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]

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[24] R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).

[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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[1] Presented in part at the Northwest Regional Meeting of the American Chemical Society, Portland, Ore., June 1968, and at the 2nd European Symposium on Fluorine Chemistry, Göttingen, Germany, Aug 1968.

[2] R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, **5**, 1464 (1966).

[3] (a) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966); (b) M. Lustig, J. K. Ruff, and C. B. Colburn, *ibid.*, **88**, 3875 (1966).

[4] R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

[5] J. M. Shreeve, *J. Inorg. Nucl. Chem.*, **30**, 3375 (1968).

[6] M. Lustig and W. E. Hill, *Inorg. Chem.*, **6**, 1448 (1967).

[7] R. W. Parry and L. F. Centofanti, 2nd European Symposium on Fluorine Chemistry, Göttingen, Germany, Aug 1968; *Inorg. Chem.*, **7**, 1005 (1968).

[8] H. S. Booth and A. R. Bozarth, *J. Am. Chem. Soc.*, **61**, 2927 (1939).

[9] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, **2**, 433 (1963).

[10] R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

[11] H. S. Booth and S. G. Frary, *J. Am. Chem. Soc.*, **61**, 2930 (1939).

[12] H. H. Anderson, *ibid.*, **69**, 2495 (1947).

TABLE I

INFRARED SPECTRA (FREQUENCIES IN cm^{-1})

$CF_3C(O)OPF_2$	$CF_3CF_2C(O)OPF_2$	$C_3F_7C(O)OPF_2$	$CH_3C(O)OPF_2$	PF_2NCO
1809 vs	1809 s	1805 s	1780 vs	2400 m
1351 s	1350 m	1382 m	1423 w	2285 vvs
1247 vs	1300 s	1300 s	1375 s	1435 m
1196 vs	1238 vs	1243 vvs	1202 s	1405 m
1124 vs	1210 s, sh	1224 vvs	1007 s	857 vs, br
1087 s	1153 vs	1198 s	898 s	715 s, br
880 vs, br	1030 vs	1143 vs	856 vs, br	
835 m, sh	888 vs	1080 s	782 s	
777 s	872 vs	968 s		
757 vs	818 m	932 s		
	755 vs, br	886 vs		
		868 vs		
		814 m		
		752 s, br		

TABLE II

^{19}F NMR SPECTRA (ϕ^*)

CF_3------$C(O)O$------PF_2

Singlet	Doublet
3.1[a]	2.0
76.5	49.9

$J_{P-F} = 1389$ cps

CF_3------$CF_2C(O)O$-------PF_2

Triplet	Quartet	Doublet
3.0	2.0	2.0
83.8	122.1	49.7

$J_{CF_3-CF_2} = 1.5$ cps

$J_{P-F} = 1389$ cps

CF_3-------CF_2------$CF_2C(O)O$-------PF_2

Triplet	Singlet	Quartet	Doublet
3.0	2.0	2.0	1.9
81.4	127.2	119.7	49.7

$J_{CF_3-\alpha CF_2} = 8.5$ cps

$J_{P-F} = 1388$ cps

CH_3-------$C(O)O$-------PF_2

Singlet	Doublet
2.1	54.4

$J_{P-F} = 1350$ cps

PF_2NCO

Doublet
39.2

$J_{P-F} = 1361$ cps

[a] Relative peak area.

TABLE III

MASS SPECTRA (MASS NUMBER, SPECIES, RELATIVE ABUNDANCE)

$CF_3C(O)OPF_2$

31 (CF^+, P^+) 3.4, 43 (C_2F^+) 3.5, 44 (CO_2^+) 3.4, 45 ($COOH^+$) 3.0, 47 (PO^+) 4.3, 50 (CF_2^+, PF^+) 9.0, 66 (PFO^+ 1.8, 69 (CF_3^+, PF_2^+) 100.0, 85 (PF_2O^+) 2.7, 88 (PF_3^+, CF_4^+) 8.5, 97 ($C_2F_3O^+$) 4.8, 113 ($CO_2PF_2^+$, $C_2F_3O_2^+$) 9.7, 135 (PF_2OPF^+) 0.5, 154 ($PF_2OPF_2^+$) 2.8

$C_2F_5C(O)OPF_2$

31 (CF^+, P^+) 5.8, 44 (CO_2^+) 4.5, 45 ($COOH^+$) 5.6, 47 (PO^+) 6.1, 50 (CF_2^+, PF^+) 10.0, 51 (CF_2H^+) 2.8, 66 (PFO^+) 3.3, 69 (CF_3^+, PF_2^+) 100.0, 85 (PF_2O^+) 3.7, 86 (HPF_2O^-) 4.5, 88 (PF_3^+, CF_4^+) 7.6, 97 ($C_2F_3O^+$) 3.2, 100 ($C_2F_4^+$) 3.7, 113 ($CO_2PF_2^+$, $C_2F_3O_2^+$) 8.1, 119 ($C_2F_5^+$) 15.1, 135 (PF_2OPF^+) 2.4, 147 ($C_3F_5O^+$) 5.4, 154 ($PF_2OPF_2^+$) 1.9, 232 ($C_2F_5CO_2PF_2^+$) trace

$C_3F_7C(O)OPF_2$

31 (CF^+, P^+) 3.0, 43 (C_2F^+) 6.7, 44 (CO_2^+) 5.5, 45 ($COOH^+$) 1.3, 47 (PO^+) 5.5, 50 (CF_2,$^+$ PF^+) 5.1, 55 (C_3F^+) 4.2, 56 ($C_2O_2^+$) 2.1, 57 ($C_2O_2H^+$) 3.2, 64 (CFO_2H^+) 3.1, 66 (PFO^+) 2.3, 69 (CF_3^+, PF_2^+) 100.0, 81 ($C_2F_3^+$) 4.1, 85 (PF_2O^+) 3.8, 86 (HPF_2O^+) 2.3, 88 (PF_3^+, CF_4^+) 6.0, 97 ($C_2F_3O^+$) 1.3, 100 ($C_2F_4^+$) 9.8, 104 (PF_3O^+) 2.0, 109 ($C_3F_3O^+$) 2.4, 113 ($CO_2PF_2^+$, $C_2F_3O_2^+$) 10.2, 119 ($C_2F_5^+$) 17.8, 131 ($C_3F_5^+$) 2.1, 135 (PF_2OPF^+) 4.2, 147 ($C_3F_5O^+$) 2.0, 150 ($C_3F_6^+$) 3.8, 154 ($PF_2OPF_2^+$) 1.7, 169 ($C_3F_7^+$) 25.9, 197 ($C_3F_7CO^+$) 8.2, 282 ($C_3F_7CO_2PF_2$) trace

$CH_3C(O)OPF_2$

13 (CH^+) 1.9, 14 (CH_2^+) 6.1, 15 (CH_3^+) 41.2, 28 (N_2^+, CO^+) 6.5, 29 (HCO^+) 6.0, 31 (P^+) 1.3, 41 (HC_2O^+) 2.0, 42 ($H_2C_2O^+$) 10.6, 43 ($C_2H_3O^+$) 100.0, 44 (CO_2^+) 2.7, 45 ($COOH^+$) 9.7, 47 (PO^+) 3.2, 50 (PF^+) 6.3, 60 (CH_3COOH^+) 4.1, 66 (PFO^+) 1.4, 69 (PF_2^+) 28.0, 85 (PF_2O^+) 2.4, 88 (PF_3^+) 4.1, 113 ($CO_2PF_2^+$) 0.7

PF_2NCO

28 (N_2^+, CO^+) 19.1, 31 (P^+) 7.4, 42 (NCO^+) 9.2, 43 (HNCO) 3.7, 44 (CO_2^+) 3.8, 45 (PN^+) 10.1, 46 ($PFNCO^+$) 2.0, 47 (PO^+) 8.5, 50 (PF^+) 20.0, 64 (PFN^+) 6.2, 69 (PF_2^+) 100.0, 92 ($PFNCO^+$) 37.8, 111 (PF_2NCO^+) 59.5

HA-100 spectrometer operating at 94.1 Mc. Trichlorofluoromethane (Matheson Co.) which had been dried over P_4O_{10} or tetramethylsilane was used as an internal reference. Mass spectra (Table III) were obtained with a Hitachi Perkin-Elmer Model RMU-6E spectrometer operating at an ionization potential of 70 eV. Vapor densities were determined by the method of Regnault using a Pyrex bulb equipped with a Teflon stopcock.

Elemental analyses (Table IV) were performed by Alfred Bernhardt Microanalytisches Laboratorium, Max Planck Institut, Mulheim (Ruhr), West Germany.

Reagents.—PF_2I, PF_2Br, and PF_2Cl were prepared by the reaction of appropriate hydrogen halide with $(CH_3)_2NPF_2$.[2,3b,10] HI, HBr, and HCl were obtained from the Matheson Co. and were used without further purification. CF_3CO_2Ag and $C_2F_5CO_2Ag$ were obtained from Columbia Organic Chemicals Co., n-$C_3F_7CO_2Ag$ was from Peninsular ChemResearch, CH_3CO_2Ag was from Allied Chemical Co., AgOCN was from Eastman Organic Chemicals, and AgCN was from Fisher Scientific Co. Before use, the silver salts were ground to a fine powder and dried by heating under dynamic vacuum at 100° for 30 min.

General Procedure.—Essentially the same method was followed for the preparation of all compounds. PF_2Cl, PF_2Br, or PF_2I reacted rapidly and nearly quantitatively toward the silver salts used. In a typical reaction, PF_2Cl (3.38 mmol) was condensed onto a slight excess of dry silver trifluoroacetate (4.57 mmol) at $-183°$ and the reaction bulb was allowed to warm to 25°. That reaction occurred below room temperature was evidenced by a jumping action and a simultaneous color change of the salt. The reaction was complete by the time ambient temperature was reached (10 min). The volatile reaction products were removed and separated giving 82.5% $CF_3C(O)OPF_2$, 8.5% $(CF_3CO)_2O$, and 8.5% PF_2OPF_2, accompanied by a trace of PF_3. In all preparations, small amounts of the corresponding acid anhydride and PF_2OPF_2 were observed.

In the preparation of $CF_3C(O)OPF_2$, $C_2F_5C(O)OPF_2$, and n-$C_3F_7C(O)OPF_2$, separation of reaction products and subsequent purification of the desired compound were accomplished

TABLE IV

Compound	Mol wt		% C		% F		% P		Log $P_{mm} = (-X/T(°K)) + Y$			ΔH_v,	ΔS_v,
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	X	Y	Bp, °C[a]	kcal	eu
$CF_3C(O)OPF_2$	182	182	13.20	13.34	...	...	17.02	16.76	1535	5.317	17.3	7.02	24.1
$C_2F_5CO(O)PF_2$	232	234	15.53	15.39	57.33	57.29	13.35	13.44	1662	5.313	35.5	7.58	24.5
n-$C_3F_7C(O)OPF_2$	282	277	17.04	17.19	60.63	60.76	10.98	11.03	1676	4.685	62.9	7.68	22.9
$CH_3C(O)OPF_2$	128	130	...	...	...	...	24.20	24.32	...	...	*b*	...	...

[a] Extrapolated. [b] Vapor pressure about 120 mm at 24°.

by gas chromatography employing a 7 or 11 ft × 0.25 in. aluminum tube packed with 20% by weight Kel-F No. 3 polymer oil (3M Co.) on acid-washed Chromasorb P (Wilkens Instrument and Research, Inc.). Purification of $CH_3C(O)OPF_2$, PF_2CN, and PF_2NCO was brought about by trap-to-trap distillation. Trap temperatures of −60, −78, and −183° were used for $CH_3C(O)OPF_2$; −60, −96, and −183° were used for PF_2CN and PF_2NCO. $CH_3C(O)OPF_2$ was retained at −78° and PF_2CN and PF_2NCO were retained at −95°.

Results and Discussion

All of the new difluorophosphines at room temperature are colorless, volatile liquids which react readily with water but do not attack glass or mercury. While the $R_fC(O)OPF_2$ compounds ($R_f = CF_3$, C_2F_5, C_3F_7) may be stored at 25° under vacuum for extended periods of time without decomposition, $CH_3C(O)OPF_2$ decomposes to a red polymeric material within 24 hr under the same conditions. However, the latter may be transferred in a vacuum system and stored at −183° without polymerization occurring. Because of this thermal instability, the normal boiling point was not determined.

The hydrolysis of each of the $RC(O)OPF_2$ compounds was followed qualitatively by infrared spectroscopy. The admission of a small amount of moist air into an infrared cell which contained a sample of the pure compound resulted in a spectrum that showed bands attributable to $(RC(O))_2O$ and PF_2OPF_2 accompanied by a decrease in the intensity of the original bands. Additional moist air converted the anhydride to $RC(O)OH$.

Since chloro-, bromo-, and iododifluorophosphines react with these silver salts with equal ease, it is preferable to use either the chloro or bromo compound because of its relatively greater stability. PF_2I tends to disproportionate into PF_3 and PI_3.[2]

Characteristic P–F stretching frequencies in the infrared region (Table I) occur in the range from 850 to 900 cm^{-1}. In $R_fC(O)OPF_2$ ($R_f = CF_3$, C_2F_5, and n-C_3F_7) bands between 1805 and 1809 cm^{-1} are due to C=O; while for $CH_3C(O)OPF_2$ this band shifts to 1780 cm^{-1}. The CF stretching region in $R_fC(O)OPF_2$ encompasses a wide range (1000–1400 cm^{-1}). The bands in PF_2NCO may be assigned as follows: 2400 and 2285 cm^{-1} NCO pseudoantisymmetric stretch, in and out of phase; 1435 and 1405 cm^{-1}, NCO pseudosymmetric stretch, in and out of phase; 857 cm^{-1}, PF_2 stretch; 715 cm^{-1}, PNCO deformation, in plane.[13] Since bands occur in the 1400–1500-cm^{-1} region and a cyanate is not expected to have any fundamentals between 1200 and 2000 cm^{-1}, the compound formed in the reaction of PF_2Cl with AgOCN must be the isocyanate PF_2NCO. The mass spectral evidence below also helps to verify this conclusion. PF_2CN was identified from its previously reported infrared spectrum.[3a]

The ^{19}F nmr spectra of $R_fC(O)OPF_2$ and $RC(O)OPF_2$ are consistent with the postulated compounds. Fluorine chemical shifts of PF_2 groups in the region between ϕ^* 44 and 50 are analogous to those in $ROPF_2$ compounds (R = alkyl, phenyl).[14] No spin–spin coupling is observed between fluorine bonded to phosphorus and fluorine or hydrogen in the carboxalato groups. The J_{P-F} values found are about 1380 cps for the perfluoro compounds and decrease slightly when phosphorus is bonded to NCO or $CH_3C(O)O$. This is also observed as fluorine is replaced by less electronegative groups in the series PF_3, CF_3PF_2, and CH_3PF_2.[14]

Although molecular ions in the mass spectra (Table III) are observed for all compounds except $CF_3C(O)OPF_2$ and $CH_3C(O)OPF_2$, only in the case of PF_2NCO does this species occur in appreciable relative abundance (59.5). In PF_2CN, the parent ion is also the second most abundant peak.[3a] The presence of peaks at m/e 45 (PN^+) and m/e 64 (PF_2N^+) and the absence of m/e 85 (PF_2O^+) lend support to the infrared evidence that the compound is an isocyanate rather than a cyanate. Existence of peaks at m/e 47 (PO^+) and m/e 43 (HNCO) for PF_2NCO and analogous fragments for the other compounds can arise from hydrolysis, *e.g.*, m/e 45 ($COOH^+$), m/e 135 (PF_2OPF^+), and m/e 154 ($PF_2OPF_2^+$). Also, for $CH_3C(O)OPF_2$, m/e 60 ($CH_3C(O)OH$) and for $C_2F_5C(O)OPF_2$ and $C_3F_7C(O)OPF_2$, m/e 86 (HPF_2O) are observed. Fragmentation patterns for all compounds contain some ions derived from rearrangement, *e.g.*, m/e 88 (CF_4^+, PF_3^+). For $R_fC(O)OPF_2$ ($R_f = CF_3$, C_2F_5, C_3F_7), fragments, including some which are a result of rearrangement, *e.g.*, CF_2H^+, CF_3CO^+, and $CF_3CO_2^+$, typically associated with perfluorocarboxylic acids occur.[15]

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[13] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **17,** 977 (1961).

[14] R. Schmutzler, *Advan. Fluorine Chem.*, **5,** 254 (1965).

[15] J. R. Majer, *ibid.*, **2,** 70 (1961).