated at 380 K for 17 h. Products were Me$_3$SiF (3·1 mmol), S(:O)F$_4$ (6·0 mmol), SO$_2$F$_2$ (trace), C$_6$H$_5$·O·SiMe$_3$ (3·9 mmol), and (C$_6$F$_5$O)$_3$S(:O)F (2·1 mmol) (Found for *trispentafluorophenoxythionyl fluoride*: C, 35·2; F, 49·8; S, 5·4. C$_{18}$F$_{16}$OS requires C, 35·0; F, 49·4; S, 5·2%). The mass spectrum is exceedingly complex with the highest *m*/*e* observed at 414 (C$_6$F$_5$O)$_2$SO$^+$ *m*/*e* = 414).

MeO·SiMe$_3$. 1 : 1 *Reaction.* MeO·SiMe$_3$ (10·4 mmol) and S(:O)F$_4$ (11·0 mmol) reacted together immediately at 190 K. Me$_3$SiF (10·3 mmol), SO$_2$F$_2$ (10·2 mmol), MeF (10·2 mmol), and unchanged S(:O)F$_4$ (trace) were identified amongst the products.

EtO·SiMe$_3$. 1 : 1 *Reaction.* EtO·SiMe$_3$ (10·8 mmol) and S(:O)F$_4$ (11·0 mmol) were set aside at room temperature for 2 h. Me$_3$SiF (10·4 mmol), SO$_2$F$_2$ (10·1 mmol), EtF (10·1 mmol), and unchanged S(O)F$_4$ (trace) were identified amongst the products.

Reactions between S(:O)F$_4$ and Me$_3$Si·O·CH$_2$·CH$_2$·O·SiMe$_3$, Me$_3$Si·O·CH$_2$·CF$_3$, Me$_3$Si·O·C$_6$H$_{11}$, and (Me$_3$Si)$_2$O all gave Me$_3$SiF as one product but no alkoxythionyl derivatives were identified.

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