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Preparation and Characterization of Trimethylhydrazino- and Dimethylhydroxylaminochloro- and -fluorophosphine[1]

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$Cl_2PN(CH_3)N(CH_3)_2$, $ClP[N(CH_3)N(CH_3)_2]_2$, $Cl_2PN(CH_3)OCH_3$, and $ClP[N(CH^3)OCH_3]_2$ can be prepared by the reaction of phosphorus trichloride with 1,1,2-trimethylhydrazine or O,N-dimethylhydroxylamine. $ClP[N(CH_3)N(CH_3)_2]_2$ and $ClP[N(CH_3)OCH_3]_2$ are also formed by the reaction of $Cl_2PN(CH_3)N(CH_3)_2$ with $HN(CH_3)N(CH_3)_2$ and $Cl_2PN(CH_3)OCH_3$ with $HN(CH_3)OCH_3$, respectively. These chlorophosphines can be fluorinated with metal fluorides to yield the corresponding fluorophosphines.

While investigations of the alkylaminohalophosphines have been reported in a number of recent papers[3,4] and several organophosphine[5-7] and bis(trifluoromethyl)phosphine[8] derivatives of various hydrazines and one cyclic hydrazinochlorophosphine[9] have been synthesized, no acyclic halophosphine derivatives of any nitrogen bases other than amines are known. This paper describes the preparation and characterization of several chloro- and fluorophosphine derivatives of 1,1,2-trimethylhydrazine and O,N-dimethylhydroxylamine. The synthesis of these compounds is a direct extension of studies of the aminohalophosphines since the substitution of the amino moiety by hydrazino or hydroxylamino groups may allow the effect of the basicity of the nitrogen on the P–N bond and the chemistry of the halophosphines to be investigated.

Experimental Section

All manipulations were performed in a vacuum line or under a dry nitrogen atmosphere. PCl_3, NaF, and SbF_3 were purchased from Matheson Coleman and Bell, Baker and Adamson, and Alfa Chemical Co., respectively. O,N-Dimethylhydroxylamine was obtained from a solution of O,N-dimethylhydroxylamine hydrochloride (Aldrich Chemical Co.) in concentrated NaOH by vacuum line distillation. 1,1,2-Trimethylhydrazine was prepared by the method of Class, Aston, and Oakwood.[10] All solvents and reactants were dried and purified by appropriate means before use.

Nmr spectra were recorded in CCl_4 solutions at about 35° using a Varian A-60 spectrometer. All chemical shifts are referenced to internal tetramethylsilane. Ir spectra were run from 5000 to 600 cm^{-1} on Beckman Ir-5 and Ir-10 spectrometers. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of $Cl_2PN(CH_3)N(CH_3)_2$.—$HN(CH_3)N(CH_3)_2$ (26.9 g, 0.40 mol) dissolved in 40 ml of dry ether was slowly added to a stirred solution of 31.6 g (0.23 mol) of PCl_3 in 20 ml of ether. The temperature of the reacting mixture was held at 0°. When the addition had been completed the mixture was allowed to warm to room temperature and stirring was continued for 1 hr. The $(CH_3)_2NN(CH_3)H_2^+Cl^-$ which had formed was removed by filtration and washed with several portions of dry ether. Vacuum evaporation at 0° of the ether and excess PCl_3 from the combined filtrates left a liquid which was purified by vacuum distillation at 28° yielding 15.8 g (0.090 mol) of the clear liquid $Cl_2PN(CH_3)N(CH_3)_2$. *Anal.* Calcd for $Cl_2PN(CH_3)N(CH_3)_2$: C, 20.59; H, 5.18; N, 16.01. Found: C, 20.73; H, 5.31; N, 16.08. Major peaks in the ir spectrum are: 2940 s, 2850 s, 2760 ms, 2740 sh, 2680 ms, 2480 m, 1590 mw, 1455 s, 1405 m, 1240 ms, 1210 mw, 1150 mw, 1105 ms, 1035 w, 1020 m, 987 w, 951 w, 928 w, 842 s, 776 mw, 669 m cm^{-1}.

Preparation of $ClP[N(CH_3)N(CH_3)_2]_2$.—(a) Using the procedure described for the preparation of $Cl_2PN(CH_3)N(CH_3)_2$, 4.48 g (0.060 mol) of $HN(CH_3)N(CH_3)_2$ was allowed to react with 2.10 g (0.015 mol) of PCl_3. Following filtration of the reaction mixture and evaporation of the ether from the filtrate, the remaining liquid was vacuum distilled at 62° giving 1.12 g (0.0053 mol) of the clear liquid $ClP[N(CH_3)N(CH_3)_2]_2$.

(b) In a vacuum line 4.37 g (0.059 mol) of $HN(CH_3)N(CH_3)_2$ was frozen, a few millimoles at a time, into a reaction tube containing 5.29 g (0.030 mol) of $Cl_2PN(CH_3)N(CH_3)_2$ held at −196°. After each portion of $HN(CH_3)N(CH_3)_2$ was added the tube was warmed to room temperature and the mixture was allowed to react for a few minutes. When the addition of $HN(CH_3)N(CH_3)_2$ was complete, the reactants were held at room temperature for 1 additional hr. The resulting mixture was extracted with ether and the extract was treated as described above to give 3.77 g (0.018 mol) of $ClP[N(CH_3)N(CH_3)_2]_2$. *Anal.* Calcd for $ClP[N(CH_3)N(CH_3)_2]_2$: C, 33.89; H, 8.53; N, 26.35. Found: C, 33.57; H, 8.69; N, 26.18. Ir spectrum: 2940 s, 2880 s, 2860 s, 2680 ms, 2460 m, 2350 m, 1455 s, 1405 mw, 1235 ms, 1190 m, 1150 br, m, 1105 ms, 1015 m, 991 m, 864 s, 838 s, 778 mw, 692 w, 661 mw cm^{-1}.

Preparation of $Cl_2PN(CH_3)OCH_3$.—On a vacuum line 14.2 g (0.23 mol) of $HN(CH_3)OCH_3$ was distilled into a reaction vessel containing a stirred solution of 16.6 g (0.12 mol) of PCl_3 and about 30 ml of ether at −78°. The mixture was warmed to room temperature and allowed to react for 2 hr after which the volatile components were passed through cold traps held at −23, −78, and −196°. The ether, collected in the −196° trap, was distilled back into the reaction vessel, stirred, and distilled through the same traps. Excess PCl_3 and some ether was detected in the −78° trap and 16.7 g (0.10 mol) of $Cl_2PN(CH_3)OCH_3$ was recovered from the −23° trap. *Anal.* Calcd for $Cl_2PN(CH_3)OCH_3$: C, 14.83; H, 3.73; N, 8.65. Found: C, 14.79; H, 3.79; N, 8.41. A vapor pressure of 11 mm

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[2] (a) NSF Undergraduate Research Participant, Summers 1966–1967; (b) NSF Undergraduate Research Participant, Summer 1968.

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at 25° was observed for $Cl_2PN(CH_3)OCH_3$ and its ir spectrum was: 2930 ms, 2900 ms, 2820 ms, 2680 s, 2480 ms, 1485 m, 1455 ms, 1440 ms, 1400 w, 1265 m, 1225 m, 1205 m, 1155 mw, 1135 m, 1075 s, 1045 ms, 1020 s, 996 s, 964 ms, 947 ms, 894 ms, 858 s, 671 s cm^{-1}.

Preparation of $ClP[N(CH_3)OCH_3]_2$.—Following the procedure described for the preparation of $Cl_2PN(CH_3)OCH_3$, 2.45 g (0.018 mol) of PCl_3 was allowed to react with 4.27 g (0.070 mol) of $HN(CH_3)OCH_3$. The volatile components of the reaction mixture were removed by evaporation on a vacuum line through traps held at −23 and −196°. The −23° trap held 2.20 g (0.012 mol) of $ClP[N(CH_3)OCH_3]_2$.

$ClP[N(CH_3)OCH_3]_2$ decomposes slowly at room temperature; consequently, good elemental analyses could not be obtained. Typical data are: *Anal.* Calcd for $ClP[N(CH_3)OCH_3]_2$: C, 25.7; H, 6.4; N, 15.0. Found: C, 24.1; H, 6.7; N, 13.7. The compound was further characterized by its ir and nmr spectra. The major ir peaks are: 2930 s, 2880 s, 2800 ms, 2680 ms, 2470 m, 1460 ms, 1435 ms, 1400 w, 1265 w, 1205 m, 1155 w, 1130 w, 1070 s, 1045 s, 1025 s, 996 ms, 963 m, 883 ms, 858 ms, 671 s, 658 s cm^{-1}.

$ClP[N(CH_3)OCH_3]_2$ can also be isolated from the reaction of $Cl_2PN(CH_3)OCH_3$ with $HN(CH_3)OCH_3$ employing procedure b described for the preparation of $ClP[N(CH_3)N(CH_3)_2]_2$.

Preparation of $F_2PN(CH_3)N(CH_3)_2$.—SbF_3 (1.15 g, 0.0061 mol) was added to a reaction tube containing 0.79 g (0.0045 mol) of $Cl_2PN(CH_3)N(CH_3)_2$ frozen at −196°. The reaction tube was attached to the vacuum line, evacuated, and slowly warmed to room temperature while being stirred. The formation of volatile products was observed as the $Cl_2PN(CH_3)N(CH_3)_2$ melted. These gasses were immediately distilled from the reaction vessel through traps held at −78 and −196°. When the reaction had ceased, a small amount of PF_3 was detected in the −196° trap and 0.24 g (0.0017 mol) of the colorless liquid $F_2PN(CH_3)N(CH_3)_2$ remained in the −78° trap. *Anal.* Calcd for $F_2PN(CH_3)N(CH_3)_2$: C, 25.36; H, 6.38; N, 19.38; mol wt, 142. Found: C, 25.13; H, 6.46; N, 19.59; mol wt, 142 (mass spectrum), 138 (vapor density). The vapor pressure of $F_2PN(CH_3)N(CH_3)_2$ can be expressed as $\log P_{mm} = (-1.38 \times 10^3/T) + 6.11$. Its ir spectrum is: 2990 mw, 2970 m, 2870 mw, 2790 mw, 1245, 1115 m, 1005 mw, 905 mw, 890 m, 866 s, 853 sh, 815 sh, 810 s, 761 ms, 679 mw cm^{-1}.

Preparation of $FP[N(CH_3)N(CH_3)_2]_2$.—A 7.59-g (0.036-mol) sample of $ClP[N(CH_3)N(CH_3)_2]_2$ and 3.01 g (0.072 mol) of NaF were refluxed in 25 ml of tetramethylene sulfone for 2 hr under reduced pressure. The mixture was distilled under vacuum at 30° yielding 1.46 g (0.0075 mol) of $FP[N(CH_3)N(CH_3)_2]_2$. During the reflux some $F_2PN(CH_3)N(CH_3)_2$ was formed and immediately distilled from the reaction vessel. Unreacted $ClP[N(CH_3)N(CH_3)_2]_2$ was collected as a separate fraction boiling at 60°. *Anal.* Calcd for $FP[N(CH_3)N(CH_3)_2]_2$: C, 36.73; H, 9.25; N, 28.55. Found: C, 36.59; H, 9.22; N, 28.71. Ir spectrum: 2930 s, 2850 s, 2770 s, 2680 s, 2460 s, 2340 mw, 2020 w, 1580 mw, 1455 s, 1420 m, 1300 w, 1235 ms, 1200 m, 1150 m, 1110 s, 1090 s, 1035 mw, 1015 ms, 993 m, 951 mw, 928 mw, 847 vbr, s, 778 m, 679 ms, 662 ms cm^{-1}.

Attempts to prepare $FP[N(CH_3)N(CH_3)_2]_2$ by reaction of $F_2PN(CH_3)N(CH_3)_2$ with $HN(CH_3)N(CH_3)_2$ were unsuccessful. Nmr spectroscopy indicates that no reaction occurs in a mixture of $F_2PN(CH_3)N(CH_3)_2$ and $HN(CH_3)N(CH_3)_2$ even after several weeks at room temperature.

Preparation of $F_2PN(CH_3)OCH_3$.—Using the procedure described for the preparation of $F_2PN(CH_3)N(CH_3)_2$, 4.90 g (0.030 mol) of $Cl_2PN(CH_3)OCH_3$ was allowed to react with 8.15 g (0.046 mol) of SbF_3. $F_2PN(CH_3)OCH_3$ (2.4 g, 0.019 mol) was collected in a −96° cold trap.

Owing to the instability of this compound, good elemental analyses were not obtained. Its composition is supported by molecular weight [theoretical, 129; found, 129 (mass spectrum), 128 (vapor density)], nmr and ir data, and its mode of preparation. Vapor pressure can be expressed as $\log P_{mm} = (-1.34 \times 10^3/T) + 5.78$. Ir spectrum: 2940 mw, 2890 mw, 2810 w, 1455 w, 1225 w, 1085 mw, 1040 mw, 976 s, 891 m, 866 s, 851 s, 832 s, 808 m, 792 ms, 683 m cm^{-1}.

Preparation of $FP[N(CH_3)OCH_3]_2$.—On a vacuum line 1.5 g (0.12 mol) of $F_2PN(CH_3)OCH_3$ and 2.9 g (0.48 mol) of $HN(CH_3)OCH_3$ were frozen into a reaction tube at −196°. The tube was warmed to room temperature and the reaction was allowed to proceed for 24 hr. The reactants and products were then distilled from the reaction tube at room temperature, through traps held at −23, −78, and −196°. $FP[N(CH_3)OCH_3]_2$ (0.4 g, 2.3×10^{-3} mol) was collected in the −23° trap. *Anal.* Calcd for $FP[N(CH_3)OCH_3]_2$: C, 28.2; H, 7.1; N, 16.4. Found: C, 29.0; H, 7.6; N, 15.6. Major peaks in the ir spectrum are: 2941 s, 2890 s, 2801 m, 1464 s, 1439 s, 1250 m, 1217 ms, 1188 m, 1153 mw, 1133 mw, 1073 s, 1052 s, 1029 vw, 970 w, 889 s, 838 ms, 752 s, 701 s, 668 s cm^{-1}.

$FP[N(CH_3)OCH_3]_2$ can also be prepared by reaction of $ClP[N(CH_3)OCH_3]_2$ with SbF_3 using the procedure outlined for the preparation of $F_2PN(CH_3)N(CH_3)_2$.

Results and Discussion

The trimethylhydrazino- and dimethylhydroxylaminohalophosphines are chemically quite similar to the alkylaminohalophosphines. The preparation of the chloro compounds by solvolysis of PCl_3

$$PCl_3 + 2nHN(CH_3)Y \rightarrow Cl_{3-n}P[N(CH_3)Y]_n + nHN(CH_3)Y \cdot HCl$$

[$n = 1$ or 2, $Y = N(CH_3)_2$ or OCH_3] and their subsequent fluorination with metal fluorides

$$Cl_{3-n}P[N(CH_3)Y]_n \xrightarrow[\text{fluoride}]{\text{metal}} F_{3-n}P[N(CH_3)Y]_n$$

closely parallel reactions commonly employed in the synthesis of the alkylaminohalophosphines.[11,12] The hydroxylaminolysis of $F_2PN(CH_3)OCH_3$

$$F_2PN(CH_3)OCH_3 + 2HN(CH_3)OCH_3 \rightarrow FP[N(CH_3)OCH_3] + HN(CH_3)OCH_3 \cdot HF$$

is analogous to the preparation[13] of $FP[N(CH_3)_2]_2$ from $F_2PN(CH_3)_2$ and $HN(CH_3)_2$. The failure of $F_2PN(CH_3)N(CH_3)_2$ to undergo further hydrazinolysis while $Cl_2PN(CH_3)N(CH_3)_2$ readily reacts with $HN(CH_3)N(CH_3)_2$ also finds parallels in aminohalophosphine chemistry where the P–F bond has been observed to be relatively nonreactive, with even PF_3 failing to undergo aminolysis with some amines which react rapidly with PCl_3.[14] From these results it would appear that many of the preparative routes developed for the aminohalophosphines may be equally applicable to the synthesis of halophosphine derivatives of a wide variety of nitrogen-containing bases.

The ^1H nmr spectra (Table I) are in complete agreement with the formulations of the compounds as hydrazino- and hydroxylaminohalophosphines. The relative peak intensities and small chemical shift differences observed between CH_3 resonances in the halophosphines and the parent hydrazine or hydroxylamine demonstrate that no rearrangements of the nitrogen moieties have occurred. The $(PNCH)$ coupling con-

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TABLE I

PROTON MAGNETIC RESONANCE DATA

Compound	Rel intens	Chem shift, ppm (TMS ref)	Multiplicity		Assignment
$Cl_2PN(CH_3)N(CH_3)_2$	1	−2.79	Doublet	J_{PNCH} = 7.2 cps	$\mathrm{N{-}C}H_3$
	2	−2.57	Doublet	J_{PNNCH} = 0.9 cps	$\mathrm{N(C}H_3)_2$
$ClP[N(CH_3)N(CH_3)_2]_2$	1	−2.69	Doublet	J_{PNCH} = 7.3 cps	$\mathrm{N{-}C}H_3$
	2	−2.49	Singlet		$\mathrm{N(C}H_3)_2$
$F_2PN(CH_3)N(CH_3)_2$	1	−2.61	Doublet of	J_{PNCH} = 5.2 cps	$\mathrm{N{-}C}H_3$
			triplets	J_{FPNCH} = 3.1 cps	
	2	−2.53	Singlet		$\mathrm{N(C}H_3)_2$
$FP[N(CH_3)N(CH_3)_2]_2$	1	−2.58	Doublet of	J_{PNCH} = 5.7 cps	$\mathrm{N{-}C}H_3$
			doublets	J_{FPNCH} = 3.5 cps	
	2	−2.46	Singlet		$\mathrm{N(C}H_3)_2$
$Cl_2PN(CH_3)OCH_3$	1	−3.00	Doublet	J_{PNCH} = 12.5 cps	$\mathrm{N{-}C}H_3$
	1	−3.70	Doublet	J_{PNOCH} = 0.5 cps	$\mathrm{O{-}C}H_3$
$ClP[N(CH_3)OCH_3]_2$	1	−2.92	Doublet	J_{PNCH} = 14.0 cps	$\mathrm{N{-}C}H_3$
	1	−3.58	Singlet		$\mathrm{O{-}C}H_3$
$F_2PN(CH_3)OCH_3$	1	−2.90	Doublet of	J_{PNCH} = 10.0 cps	$\mathrm{N{-}C}H_3$
			triplets	J_{FPNCH} = 3.6 cps	
	1	−3.66	Singlet		$\mathrm{O{-}C}H_3$
$FP[N(CH_3)OCH_3]_2$	1	−2.87	Doublet of	J_{PNCH} = 10.5 cps	$\mathrm{N{-}C}H_3$
			doublets	J_{FPNCH} = 1.8 cps	
	1	−3.58	Singlet		$\mathrm{O{-}C}H_3$
$HN(CH_3)N(CH_3)_2$	1	−2.21	Singlet		$\mathrm{N{-}C}H_3$
	2	−2.01	Singlet		$N(CH_3)_2$
$HN(CH_3)OCH_3$	1	−2.58	Singlet		$N(CH_3)$
	1	−3.40	Singlet		OCH_3

stants, calculated from the splitting of the $\mathrm{N{-}C}H_3$ signals, are of the same magnitude as the J_{PNCH} = 8–15 cps observed in a variety of alkylaminophosphorus compounds,[14–17] and argue strongly for the existence of the P–N–CH_3 linkage. The FPNCH coupling constants observed in the spectra of the fluoro derivatives are all in the range of 2–5 cps reported[15] for similar couplings in other fluorophosphorus compounds. In every case the postulated number of fluorines is confirmed by the multiplicity of the $\mathrm{N{-}C}H_3$ resonances.

Nixon and Schmutzler[16] have reported that J_{PNCH} decreases going from an aminochloro- to the analogous aminofluorophosphine. A similar trend is apparent in the hydrazino and hydroxylamino compounds. However, the increase in J_{PNCH} from $ClP(NR_2)_2$ to Cl_2PNR_2 (R = alkyl) noted by Cowley and Pinnell[17] does not occur in the compounds studied here. Long-range PNNCH and PNOCH coupling is seen in the spectra of $Cl_2PN(CH_3)N(CH_3)_2$ and $Cl_2PN(CH_3)OCH_3$, respectively. As with the PNCCH coupling observed by Kaplan, Singh, and Zimmer[18] its magnitude must be quite sensitive to molecular environment as this long-range coupling could not be resolved in the other compounds studied. Variations in the $\mathrm{N{-}C}H_3$ chemical shifts are similar in the amino-,[15–17] hydrazino-, and hydroxylaminohalophosphines decreasing with increasing halogen substitution and from fluoro to chloro derivatives.

With the exception of peaks arising from the N–H vibrations, the infrared spectra of 1,1,2-trimethylhydrazine[19,20] and O,N-dimethylhydroxylamine[21] between 900 and 4000 cm^{-1} are quite similar to the spectra of their respective halophosphine derivatives. These results strongly support the nmr data which indicate that no rearrangements have taken place within the nitrogen moieties. P–N[22] and P–F[23] stretches often are observed in the 700–900-cm^{-1} region, and the spectral variations apparent in this range probably reflect differences in these modes which would be expected to occur between the various compounds. While no detailed ir analysis has been attempted, it is reassuring that the ir spectra are in qualitative agreement with the proposed formulations.

Quantitative thermal stability data were not obtained. Nonetheless, the hydrazino derivatives which can be stored for at least several weeks at room temperature are clearly more stable than the corresponding hydroxylamino compounds, some of which begin to decompose only minutes after being warmed to room temperature. The replacement of a Y = $N(CH_3)_2$ group by the more electronegative OCH_3 group in the compounds $X_{3-n}P[N(CH_3)Y]_n$ might be expected to effect the withdrawal of electrons from the nitrogen accompanied by a concomitant weakening of the P–N bond. While the relative stabilities of the two classes of compounds may be the result of a number of factors, it is interesting to speculate that the overall trend reflects such a difference in P–N bond strengths.

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Experiments involving the bishydrazino or bishydroxylamino compounds were frequently complicated by the production of the appropriate monohydrazino or monohydroxylamino derivative as a major by-product. Schmutzler[24] has observed the slow disproportionation

$$2FP(NR_2) \rightarrow F_2PNR_2 + P(NR_2)_3 \quad [R = \text{alkyl}]$$

Similar reactions involving the compounds studied here would not be unexpected. Thus, even though the tris-substituted phosphines were not isolated in these studies, such a disproportionation may also occur with hydrazino- and hydroxylaminohalophosphines.[25]

Acknowledgment.—Acknowledgment is gratefully made to the Petroleum Research Fund administered by the American Chemical Society for support of the research. The mass spectrometer was obtained through NSF Equipment Grant GP 5813.

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[25] Note Added in Proof.—Since submission of this paper mass spectral molecular weights have been obtained for $ClP[N(CH_3)N(CH_3)_2]_2$ theory, 212; found, 212; $Cl_2PN(CH_3)OCH_3$ theory, 161; found, 161; $ClP[N(CH_3)OCH_3]_2$ theory, 186; found, 186; $FP[N(CH_3)N(CH_3)_2]_2$ theory, 196; found, 196; and $FP[N(CH_3)OCH_3]_2$ theory, 170; found, 170. These spectra were run using liquid samples injected into a Perkin-Elmer Hitachi RMU-6D spectrometer.

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Reactions of Halodifluorophosphines with Silver Salts[1]

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The reactions of PF_2I, PF_2Br, or PF_2Cl with silver salts have been shown to provide an excellent route to new PF_2-containing compounds. Compounds prepared and characterized are $CF_3C(O)OPF_2$, $CF_3CF_2C(O)OPF_2$, $CF_3CF_2CF_2C(O)OPF_2$, and $CH_3C(O)OPF_2$. In addition, the previously reported compounds PF_2CN and PF_2NCO are easily prepared by this method.

Recent investigations have shown the utility of using difluoroiodophosphine[2] as a reagent for the syntheses of compounds which contain the PF_2 moiety. Thus, PF_2I has been found to react with mercury to give tetrafluorodiphosphine,[3] with mercury and hydrogen iodide to give difluorophosphine,[4] with copper(I) oxide to give μ-oxo-bisdifluorophosphine,[3] and with copper(I) cyanide to give cyanodifluorophosphine.[3a] With sulfur, iodothiophosphoryl difluoride is formed.[5] Both PF_2I and PF_2Br have been found to add across the carbonyl double bond in hexafluoroacetone,[6] and to react with hydrogen chalcogenides and trimethyltin hydroxide.[7] Chlorodifluorophosphine[8–10] and bromodifluorophosphine[3b,11] have been known for a considerable time, but little of their chemistry has been studied.

Reactions of the halodifluorophosphines with silver salts at room temperature provide an excellent general route to PF_2X compounds; *e.g.*, the new compounds, trifluoroacetatodifluorophosphine, $CF_3C(O)OPF_2$, pentafluoropropionatodifluorophosphine, $CF_3CF_2C(O)OPF_2$, heptafluoro-*n*-butyratodifluorophosphine, $CF_3CF_2CF_2C(O)OPF_2$, and acetatodifluorophosphine, $CH_3C(O)OPF_2$, have been prepared and characterized. The previously reported compounds, cyanodifluorophosphine,[3a] PF_2CN, and isocyanatodifluorophosphine,[12] PF_2NCO, also were readily prepared by this method.

Although the perfluorocarboxylatodifluorophosphines are hydrolyzed rapidly by moisture, they seem to have considerable thermal stability; *e.g.*, $C_2F_5C(O)OPF_2$ showed no indication of decarboxylation or decomposition after several days at 150°.

Experimental Section

Apparatus.—A standard Pyrex high-vacuum system was used for manipulation of volatile compounds. Glass stopcocks were lubricated with Kel-F No. 90 grease (3M Co.). Reactions were carried out in 100-ml Pyrex flasks fitted with a Teflon stopcock (Fischer and Porter Co.) and a side arm for admission of the silver salt.

Infrared spectra (Table I) were recorded in the gas phase with a Beckman IR5A or a Perkin-Elmer Model 137 Infracord spectrophotometer. The samples were contained in a Pyrex cell (6-mm path length) equipped with NaCl windows. High-resolution ^{19}F nmr spectra (Table II) were obtained using a Varian Model

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