

**868.** *Phosphorus-Fluorine Chemistry. Part VIII.<sup>1</sup> Some Comments on the "Group Shift Theory," as applied to the <sup>31</sup>P Nuclear Magnetic Resonance Spectra of Certain Phosphorus Fluorides.*

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During early <sup>31</sup>P n.m.r. studies, attempts were made to establish group shifts typical of certain substituents attached to tervalent phosphorus. Special discrepancies between calculated and measured values were noted for "ethylchlorofluorophosphine," "ethyldifluorophosphine," and "isopropyl ethylphosphonofluoridite." It is now demonstrated by means of <sup>31</sup>P n.m.r. spectroscopy, and also from chemical evidence, that all three compounds are derivatives of quinquevalent phosphorus.

In one of the early reports<sup>2</sup> on the application of <sup>31</sup>P n.m.r. spectroscopy to phosphorus compounds, an attempt was made to correlate data obtained on a great number of compounds in terms of constant contributions of various groups attached to tervalent phosphorus. The postulation of the existence of "group shifts," which can be calculated, seemed to be justified in numerous instances, and predicted and observed values were frequently correct within  $\pm 10$ – $20$  p.p.m. Other authors,<sup>3,4</sup> however, reached the conclusion that no convenient quantitative correlation between the <sup>31</sup>P chemical shift and the nature of the atoms or groups bonded to phosphorus was possible. In particular, Jones and Katritzky<sup>4</sup> examined the suggested group-shift values of Van Wazer and his co-workers<sup>2</sup> statistically. For tervalent phosphorus compounds, discrepancies ranging between  $-101$  and  $+93$  p.p.m. were found, and for forty-one compounds the standard deviation was  $37$  p.p.m., which is far larger than that suggested originally.<sup>2</sup>

It had been noted by the original workers that a number of compounds showed exceptional deviations from the predicted values.<sup>2</sup> Thus, for EtPClF, a <sup>31</sup>P chemical shift of  $-85$  p.p.m. was calculated using the increments given by Van Wazer *et al.*<sup>2</sup> for the alkyl group, chlorine, and fluorine. The observed value was  $+20$  p.p.m. Similarly, data on two further compounds reported to be fluorides of tervalent phosphorus, namely, EtPF<sub>2</sub> and EtPF<sub>2</sub>OPr<sup>i</sup>, were difficult to understand in view of our observations on a great variety

<sup>1</sup> Part VII, Schmutzler, *Chem. Ber.*, 1963, **96**, 2435.

<sup>2</sup> Van Wazer, Callis, Shoolery, and Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 5715.

<sup>3</sup> Muller, Lauterbur, and Goldenson, *J. Amer. Chem. Soc.*, 1956, **78**, 3557.

<sup>4</sup> Jones and Katritzky, *Angew. Chem. (Internat. Edn.)*, 1962, **1**, 32.

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of authentic fluorides of trivalent phosphorus.<sup>1,5,6</sup> Without exception, fluorides of trivalent phosphorus showed large negative <sup>31</sup>P chemical shifts, usually between -100 and -150 p.p.m., and the results of Van Wazer *et al.*<sup>2</sup> were difficult to reconcile to these findings. Therefore, a reinvestigation of the three compounds reported to be EtPF<sub>2</sub>, EtPClF, and EtPF·OPr<sup>i</sup> was carried out, after further information on their preparation and properties had been obtained from Dr. E. E. Weaver<sup>7</sup> who supplied the samples used in the previous investigation.<sup>2</sup>

## RESULTS AND DISCUSSION

Both EtPF<sub>2</sub> and EtPClF were reported to be formed simultaneously upon fluorination of ethyldichlorophosphine with antimony trifluoride.<sup>7</sup> It was recognized in the meantime, however, that the usual interaction of chlorophosphines and Group V trifluorides such as those of arsenic or antimony not only involves the simple exchange of chlorine for fluorine, but almost invariably leads to oxidation of the trivalent phosphorus to the quinquevalent state. Thus, fluorophosphoranes, R<sub>n</sub>PF<sub>5-n</sub>, are usually obtained upon fluorination of chlorophosphines, R<sub>n</sub>PCl<sub>3-n</sub> (*n* = 1 or 2), with arsenic or antimony trifluoride.<sup>8</sup>

That the "EtPF<sub>2</sub>" used in the <sup>31</sup>P n.m.r. study was actually the tetrafluorophosphorane, EtPF<sub>4</sub>, was readily confirmed by a comparison of some physical properties with those of authentic EtPF<sub>4</sub>:<sup>8b,c,9</sup> "EtPF<sub>2</sub>" had b. p. 32.5°<sup>7</sup> and that of EtPF<sub>4</sub> is 32-33°;<sup>8b,c</sup> the observed molecular weight is 124 or 125, and the calculated values are 98.0 and 136.0, respectively. The infrared spectra were the same.

In the original communication on the <sup>31</sup>P n.m.r. spectrum of "EtPF<sub>2</sub>," only a 1 : 2 : 1 triplet, indicative of a PF<sub>2</sub> compound, was reported.<sup>2</sup> It is now apparent that two weak outside peaks were missed, and in the present work a clear 1 : 4 : 6 : 4 : 1 quintuplet was observed for the <sup>31</sup>P spectrum of EtPF<sub>4</sub>, resulting from coupling between <sup>31</sup>P and four equivalent fluorine nuclei. The apparent equivalence of fluorine atoms in tetrafluorophosphoranes was also observed in their <sup>19</sup>F n.m.r. spectra.<sup>10</sup> Also, the <sup>31</sup>P chemical shift reported for "EtPF<sub>2</sub>" (+30 ± 3 p.p.m.) is in excellent agreement with that for authentic ethyltetrafluorophosphorane (+30.2 p.p.m.) and other alkyltetrafluorophosphoranes. Some representative <sup>31</sup>P chemical shifts for fluorophosphoranes are given in Table 1; the relatively narrow range for alkyltetrafluorophosphoranes distinguishes them from other members of the series.

TABLE 1.

<sup>31</sup> P n.m.r. data for some fluorophosphoranes, R <sub>n</sub> PF <sub>5-n</sub> .		
Compound	J <sub>P-F</sub> (c./sec.) *	δ (p.p.m.)
"EtPF <sub>2</sub> " (refs. 2 and 7) .....	980	+30 ± 3
MePF <sub>4</sub> .....	965	+29.6
EtPF <sub>4</sub> .....	1000	+30.2
CICH <sub>2</sub> ·PF <sub>4</sub> .....	1012	+43.7
PhPF <sub>4</sub> .....	973	+51.7
Me <sub>2</sub> PF <sub>3</sub> .....	axial, 787; eq., 975 †	-8.95
Et <sub>2</sub> PF <sub>3</sub> .....	axial, 830; eq., 1000 †	-6.2
MePhPF <sub>3</sub> .....	axial, 800; eq., 950 †	+13.1
Ph <sub>2</sub> PF <sub>3</sub> .....	axial, 834; eq., 968 †	+34.8
PF <sub>3</sub> .....	915 (average at room temp.)	-29.6
Bu <sup>n</sup> <sub>3</sub> PF <sub>2</sub> .....	560	+15.5

\* The values of the P-F coupling constants agree with those obtained from the <sup>19</sup>F n.m.r. spectra.<sup>10</sup>

† For the assignment of axial and equatorial coupling constants see ref. 10.

<sup>5</sup> Schmutzler, *Inorg. Chem.*, 1964, **3**, 416.

<sup>6</sup> Reddy and Schmutzler, unpublished results.

<sup>7</sup> (a) Weaver, personal communication; (b) Hovorka and Weaver, presented at the Meeting of the American Chemical Society, Buffalo, March 1952.

<sup>8</sup> (a) Yagupol'skii and Ivanova, *Zhur. obshchei Khim.*, 1959, **29**, 3766; (b) Schmutzler, *Chem. and Ind.*, 1962, 1868; (c) Schmutzler, *Inorg. Chem.*, 1964, **3**, 410.

<sup>9</sup> Komkov, Ivin, Karavanov, and Smirnov, *Zhur. obshchei Khim.*, 1962, **32**, 301.

<sup>10</sup> Muetterties, Mahler, and Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

As with the other two presumed fluorides of trivalent phosphorus (see below), attention has already been drawn to the particularly puzzling fact that the  $^{31}\text{P}$  chemical shift of "EtPF<sub>2</sub>" is positive, while other fluorides of trivalent phosphorus, including PF<sub>3</sub>, invariably show large negative shifts.<sup>6</sup> Also, the P-F coupling constant reported for "EtPF<sub>2</sub>" is unusually low for a fluoride of trivalent phosphorus, as are the coupling constants of the other two fluorides.

Next, doubt arose as to the identity of the presumed ethylchlorofluorophosphine, EtPClF. For this compound, a  $^{31}\text{P}$  chemical shift of  $-26 \pm 2$  p.p.m. (not  $+20 \pm 2$  p.p.m.<sup>2</sup>) has been observed, as is evident from a reinspection of the original spectrum.<sup>2,7</sup> The spectrum is a 1 : 2 : 1 triplet, not a 1 : 1 doublet,<sup>2</sup> suggesting a PF<sub>2</sub> compound. Also, the P-F coupling constant for "EtPClF" is not 570, but 1140 c./sec. This value is indicative of a phosphonic difluoride, EtPOF<sub>2</sub>, which is also confirmed by the  $^{31}\text{P}$  chemical shift (see Table 2) characteristic of an alkylphosphonic difluoride.

TABLE 2.

$^{31}\text{P}$  n.m.r. data for some fluorides of phosphonic and phosphinic acids.

Compound	$J_{\text{P-F}}$ (c./sec.)	$\delta$ (p.p.m.)
"EtPClF" (refs. 2, 7) .....	1140	$-26 \pm 2$
EtPOF <sub>2</sub> .....	1130	$-29.2$
Bu <sup>n</sup> POF <sub>2</sub> .....	1140	$-29.3$
i-C <sub>2</sub> H <sub>11</sub> POF <sub>2</sub> .....	1135	$-27.2$
ClCH <sub>2</sub> POF <sub>2</sub> .....	1142	$-12.0$
PhPOF <sub>2</sub> .....	1115	$-11.4$
Me <sub>2</sub> POF .....	990	$-66.3$
Ph <sub>2</sub> POF .....	1020	$-40.0$

The identity of "EtPClF" with the known EtPOF<sub>2</sub><sup>11</sup> is further suggested by the similarity of some of the physical properties (boiling point of "EtPClF" 102°, and of EtPOF<sub>2</sub> 109°; melting points  $-63$  and  $-51^\circ$  to  $-50^\circ$ , respectively. Furthermore, the infrared spectra of "EtPClF"<sup>7</sup> and EtPOF<sub>2</sub><sup>11</sup> are superimposable. No distinction between EtPClF and EtPOF<sub>2</sub> can be made on the basis of an analysis for carbon, hydrogen, and phosphorus.

Finally, it is suggested that the compound "EtPF·OPri"<sup>2,7</sup> is actually the phosphonofluoridate, EtP(O)F·OPri. This is strongly indicated by a comparison of the  $^{31}\text{P}$  n.m.r. data for the latter compound, obtained by three independent methods, with the values reported for "EtPF·OPri"<sup>2,7</sup> (see Table 3).

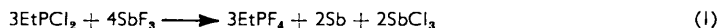
TABLE 3.

$^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r. data for isopropyl ethylphosphonofluoridate.

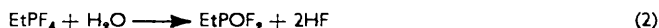
Method of preparation *	$^{19}\text{F}$		$^{31}\text{P}$	
	$J_{\text{P-F}}$ (c./sec.)	$\delta$ (p.p.m.)	$J_{\text{P-F}}$ (c./sec.)	$\delta$ (p.p.m.)
(a) .....	1062	$+66.0$	1040	$-30.7$
(b) .....	1065	$+65.0$	1060	$-30.2$
(c) .....	1062	$+66.0$	—	—
"EtPF·OPri" (refs. 2 and 7) ...	—	—	$\sim 1000$	$-29 \pm 3$

\* See Experimental section.

In the original work the reaction of ethyldichlorophosphine with antimony trifluoride was believed to have given both EtPClF and EtPF<sub>2</sub>. Reaction of the former with propan-2-ol gave what was believed to be EtPF·OPri. It is now proposed that the reaction was:



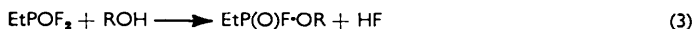
Traces of water (and/or glass) will convert ethyltetrafluorophosphorane into the phosphonic difluoride:



<sup>11</sup> Schmutzler, *J. Inorg. Nuclear Chem.*, 1963, **25**, 335.

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The phosphonic difluoride can react with alcohols to give ethylphosphonofluoridates:

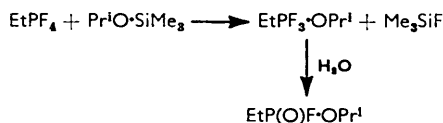


All three types of reaction, (1)—(3), are known to occur.<sup>8,9-11</sup> Thus, in the present work, one of the routes for making isopropyl ethylphosphonofluoridate followed reaction (3). Another preparation employed,

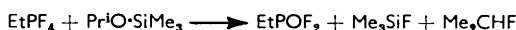


is also known in principle.

As a possible third route to isopropyl ethylphosphonofluoridate, the reaction between ethyltetrafluorophosphorane and isopropyl trimethylsilyl ether was considered, the following being expected:

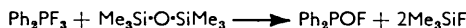


It was known from previous work<sup>8c</sup> that Lewis-acid phosphorus fluorides such as phenyltetrafluorophosphorane are capable of splitting oxygen bridges, *e.g.*, in acid anhydrides or disiloxanes. In the above case, a smooth reaction occurred, which proceeded to a large extent (<90%) according to the following stoichiometry:



Only a minute amount of the phosphonofluoridate was obtained, and ethylphosphonic difluoride was isolated in over 90% yield. Cleavage of the Si-O as well as the O-C bond in the silyl ether is apparent from the formation of trimethylfluorosilane and 2-fluoropropane as the only other products. Both compounds were readily characterized by their <sup>19</sup>F n.m.r. spectra (see Experimental section).

It is of interest, in this connection, that diphenylphosphinic fluoride,<sup>11</sup> Ph<sub>2</sub>POF, could be obtained by a similar route, involving cleavage of the Si-O-Si bridge in hexamethyl-disiloxane by diphenyltrifluorophosphorane:



In accordance with the reduced Lewis-acid strength of diphenyltrifluorophosphorane, compared to phenyltetrafluorophosphorane,<sup>8c</sup> the reaction was much less vigorous than with the latter. Nevertheless, a quantitative conversion of Ph<sub>2</sub>PF<sub>3</sub> into Ph<sub>2</sub>POF was achieved upon refluxing the fluorophosphorane with a slight molar excess of the disiloxane for 16 hours.

Although the three phosphorus-fluorine compounds under discussion have been identified as containing quinquevalent phosphorus, a check on a series of authentic fluorides of trivalent phosphorus, (RO)<sub>n</sub>PF<sub>3-n</sub> and (R<sub>2</sub>N)<sub>n</sub>PF<sub>3-n</sub> (*n* = 1 or 2), still reveals large deviations, and the data cannot be considered sufficiently meaningful as a criterion for a given type of compound.

A more detailed discussion of <sup>31</sup>P chemical shifts, and further information on the <sup>19</sup>F n.m.r. spectra of various types of phosphorus-fluorine compound, including fluorides of phosphonic and phosphinic acid, and fluorophosphoranes, will be published separately.<sup>12</sup>

#### EXPERIMENTAL

The usual precautions required in handling moisture-, and, sometimes, air-sensitive phosphorus compounds were observed.

<sup>31</sup>P and <sup>19</sup>F n.m.r. spectra were obtained on a Varian Associates n.m.r. spectrometer model 4300 B, with a 12-in. electromagnet with flux-stabilization. Non-spinning 10-mm. tubes were

<sup>12</sup> Nixon and Schmutzler, unpublished results.

used for the  $^{31}\text{P}$  spectra, and 5-mm. spinning tubes for the  $^{19}\text{F}$  spectra.  $^{31}\text{P}$  spectra were obtained at 16.2 and  $^{19}\text{F}$  spectra at 40 Mc./sec., with a magnetic field of 9400 gauss.

Sealed capillaries containing 85% phosphoric acid were inserted into the phosphorus n.m.r. tubes as a reference, and trichlorofluoromethane was used as an internal standard for the  $^{19}\text{F}$  spectra. The data presented are based on one or the other of these.

Spectra were recorded both at increasing and decreasing field; the data reported are the averages from 2—10 measurements. Undiluted samples were used throughout. Calibration of spectra was effected by superimposing an audiofrequency on the sweep field to produce sidebands to the  $\text{H}_3\text{PO}_4$  or  $\text{CFCl}_3$  reference.<sup>13</sup>

*Preparation of Fluorophosphoranes.*—These have all been described.<sup>8b,c, 14</sup>

*Preparation of Fluorides of Phosphonic and Phosphinic Acid.*—Most of the compounds were available from previous studies.<sup>11</sup> The following compounds were prepared by modified or new procedures.

*Chloromethylphosphonic difluoride.*<sup>11</sup> Hexamethyldisiloxane was added dropwise with ice-cooling and stirring to chloromethyltetrafluorophosphorane<sup>8c</sup> in a slightly more than 1 : 1 molar ratio.<sup>8c</sup> Trimethylfluorosilane escaped, and the phosphonic difluoride was left as a higher-boiling residue which was used directly in the spectroscopic measurements.

*Ethylphosphonic difluoride.*<sup>11</sup> With exclusion of moisture, antimony trifluoride (60 g., 0.34 mole) was added with stirring to ethylphosphonic dichloride<sup>15</sup> (76 g., 0.52 mole) at an inner temperature not exceeding 50° (0.5 g.). The crude product was recovered by vacuum distillation, b. p. 50—70°/60—70 mm. A check by  $^{19}\text{F}$  and  $^{31}\text{P}$  n.m.r., revealed, besides the desired  $\text{EtPOF}_2$ , <10% of  $\text{EtO}\cdot\text{POF}_2$ . Contamination of the starting  $\text{EtPOCl}_2$  with  $\text{EtO}\cdot\text{POCl}_2$  ( $\delta_{\text{P}} = -4.0$  p.p.m.) had been detected previously by  $^{31}\text{P}$  n.m.r. The following data were obtained for  $\text{EtO}\cdot\text{POF}_2$ .  $^{31}\text{P}$  n.m.r.:  $J_{\text{P-F}} = 1014$  c./sec.;  $\delta = +20.2$  p.p.m. (lit.,<sup>16</sup> 1010 and +21.2);  $^{19}\text{F}$  n.m.r.:  $J_{\text{P-F}} = 1008$  c./sec.;  $\delta = +85.0$  p.p.m. ( $\text{PhO}\cdot\text{POF}_2$ :<sup>6</sup> 1027 and +84.1). The  $\text{EtO}\cdot\text{POF}_2$  impurity was readily removed by fractional distillation, to yield ethylphosphonic difluoride (43.4 g., 73%), b. p. 110—111°,  $n_{\text{D}}^{20}$  1.3376. These data are in agreement with previous values.<sup>11</sup>

*n-Butylphosphonic difluoride.*<sup>11</sup> This was obtained by fluorination of the chloride with antimony trifluoride, and was used without further separation and purification.

*n-Pentylphosphonic difluoride.* n-Pentylphosphonic dichloride (8g., 0.042 mole) was fluorinated with antimony trifluoride (7.15 g., 0.04 mole), as described for  $\text{EtPOF}_2$ . The product (4.9 g., 75%) had b. p. 68—70°/15 mm. (Found: C, 37.2; H, 7.3.  $\text{C}_5\text{H}_{11}\text{F}_2\text{OP}$  requires C, 38.5; H, 7.1%).

*Phenylphosphonic difluoride.*<sup>11</sup> This was prepared in an entirely analogous manner from phenylphosphonic dichloride (19.5 g., 0.1 mole) and antimony trifluoride (18 g., 0.1 mole), b. p. 78°/15 mm.,  $n_{\text{D}}^{20}$  1.4680 (lit.,<sup>11</sup> b. p. 69°/10 mm.,  $n_{\text{D}}^{20}$  1.4669).

*Diphenylphosphinic fluoride.*<sup>11</sup> No exothermic interaction was noted when diphenyltrifluorophosphorane<sup>8b,c</sup> (12.1 g., 0.05 mole) was added dropwise with stirring to hexamethyldisiloxane (12.2 g., 0.075 mole). A volatile product, solidifying in a  $-78^\circ$  trap, was formed in gradually increasing amount upon refluxing the mixture for 18 hr. The cooling water in the reflux condenser was held at  $50 \pm 10^\circ$  during this heating period. A total of 7.2 g. (78%) of gas was collected, and identified as pure trimethylfluorosilane from its infrared spectrum<sup>17</sup> (10-cm. cell; 10-mm. gas pressure). Distillation of the residue at atmospheric pressure gave 3.1 g. (76% based on excess of siloxane employed) of unreacted hexamethyldisiloxane, b. p. 99—102°, identified by its refractive index.

A  $^{31}\text{P}$  n.m.r. check on the higher-boiling residue indicated that no unreacted diphenyltrifluorophosphorane was present. Distillation gave diphenylphosphinic fluoride (9.9 g., 90%), b. p. 132°/0.15 mm.,  $n_{\text{D}}^{20}$  1.3780 (Found: P, 14.1. Calc. for  $\text{C}_{12}\text{H}_{10}\text{FOP}$ : P, 14.1%).

*Isopropyl Ethylphosphonofluoridate.*—Phosphonofluoridates are powerful anticholinesterase agents.<sup>18</sup> Therefore, careful precautions against any effects caused by the potential toxicity of isopropyl ethylphosphonofluoridate were taken during its preparation.

<sup>13</sup> Arnold and Packard, *J. Chem. Phys.*, 1951, **19**, 1608.

<sup>14</sup> Schmutzler, *Inorg. Chem.*, 1964, **3**, 421.

<sup>15</sup> Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme Verlag, Stuttgart, 1963, Vol. XII, Part 1, p. 388.

<sup>16</sup> Moedritzer, Maier, and Groenweghe, *J. Chem. and Eng. Data*, 1962, **7**, 307.

<sup>17</sup> Kriegsmann, *Z. anorg. Chem.*, 1958, **294**, 113.

<sup>18</sup> Saunders, "Some Aspects of the Chemical and Toxicological Action of Organic Compounds containing Phosphorus and Fluorine," Cambridge University Press, 1957.

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(a) *Reaction of ethylphosphonic dichloride with sodium fluoride-propan-2-ol.* Ethylphosphonic dichloride<sup>15</sup> (44.1 g., 0.3 mole) in benzene (35 ml.) was added dropwise with stirring to a suspension of sodium fluoride (58.8 g., 1.4 mole) (dried at 500° for 20 hr.) in benzene (100 ml.) and propan-2-ol (25.3 g., 0.42 mole) at 70–80°. Stirring at a temperature slightly below reflux was continued for 2 hr. after the addition was complete. The mixture was filtered and the filtrate distilled, first to remove the benzene solvent. The higher-boiling product was distilled *in vacuo* through a 20-cm. Vigreux column. A colourless liquid (36 g., 78%) was obtained, which was characterized by its <sup>31</sup>P and <sup>19</sup>F n.m.r. spectra. Both spectra revealed a 10–15% content of diethyl phosphorofluoridate, (EtO)<sub>2</sub>POF, whose formation is due to the presence of some EtO·POCl<sub>2</sub> in the starting ethylphosphonic dichloride. Diethyl phosphorofluoridate could not be separated from isopropyl ethylphosphonofluoridate by fractional distillation. N.m.r. data: <sup>31</sup>P,  $J_{P-F} = 960$  c./sec.,  $\delta = +11.0$  p.p.m.; <sup>19</sup>F, 970 and +77.5, respectively. The <sup>19</sup>F data agree with those found<sup>6</sup> for authentic (EtO)<sub>2</sub>POF.

(b) *Reaction of ethylphosphonic difluoride with propan-2-ol in the presence of triethylamine.* To ethylphosphonic difluoride (11.4 g., 0.1 mole) in benzene (20 ml.) was added with stirring a mixture of propan-2-ol (7.5 g., 0.125 mole) and triethylamine (10.1 g., 0.1 mole) (dried over P<sub>4</sub>O<sub>10</sub>). A mildly exothermic reaction occurred, and the temperature was held between 10 and 15° by cooling with ice. A precipitate was formed, which was filtered off after the mixture had been allowed to stand overnight. The filtrate was fractionally distilled through a 20-cm. Vigreux column. After removal of the benzene solvent, the product (13.2 g., 84%), b. p. 74°/16 mm., was collected. Both <sup>31</sup>P and <sup>19</sup>F n.m.r. spectra showed the product to be identical with isopropyl ethylphosphonofluoridate prepared as described under (a), and indicated that no other phosphorus- or fluorine-containing species was present (Found: C, 39.4; H, 7.5. Calc. for C<sub>5</sub>H<sub>12</sub>FO<sub>2</sub>P: C, 39.7; H, 8.1%).

In view of the expected toxicity, no further analytical characterization was undertaken. The identity of the products obtained according to (a) or (b) was further confirmed by a comparison of their infrared spectra (pure liquids), strong absorptions being observed at 1290 (P=O), 1010–1020 (P–O–C aliphatic), and 850 cm.<sup>-1</sup> (P–F). These data agree well with those for the related MePO(F)·OPr<sup>i</sup>,<sup>19</sup> for instance, 1285 (P=O), 842 cm.<sup>-1</sup> (P–F).

(c) *Reaction of isopropyl trimethylsilyl ether with ethyltetrafluorophosphorane.* Trimethylchlorosilane (57.5 g., 0.53 mole) was gradually added with stirring to propan-2-ol (30.05 g., 0.5 mole) and dimethylaniline (66.7 g., 0.55 mole). A mildly exothermic reaction occurred, and the dense precipitate formed was filtered off and washed with ether. The filtrate was fractionally distilled through a 30-cm. Vigreux column. Isopropyl trimethylsilyl ether (31 g., 47%) was obtained as a colourless liquid, b. p. 87°,  $n_D^{20} 1.3794$  (lit.,<sup>20</sup> b. p. 88°,  $n_D^{20} 1.3788$ ).

The reaction of the ether with the phosphorane was conducted in a 50-ml. two-necked flask equipped with a dropping funnel with side-arm, and a water-cooled reflux condenser, topped by a solid-carbon dioxide condenser, the latter being protected by a drying tube. A vigorous reaction occurred upon dropwise addition of ethyltetrafluorophosphorane (8.16 g., 0.06 mole) to the silyl ether, and the reaction was controlled by cooling with ice. After the addition was completed (0.5 hr.) material volatile at a bath temperature of 40–50° was driven off, and a colourless liquid (8.7 g.) was collected in a –78° trap. Two major and one minor product were detected by gas chromatography. Characterization was by <sup>19</sup>F n.m.r., the components being identified as follows. Me<sub>3</sub>SiF (ca. 45%):  $\delta_F = +157.2$  p.p.m.;  $J_{F-H} = ca. 8$  c./sec. Eight of the expected ten lines, due to F–H coupling are readily distinguished. Me<sub>2</sub>( $\beta$ )CH( $\alpha$ )F (ca. 35%):  $\delta_F = +164.0$  p.p.m.;  $J_{F-H\alpha} = 54.5$  c./sec.;  $J_{F-H\beta} = 25.5$  c./sec. A basic doublet ( $J_{F-H\alpha}$ ) is further split into two overlapping septets by equal coupling of fluorine with the six  $\beta$ -protons. 2-Fluoropropane is a known compound.<sup>21</sup> EtPF<sub>4</sub> (ca. 20%):  $J_{P-F} = 972$  c./sec.;  $\delta_F = 50.6$  p.p.m. EtPOF<sub>2</sub> (<1%):  $J_{P-F} = 1132$  c./sec.;  $\delta_F = 67.5$  p.p.m. There was only a trace of the phosphonic difluoride, which was probably formed in the n.m.r. tube.

The higher-boiling product which remained after removal of the volatile components, was also checked by <sup>19</sup>F n.m.r., and was found to contain two components. EtPOF<sub>2</sub> (ca. 95%):  $J_{P-F} = 1130$  c./sec.;  $\delta_F = 68.6$  p.p.m. EtP(O)F·OPr<sup>i</sup> (ca. 5%):  $J_{P-F} = 1060$  c./sec.;  $\delta_F = 66.0$  p.p.m. Distillation of the higher-boiling product through a 4-in. Vigreux microstill gave

<sup>19</sup> Larsson, *Arkiv Kemi*, 1958, **13**, 259.

<sup>20</sup> Abel, *J.*, 1961, 4933.

<sup>21</sup> Sweeney and Woolf (to Allied Chemical Corp.), U.S.P. 2,917,559/1959.

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pure ethylphosphonic difluoride (5.9 g., 86%), b. p. 109°,  $n_D^{20}$  1.3356 (lit.,<sup>11</sup> b. p. 53°/100 mm.,  $n_D^{25}$  1.3365).

The stoichiometry of the reaction is thus established.

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