### Phosphorus–Fluorine Chemistry. Part XXII.<sup>1</sup> Alkylthio- and Arylthiosubstituted Fluorophosphoranes

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Alkylthio-and arylthio-fluorophosphoranes of the types  $R^{1}SPF_{4}$ ,  $R^{1}S(R^{2})PF_{3}$ , and  $R^{1}S(R^{2})_{2}PF_{2}$  ( $R^{1} = Me$ , Et, or Ph;  $R^2$  = Me or Ph) are prepared in good yields by the cleavage of sulphur-silicon bonds in trimethylsilylsulphides by fluorophosphoranes. The structures of the new compounds are deduced from <sup>19</sup>F and <sup>31</sup>P n.m.r. data.

THE structures of fluorophosphoranes which contain hetero-atoms are of considerable interest,<sup>2</sup> and since few compounds in this class were known, apart from those containing nitrogen as a hetero-atom, we were interested in preparing a series of mercapto-substituted fluorophosphoranes. These compounds were of particular interest since we expected that they would have greater thermal stability than their alkoxy-analogues which have a great tendency to decompose to (tetra-co-ordinate) phosphoryl species.<sup>2</sup>

Aminofluorophosphoranes of the general formula  $R_2^1 NPR_n^2 F_{4-n}$  ( $R^1 = Me$ , Et, or Ph;  $R^2 = Me$ , Et, or Ph; n = 0, 1, or 2),<sup>3</sup> are readily synthesised by the cleavage of the silicon-nitrogen bonds of aminosilanes by fluoro-

<sup>1</sup> Part XXI, M. Fild and R. Schmutzler, J. Chem. Soc. (A), 1969, 840.

<sup>2</sup> For a recent review of fluorophosphoranes, including structural aspects see R. Schmutzler in 'Halogen Chemistry, ed. V. Gutmann, Academic Press, London and New York, 1967, vol. 2,

p. 31. <sup>3</sup> R. Schmutzler, Angew. Chem., 1964, **76**, 570; Angew. Chem. Internat. Edn., 1964, **3**, 513.

phosphoranes; recently a series of aryloxyfluorophosphoranes of the general formula  $(PhO)_n PR_{3-n}F_2$  (R = Me or Ph; n = 1 or 2)<sup>4</sup> has been prepared by cleavage of the silicon-oxygen bond of phenyl trimethylsilyl ether by fluorophosphoranes.

Bisdialkylaminofluorophosphoranes of composition  $(R_2N)_2PF_3$  have also been prepared by disubstitution of fluorine atoms in phosphorus pentafluoride by aminogroups from the corresponding amino-silanes. However, this disubstitution reaction occurs only under forcing conditions,<sup>5</sup> unless unsymmetrically substituted aminogroups are employed.<sup>6</sup>

In contrast, the preparation of aryloxyfluorophosphoranes from fluorophosphoranes which contain a single

<sup>4</sup> S. C. Peake and R. Schmutzler, Chem. Comm., 1968, 665, and unpublished results.

 <sup>5</sup> R. Schmutzler, Angew. Chem., 1964, 76, 893; Angew. Chem. Internat. Edn., 1964, 3, 753.
 <sup>6</sup> (a) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, Zhur. strukt. Khim., 1967, 8, 1097; (b) S. C. Peake and R. Schmutzler, unpublished observations on benzylmethylamino-substituted fluorophosphoranes.

equatorial fluorine atom, results only in mono-substituted products,

$$R_2PF_3 + PhO \cdot SiMe_3 \longrightarrow R_2(PhO)PF_2 + FSiMe_3$$

whereas in the reaction,

$$RPF_4 + 2PhO \cdot SiMe_3 \longrightarrow R(PhO)_2PF_2 + 2FSiMe_3$$

no trace of the trifluorophosphorane species is observed. In the cleavage reaction of phenyl trimethylsilyl ether by phosphorus pentafluoride there is again no evidence for the mono-substituted phenoxytetrafluorophosphorane.7

of trimethylsilyl sulphides with fluorophosphoranes gives only mono-substituted thiofluorophosphoranes: 4,12

$$R^{1}S:SiMe_{3} + R^{2}{}_{n}PF_{5-n} \longrightarrow R^{1}S(R^{2})_{n}PF_{4-n} + FSiMe_{3}$$
  
(*n* = 0, 1, or 2;  $R^{1} = Me$ , Et, or Ph;  $R^{2} = Me$  or Ph)

This contrasts with observations by Ivin and his coworkers 13 who introduced two mercapto-groups into fluorophosphoranes, employing the reaction

$$R^{1}PF_{4} + 2R^{2}SNa \longrightarrow R^{1}PF_{2}(SR^{2})_{2} + 2NaF$$

Table 1 lists the compounds we have prepared by this route.

TABLE 1

Alkylthio- and arylthio-fluorophosphoranes from the cleavage of trimethylsilylsulphides by fluorophosphoranes

Deceterate	Reaction conditions,	\$71 1 1			Analysis				
(moles)	nr. (temp.)	(%)	B.p., °C/mm.		Ċ	H	<b>λ</b> F	P	S
$PF_{5}$ (0.033), MeS·SiMe_{3} (0.030)	1 (-50°)	100	Decomp. at 0°						
PF <sub>5</sub> (0.029), EtS·SiMe <sub>3</sub> (0.020)	1 (-50)	100	Decomp. at $0^{\circ}$						
PF <sub>5</sub> (0·047), PhS·SiMe <sub>3</sub> (0·046)	4 (20)	58	7576/40	Calc. Found			$35 \cdot 2 \\ 34 \cdot 8$		
MePF <sub>4</sub> (0·10), MeS·SiMe <sub>3</sub> (0·10)	12 (20)	75	47/75	Calc. Found	$16.0 \\ 16.1$	4∙0 4∙1		$20.6 \\ 20.9$	
MePF <sub>4</sub> (0·11), EtS·SiMe <sub>3</sub> (0·10)	10 (20)	69	40-42/60	Calc. Found	$21 \cdot 9 \\ 21 \cdot 7$	$4.9 \\ 5.2$	$34.7 \\ 35.1$		
PhPF <sub>4</sub> (0·13), MeS·SiMe <sub>3</sub> (0·13)	4 (80)	72	<b>47</b> —50/0·02	Calc. Found	$39.7 \\ 40.6$	3∙8 4∙4		$14.6 \\ 13.4$	$15 \cdot 1 \\ 14 \cdot 1$
PhPF <sub>4</sub> (0·05), EtS·SiMe <sub>3</sub> (0·05)	4 (80)	69	59-60/0.01	Calc. Found	$42.55 \\ 42.2$	$4.5 \\ 4.1$			$14 \cdot 15 \\ 15 \cdot 1$
PhPF <sub>4</sub> (0.031), PhS·SiMe <sub>3</sub> (0.031)	12 (60)	96	Decomp. at $100^{\circ}$	Calc. Found	$52.5 \\ 52.6$	$3.7 \\ 3.7$	$20.7 \\ 20.4$		$11.75 \\ 12.4$
Ph <sub>2</sub> PF <sub>3</sub> (0·20), MeS·SiMe <sub>3</sub> (0·20)	6 (100)	50	$148 - 150/2 \cdot 0$	Calc. Found	57·75 56·6	$4.9 \\ 4.5$	$14.05 \\ 14.6$		
Ph <sub>2</sub> PF <sub>3</sub> (0·20), EtS·SiMe <sub>3</sub> (0·20)	7 (105)	<b>52</b>	160	Calc. Found	$59 \cdot 2 \\ 61 \cdot 3$	$5.35 \\ 5.5$		$10.8 \\ 12.3$	
Ph <sub>2</sub> PF <sub>3</sub> (0.05), PhS·SiMe <sub>3</sub> (0.05)	9 (80)	_	Decomp. at 140° a						
	$\begin{array}{c} Reactants \\ (moles) \\ PF_5 (0.033), \\ MeS\cdotSiMe_3 (0.030) \\ PF_5 (0.029), \\ EtS\cdotSiMe_3 (0.020) \\ PF_5 (0.047), \\ PhS\cdotSiMe_3 (0.046) \\ MePF_4 (0.10), \\ MeS\cdotSiMe_3 (0.10) \\ MePF_4 (0.11), \\ EtS\cdotSiMe_3 (0.10) \\ PhFF_4 (0.13), \\ MeS\cdotSiMe_3 (0.13) \\ PhPF_4 (0.05), \\ EtS\cdotSiMe_3 (0.05) \\ PhPF_4 (0.031), \\ PhS - SiMe_3 (0.031) \\ Ph_2 PF_3 (0.20), \\ MeS\cdotSiMe_3 (0.20) \\ Ph_2 PF_3 (0.20), \\ EtS\cdotSiMe_3 (0.20) \\ Ph_2 PF_3 (0.05), \\ EtS\cdotSiMe_3 (0.20) \\ Ph_2 PF_3 (0.05), \\ PhS-SiMe_3 (0.05) \\ PhS\cdotSiMe_3 (0.05) \\ \end{array}$	$\begin{array}{c} & \mbox{Reaction} \\ & \mbox{conditions,} \\ & \mbox{conditions,} \\ & \mbox{conditions,} \\ & \mbox{conditions,} \\ & \mbox{hr.} \\ & \mbox{conditions,} \\ & \mbox{hr.} \\ & \mbox{conditions,} \\ & \mbox{hr.} \\ & \mbox{hr.} \\ & \mbox{temp.} \\ \hline PF_5 (0.033), & 1 (-50^\circ) \\ & \mbox{MeS-SiMe_3 (0.040)} \\ \hline PF_5 (0.029), & 1 (-50) \\ & \mbox{EtS-SiMe_3 (0.040)} \\ \hline MePF_4 (0.10), & 12 (20) \\ & \mbox{MeS-SiMe_3 (0.10)} \\ & \mbox{MePF_4 (0.11),} & 10 (20) \\ & \mbox{EtS-SiMe_3 (0.10)} \\ \hline PhPF_4 (0.13), & 4 (80) \\ & \mbox{MeS-SiMe_3 (0.13)} \\ PhPF_4 (0.05), & 4 (80) \\ & \mbox{EtS-SiMe_3 (0.05)} \\ \hline PhPF_4 (0.031), & 12 (60) \\ & \mbox{PhS-SiMe_3 (0.20)} \\ \hline Ph_2 PF_3 (0.20), & 6 (100) \\ & \mbox{MeS-SiMe_3 (0.20)} \\ \hline Ph_2 PF_3 (0.20), & 7 (105) \\ & \mbox{EtS-SiMe_3 (0.05)} \\ \hline \end{array}$	$\begin{array}{c c} & \mbox{Reaction} \\ \mbox{conditions,} \\ \mbox{conditions,} \\ \mbox{hr. Conditions,} \\ $	$\begin{array}{c cccc} & \mbox{Reaction} & \mbox{conditions,} & \mbox{Reactants} & \mbox{hr.} & \mbox{Yield} & \mbox{(moles)} & \mbox{(temp.)} & \mbox{(\%)} & \mbox{B.p., °C/mm.} \\ \mbox{PF}_5 & (0.033), & 1 & (-50^\circ) & 100 & \mbox{Decomp. at } 0^\circ & \mbox{MeS-SiMe}_3 & (0.030) & \mbox{PF}_5 & (0.029), & 1 & (-50) & 100 & \mbox{Decomp. at } 0^\circ & \mbox{EtS-SiMe}_3 & (0.020) & \mbox{PF}_5 & (0.047), & 4 & (20) & 58 & 75-76/40 & \mbox{PhS-SiMe}_3 & (0.046) & \mbox{MePF}_4 & (0.10), & 12 & (20) & 75 & 47/75 & \mbox{MeS-SiMe}_3 & (0.046) & \mbox{MePF}_4 & (0.11), & 10 & (20) & 69 & 40-42/60 & \mbox{EtS-SiMe}_3 & (0.10) & \mbox{MePF}_4 & (0.13), & \mbox{MeS-SiMe}_3 & (0.10) & \mbox{PhF}_4 & (0.13), & \mbox{MeS-SiMe}_3 & (0.13) & \mbox{PhF}_4 & (0.05), & \mbox{A } & \mbox{(80)} & 72 & \mbox{A750/0.02} & \mbox{MeS-SiMe}_3 & (0.13) & \mbox{PhF}_4 & (0.05), & \mbox{A } & \mbox{(80)} & \mbox{69} & \mbox{5960/0.01} & \mbox{EtS-SiMe}_3 & \mbox{(0.031)} & \mbox{PhF}_4 & \mbox{(0.031)} & \mbox{PhF}_4 & \mbox{(0.031)} & \mbox{PhF}_4 & \mbox{(0.031)} & \mbox{PhF}_5 & \mbox{(0.20)} & \mbox{Ph}_2 & \mbox{Ff}_3 & \mbox{(0.20)} & \mbox{Ph}_2 & \mbox{Ff}_3 & \mbox{(0.20)} & \mbox{Ph}_2 & \mbox{(0.20)} & \mbox{Ph}_2 & \mbox{(0.20)} & \mbox{Ph}_2 & \mbox{(0.20)} & \\mbox{Ph}_2 & \\mbox{(0.20)} & \\mbox{Ph}_2 & \\mbox{(0.20)} & \\mbox{Ph}_2 & \\mbox{(0.20)} & \\mbox{(0.20)} & \\mbox{Ph}_2 & \\mbox{(0.20)} & \(0$	$\begin{array}{c ccccc} & \mbox{Reaction} & \mbox{conditions,} & \mbox{hr.} & \mbox{Yield} & \mbox{(moles)} & \mbox{(temp.)} & \mbox{(\%)} & \mbox{B.p., °C/mm.} \\ \mbox{PF}_5 (0.033), & 1 (-50°) & 100 & \mbox{Decomp. at } 0° & \mbox{MeS-SiMe}_3 (0.020) & \mbox{PF}_5 (0.029), & 1 (-50) & 100 & \mbox{Decomp. at } 0° & \mbox{EtS-SiMe}_3 (0.020) & \mbox{PF}_5 (0.047), & \mbox{4} (20) & 58 & 75-76/40 & \mbox{Calc.} & \mbox{Found} & \mbox{Found} & \mbox{Found} & \mbox{Found} & \mbox{Found} & \mbox{Found} & \mbox{MePF}_4 (0.10), & 12 (20) & 75 & \mbox{47/75} & \mbox{Calc.} & \mbox{Found} $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Reaction conditions, mescatants hr. Yield (moles) (temp.) ( $\%$ ) B.p., $^{\circ}C/mm$ . Decomp. at 0°AnalysisPF (moles)(temp.) ( $\%$ )( $\%$ ) B.p., $^{\circ}C/mm$ . Decomp. at 0°C HH FPF (0.033), EtS:SiMe (0.020)1 (-50)100Decomp. at 0°Calc. Found35.2PF (0.047), (0.047), (0.046)1 (-50)100Decomp. at 0°34.8MePF (0.10), meSrSiMe (0.10)12 (20)7547/75Calc. Found16.0400 meSrSiMe (0.10)10 (20)6940-42/60Calc. Found21.94.94434.8Found11.44.14.1MePF (0.11), PhF (0.13), (0.05)10 (20)6940-42/60Calc. Found21.75.235.1PhPF (0.13), PhF (0.05), HaPF (0.05), PhapF (0.031), PhapF (0.031), PhapF (0.20), PhapF (0.20), (0.031)12 (60)96Decomp. at 100°Calc. Calc. Found52.63.720.7PhapF (0.20), PhapF (0.20), PhapF (0.20), PhapF (0.20),52160-163/0.1 Calc. FoundCalc. 59.25.355.35PhapF (0.20), PhapF (0.20), PhapF (0.20),9 (80)Decomp. at 140° aHalo'aPhapF (0.20), PhapF (0.20), PhapF (0.20),9 (80)Decomp. at 140° aHalo'a	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

<sup>a</sup> Product characterized by <sup>19</sup>F n.m.r. only.

Rearrangement of the amino- and oxy-fluorophosphoranes to give ionic products has also been reported, particularly for trifluorophosphoranes: 8-11

$$2\mathrm{Me}_{2}\mathrm{N}(\mathrm{Ph})\mathrm{PF}_{3} \longrightarrow [(\mathrm{Me}_{2}\mathrm{N})_{2}\mathrm{Ph}\mathrm{PF}]^{+}[\mathrm{PF}_{5}\mathrm{Ph}]^{-}$$
$$2(\mathrm{Me}_{2}\mathrm{N})(\mathrm{Ph}\mathrm{O})\mathrm{PF}_{3} \longrightarrow [(\mathrm{Me}_{2}\mathrm{N})_{2}(\mathrm{Ph}\mathrm{O})_{2}\mathrm{P}]^{+}[\mathrm{PF}_{6}]^{-}$$
$$2\mathrm{P}(\mathrm{OPh})_{2}\mathrm{F}_{3} \longrightarrow [\mathrm{P}(\mathrm{Ph}\mathrm{O})_{4}]^{+}[\mathrm{PF}_{6}]^{-}$$

It is of interest, therefore, to compare these properties as well as the molecular structures of the aminofluorophosphoranes and the oxyfluorophosphoranes with those of the corresponding arylthio- and alkylthiosubstituted fluorophosphoranes.

### RESULTS AND DISCUSSION

Despite the use of forcing conditions and varying molar ratios of reactants we have found that cleavage

The thermal stability of the thiofluorophosphoranes is dependent both on the number of fluorine atoms in the molecule and the nature of the organothio-group.

The thiotetrafluorophosphoranes,  $RSPF_4$ , are of moderate thermal stability. The methylthio- and ethylthio-analogues decompose completely during 1 hr. at room temperature to give phosphorus pentafluoride and a mixture of solids. All the thiotetrafluorophosphoranes may be stored for extended periods in Teflon containers at  $-70^{\circ}$ . Phenylthiotetrafluorophosphorane is, however, considerably more stable than its analogues and may be distilled under reduced pressure. The resulting colourless, mobile liquid decomposes during 3 days at room temperature to yield diphenyl disulphide, PhS·SPh, phosphorus pentafluoride, and a solid which appears

<sup>&</sup>lt;sup>7</sup> S. C. Peake and R. Schmutzler, unpublished observations. <sup>8</sup> R. Schmutzler, J. Amer. Chem. Soc., 1964, **86**, 4500; R. Schmutzler, J. Chem. Soc., 1965, 5630; G. S. Reddy and R. Schmutzler, Inorg. Chem., 1966, **5**, 164; R. Schmutzler, unpublished works lished work.

<sup>&</sup>lt;sup>9</sup> S. C. Peake and R. Schmutzler, *Chem. and Ind.*, 1968, 1482.
<sup>10</sup> L. Kolditz, K. Lehmann, W. Wieker, and A. R. Grimmer, *Z. anorg. Chem.*, 1968, **360**, 257.
<sup>11</sup> S. C. Peake and R. Schmutzler, unpublished work.
<sup>12</sup> S. C. Peake and R. Schmutzler, *Chem. Comm.*, 1968, 1662.
<sup>13</sup> S. Z. Ivin, K. V. Karavanov, V. V. Lysenko, and I. D. Schalekov, *Chur. chek.ki Khim*, 1067, 27, 1241.

Shelakova, Zhur. obshchei Khim., 1967, 37, 1341.

from <sup>19</sup>F n.m.r., <sup>31</sup>P n.m.r., and analytical data to be  $[(PhS)_4P][PF_6]$ . We suggest that the initial step in the decomposition reaction is described by

 $4 \text{PhSPF}_4 \longrightarrow 2 \text{PF}_5 + [(\text{PhS})_4 \text{P}][\text{PF}_6]$ 

Characterization of methylthio- and ethylthio-tetrafluorophosphorane, was by <sup>19</sup>F and <sup>31</sup>P n.m.r. spectroscopy only, since the instability of the compounds prevented any fractionation. Phenylthiotetrafluorophosphorane was characterized by its <sup>19</sup>F n.m.r., <sup>31</sup>P n.m.r., and mass spectra and by a fluorine analysis.

The thiotrifluorophosphoranes are a series of relatively stable compounds. All are colourless, distillable liquids, except for phenyl(phenylthio)trifluorophosphorane which decomposes at 100° and thus makes distillation impossible. The products of this decomposition are diphenyl disulphide, phenyltetrafluorophosphorane, and a liquid product inseparable from diphenyl disulphide which is characterized by its <sup>31</sup>P n.m.r. shift and elemental analysis as diphenyl phenylphosphonodithioite, PhP-(SPh)<sub>2</sub>. The decomposition of phenyl(phenylthio)trifluorophosphorane is, therefore, represented by the equation

$$4(PhS)P(Ph)F_3 \longrightarrow 3PhPF_4 + PhS \cdot SPh + PhP(SPh)_2$$

The ethylthio- and methylthio-substituted analogues of this compound show no tendency to decompose on distillation *in vacuo*. The methyl substituted analogues,  $EtSP(Me)F_3$  and  $MeSP(Me)F_3$ , however, do decompose partially when distilled at atmospheric pressure (b.p. 122° and 100° respectively), while distillation at reduced pressure gives substantially increased yields.

Diphenyl(phenylthio)difluorophosphorane also shows some tendency to decompose thermally. When heated at 140° for several hours, a strong singlet of  $\delta_{\rm P} = -33\cdot 2$ p.p.m. gradually appeared in the <sup>31</sup>P n.m.r. spectrum. At the same time crystals of diphenyl disulphide were deposited, and large quantities of diphenyltrifluorophosphorane were produced; this was identified by its <sup>31</sup>P and <sup>19</sup>F n.m.r. spectra and its boiling point. We postulate that this is the result of the following decomposition:

$$3PhS(Ph)_2PF_2 \longrightarrow (PhS)_2 + 2Ph_2PF_3 + Ph_2P(SPh)$$

Phenyl diphenylphosphinothioite, Ph<sub>2</sub>P(SPh), is characterized as a product in this reaction by comparison of its <sup>31</sup>P n.m.r. shift with that of an authentic sample.

Methylthio- and ethylthio-diphenyldifluorophosphorane are colourless, distillable liquids;  $MeSPPh_2F_2$ solidifies if seeded.

Nuclear Magnetic Resonance Spectra.—Table 2 lists room-temperature <sup>19</sup>F and <sup>31</sup>P n.m.r. spectra data for the various compounds.

The room-temperature <sup>31</sup>P and <sup>19</sup>F n.m.r. spectra of the compounds reported are consistent with trigonal bipyramidal geometry in every case. There is a close analogy between the <sup>19</sup>F and <sup>31</sup>P n.m.r. spectra of the thiofluorophosphoranes, and those reported for the aminofluorophosphoranes.<sup>14</sup> In both series, each compound shows two equivalent axial fluorine atoms in the

#### TABLE 2

Room-temperature <sup>19</sup>F and <sup>31</sup>P n.m.r. data for alkylthioand arylthio-fluorophosphoranes <sup>*a*</sup>

	JP-F	$J_{F-F}$	δ <sub>F</sub>	δ <sub>P</sub>
Compound	(c./sec.)	(c./sec.)	(p.p.m.) »	(p.p.m.) *
MeS·PF, d	1032		+45.5	+34.2
EtS PF d	1045		+42.1	+34.0
PhS•PF4	1060		+45.1	+38.3
MeS·P(Me)F <sub>3</sub>	925 (ax)	62.0	$-1\cdot 2 (ax)$	-2.0
	1062 (eq)		+75.2 (eq)	
$EtS \cdot P(Me)F_3$	897 (ax)	е	$-1\cdot 2$ (ax)	-1.0
	$1022 \ (eq)$		+72.7 (eq)	
$MeS \cdot P(Ph)F_3$	942 $(ax)$	60.5	+15.0(ax)	+18.9
	$1042 \ (eq)$		+71.9 (eq)	
EtS·P(Ph)F <sub>3</sub>	938 (ax)	59.3	+15.7 (ax)	+18.3
	$1049 \ (eq)$		+71.3~(eq)	
$PhS \cdot P(Ph)F_3$	970 (ax)	60.0	+13.6(ax)	+23.6
	$1066 \ (eq)$		+71.3~(eq)	
$MeS \cdot P(Ph)_2 F_2^{f}$	760		+25.0	+39.0
$EtS \cdot P(Ph)_2F_2$	752		+25.2	+39.2
$PhS \cdot P(Ph)_2F_2$	796		$+23 \cdot 5$	g

<sup>a</sup> All values refer to neat liquids except where otherwise stated. <sup>b</sup> All fluorine shifts were measured relative to  $CCl_3F$  as an internal reference. <sup>e</sup> Phosphorus shifts were measured relative to 85% H<sub>3</sub>PO<sub>4</sub> as an external reference. <sup>d</sup> Solution in Me<sub>3</sub>SiF. <sup>e</sup> F-F coupling not resolved at room temperature. <sup>f</sup> Solution in benzene. <sup>g</sup> <sup>31</sup>P n.m.r. shift unobtainable owing to rapid decomposition.

trigonal bipyramid, which have lower chemical shifts in the <sup>19</sup>F n.m.r. spectra than the equatorial fluorine atoms. In every case the hydrocarbon, amino-, and mercaptogroups appear to be in equatorial positions of the trigonal bipyramid.

In both the amino- and the mercapto-substituted series, the tetrafluorophosphoranes undergo positional exchange of axial and equatorial fluorine atoms. Consequently, the room-temperature <sup>19</sup>F n.m.r. spectra of these compounds show broad doublets instead of the more complicated spectra which would be expected from a rigid molecule. This 'pseudorotation' process is common in mono-substituted fluorophosphoranes and is thought to occur in the parent compound, tetrafluorophosphorane, as well.<sup>15</sup>

As with their  $R_2NPF_4$  analogues,<sup>2,14</sup> the fluorine atom exchange in  $RSPF_4$  can be slowed down, relative to the n.m.r. time scale, so as to permit the observation of distinct environments for axial and equatorial fluorine atoms.

The mercapto-tetrafluorophosphoranes, however, show another change, quite distinct from the 'freezing' of pseudorotation as the temperature is lowered. This change appears to be due to hindrance of free rotation about the P-S bond and it is manifest in nonequivalence of the two axial fluorine atoms in the low-temperature <sup>19</sup>F n.m.r. spectra of all the thiotetrafluorophosphoranes.<sup>12</sup> The same phenomenon is also observed in all the thio-tri- and di-fluorophosphoranes that we have investigated <sup>12</sup> (cf. Table 3).

With the tetrafluorothiophosphoranes all resonances due to the axial fluorine atoms in the low-temperature <sup>19</sup>F n.m.r. spectra are split into 1:2:1 triplets, indicating

<sup>15</sup> R. S. Berry, J. Chem. Phys., 1960, **32**, 933.

<sup>&</sup>lt;sup>14</sup> E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298; F. N. Tebbe and E. L. Muetterties, *ibid.*, 1968, **7**, 172.

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that the two equatorial fluorine atoms are still equivalent. In methylthio- and ethylthio-tetrafluorophosphorane,  $MeSPF_4$  and  $EtSPF_4$ , coupling of only one of the axial fluorine atom environments with the protons of the alkylthio-group is observed, whilst the peaks due to the other axial fluorine atom remain unsplit by protons.

We suggest, in the light of this evidence, that the observed non-equivalence of the axial fluorine atoms in the low-temperature <sup>19</sup>F n.m.r. spectra of the series of alkylthio- and arylthio-substituted fluorophosphoranes is due to a slowing down of free rotation about the phosphorus-sulphur bond, with respect to the n.m.r. time scale. This appears to cause the hydrocarbon group to be held in close proximity to one axial fluorine atom as represented in Figure 1, thus changing the respective environments of the two axial fluorine atoms. It also appears that the sulphur-carbon bond and both P-F (axial) bonds lie in a mutually common plane for the tetrafluorophosphoranes, and, by analogy, this may also be the case in the di- and tri-fluorophosphoranes.

Figure 2 shows the change observed in the <sup>19</sup>F n.m.r. spectrum of methylthiotetrafluorophosphorane when it is cooled from room temperature to  $-90^{\circ}$ . The broad doublet observed at room temperature breaks down into a 32-line spectrum at  $-80^{\circ}$ . This may be compared with the 12-line spectrum observed for diethylamino-tetrafluorophosphorane at  $-80^{\circ}$ ,<sup>14</sup> where the axial fluorine atoms are still equivalent. Table 3 shows  $\delta_{\rm F}$  and  $J_{\rm P-F}$  values for the low-temperature <sup>19</sup>F n.m.r. spectra of the various compounds investigated.

#### EXPERIMENTAL

The usual precautions required in handling moisturesensitive phosphorus compounds were observed.

Room-temperature <sup>31</sup>P and <sup>19</sup>F n.m.r. spectra were obtained on a Perkin-Elmer 60 Mc./sec. R.10 spectrometer,



FIGURE 2 <sup>19</sup>F n.m.r. spectra of MeS·PF<sub>4</sub> at room temperature (top) and at  $-90^{\circ}$  (bottom). Scale expansion of the lower axial fluorine atom peaks (F<sub>1</sub>), reveals quartet fine structure in each. Data in Table 3 are from a scale-expanded spectrum at  $-100^{\circ}$ 

### TABLE 3

Low-temperature <sup>19</sup>F n.m.r. data for alkylthio- and arylthio-fluorophosphoranes <sup>a</sup>

	-						
Compound	Temp	$J_{\mathbf{P}-\mathbf{F}}$		$J_{\mathbf{F}-\mathbf{F}}$		$\delta_{\mathbf{F}}$	
MeS·PF <sub>4</sub>	-100°	$J_{P, F(1)}$ $J_{P, F(2)}$ $J_{P, F(3)}$	$930 \\1088 \\1075$	$J_{F(1), F(2)}$ $J_{F(1), F(3)}$ $J_{F(2), F(3)}$	19 104 91	(P·P δ <sub>F(1)</sub> δ <sub>F(2)</sub> δ <sub>F(3)</sub>	14·1 19·8 66·1
EtS·PF4	-70	$J_{P, F(1)}$ $J_{P, F(2)}$ $J_{P, F(3)}$	$950 \\ 1082 \\ 1074$	$\begin{array}{c} J_{\rm F(1),F(2)} \\ J_{\rm F(1),F(3)} \\ J_{\rm F(2),F(3)} \end{array}$	$\begin{array}{c} 20\\88\\103 \end{array}$	δ <sub>F(1)</sub> δ <sub>F(2)</sub> δ <sub>F(3)</sub>	15·1 21·7 65·8
$PhS \cdot PF_4$	80	$J_{ m P, F(1)}$ $J_{ m P, F(2)}$ $J_{ m P, F(3)}$	$1071 \\ 943 \\ 1064$	$\int \mathbf{F}(1), \mathbf{F}(2) \\ \int \mathbf{F}(1), \mathbf{F}(3) \\ \int \mathbf{F}(2), \mathbf{F}(3)$	$18 \\ 113 \\ 96$	δf(1) δf(2) δf(3)	13·9 16·9 65·0
$MeS \cdot P(Me)F_3$	-90	$J_{P, F(1)}$ $J_{P, F(2)}$ $J_{P, F(3)}$	$854 \\ 999 \\ 1058$	J <sub>F(1), F(3)</sub> J <sub>F(2), F(3)</sub>	$\begin{array}{c} 50 \\ 65 \end{array}$	δ <sub>F(1)</sub> δ <sub>F(2)</sub> δ <sub>F(3)</sub>	$-5.4 \\ 2.2 \\ 73.1$
$EtS \cdot P(Me)F_3$	80	$J_{P,F(1)}$ $J_{P,F(2)}$ $J_{P,F(3)}$	$841 \\ 953 \\ 1038$	$J_{F(1), F(3)}$ $J_{F(2), F(3)}$	$\begin{array}{c} 62 \\ 62 \end{array}$	$\delta_{F(1)} \\ \delta_{F(2)} \\ \delta_{F(3)}$	$-4.8 \\ 3.2 \\ 71.4$
$EtS \cdot P(Ph)F_3$	60	$J_{P, F(1)}$ $J_{P, F(2)}$ $J_{P, F(3)}$	$871 \\ 1015 \\ 1049$	$J_{F(1), F(2)}$ $J_{F(1), F(3)}$ $J_{F(2), F(3)}$	$32 \\ 62 \\ 62$	δ <sub>F(1)</sub> δ <sub>F(2)</sub> δ <sub>F(3)</sub>	13·1 21·4 70·5
$MeS \cdot P(Ph)_2F_2$	80	$J_{\mathbf{P},\mathbf{F}(1)}$ $J_{\mathbf{P},\mathbf{F}(2)}$	$\begin{array}{c} 694 \\ 823 \end{array}$	$J_{\mathbf{F(1)}, \mathbf{F(2)}}$	28	$\delta_{F(1)} \\ \delta_{F(2)}$	$22 \cdot 2 \\ 31 \cdot 1$
$\mathrm{EtS}{\boldsymbol{\cdot}}\mathrm{P}(\mathrm{Ph})_{2}\mathrm{F}_{2}$	-85	$J_{\mathbf{P}, \mathbf{F}(1)}$	$\begin{array}{c} 700 \\ 800 \end{array}$	С		$\delta_{F(1)}$ $\delta_{F(2)}$	$23.0 \\ 32.2$

• F(1) and F(2) are axial fluorine atoms: F(3) represents the equatorial fluorine atom (or atoms). • The low temperature <sup>10</sup>F n.m.r. data for this compound were incorrectly reported in *Chem. Comm.*, 1968, 1662. • F(ax)-F(ax)coupling is not resolved due to the high viscosity of the toluene solutions of this compound at -80 to  $-100^{\circ}$ .



FIGURE 1 Postulated structure of alkylthio- and arylthio-substituted fluorophosphoranes at low temperatures (X = Y = F;  $X \neq Y = Me$ , Ph, or F; R = Me, Et, or Ph)

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and low-temperature <sup>19</sup>F n.m.r. spectra were recorded on a Varian Associates 100 Mc./sec. HA 100 spectrometer and on a Perkin-Elmer R.10 spectrometer.

Sealed capillaries containing 85% phosphoric acid solution were used as an external reference for the phosphorus spectra, and fluorotrichloromethane was used as an internal reference in all the <sup>19</sup>F n.m.r. spectra. The data presented are all based on one or the other of these. All low-temperature spectra were run in toluene solution.

Preparation of Thiofluorophosphoranes.—The following examples of the syntheses of tetra-, tri-, and di-fluorophosphorane illustrate the procedures used in the preparation of all the mercapto-fluorophosphoranes. It may be noted that the amount of trimethylfluorosilane in all the reactions was determined. It invariably corresponded to a quantitative or nearly quantitative yield, assuming the cleavage of one P-F bond per molecule of the original fluorophosphorane.

Phenylthiotetrafluorophosphorane.-Phosphorus pentafluoride (5.9 g., 0.047 mole) was condensed onto phenyltrimethylthiosilane (8.5 g., 0.046 mole) in vacuo in a glass reaction tube at  $-196^{\circ}$ . The tube was sealed and warmed to  $0^{\circ}$  overnight. After the tube was opened, trimethylfluorosilane was allowed to evaporate at room temperature and the remaining liquid was distilled under reduced pressure from a large (50-ml.) flask fitted with an efficient magnetic stirrer to control the extensive foaming caused by partial decomposition of the product during distillation. Phenylthiotetrafluorophosphorane was collected as a colourless liquid of b.p. 72-76°/36 mm. Immediate fractionation through an 8-in. vacuum-jacketed column yielded the pure compound (5.8 g., 59%), b.p. 75-76°/40 mm. as a colourless, mobile, fuming liquid. This was quickly transferred to a Teflon vial in a sealed secondary container and stored in a Dewar packed with dry ice, in order to prevent decomposition.

Ethylthiophenyltrifluorophosphorane .--- No exothermic reaction was observed when phenyltetrafluorophosphorane (9.2 g., 0.05 mole) was added dropwise, with stirring, to ethyltrimethylthiosilane (6.7 g., 0.05 mole) at room temperature. The mixture was warmed to  $60^{\circ}$  when a vigorous evolution of colourless gas occurred. After the mixture had been heated at 80° for 4 hr. the reaction appeared to be complete; a total of  $4 \cdot 1$  g. (91%) of gas was collected in a  $-78^{\circ}$  trap and was identified as trimethylfluorosilane from its i.r. spectrum.<sup>16</sup> Distillation of the residue in vacuo yielded ethylthiophenyltrifluorophosphorane (7.8 g., 69%), b.p. 59-60°/0.01 mm., as a colourless, mobile liquid of pungent odour.

Methylthiodiphenyldifluorophosphorane.— Diphenyltrifluorophosphorane (48.6 g., 0.2 mole) was added, with stirring, to methyltrimethylthiosilane (24.0 g., 0.2 mole), and the mixture was heated under reflux at 100° for 6 hr. Trimethylfluorosilane (16.4 g., 89%) collected in a  $-78^{\circ}$ trap and was identified by its gas i.r. spectrum. The viscous residue was distilled through an 8-in. vacuumjacketed column to yield a colourless liquid (42.1 g.; b.p. 140-150°/2·0 mm.) which crystallised spontaneously on contact with a broken glass surface. A repeat fractionation

of this solid yielded pure methylthiodiphenyldifluorophosphorane (37.0 g., 66%), b.p. 148-150°/2.0 mm., as a colourless, viscous liquid which crystallised, when seeded, to give a white crystalline solid.

Thermal Decomposition of Phenylthiofluorophosphoranes.— Phenylthiotetrafluorophosphorane. Phenylthiotetrafluorophosphorane (10.8 g., 0.05 mole), redistilled and checked for purity by its <sup>19</sup>F n.m.r. spectrum, was kept at room temperature for 3 days in a weighed Monel cylinder attached by PVC tubing to a weighed trap held at liquid-nitrogen temperature. The whole apparatus was kept at a pressure of 60 mm. during the decomposition period. The colourless liquid decomposed completely to give a white solid product (8.0 g.) and a colourless gas (3.3 g.) which solidified in the cold trap. The gaseous product was identified as a mixture of trifluorophosphine oxide, 17, 18 and phosphorus pentafluoride 19 by its gas-phase i.r. spectrum. Since the proportion of trifluorophosphine oxide varied from one experiment to another, its presence is undoubtedly the result of partial hydrolysis of phosphorus pentafluoride which occurs rapidly in glass apparatus. The white crystalline solid product was a mixture of two compounds, separation of which was achieved by extracting the powdered solid several times with cold benzene. On evaporation of the benzene a small quantity (0.2 g.) of diphenyl disulphide, characterized by its m.p., analysis, and i.r. spectrum,<sup>20</sup> was obtained. The remaining solid (7.8 g.) was hygroscopic and soluble only in acetonitrile. A solution of this solid in acetonitrile showed only a doublet of  $\delta_{\rm F} = 73.5$  p.p.m. and  $J_{\rm PF} = 716$  c./sec. in its <sup>19</sup>F n.m.r. spectrum; characteristic of the [PF<sub>8</sub>]<sup>-</sup> anion. The <sup>31</sup>P n.m.r. spectrum of the same solution showed a singlet at  $\delta_P = -121{\cdot}8$  p.p.m. No signals attributable to  $[PF_6]^-$  were seen in the <sup>31</sup>P n.m.r. spectrum; this may, however, be due to the fact that a dilute solution only could be used, as concentrated solutions of ionic solids in polar media appear to cause interference with <sup>31</sup>P n.m.r. measurements.<sup>21</sup> The presence of  $[PF_6]$  was confirmed by an intense band at 839 cm.<sup>-1</sup> in the i.r. spectrum.<sup>22,23</sup> We suggest that this product may be  $[(PhS)_4P]^+[PF_6]^-$  (Found: C, 50.6; H, 4.3; F, 16.4; S, 20.2. [(PhS)<sub>4</sub>P][PF<sub>6</sub>] requires C, 47.1; H, 3.6; F, 18.6; S, 20.9%. The occurrence of diphenyl disulphide as a decomposition product might be ascribable to partial decomposition of  $[(PhS)_4P]^+[PF_6]^-$ , since upon repeated extraction of purified  $[(PhS)_4P]^+[PF_6]^$ with boiling benzene, diphenyl disulphide was taken up on every occasion. White gaseous fumes were also observed.

Phenylthiophenyltrifluorophosphorane.— Phenvlthiophenyltrifluorophosphorane (10.9 g.; 0.04 mole) was heated and magnetically stirred in a round-bottom flask attached through a reflux condenser to a trap held at liquid nitrogen temperature, in series with an oil pump. The liquid was heated at 140° for 3 days at a pressure of 0.1 mm. Phenyltetrafluorophosphorane (5.1 g.; 0.028 mole) was collected in the cold trap and identified by its b.p., and <sup>19</sup>F and <sup>31</sup>P n.m.r. spectra. Diphenyl disulphide (1.0 g.) sublimed into the reflux condenser. The involatile liquid residue showed a singlet in its <sup>31</sup>P n.m.r. spectrum at  $\delta_P =$ -90.8 p.p.m. Separation of this compound from diphenyl disulphide was achieved with some difficulty by careful

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extraction of the diphenyl disulphide with light petroleum (b.p. 40-60°) in which the diphenyl disulphide is slightly more soluble than the liquid product. The separated liquid product of b.p. 221-223°/0·1 mm. had an analysis consistent with its formulation as diphenyl phenylphosphonodithioite (Found: C, 64·3; H, 4·6; S, 19·7. Calc. for  $C_{19}H_{15}PS_2$ : C, 66·3; H, 4·6; S, 19·3%). Complete characterisation of the compound was achieved by synthesis of the authentic compound by the reaction of benzene thio with phenyldichlorophosphine and triethylamine in ether under dry nitrogen. The <sup>31</sup>P n.m.r. chemical shifts of the two reaction products were in agreement.

Phenylthiodiphenyldifluorophosphorane.—A mixture of phenyl trimethylsilyl sulphide (9·2 g., 0·05 mole) and diphenyltrifluorophosphorane (12·1 g., 0·05 mole) was heated at 140° and magnetically stirred in a round-bottom flask fitted with a reflux condenser and drying tube. The course of the reaction was followed by observation of the <sup>19</sup>F n.m.r. spectrum of samples taken at hourly intervals. During the first 2 hr. the intensity of the peaks due to diphenyltrifluorophosphorane decreased, and the doublet due to the product, phenylthiodiphenyldifluorophosphorane, PhS(Ph)<sub>2</sub>-PF<sub>2</sub> appeared and increased in intensity. After 3 hr., however, this doublet began to decrease in intensity and it disappeared completely after 8 hr. During this period the

<sup>24</sup> B. E. Job, R. A. N. McLean, and D. J. Thompson, Chem. Comm., 1966, 895.

peaks due to diphenyltrifluorophosphorane increased to approximately their original intensity. Crystals of diphenyl disulphide were found to be deposited when the mixture was cooled after being heated for 4 hr. <sup>31</sup>P N.m.r. spectra of the final product after it had been heated for 24 hr. in benzene solution showed peaks due to diphenyltrifluorophosphorane and a singlet at  $\delta_P = -33 \cdot 2$  p.p.m., indicating another fluorine-free product. The <sup>31</sup>P n.m.r. chemical shift of this compound is identical with the phosphorus shift of phenyl diphenylphosphinothioite Ph<sub>2</sub>PSPh,<sup>24,25</sup>

The authors thank the following for gifts of chemicals; Professor H. Hoffmann, Farbenfabriken Bayer, Wuppertal-Elberfeld, Germany, Dr. W. E. White, Ozark-Mahoning Co., Tulsa, Oklahoma, U.S.A., Dr. N. C. Lloyd, Midland Silicones, Barry, Glamorgan, and Dr. A. F. Childs, Albright and Wilson Ltd., Oldbury, Birmingham. The assistance of Dr. D. Shaw of Varian Associates Ltd., Walton, Surrey, and Dr. M. Murray of Technische Universität, Braunschweig, Germany, in obtaining low-temperature n.m.r. spectra, and of Dr. I. K. Gregor of University College, London, in running the mass spectra of various compounds is greatly appreciated. S. C. P. acknowledges a S.R.C. Research Studentship.

[9/1395 Received, 14th August, 1969]

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