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## Phosphorus-Fluorine Chemistry. IV. The Reaction of Chlorophosphines with Group V Fluorides: Synthesis of Fluorophosphoranes<sup>1a</sup>

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The reaction of chlorophosphines,  $R_n\text{P}\text{Cl}_{3-n}$ , with arsenic or antimony trifluoride provides a simple route to fluorophosphoranes,  $R_n\text{P}\text{F}_{3-n}$  ( $n = 1$  or  $2$ ). The syntheses of a variety of fluorophosphoranes and some of their properties are reported. The behavior of antimony trifluoride toward dialkylaminodichlorophosphines, alkyl- or arylchlorophosphites, and dihaloarsines has also been studied.

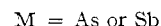
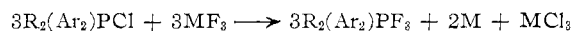
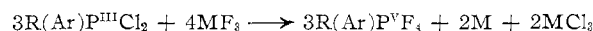
### Introduction

A few years ago, a new type of phosphorus fluoride, derived from phosphorus pentafluoride by substitution of fluorine atoms with organic hydrocarbon groups, was first referred to in the patent literature.<sup>2</sup> Since then, several methods of synthesis of these "fluorophosphoranes,"  $R_n\text{P}\text{F}_{5-n}$  ( $n = 1-3$ ) have been reported, including: (a) fluorination of the complexes  $[\text{R}\text{P}\text{Cl}_3]\text{-}[\text{AlCl}_4]$  and  $[\text{R}_2\text{P}\text{Cl}_2][\text{AlCl}_4]$  with hydrogen fluoride, alkali fluorides, and arsenic or antimony trifluoride<sup>3,3</sup>; (b) fluorination of dichlorophosphines with antimony pentafluoride or a mixture of antimony trifluoride with a stoichiometric amount of antimony pentachloride<sup>4</sup>; (c) oxidative chlorination of dichlorophosphines and fluorination of the resulting tetrachlorophosphoranes with antimony trifluoride<sup>3,5</sup>; and (d) reaction of phosphonic or phosphinic acids, phosphonic difluorides, and phosphine oxides with sulfur tetrafluoride under autogenous pressure.<sup>6</sup> In the course of a study of the synthesis and coordination chemistry of fluorophosphines,  $R_n\text{P}\text{F}_{3-n}$  ( $n = 1, 2$ ), oxidation-reduction reactions were encountered when various reagents were employed in the fluorination of chlorophosphines, and compounds containing pentavalent phosphorus, instead of the expected fluorophosphines, were frequently obtained.<sup>7-10</sup>

### Results and Discussion

Most interesting was the reaction of chlorophosphines with trifluorides of group V elements, such as  $\text{AsF}_3$  or  $\text{SbF}_3$ , the former being expected particularly advan-

tageous in that it would permit a fluorination in a liquid-liquid system. Vigorous interaction was noted indeed upon contact of chlorophosphines with these fluorinating agents. The reaction mixtures were found to turn dark rapidly due to precipitation of elemental arsenic or antimony, respectively. The fluorination products were not the expected fluorophosphines ( $R_n\text{P}\text{F}_{3-n}$ ) but the corresponding fluorophosphoranes ( $R_n\text{P}\text{F}_{5-n}$ ), and the following stoichiometry for this very general type of oxidation-reduction reaction was established



The above stoichiometry was further confirmed by the isolation and identification of elemental arsenic or antimony in nearly quantitative yields. Mono- and dichlorophosphines in most instances reacted smoothly with  $\text{AsF}_3$  or  $\text{SbF}_3$  to give tri- and tetrafluorophosphoranes, the choice of the fluorinating agent depending only on the respective boiling points of starting materials and products. Thus, in the case of the low boiling fluorophosphoranes, antimony trifluoride was the preferred reagent (b.p. of  $\text{SbCl}_3$   $224^\circ$ ) while arsenic trifluoride was employed in the preparation of higher boiling compounds (b.p. of  $\text{AsCl}_3$   $130.5^\circ$ ). Fluorophosphoranes were obtained from chlorophosphines regardless of whether the chlorophosphine or the fluoride was employed in excess over the other reactant.

The results obtained upon fluorination of nearly twenty chlorophosphines with arsenic or antimony trifluoride (*cf.* Tables I and II) suggest that the above type of oxidation-reduction reaction is very general and that most any fluorophosphorane is accessible, if the respective chlorophosphine is known. This may also apply, for instance, to the as yet unknown bis-tetrafluorophosphoranes,  $\text{F}_4\text{P}(\text{CH}_2)_n\text{PF}_4$ . Some of the required starting compounds of the type  $\text{Cl}_2\text{P}(\text{CH}_2)_n\text{-PCl}_2$  became available recently,<sup>11</sup> and a single, small-scale experiment on the reaction of  $\text{Cl}_2\text{P}(\text{CH}_2)_6\text{PCl}_2$  with  $\text{SbF}_3$  was conducted. Although 95% of the

(1) (a) Preceding paper in this series: R. Schmutzler, *Chem. Ind. (London)*, 1868 (1962); (b) University Chemical Laboratory, Cambridge, England.

(2) H. Coates and P. R. Carter (to Great Britain Ministry of Supply), British Patent 734,187 (July 27, 1955); U. S. Patent 2,853,515 (Sept. 23, 1958).

(3) I. P. Komkov, S. Z. Ivin, K. W. Karavanov, and L. E. Smirnov, *Zh. Obshch. Khim.*, **32**, 301 (1962).

(4) W. C. Smith (to E. I. du Pont de Nemours and Company, Inc.), U. S. Patent 2,904,588 (Sept. 15, 1959).

(5) (a) L. M. Yagupol'skii and Zh. M. Ivanova, *Zh. Obshch. Khim.*, **29**, 3766 (1959); (b) *ibid.*, **30**, 4026 (1960).

(6) (a) W. C. Smith (to E. I. du Pont de Nemours and Company, Inc.), U. S. Patent 2,950,306 (Aug. 23, 1960); (b) W. C. Smith, *J. Am. Chem. Soc.*, **82**, 6176 (1960).

(7) F. Seel, K. Ballreich, and R. Schmutzler, *Chem. Ber.*, **94**, 1173 (1961).

(8) F. Seel, K. Ballreich, and R. Schmutzler, *ibid.*, **95**, 199 (1962).

(9) R. Schmutzler, *J. Inorg. Nucl. Chem.*, **25**, 335 (1963).

(10) R. Schmutzler, *Advances in Chemistry Series*, No. 37. American Chemical Society, Washington, D. C., 1963, p. 150.

(11) M. Sander, *Chem. Ber.*, **95**, 473 (1962); the author is indebted to Dr. Sander for providing a sample of the intermediate hexamethylene-1,6-bis-diethylphosphinite.

stoichiometric amount of elemental antimony was found, the bis-tetrafluorophosphorane could not be isolated. There can be no doubt, however, that bis-tetrafluorophosphoranes may be obtained by this route.

A compound of special interest in view of its stereochemistry<sup>12</sup> is cyclotetramethylenetrifluorophosphorane,  $C_4H_8PF_3$ , which could be obtained from the recently reported chlorophosphine,  $C_4H_8PCl$ . The structure of  $C_4H_8PF_3$  could be confirmed by its synthesis using an entirely different route.<sup>13</sup>

In further experiments it was established that dihaloarsines will react with antimony trifluoride to give difluoroarsines, without an indication of an oxidation-reduction reaction.<sup>14</sup> Methyl-diiodoarsine and phenyldichloroarsine both could be fluorinated to the previously described difluoroarsines.<sup>15</sup> It is noteworthy that methyl-diiodoarsine reacted smoothly with antimony trifluoride whereas the same reagent, with or without catalysts, has been reported to be without action on methyl-dichloroarsine at  $100^\circ$ .<sup>15</sup>

It was also obvious in this connection to investigate the reaction of  $AsF_3$  or  $SbF_3$  with other substitution products of  $PCl_3$ , such as chlorophosphites,  $(RO)_nPCl_{3-n}$ , or dialkylaminochlorophosphines,  $(R_2N)_nPCl_{3-n}$ . No evidence for oxidation-reduction reactions leading to fluorophosphoranes of the composition  $(RO)_nPF_{5-n}$  or  $(R_2N)_nPF_{5-n}$  was obtained.<sup>16</sup>

On the basis of these observations, some conclusions may be drawn as to the generality of the reaction between chlorophosphines and group V trifluorides: electron-donating substituents in the chlorophosphine, e.g., in  $R_2PCl$  compounds, particularly seem to promote the oxidation-reduction reaction, which occurs somewhat less readily in dichlorophosphines such as  $C_6H_5PCl_2$ , and does not take place at all in certain halophosphines containing strongly electronegative perfluoroalkyl substituents. Formation of fluorophosphines as the only products was observed upon reaction of  $CF_3PI_2$ ,<sup>17</sup>  $(CF_3)_2PI$ ,<sup>17,18</sup> and  $CF_2=CFPCl_2$  and  $(CF_2=CF)_2PCl$ <sup>19</sup> with antimony trifluoride. It may also be noted that during the present study a chlorophosphine,  $ClCH_2PCl_2$ , was found to be fluorinated smoothly by  $SbF_3$  to the corresponding fluorophosphine,  $ClCH_2PF_2$ ,<sup>10</sup> a liquid spontaneously flammable in the atmosphere. The fluorophosphorane,  $ClCH_2PF_4$ , could be obtained only upon fluorination

of  $ClCH_2PCl_2$  with  $SbF_5$ . This example is particularly illustrative in that the closely related compound  $CH_3PCl_2$  under the same conditions reacted smoothly to form  $CH_3PF_4$ .

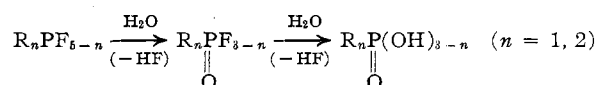
The presence of at least one chlorine atom bonded to trivalent phosphorus seems to be a requirement to bring about a facile oxidation of the phosphorus to the pentavalent state. A very slow reaction between a tertiary aliphatic phosphine such as  $(n-C_4H_9)_3P$  and  $SbF_3$  with precipitation of elemental antimony was also noted, but it is uncertain if  $(n-C_4H_9)_3PF_2$  was produced in this reaction.

### Properties of Fluorophosphoranes

Except for methyltetrafluorophosphorane, being a gas of b.p.  $10^\circ$ , all fluorophosphoranes described in this paper were distillable, colorless liquids, no evidence for disproportionation during distillation being observed. The boiling points of tetrafluorophosphoranes were normally found ca.  $80^\circ$  lower than those of the corresponding dichlorophosphines, whereas trifluorophosphoranes had boiling points ca.  $20^\circ$  lower than the monochlorophosphines.

All fluorophosphoranes could be handled in glass apparatus, but slow attack on glass was apparent in many instances, even under strictly anhydrous conditions, particularly on prolonged storage in glass. The compounds could be stored unchanged indefinitely in stainless steel or Teflon containers.

Most of the fluorophosphoranes readily undergo reaction with water, the first step of hydrolysis being the phosphonic or phosphinic fluoride, respectively, which, under more vigorous conditions or over longer periods, will be converted into the corresponding phosphonic or phosphinic acid



Tetrafluorophosphoranes and dialkyltrifluorophosphoranes were found to hydrolyze most readily, although a compound such as *i*- $C_8H_{16}PF_4$  proved to be comparatively more stable than fluorophosphoranes containing lower alkyl groups. Dialkyltrifluorophosphoranes are particularly subject to hydrolysis, whereas diphenyltrifluorophosphorane could be stored unchanged in glass over extended periods. The formation of phosphonic or phosphinic fluorides as the first step in the hydrolysis was frequently observed upon the preparation of fluorophosphoranes, if moisture was not rigorously excluded. A number of these compounds have been characterized and described.<sup>9</sup> The hydrolysis of fluorophosphoranes to give largely the phosphonic or phosphinic fluorides could be effected at controlled temperatures, preferably below  $0^\circ$ . More vigorous conditions lead to the formation of the corresponding acids, providing further proof that the trivalent phosphorus in the starting chlorophosphine had been oxidized to the pentavalent state during the fluorination.

(12) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(13) R. Schmutzler, *Inorg. Chem.*, **3**, 421 (1964).

(14) The only organoarsenic(V) fluoride known is  $C_6H_5AsF_4$ , obtained from the arsonic acid and sulfur tetrafluoride.<sup>6a,b</sup>

(15) L. H. Long, H. J. Emeléus, and H. V. A. Briscoe, *J. Chem. Soc.*, 1123 (1946).

(16) For more detailed reports on synthesis, properties, and coordination chemistry of fluorophosphites and dialkylaminodifluorophosphines, see R. Schmutzler, *Chem. Ber.*, **96**, 2435 (1963); R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

(17) V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii, *Zh. Obshch. Khim.*, **29**, 3957 (1959).

(18) (a) A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958);

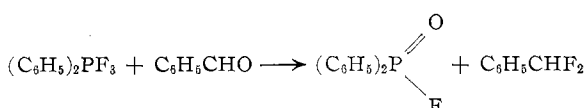
(b) A. B. Burg and G. Brendel (to American Potash & Chemical Corp.), U. S. Patent 2,959,820 (Nov. 8, 1960).

(19) R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1991 (1960).

An interesting observation in connection with an  $F^{19}$  n.m.r. study on fluorophosphoranes,<sup>12</sup> whose synthesis is based on substituted aromatic dichlorophosphines, was that these compounds invariably contain at least two isomers. The substituted aromatic dichlorophosphines were obtained from the corresponding hydrocarbon and phosphorus trichloride in the presence of aluminum chloride. The isomers were surprisingly identified as *para* and *meta*, in an approximate 7:3 ratio.<sup>9</sup>

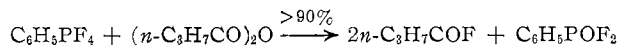
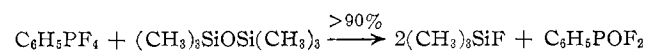
Some scouting experiments were undertaken on the chemistry of fluorophosphoranes, particularly of phenyltetrafluorophosphorane. There was some probability that fluorophosphoranes might resemble sulfur tetrafluoride<sup>20</sup> as a fluorinating agent while being liquids which can be handled conveniently at atmospheric pressure. It has also been reported that an organic derivative of sulfur tetrafluoride,  $C_6H_5SF_3$ , effected fluorination of carbonyl groups, thus acting as a "liquid sulfur tetrafluoride."<sup>21</sup>

Vigorous interaction was noted in almost every case when a variety of carbonyl compounds, mostly aldehydes or ketones, were allowed to react with phenyltetrafluorophosphorane or, in some instances, with diphenyltrifluorophosphorane. Polymerization seemed to be the predominant reaction in most instances and no evidence for a fluorination of carbonyl groups was found except for the system benzaldehyde-diphenyltrifluorophosphorane, where  $\alpha,\alpha$ -difluorotoluene was isolated in low yield



There was no evidence for a conversion of  $-COF$  into  $-CF_3$  groups by means of fluorophosphoranes.

The following reactions, involving cleavage of oxygen bridges, could be effected under mild conditions



Maleic anhydride upon 1-hr. interaction with phenyltetrafluorophosphorane at  $100^\circ$  did not give any maleic acid difluoride,<sup>20b</sup> but an 89% yield of phenylphosphonic difluoride was isolated after 10-hr. interaction of the same reactants. No maleic acid difluoride, however, was isolated in the latter case, and a presumably polymeric material was formed instead.

Succinic anhydride and phenyltetrafluorophosphorane, heated for 6 hr. at  $120$ – $140^\circ$ , formed succinic acid difluoride, but unreacted anhydride was still detected after this comparatively long reaction period. It is evident that the cyclic anhydride reacts much less readily with the fluorophosphorane than the open chain compound, butyric acid anhydride.

(20) (a) W. C. Smith (to E. I. du Pont de Nemours and Co., Inc.), U. S. Patent 2,859,245 (Nov. 4, 1958); (b) W. C. Smith, W. R. Hasek, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

(21) (a) W. A. Sheppard, *J. Am. Chem. Soc.*, **82**, 4751 (1960); (b) W. A. Sheppard, *ibid.*, **84**, 3058 (1962).

## Experimental

**General.**—Since most of the phosphorus and fluorine compounds employed were sensitive toward oxygen or moisture or both, experiments were conducted throughout in an atmosphere of dry nitrogen. Reaction systems were flushed with nitrogen or, in many instances, carefully evacuated and filled with nitrogen, the latter operation being done repeatedly. The apparatus used was protected toward the atmosphere with drying tubes.

Glass apparatus could be used throughout in these experiments, if the above conditions were observed. Distillation of fluorophosphoranes over sodium fluoride was found advantageous in removing traces of hydrogen fluoride. Most of the fluorophosphoranes, particularly those of the  $RPF_4$  series and dialkyltrifluorophosphoranes, attacked glass on standing, and Teflon bottles or stainless steel cylinders were used for the storage of fluorophosphoranes. Less reactive compounds could well be stored in glass bottles. Thus, diphenyltrifluorophosphorane was found unchanged after 2 years storage in a glass bottle.

**Materials.**—Sources of most of the starting materials are indicated in the tables. Arsenic and antimony trifluoride were employed as obtained from Ozark Mahoning Co. Antimony pentafluoride was used as obtained from Allied Chemical Co.

(A) **Preparation of Fluorophosphoranes from Chlorophosphines and Arsenic or Antimony Trifluoride.**—The compounds synthesized and the experimental conditions are given in Tables I and II. Some typical procedures are given below.

(a) **Phenyltetrafluorophosphorane.**—A 1-l. four-necked flask was equipped with a reflux condenser with a drying tube, a thermometer, a mechanical stirrer, and a hose-connected solid addition funnel. The latter was charged with 787 g. (4.4 moles) of antimony trifluoride, after the system had been flushed carefully with nitrogen. Phenylchlorophosphine (537 g., 3 moles) was placed in the flask, and the antimony trifluoride was added in small portions with stirring. An inner temperature of  $40$ – $50^\circ$  during the slightly exothermic reaction was maintained by controlling the rate of addition of the antimony trifluoride (2 hr.). After stirring the black mixture for 1 hr. at  $60^\circ$ , the fluorophosphorane was isolated by distillation *in vacuo*, 520 g. (94%) of material of b.p.  $60$ – $80^\circ$  (60 mm.) [mainly  $65^\circ$  (60 mm.)] being collected. The product was redistilled at atmospheric pressure through a 10-in. glass helix-packed column; b.p.  $134.5$ – $136^\circ$ . Phenyltetrafluorophosphorane is a colorless liquid, fuming in the atmosphere.

(b) **Diphenyltrifluorophosphorane.**—The apparatus used was similar to that above. A slightly exothermic reaction occurred when 185.5 g. (0.85 mole) of diphenylchlorophosphine was added dropwise with stirring to 170 g. (1.2 moles) of arsenic trifluoride. Black elemental arsenic was precipitated immediately. The addition being completed within 1 hr., the mixture was stirred for 5 hr. at *ca.*  $50^\circ$ . The more volatile products (arsenic trichloride, excess arsenic trifluoride) were removed *in vacuo* [*ca.*  $50^\circ$  (15 mm.)]. The residue was distilled through a 10-in. glass helix-packed column under high vacuum; 160 g. (77.6%) of colorless liquid of b.p.  $92$ – $93^\circ$  (0.4 mm.),  $n_D^{25}$  1.5425, being obtained.

(B) **Preparation of Chloromethyltetrafluorophosphorane.**—A 50-ml. three-necked flask was fitted with a combination of a water cooled reflux condenser and a Dry Ice condenser with a drying tube on top, a dropping funnel, and a thermometer. The system was evacuated and filled with nitrogen, and 30.2 g. (0.2 mole) of chloromethylchlorophosphine<sup>22</sup> was placed in the flask. Antimony pentafluoride (65.4 g., 0.3 mole) was added dropwise to the chlorophosphine with magnetic stirring, an extremely vigorous reaction taking place. By cooling with ice a temperature below  $50^\circ$  was maintained during the addition (2 hr.), and stirring was continued for another hour. Distillation at atmospheric pressure gave 26.0 g. (83.4%) of chloromethyltetrafluorophosphorane, b.p.  $47^\circ$ , which was once redistilled prior to analysis.

(22) E. Uhing, K. Rattenbury, and A. D. F. Toy *J. Am. Chem. Soc.* **83**, 2299 (1961).

TABLE I  
 ALKYL- AND ARYLTETRAFLUOROPHOSPHORANES

Compound	Reactants, moles	Reaction conditions, hr. (temp.)	Yield, %	B.p., °C. (mm.)	Analyses				Lit. ref.		
					C	H	F	P			
CH <sub>3</sub> PF <sub>4</sub>	CH <sub>3</sub> PCl <sub>2</sub> <sup>a</sup>	0.9	4.5 (≤15°)	36.8 <sup>b</sup>	10° <sup>c</sup>	Calcd.	...	...	...	2, 3	
	AsF <sub>3</sub>	1.5				Found	...	...	...		
	Benzene (35 ml.)										
C <sub>2</sub> H <sub>5</sub> PF <sub>4</sub>	CH <sub>3</sub> PCl <sub>2</sub>	1.5	30 <sup>b</sup>	10°	Calcd.	...	62.4	25.4			
	SbF <sub>3</sub>	2	4 (20°)		Found	...	59.4	23.3			
C <sub>2</sub> H <sub>5</sub> PF <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> PCl <sub>2</sub> <sup>d</sup>	0.5	4 (40°)	84	33–34°	Calcd.	17.6	3.7	55.9	22.8	3
	SbF <sub>3</sub>	2				Found	17.1	3.0	55.7	23.3	
<i>n</i> -C <sub>4</sub> H <sub>9</sub> PF <sub>4</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub> PCl <sub>2</sub> <sup>e</sup>	0.1	1 (40°)	68.5	85–86°	Calcd.	29.3	5.5	46.3	18.9	...
	SbF <sub>3</sub>	0.15	2 (60–80°)			Found	29.2	5.1	43.1 <sup>f</sup>	18.7	
<i>i</i> -C <sub>8</sub> H <sub>15</sub> PF <sub>4</sub>	<i>i</i> -C <sub>8</sub> H <sub>15</sub> PCl <sub>2</sub> <sup>g</sup>	0.2	5 (100°)	65.6	43° (9)	Calcd.	44.0	6.9	...	14.2	4
	SbF <sub>3</sub>	0.33			<i>n</i> <sup>24, 25</sup> D 1.3931	Found	44.4	7.0	...	14.1	
C <sub>6</sub> H <sub>5</sub> PF <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> PCl <sub>2</sub> <sup>h</sup>	3	2 (40°)	94	58° (60)	Calcd.	39.2	2.8	...	...	4–6
	SbF <sub>3</sub>	4.4	1 (60°)		134.5–136°	Found	39.1	2.7	...	...	
CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> ·PF <sub>4</sub> ( <i>m</i> , <i>p</i> ) <sup>i</sup>	CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> ·PCl <sub>2</sub> <sup>i</sup>	0.3	5 (≤100°)	80	44° (4)	Calcd.	42.5	3.5	38.4	15.7	5a
	SbF <sub>3</sub>	0.5				Found	42.6	3.7	38.2	15.8	
(CH <sub>3</sub> ) <sub>2</sub> CH·C <sub>6</sub> H <sub>4</sub> ·PF <sub>4</sub> ( <i>m</i> , <i>p</i> )	(CH <sub>3</sub> ) <sub>2</sub> CH·C <sub>6</sub> H <sub>4</sub> ·PCl <sub>2</sub> <sup>i</sup>	0.1	1 (60°)	21.6	84–85.5° (18)	Calcd.	47.8	4.9	33.6	13.7	...
	AsF <sub>3</sub>	0.15	Overnight (20°)			Found	47.7	4.7	32.8	14.0	
	(CH <sub>3</sub> ) <sub>2</sub> CH·C <sub>6</sub> H <sub>4</sub> ·PCl <sub>2</sub>	0.15	3 (60°)	61.5	64° (8)	Calcd.	47.8	4.9	33.6	13.7	
2.5(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ·PF <sub>4</sub>	2.5(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ·PCl <sub>2</sub> <sup>m</sup>	0.15	1.5 (50°)	85	56° (9)	Calcd.	45.3	4.3	33.8	14.6	...
	SbF <sub>3</sub>	0.23				Found	44.9	4.5	31.9 <sup>f</sup>	14.7	
	CH <sub>3</sub> O·C <sub>6</sub> H <sub>4</sub> ·PCl <sub>2</sub> <sup>k</sup>	0.1	3 (60–80°)	24.4	95–96° (20)	Calcd.	39.2	3.3	...	14.5	
CH <sub>3</sub> O·C <sub>6</sub> H <sub>4</sub> ·PF <sub>4</sub> ( <i>m</i> , <i>p</i> )	AsF <sub>3</sub> <sup>l</sup>	0.19				Found	39.5	3.1	...	14.6	
	Cl·C <sub>6</sub> H <sub>4</sub> ·PF <sub>4</sub> ( <i>m</i> , <i>p</i> )	Cl·C <sub>6</sub> H <sub>4</sub> ·PCl <sub>2</sub> <sup>h</sup>	0.2	1 (40°)	68.6	49° (9)	Calcd.	33.0	1.8	34.8	14.2
SbF <sub>3</sub>	0.3	1 (60–70°)			Found	31.9	2.1	33.9	14.4		
C <sub>6</sub> H <sub>5</sub> ·CH=CH·PF <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> ·CH=CH·PCl <sub>2</sub> <sup>g</sup>	0.2	2 (70°)	70.7	97.5–98° (23)	Calcd.	45.7	3.4	36.2	14.7	...
	AsF <sub>3</sub>					Found	44.8	3.8	35.7	14.9	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> PF <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> PCl <sub>2</sub> <sup>n, o</sup>	0.1	1.5 (60–80°)	38	53° (15)	Calcd.	42.4	3.6	38.4	15.6	...
	SbF <sub>3</sub>	0.15				Found	42.4	3.7	37.1 <sup>f</sup>	15.8	

<sup>a</sup> Army Chemical Center, Maryland. <sup>b</sup> The low yield of CH<sub>3</sub>PF<sub>4</sub> in both preparations is due to mechanical losses. From the amount of elemental arsenic or antimony, respectively, it can be concluded that the reaction in both cases was nearly complete. <sup>c</sup> CH<sub>3</sub>PF<sub>4</sub> was distilled through a 20-in. helix-packed low temperature column. Due to difficulties on chemical analysis of the volatile, moisture-sensitive material it was characterized by mass spectroscopy, some of the most indicative fragments being (relative intensities in parentheses): *m/e* = 107 (100): PF<sub>4</sub><sup>+</sup>; 103 (58.3): CH<sub>3</sub>PF<sub>3</sub><sup>+</sup>; 15 (19.7): CH<sub>3</sub><sup>+</sup>. <sup>d</sup> I. P. Komkov, K. W. Karavanov, and S. Z. Ivin, *Zh. Obshch. Khim.*, **28**, 2963 (1958). <sup>e</sup> M. Sander, *Chem. Ber.*, **93**, 1220 (1960). <sup>f</sup> Fluorine analyses in several cases should be obtained only after prolonged storage of the extremely hygroscopic compounds and were, consequently, found low. <sup>g</sup> E. N. Walsh, T. M. Beck, and W. H. Woodstock, *J. Am. Chem. Soc.*, **77**, 929 (1955). <sup>h</sup> Victor Chemical Works, technical grade. <sup>i</sup> B. Buchner and L. G. Lockart, *J. Am. Chem. Soc.*, **73**, 755 (1951). <sup>j</sup> The procedure described for the synthesis of substituted aromatic dichlorophosphines<sup>j</sup> invariably leads to mixtures of *meta* and *para* isomers,<sup>9</sup> which in the corresponding fluorophosphoranes are readily distinguished by their F<sup>19</sup> n.m.r. spectra (E. L. Muetterties, personal communication). <sup>k</sup> W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 276 (1944). <sup>l</sup> CH<sub>3</sub>O·C<sub>6</sub>H<sub>4</sub>PF<sub>4</sub> could also be obtained when antimony trifluoride was employed as a fluorinating agent, but separation of products was more difficult since the boiling points of SbCl<sub>3</sub> and the fluorophosphorane are close. <sup>m</sup> A. Michaelis and C. Panek, *Ann.*, **212**, 203 (1882). <sup>n</sup> Prepared from benzyl chloride and white phosphorus under autogenous pressure at 300° according to the directions of K. A. Petrov, V. V. Smirnov, and V. I. Yemeljanov, *Zh. Obshch. Khim.*, **31**, 3027 (1961). <sup>o</sup> The F<sup>19</sup> n.m.r. spectrum of the fluorophosphorane (E. L. Muetterties, personal communication) revealed the presence of an isomeric tolyltetrafluorophosphorane in addition to benzyltetrafluorophosphorane. It is therefore reasonable to assume that the starting product already contains tolyldichlorophosphine, resulting from isomerization of the benzyl compound.

*Anal.* Calcd. for ClCH<sub>2</sub>PF<sub>4</sub>: C, 7.7; H, 1.3; F, 48.6; P, 19.8. Found: C, 7.8; H, 1.6; F, 47.2; P, 19.4.

(C) **Conversion of Fluorophosphoranes into Phosphonic or Phosphinic Acids.**—Small samples of the fluorophosphoranes were repeatedly evaporated with excess water on a steam bath, after the first exothermic reaction had subsided. Recrystallization of the acids was either from water [C<sub>6</sub>H<sub>5</sub>PO(OH)<sub>2</sub>, CH<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>PO(OH)<sub>2</sub>, 2,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>PO(OH)<sub>2</sub>, CH<sub>3</sub>O·C<sub>6</sub>H<sub>4</sub>PO(OH)<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH=CH·PO(OH)<sub>2</sub>], aqueous ethanol [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>POOH], or benzene [*n*-C<sub>4</sub>H<sub>9</sub>PO(OH)<sub>2</sub>].

(D) **Reaction of Dihalooarsines with Antimony Trifluoride.**

(a) **Reaction of Methyl-diiodoarsine with Antimony Trifluoride.**—

A mixture of 20.6 g. (0.06 mole) of methyl-diiodoarsine<sup>23</sup> and 11 g. (0.06 mole) of antimony trifluoride was heated with magnetic stirring at 80–100° for 2.5 hr. The red-orange solution thus obtained gave 5.89 g. (76.5%) of methyl-difluoroarsine, b.p. 75–78°. The material was once redistilled; b.p. 76.5°, in agreement with the literature value.<sup>16</sup>

*Anal.* Calcd. for CH<sub>3</sub>AsF<sub>2</sub>: C, 9.4; H, 2.4; F, 29.7. Found: C, 8.1; H, 2.2; F, 28.4.

(b) **The reaction of phenyldichloroarsine with antimony trifluoride** was investigated more qualitatively, no oxidation-reduction reaction with formation of elemental antimony being

(23) V. Auger, *Compt. rend.*, **142**, 1151 (1906).

TABLE II  
 DIALKYL- AND DIARYLTRIFLUOROPHOSPHORANES

Compound	Reactants, moles	Reaction conditions, hr. (temp.)	Yield, %	B.p., °C. (mm.)	Analyses				Lit. ref.		
					C	H	F	P			
(CH <sub>3</sub> ) <sub>2</sub> PF <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> PCl <sup>a</sup>	0.056	1 (50°)	67	62°	Calcd.	20.3	5.1	48.3	...	3
	SbF <sub>3</sub>	0.084				Found	19.9	4.8	46.8 <sup>b</sup>	...	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> PF <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> PCl <sup>c</sup>	0.062	3 (40°)	79.5	50° (100)	Calcd.	32.9	6.9	...	21.2	3
	SbF <sub>3</sub>	0.067				Found	33.1	6.9	...	21.1	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PF <sub>3</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCl	2	5 (50°)	67	92–93° (0.4) <i>n</i> <sup>20D</sup> 1.5410	Calcd.	59.5	4.2	23.5	...	6b
	AsF <sub>3</sub>	2.7				Found	59.8	4.1	23.1	...	
$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{CH}_2-\text{CH}_2 \end{array} \begin{array}{l} \diagup \text{P} \diagdown \\ \diagdown \text{F} \diagup \\ \diagdown \text{F} \diagup \\ \diagdown \text{F} \diagup \end{array}$	C <sub>4</sub> H <sub>9</sub> PCl <sup>d</sup>	0.045	5 (–80 to 0°)	44.7	62° (90) <sup>e</sup>	Calcd.	33.4	5.6	39.5	...	...
	SbF <sub>3</sub>	0.056				1 (60–80°)	Found	33.6	5.7	38.3 <sup>b</sup>	

<sup>a</sup> Prepared according to the directions of G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960). Since the main product in this reaction is (CH<sub>3</sub>)<sub>2</sub>PSCl rather than (CH<sub>3</sub>)<sub>2</sub>PCl, the yield of the latter compound could be more than doubled by redistillation of the crude product over tributylphosphine, which served to desulfurize (CH<sub>3</sub>)<sub>2</sub>PSCl. <sup>b</sup> Fluorine analyses on the hygroscopic compounds were consistently low in some instances where the samples had to be stored over extended periods prior to analysis. <sup>c</sup> K. Issleib and W. Seidel, *Chem. Ber.*, **92**, 2681 (1959). <sup>d</sup> A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **82**, 2148 (1960). This method involves a very low yield step (C<sub>4</sub>H<sub>9</sub>P·N(CH<sub>3</sub>)<sub>2</sub>). The reported yield of 8% was substantially improved (to 27%) when a commercial di-Grignard reagent was employed. In the present work, the cleavage of the P–N bond in the aminophosphine was effected by HCl, generated from the stoichiometric amount of NH<sub>4</sub>Cl + concentrated H<sub>2</sub>SO<sub>4</sub>. <sup>e</sup> C<sub>4</sub>H<sub>9</sub>PF<sub>3</sub> attacked glass readily and was directly distilled into Teflon vials.

 TABLE III  
 ACID DERIVATIVES OF FLUOROPHOSPHORANES

Starting compound	Acid	M.p., °C.	Analyses			Remarks	
			C	H	P		
<i>n</i> -C <sub>4</sub> H <sub>9</sub> PF <sub>4</sub>	$n\text{-C}_4\text{H}_9\text{P}(\text{OH})_2$	100–103° (sealed capillary)	Calcd. ...	...	22.4	<sup>a</sup>	
			Found	...	21.3		
<i>i</i> -C <sub>3</sub> H <sub>7</sub> PF <sub>4</sub>	$i\text{-C}_3\text{H}_7\text{P}(\text{OH})_2$	Liquid	Calcd.	50.0	8.9	...	<sup>b</sup>
			Found	49.5	8.9	...	
C <sub>6</sub> H <sub>5</sub> PF <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> P(OH) <sub>2</sub>	161–163° <sup>c</sup>	Calcd.	45.6	4.4	...	..
			Found	45.7	4.7	...	
CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> PF <sub>4</sub> ( <i>m</i> , <i>p</i> )	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> P(OH) <sub>2</sub> ( <i>m</i> , <i>p</i> )	Softening at 163°; m.p. 181.5–184°	Calcd.	48.9	5.3	...	<sup>d</sup>
			Found	48.6	5.3	...	
2.5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> PF <sub>4</sub>	2.5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> P(OH) <sub>2</sub>	179–180° <sup>e</sup>	Calcd.	51.6	6.0	16.6	..
			Found	51.3	6.0	16.9	
CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> PF <sub>4</sub> ( <i>m</i> , <i>p</i> )	CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> P(OH) <sub>2</sub>	169.5–171.5° <sup>f</sup>	Calcd.	44.7	4.8	16.4	..
			Found	45.1	5.0	16.1	
C <sub>6</sub> H <sub>5</sub> CH=CHPF <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> CH=CHP(OH) <sub>2</sub>	150.5–152° <sup>g</sup>	Calcd.	52.2	4.9	16.8	..
			Found	52.4	5.0	16.8	
(CH <sub>3</sub> ) <sub>2</sub> PF <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> POH	87–89° <sup>h</sup>	...	...	...	...	
			...	...	...	...	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PF <sub>3</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> POH	193.5–195° <sup>i</sup>	Calcd.	66.0	5.1	...	..
			Found	66.1	5.2	...	

<sup>a</sup> A melting point of 103.4–104° has been reported for *n*-butylphosphonic acid: G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67**, 1180 (1945).

<sup>b</sup> The acid was obtained as a liquid, which was dried *in vacuo* over phosphorus pentoxide. Crystallization commenced slowly upon standing over a period of several months. According to evidence by the F<sup>19</sup> n.m.r. spectrum (E. L. Muetterties, personal communication) the fluorophosphorane and, consequently, the starting dichlorophosphine contain two isomers. <sup>c</sup> Reported melting point 161–162°: A. D. F. Toy, *J. Am. Chem. Soc.*, **70**, 186 (1948). <sup>d</sup> A. B. Burger and N. D. Dawson, *J. Org. Chem.*, **16**, 1250 (1951), reported m.p. 188.5–190° for pure *p*-tolylphosphonic acid; pure *m*-tolylphosphonic acid melts at 125–126°: J. M. Denham and R. K. Ingham, *J. Org. Chem.*, **23**, 1298 (1958). <sup>e</sup> J. Weller, *Ber.*, **21**, 1492 (1888), reported m.p. 179–180° for 2,5-dimethylphenylphosphonic acid. <sup>f</sup> A. Michaelis, *Ann.*, **293**, 193 (1896); **294**, 1 (1896), reported m.p. 158° for *p*-methoxyphenylphosphonic acid. <sup>g</sup> E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930), reported two stereoisomers of styrene phosphonic acid, the melting points being 146 and 150°, respectively. <sup>h</sup> Mixture melting point with authentic dimethylphosphonic acid (H. Reinhardt, D. Bianchi, and D. Mölle, *Chem. Ber.*, **90**, 1656 (1957)): 85–88°. <sup>i</sup> A. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, **42**, 395, 549 (1910), reported m.p. 195–196°.

observed when 6.7 g. (0.03 mole) of phenyldichloroarsine<sup>24</sup> and 9 g. (0.05 mole) of antimony trifluoride were heated for 1 hr. Distillation *in vacuo* gave a deliquescent product which solidified in the condenser. The observed melting point of 35–41° indicated phenyldifluoroarsine (reported<sup>15</sup> m.p. 42°) with possibly some antimony trichloride impurity (b.p. of SbCl<sub>3</sub> 95° (12 mm.)

*vs.* 112° (48 mm.) for C<sub>6</sub>H<sub>5</sub>AsF<sub>2</sub>). No evidence for the formation of phenylarsenic tetrafluoride, C<sub>6</sub>H<sub>5</sub>AsF<sub>4</sub>,<sup>24a,b</sup> was found.

(E) Reaction of Benzaldehyde with Diphenyltrifluorophosphorane.—No heat was evolved when 10.6 g. (0.1 mole) of benzaldehyde was added dropwise with stirring to 36.4 g. (0.15 mole) of diphenyltrifluorophosphorane. The mixture turned dark brown on 3.5-hr. heating at 160°. Distillation through an 8-in. helix-packed column gave 0.9 g. of a colorless liquid, b.p. 31–39°

(24) A. Michaelis and H. Lösner, *Ber.*, **27**, 263 (1894).

(15 mm.), which was found to be of 98% purity by v.p.c. Found:  $n^{24}_D$  1.4568 vs.  $n^{25}_D$  1.4552.<sup>25</sup> The identity of the material as pure  $\alpha, \alpha$ -difluorotoluene was further established by v.p.c. and infrared spectrum (comparison with authentic material).

Anal. Calcd. for  $C_7H_6F_2$ : C, 65.6; H, 4.7. Found: C, 65.3; H, 5.0.

(F) **Reaction of Hexamethyldisiloxane with Phenyltetrafluorophosphorane.**—With exclusion of moisture, 12.1 g. (0.075 mole) of hexamethyldisiloxane was placed in a 50-ml. three-necked flask, equipped with a Dry Ice reflux condenser, a thermometer, and a dropping funnel. From the dropping funnel was added 18.4 g. (0.1 mole) of phenyltetrafluorophosphorane, an exothermic reaction with formation of a low boiling material being observed. The mixture was refluxed for 1 hr. at  $\leq 40^\circ$ . A total of 12.9 g. trimethylfluorosilane (93.5%) was collected on distillation, b.p. ca.  $20^\circ$  (lit.<sup>26</sup> b.p.  $16.4^\circ$ ). The infrared spectrum (gas) was found in complete agreement with the reported spectrum.<sup>27</sup>

Distillation of the higher-boiling residue gave 3.5 g. of unreacted phenyltetrafluorophosphorane [b.p.  $34^\circ$  (13 mm.), identified by infrared analysis], followed by 10.8 g. (89%) of phenylphosphonic difluoride, b.p.  $73^\circ$  (13 mm.);  $n^{25}_D$  1.4640, in agreement with the known data.<sup>9</sup> The stoichiometry of the reaction is thus established.

(G) **Reaction of *n*-Butyric Anhydride with Phenyltetrafluorophosphorane.**—The apparatus used was the same as in the above experiment. No immediate reaction was observed when 20 g. (ca. 0.11 mole) of phenyltetrafluorophosphorane was gradually

added with stirring to 15.8 g. (0.1 mole) of butyric anhydride. Reflux of a low boiling material occurred on heating to  $80^\circ$  inner temperature (1 hr.). Distillation gave 16.4 g. (91%) of *n*-butyric fluoride, b.p.  $69-70^\circ$  (reported<sup>28</sup> b.p.  $69-70^\circ$ ).

Anal. Calcd. for  $C_4H_7FO$ : C, 53.3; H, 7.8. Found: C, 53.6; H, 7.9.

Continued distillation *in vacuo* after removal of the acid fluoride gave 15.9 g. (98%) of phenylphosphonic difluoride, b.p.  $71-73^\circ$  (11 mm.);  $n^{27}_D$  1.4610. The compound contained a small amount of impurity.

(H) **Reaction of Succinic Anhydride with Phenyltetrafluorophosphorane.**—A mixture of 10.1 g. (0.1 mole) of succinic anhydride and 20 g. (ca. 0.11 mole) of phenyltetrafluorophosphorane was heated with stirring for 6 hr. at  $120-140^\circ$ . The presence of the desired acid fluoride was detected by gas chromatographic investigation of the crude reaction product. The product was separated first by distillation through a 10-in. glass helix packed column [b.p.  $30-60^\circ$  (12 mm.)], 6.5 g. of product containing 80% of succinic fluoride (by v.p.c.) being collected. Pure succinic fluoride was obtained by preparative v.p.c. separation and was characterized by analysis and infrared spectrum.

Anal. Calcd. for  $C_4H_4F_2O_2$ : C, 39.4; H, 3.3. Found: C, 39.5; H, 3.2.

Continued distillation gave 12.0 g. of phenylphosphonic difluoride [b.p.  $69^\circ$  (10 mm.), identified by v.p.c. comparison with authentic material]. Finally, 3.1 g. of unreacted succinic anhydride was recovered. Succinic fluoride has been obtained by the fluorination of the corresponding dichloride with potassium fluorosulfinate,<sup>29</sup> reported b.p.  $47^\circ$  (12 mm.).

(25) W. A. Sheppard, personal communication.

(26) H. S. Booth and J. F. Suttle, *J. Am. Chem. Soc.*, **68**, 2658 (1946).

(27) H. Kriegsmann, *Z. anorg. allgem. Chem.*, **294**, 113 (1958).

(28) G. Olah, S. Kuhn, and S. Beke, *Chem. Ber.*, **89**, 2553 (1956).

(29) F. Seel and J. Langer, *ibid.*, **91**, 2553 (1958).

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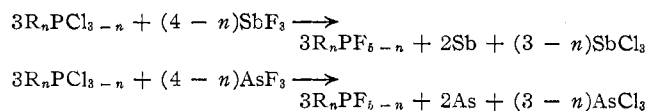
## Phosphorus-Fluorine Chemistry. V. Dialkylaminodifluorophosphines and Their Coordination Compounds with Transition Metals<sup>1a</sup>

By R. SCHMUTZLER<sup>1b</sup>

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The substituted phosphorus fluorides  $(CH_3)_2NPF_2$ ,  $(C_2H_5)_2NPF_2$ , and  $C_8H_{10}NPF_2$  ( $C_8H_{10}$  = piperidyl) have been prepared by fluorinating the corresponding chlorides  $R_2NPCl_2$  with  $SbF_3$  or a suspension of  $NaF$  in tetramethylene sulfone. These substituted phosphorus fluorides serve as interesting ligands which will displace CO from nickel and molybdenum carbonyls to give compounds of the type  $Ni(CO)_2L_2$ ,  $NiL_4$ , and  $Mo(CO)_3L_3$  (L is any of the new fluorides).

As noted in the preceding papers,<sup>2a,b</sup> chlorophosphines undergo both oxidation and fluorination with  $SbF_3$  or  $AsF_3$  to give substitution products of  $PF_3$ .



R = hydrocarbon group;  $n = 1$  or  $2$

If, however, R in the above equation is replaced by either a dialkylamino group,  $R_2N-$ , or an alkoxy group,  $RO-$ , normal exchange reaction with either  $SbF_3$  or

$NaF$  occurs to give the compounds  $R_2NPF_2$  or  $ROPF_2$ , respectively.<sup>3,4</sup> No evidence for the compounds  $R_2NPF_4$  or  $ROPF_4$ , analogous to alkyl- or aryltetrafluorophosphoranes described earlier,<sup>2</sup> has yet been obtained in these reactions.

Details of the fluorination with  $SbF_3$  for the dialkylaminodichlorophosphines are contained in Table I and

(3) The early patent literature [cf. (a) French Patent 807,769 (to I. G. Farbenindustrie A.G., Oct. 26, 1936); (b) G. Schrader and O. Bayer (to I. G. Farbenindustrie A.G.), German Patent 664,438 (Aug. 26, 1938); (c) G. Schrader and O. Bayer (to Winthrop Chemical Co.), U. S. Patent 2,146,356 (Feb. 7, 1939)] refers to the fluorination of  $(C_2H_5)_2NPCl_2$  and reports  $(C_2H_5)_2NPF_2$  as a gas which was condensed to a liquid at  $-78^\circ$ . These properties are in sharp disagreement with those found in this study (b.p. of  $(C_2H_5)_2NPF_2$   $96^\circ$  at atmospheric pressure).

(4) The reaction of  $ROPCl_2$  with  $SbF_3$  was studied earlier (D. R. Martin and P. J. Pizzolato, *J. Am. Chem. Soc.*, **72**, 4584 (1950); D. R. Martin, W. D. Cooper, D. R. Spessard, and H. S. Booth, *ibid.*, **74**, 809 (1952)). The compounds  $CH_3OPClF$ ,  $CH_3OPF_2$ , and  $ClCH_2CH_2OPF_2$  were isolated and characterized.

(1) (a) The author has been informed by personal communications of Prof. R. W. Parry and Dr. H. Nöth [cf. also H. Nöth and H. J. Vetter, *Chem. Ber.*, **96**, 1109, 1298 (1963)] that they have studied independently the synthesis and coordination chemistry of dimethylaminodifluorophosphine. (b) University Chemical Laboratory, Cambridge, England.

(2) (a) R. Schmutzler, *Chem. Ind. (London)*, 1868 (1962); (b) R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).