J. Chem. Soc. (A), 1969

## Phosphorus–Fluorine Chemistry. Part XXI.<sup>1</sup> Pentafluorophenylfluorophosphines and Pentafluorophenylfluorophosphoranes

By M. Fild and R. Schmutzler, \*† Department of Chemistry, University of Technology, Loughborough, Leicestershire

The preparation of the fluorophosphines,  $(C_6F_5)_n PF_{3-n}$ , and of the fluorophosphoranes,  $(C_6F_5)_n PF_{5-n}$ , as well as of the related oxygen species,  $(C_6F_5)_n P(:O)F_{3-n}$  (n = 1, 2) is described. <sup>19</sup>F and <sup>31</sup>P N.m.r. data for the new compounds are reported and discussed.

THE study of the chemistry of organo-substituted phosphorus-fluorine compounds has been limited, essentially, to compounds involving hydrogen-containing hydrocarbon groups.<sup>2,3</sup> Comparatively little is known about the analogous perfluoroalkyl derivatives whose properties often differ considerably from those of the corresponding C-H compounds. We became interested, therefore, in the introduction of another perfluorinated substituent, the pentafluorophenyl group, and in studying its effect on the properties of various phosphorus fluorides containing this group. Our study was concerned with compounds involving phosphorus of co-ordination number 3, 4, and 5.

In a number of cases it is now well established that fluorophosphines,  $R_n PF_{3-n}$  (n = 1,2), are unstable with regard to disproportionation into fluorophosphorane,  $RPF_4$ , and cyclopolyphosphine,  $(RP)_5$  (n = 1), or fluorophosphorane,  $R_2PF_3$ , and diphosphine,  $R_2P\cdot PR_2$  (n = 2), respectively.<sup>1,2,4</sup> Rate and extent of this disproportionation are controlled both by the electronegativity of the group R, and by the temperature. Fluorophosphines involving highly electronegative substituents are less susceptible to spontaneous disproportionation than are compounds with more electropositive groups.

This difference in reactivity is significant during the preparation of fluorophosphines. It is well established that the metathetical reaction of chlorophosphines,  $R_n PCl_{3-n}$ , with Group V trifluorides is unsuitable normally as a method of synthesizing the respective fluorophosphines,  $R_n PF_{3-n}$ , because of a simultaneous redox reaction, giving rise to exclusive formation of fluorophosphoranes,  $R_n PF_{5-n}$ .<sup>3</sup> Therefore, fluorinating agents such as the alkali fluorides, sodium fluoride, or potassium fluoride, in a polar medium which do not permit a redox reaction to occur must be employed in the metathetical synthesis.

## RESULTS AND DISCUSSION

We have found that upon fluorination of  $C_6F_5PX_2$ (X = Cl, Br) with antimony trifluoride straightforward halogen exchange takes place and the fluorophosphine,

† Present address: 33 Braunschweig, Pockelsstrasse 4, Institut für Anorganische Chemie der Technischen Universität, Germany.

<sup>1</sup> Part XX, H. G. Ang and R. Schmutzler, J. Chem. Soc. (A), 1969, 702.

<sup>2</sup> R. Schmutzler, Adv. Fluorine Chem., 1965, 5, 31.
 <sup>3</sup> R. Schmutzler, in 'Halogen Chemistry,' ed. V. Gutmann,

Academic Press, London, 1967, vol. 2, p. 31. <sup>4</sup> G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, B. I. Tetel'baum, and A. D. Varshavskii, Zhur. obschei Khim., 1967, 37, 1343.

 $C_6F_5PF_2$ , is the major product. Only trace amounts of  $C_6F_5PF_4$  may sometimes be observed.

In the case of the homologous compounds,  $(C_6F_5)_2PX$ (X = Cl, Br), the fluorophosphine,  $(C_6F_5)_2PF$ , is still the predominant product when SbF<sub>3</sub> is employed as the fluorinating agent, but a considerable amount of the trifluorophosphorane, (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PF<sub>3</sub>, is also formed.

This course of reaction is known from the analogous  $CF_3$ -substituted compounds,  $(CF_3)_n PX_{3-n}$  which, owing to the greater electronegativity of the CF<sub>3</sub> group, are converted into trifluoromethylfluorophosphines only.<sup>2</sup>

An unambiguous method of synthesis of both  $C_6F_5PF_2$ and  $(C_6F_5)_2$ PF is based on the fluorination of the respective halogenophosphines with sodium fluoride in acetonitrile. The fluorination of  $C_6F_5PX_2$  with sodium fluoride has also been attempted, using sulpholan as a reaction medium but only traces of C<sub>6</sub>F<sub>5</sub>PF<sub>2</sub> could be recovered upon distillation. This reaction has been referred to as a method of preparation of  $C_6F_5PF_2$  in a previous literature report,<sup>5</sup> but no experimental details were given. Reference to  $C_{6}F_{5}PF_{2}$ , in the absence of any analytical or physical characterization other than by <sup>19</sup>F n.m.r. has also been made by two other research groups.6,7

Both pentafluorophenylfluorophosphines are colourless and readily distillable.  $C_6F_5PF_2$ , is obtained as a liquid while  $(C_6F_5)_2$ PF solidifies on cooling in the distillation receiver. The compounds were found to be unchanged upon storage over periods of several months; in particular, there was no evidence for any redox disproportionation at room temperature. It may be noted, however, that redox disproportionation does take place upon prolonged heating of both fluorophosphines.

The preparation of the pentafluorophenylfluorophosphoranes was effected via the respective chlorophosphoranes which were fluorinated, using arsenic trifluoride as a fluorinating agent, viz.,

$$(C_6F_5)_nPCl_{3-n} \xrightarrow{Cl_4} (C_6F_5)_nPCl_{5-n} \xrightarrow{AsF_3} (C_6F_5)_nPF_{5-n}$$

 $C_6F_5PF_4$  was synthesized from pentafluorophenyldifluorophosphine, chlorine, and arsenic or antimony trifluoride:

$$C_6F_5PF_2 \xrightarrow{Cl_2} C_6F_5PF_2Cl_2 \xrightarrow{AsF_3} C_6F_5PF_4$$

<sup>5</sup> J. M. Miller, J. Chem. Soc. (A), 1967, 828.

M. Hiller, J. Chem. Soc. (11), 1001, 1001, 1001.
M. G. Barlow, M. Green, R. N. Haszeldine, and H. G. Higson, J. Chem. Soc. (B), 1966, 1025.
A. H. Cowley and R. P. Pinnell, J. Amer. Chem. Soc., 1966,

88, 4533.

Owing to its poor stability the formation of the intermediate, C<sub>6</sub>F<sub>5</sub>PF<sub>2</sub>Cl<sub>2</sub>, has not been established with certainty.

It may be noted here that oxidation of  $C_{6}F_{5}PCl_{2}$  by chlorine did not give a tetrachlorophosphorane stable enough to be isolated at room temperature, and the  $C_{6}F_{5}PCl_{2}-Cl_{2}$  reaction product readily reverts to the starting materials. Cowley and Pinnell <sup>7</sup> have suggested that this instability is a consequence of the  $C_6F_5$  group, owing to its high electronegativity, occupying the axial position of a trigonal bipyramid. We believe that these observations may also be rationalized as a result of the  $\pi$ -donor properties of the pentafluorophenyl ring which permit oxidation only in the case of very electronegative groups or atoms, such as fluorine.

intermediate between the values found for fluorophosphines containing phenyl and perfluoroalkyl groups.<sup>8</sup> The  $J_{P-F}$  values, 1211 and 1000 c./sec., respectively, are somewhat smaller than those for the analogous perfluoroalkyl-substituted compounds. Further fine structure in the spectra, due to coupling between <sup>31</sup>P and aromatic ring fluorine atoms, especially in the orthoposition, is evident.

We assume that in all compounds of type RPF, the  $\sigma$ -bond system is essentially the same. The shielding of the phosphorus atom is believed to be determined by the electronegativity of R, by the bond angle,9 and, possibly, by  $d_{\pi}-p_{\pi}$  interaction between phosphorus and the group R. On the basis of its electronegativity the  $C_{6}F_{5}$  group should give rise to strong deshielding of the

191

<sup>31</sup>P and <sup>19</sup>F N.m.r. data for pentafluorophenylphosphorus compounds

	31P		P-F		$\delta_{\mathbf{F}}$ for C(aromat.)-F (p.p.m.)		
Compound	$\delta_{\mathbf{P}}$ (p.p.m.)	$J_{\mathbf{P}-\mathbf{F}}$ (c./sec.)	$\delta_{\mathbf{F}}$ (p.p.m.)	$J_{P-F}$ (c./sec.)	ortho	para	meta
C <sub>a</sub> F <sub>5</sub> PF,	-193.4	1211	+94.5	1215	+140.3	+149.0	+164.5
$(\check{C}_{\mathfrak{g}}\check{F}_{\mathfrak{f}})_{\mathfrak{g}}\check{P}F$	-136.0	1000	+216.6	1002	$+138 \cdot 4$	+152.6	+166.0
C <sub>s</sub> F <sub>5</sub> POF <sub>2</sub>	+4.6	1130	+57.5	1128	+133.0	+145.0	$+163 \cdot 2$
$(\check{C}_{6}\check{F}_{5})_{2}POF$	9-8	1085	+55.8	1090	+136.8	+147.2	$+164 \cdot 4$
C <sub>6</sub> F <sub>5</sub> PF <sub>4</sub>	+52.2	996	+40.6	1000	+135.8	+149.0	$+163 \cdot 2$
$(C_{6}F_{5})_{2}PF_{3}$	+28.8	920	-7.0	912	$+138 \cdot 4$	+151.0	$+165 \cdot 2$
$(C_{6}F_{5})_{3}PF_{2}^{a}$	b	b	-2.5	713	+137.8	+151.6	+164.8

<sup>a</sup> In benzene. <sup>b</sup> <sup>31</sup>P N.m.r. parameters not obtained, owing to insufficient solubility of the compound in benzene, chloroform, or acetonitrile.

Tris(pentafluorophenyl)difluorophosphorane is also accessible via the reaction of the sulphide,  $(C_{6}F_{5})_{3}PS$ , with either arsenic or antimony trifluoride:

$$3(C_6F_5)_3PS + 2MF_3 \xrightarrow{} 3(C_6F_5)_3PF_2 + M_2S_3$$
 (M = As, Sb)

All three fluorophosphoranes are sensitive to hydrolysis, the primary products of the reaction with water being the corresponding phosphoryl compounds, *i.e.*,

$$(C_6F_5)_n PF_{5-n} + H_2O \longrightarrow (C_6F_5)_n P(O)F_{3-n} + 2HF \quad (n = 1,2,3)$$

The new compounds  $C_6F_5POF_2$  and  $(C_6F_5)_2POF$  (corresponding to n = 1,2) were also synthesized conveniently via an alternative route, involving the cleavage of the Si-O-Si linkage of hexamethyldisiloxane by the respective fluorophosphorane:

$$\begin{array}{ll} (\mathrm{C_6F_5})_n\mathrm{PF_{5-n}} + (\mathrm{Me_3Si})_2\mathrm{O} \longrightarrow \\ (\mathrm{C_6F_5})_n\mathrm{P({}^{\bullet}\mathrm{O}\mathrm{)F_{3-n}}} + 2\mathrm{Me_3SiF} & (n=1,2) \end{array}$$

Nuclear Magnetic Resonance Spectra.—The Table lists chemical shifts,  $\delta_{\mathbf{P}}$  and  $\delta_{\mathbf{F}}$ , as well as P-F coupling constants for the various compounds.

The  $\delta_P$  values for the fluorophosphines,  $C_6F_5PF_2$  and  $(C_6F_5)_2$ PF, show the usual highly negative values, -193.4 and -136.0 p.p.m., respectively; they are

phosphorus atom in  $C_6F_5PF_2$ . It is actually found that, though still highly negative,  $\delta_P$  for  $C_6F_5PF_2$  (-193.4 p.p.m.) is more positive than for any other aryl- or alkyldifluorophosphine. Thus, the  $C_6F_5$  group in  $C_6F_5PF_2$ appears to exhibit more pronounced  $\pi$ -donor ability than the  $C_6H_5$  group in  $C_6H_5PF_2$  ( $\delta_P - 208$  p.p.m.). A further illustration of this point is provided by a comparison of the  $\delta_P$  values for  $(C_6F_5)_2PF$  and  $(C_6H_5)_2PF^{10}$ (-136.0 p.p.m. and -168.4 p.p.m., respectively). The  $\pi$ -donor properties of the C<sub>6</sub>F<sub>5</sub> group bonded to 3-coordinate phosphorus have also been discussed by Graham and his co-workers <sup>11</sup> on the basis of <sup>19</sup>F n.m.r. studies of a series of compounds of type  $C_6F_5PR_2$ . Finally, it may be noted that stronger shielding, presumably through  $p_{\pi}-d_{\pi}$  bonding, is also observed in fluorophosphites,  $(\mathrm{RO})_n \mathrm{PF}_{3-n}$  $\operatorname{and}$ dialkylaminofluorophosphines,  $(R_2N)_n PF_{3-n}$ , where lone electron pairs are available on oxygen or nitrogen, respectively.

The n.m.r. parameters for the compounds  $C_6F_5POF_2$ and  $(C_6F_5)_2$ POF are comparable to those of other 4-co-ordinate P-F compounds.  $\delta_P$  values and P-F coupling constants are notably larger than for the analogous C<sub>6</sub>H<sub>5</sub> derivatives.

For the fluorophosphoranes,  $C_6F_5PF_4$  and  $(C_6F_5)_2PF_3$ , similar n.m.r. parameters as for the CF<sub>3</sub>-substituted compounds are observed. Thus, a simple 1:3:3:1quartet in the <sup>31</sup>P n.m.r. spectrum and a 1 : 1 doublet in the <sup>19</sup>F spectrum of  $(C_6F_5)_2PF_3$  at room temperature,

<sup>&</sup>lt;sup>8</sup> B. I. Tetel'baum, V. V. Sheluchenko, S. S. Dubov, G. I. Drozd, and S. Z. Ivin, *Zhur. Vsesoyug. Khim. obshch. im. D.I. Mendeleeva*, 1967, 12, 351.
<sup>9</sup> J. R. Van Wazer and J. R. Letcher, in 'Topics in Phosphorus Chemistry,' vol. 5, 1967, p. 169ff.

M. Murray and R. Schmutzler, unpublished results.
 M. G. Hogben, R. S. Gay, and W. A. G. Graham, J. Amer. Chem. Soc., 1966, 88, 3457.

similarly to cyclotetramethylenetrifluorophosphorane,  $(CH_2)_4PF_3$  and  $(CF_3)_2PF_3$ , are observed.

The tetrafluorophosphorane,  $C_6F_5PF_4$ , at room temperature shows the usual simplified n.m.r. pattern, characteristic of 5-co-ordinate P-F compounds undergoing positional exchange. The possibility of freezing this exchange process was considered but no change in the <sup>19</sup>F n.m.r. spectrum of a solution of  $C_6F_5PF_4$  in toluene was observed at temperatures as low as  $-60^\circ$ .

Aside from the P-F resonances, multiple n.m.r. signals are also observed for the ring fluorine atoms in the <sup>19</sup>F spectra. The smallest changes in  $\delta_F$  are observed for fluorine atoms in *meta*-positions, in 3-, 4-, and 5-coordinate compounds. A detailed discussion of the complicated fine structure of the aromatic fluorine resonances in our C<sub>6</sub>F<sub>5</sub>-phosphorus compounds will not be attempted.

## EXPERIMENTAL

The usual precautions in handling air- and moisturesensitive compounds were observed during the experimental work.

<sup>19</sup>F and <sup>31</sup>P n.m.r. spectra were obtained on a Perkin-Elmer R 10 spectrometer. <sup>19</sup>F n.m.r. spectra were obtained at 56·4 Mc./sec. and <sup>31</sup>P spectra at 24·3 Mc./sec. Nonspinning tubes (8·5 mm.) were used for the <sup>31</sup>P spectra, and 5 mm. spinning tubes for the <sup>19</sup>F spectra.

Trichlorofluoromethane was used as an internal standard for the <sup>19</sup>F spectra while sealed capillaries containing 85%  $H_3PO_4$  were inserted into the phosphorus n.m.r. tubes as <sup>31</sup>P standard. Liquid samples were measured neat, solid compounds were dissolved in benzene, chloroform, or carbon tetrachloride.

The starting pentafluorophenyl halogenophosphines and trispentafluorophenylphosphine sulphide were obtained by published methods.<sup>12,13</sup>

Pentafluorophenyldifluorophosphine.---The fluorination reaction was conducted in a two-necked flask, fitted with a tap-funnel with side-arm, and a downward condenser, set up for distillation. Pentafluorophenyldichlorophosphine<sup>12</sup> (25 g., 0.093 mole) was added dropwise with stirring (magnetic stirrer) to finely ground antimony trifluoride (15 g., 0.084 mole) during 0.5 hr., a mildly exothermic reaction commencing. Upon heating the reaction mixture to 160° (oil-bath temperature) a liquid of boiling range 126-132° distilled over. Redistillation gave pentafluorophenyldifluorophosphine (15.0 g., 68%), b.p. 129-130°. The <sup>19</sup>F n.m.r. spectrum (Table) was identical with that published by Haszeldine.<sup>6</sup> No evidence for the formation of the tetrafluorophosphorane,  $C_6F_5PF_4$ , was found in the n.m.r. spectrum of the distilled product. However, a darkening of the reaction mixture was noted during the fluorination which would suggest that a redox reaction has occurred to a small extent. Also, a trace of pentafluorophenylphosphonic difluoride,  $C_6F_5POF_2$ , was isolated from the reaction residue and was identified by n.m.r. (Table).

Bis(pentafluorophenyl)fluorophosphine—(a) Fluorination with antimony trifluoride. Using the same set-up as described in the preceding experiment, bis(pentafluorophenyl)bromophosphine <sup>12</sup> (12.7 g., 0.029 mole) was added drop-

<sup>12</sup> M. Fild, O. Glemser, and I. Hollenberg, Z. Naturforsch., 1966, **21**b, 920.

wise with stirring during 0.5 hr. to antimony trifluoride (6.1 g., 0.034 mole), a mildly exothermic reaction taking place. After heating for 2 hr. (120–140° bath temperature) the reaction mixture was distilled *in vacuo*, a liquid product boiling at 105–125°/1 mm. being obtained which solidified in the receiver flask. <sup>19</sup>F n.m.r. indicated the presence of a mixture of both the fluorophosphine,  $(C_6F_5)_2PF_3$ , which could not be separated by distillation.

(b) Fluorination with sodium fluoride in benzene. Bis-(pentafluorophenyl)bromophosphine <sup>12</sup> (14 g., 0.032 mole) was added dropwise with stirring to a suspension of sodium fluoride (10 g., 0.24 mole) in benzene (60 ml.). The mixture was refluxed for 15 hr., cooled to room temperature, and filtered. The liquid product remaining after the benzene solvent had been removed was distilled *in vacuo*. A liquid product distilled at 96—100°/0.01 mm. <sup>31</sup>P n.m.r. showed it to consist largely of unreacted (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PBr, with an estimated 10% of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PF.

(c) Fluorination with sodium fluoride in acetonitrile. The fluorination was repeated, using the same quantities of reactants and experimental set-up as in the preceding experiment. Acetonitrile (60 ml.) instead of benzene was used as a solvent. The product was recovered, after removal of the acetonitrile solvent, by direct distillation from the reaction mixture. Bis(pentafluorophenyl)fluorophosphine (8.0 g., 73%) was obtained as a liquid, b.p. 104—106°/0.02 mm., m.p. 49° (Found: C, 37.6; P, 8.1.  $C_{12}F_{11}P$  requires C, 37.5; P, 8.1).

Pentafluorophenyltetrafluorophosphorane.--Chlorine (4.46 g., 0.063 mole) was condensed at  $-196^{\circ}$  on to a mixture of pentafluorophenyldifluorophosphine (14.1 g., 0.06 mole) and arsenic trifluoride (5.5 g., 0.042 mole), contained in a 75-ml. steel cylinder. After the cylinder had been sealed its contents were allowed to warm to room temperature during 15 hr. Subsequently, the reaction mixture was heated to 100-110° for 5 hr. After cooling to room temperature the reaction products were transferred into a high-vacuum line, a small amount of a solid residue being left in the tube which was not further characterized. Fractional distillation of the liquid products at atmospheric pressure gave some unreacted AsF<sub>3</sub>, followed by pentafluorophenyltetrafluorophosphorane, b.p. 118-125°. After redistillation through an 8-in. Vigreux column, b.p. 121° was found (10.7 g., 65%) (Found: C, 26.5; F, 61.8. C<sub>6</sub>F<sub>9</sub>P requires C, 26.3; F, 62.4%). The mass spectrum clearly shows the parent ion, C<sub>6</sub>F<sub>9</sub>PF<sub>4</sub><sup>+</sup> at m/e 274, along with the expected PF- and  $C_6F_5$ -containing fragments. N.m.r. data for  $C_6F_5PF_4$  are listed in the Table.

In another experiment,  $C_6F_5PF_2$  was refluxed for 6 hr. at atmospheric pressure with a slight excess of AsF<sub>3</sub>. Only a small amount of  $C_6F_5PF_4$  was observed in the <sup>19</sup>F n.m.r. spectrum, along with some  $C_6F_5POF_2$ , presumably originating from the reaction of  $C_6F_5PF_4$  with glass, while most of the  $C_6F_5PF_2$  had remained unchanged. In order to exclude the possibility of  $C_6F_5PF_4$  reacting with glass, the reaction of the fluorophosphine,  $C_6F_5PF_2$ , with AsF<sub>3</sub> was also conducted in a steel cylinder at 100—110° for 15 hr. A much larger proportion of  $C_6F_5PF_4$  was observed in the <sup>19</sup>F n.m.r. spectrum, but its separation from unreacted  $C_6F_5PF_2$  by distillation proved impossible.

Bis(pentafluorophenyl)trifluorophosphorane.— Using the same apparatus as described in the preceding experiments, <sup>13</sup> H. J. Emeléus and J. M. Miller, J. Inorg. Nuclear Chem., 1966, **28**, 662.

arsenic trifluoride (2·2 g., 0·007 mole) was added dropwise with stirring during 0·5 hr. to bis(pentafluorophenyl)trichlorophosphorane (8·1 g., 0·072 mole). The latter was prepared from bis(pentafluorophenyl)chlorophosphine and chlorine.<sup>14</sup> After the mildly exothermic reaction had subsided (1 hr.) the mixture was distilled *in vacuo*. Arsenic trichloride was collected first and was condensed in a dryice cooled trap, followed by bis(pentafluorophenyl)trifluorophosphorane (5·5 g., 76%), b.p. 120°/1 mm., which readily solidified in the condenser, m.p. 55° (Found: C, 33·8; P, 7·05. C<sub>12</sub>F<sub>13</sub>P requires C, 34·2; P, 7·05).

Tris(pentafluorophenyl)difluorophosphorane.—A mixture of tris(pentafluorophenyl)phosphine sulphide <sup>13</sup> (3.8 g., 0.007 mole) and antimony trifluoride (1.2 g., 0.0065 mole) was prepared with exclusion of moisture in a 25-ml. roundbottom flask. The mixture was heated to 180° during 0.5 hr. and was held at this temperature for 2 hr. After cooling to room temperature two portions of 50 ml. each of benzene were added to the reaction mixture which was then filtered. Recrystallisation of the residue left after removal of the benzene solvent furnished colourless crystals of tris(pentafluorophenyl)difluorophosphorane (3.05 g., 79%), m.p. 159° (Found: C, 38.5; F, 56.9. C<sub>18</sub>F<sub>17</sub>P requires C, 37.9; F, 56.7%).

Tris(pentafluorophenyl)difluorophosphorane could also be prepared by the reaction of the dichloride,  $(C_6F_5)_3PCl_{2}$ ,<sup>14</sup> with AsF<sub>3</sub>.

Tris(pentafluorophenyl)phosphine Oxide.—Hydrolysis of  $(C_6F_5)_3PF_2$  in chloroform with an excess of water furnished  $(C_6F_5)_3PO$  which was identified from its melting point (168°; lit.,<sup>15</sup> 169—170°) and <sup>31</sup>P chemical shift ( $\delta_P + 9.9$  p.p.m.; lit.,<sup>10</sup>  $\delta_P + 8.2$  p.p.m.).

Pentafluorophenylphosphonic Difluoride.—Hexamethyldisiloxane (3·25 g., 0·02 mole) was added dropwise with 843

stirring during 0.5 hr. to pentafluorophenyltetrafluorophosphorane (5.5 g., 0.02 mole). An exothermic reaction commenced with evolution of trimethylfluorosilane which was collected in a dry-ice cooled trap in nearly theoretical yield (0.04 mole). The higher-boiling liquid product upon distillation gave pentafluorophenylphosphonic difluoride, b.p. 73°/14 mm. (4.65 g., 92%) (Found: C, 28.1; P, 12.05.  $C_6F_7OP$  requires C, 28.6; P, 12.3%).

Bis(pentafluorophenyl)phosphinic Fluoride.—As described in the preceding experiment, hexamethyldisiloxane (3.5 g., 0.02 mole) was added to bis(pentafluorophenyl)trifluorophosphorane (8.3 g., 0.02 mole). There was an exothermic reaction with formation of trimethylfluorosilane. The desired bis(pentafluorophenyl)phosphinic fluoride was obtained upon distillation of the higher-boiling product (b.p.  $100-110^{\circ}/0.02$  mm.) and solidified on cooling, m.p. 80° (Found: C, 35.3; F, 53.0; P, 7.8. C<sub>12</sub>F<sub>11</sub>OP requires C, 36.0; F, 52.3; P, 7.75%).

M. F. wishes to acknowledge the award of a Postdoctoral Fellowship by Stiftung Volkswagenwerk, Hannover, Germany. We are indebted to Drs. A. K. Barbour and M. W. Buxton of Imperial Smelting Corporation Ltd., Avonmouth, Bristol, for providing us with bromopentafluorobenzene. Dr. W. E. White of Ozark Mahoning Co., Tulsa, Oklahoma, U.S.A., kindly supplied arsenic and antimony trifluoride. Thanks are due, finally, to Drs. I. K. Gregor and C. E. Holloway of University College, London, for mass spectral and low-temperature <sup>19</sup>F n.m.r. data, respectively.

## [8/938 Received, July 4th, 1968]

 <sup>14</sup> H. G. Ang and J. M. Miller, Chem. and Ind., 1966, 945.
 <sup>15</sup> L. A. Wall, R. E. Donadio, and W. J. Pummer, J. Amer. Chem. Soc., 1960, 82, 4846.