Preparation and Properties of Difluorophosphino-derivatives of Phosphorus(v) Hydroxy-compounds †

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Phosphoric acid and other hydroxy-derivatives of phosphorus(v) react with $S(PF_2)_2$ to give difluorophosphino-esters. Tris(difluorophosphino) phosphate, $PO(OPF_2)_3$, and bis(difluorophosphino) monofluorophosphate, $PFO(OPF_2)_2$, have been prepared and characterised by n.m.r., mass, and vibrational spectroscopy. The reaction of $PO(OPF_2)_3$ with diborane is described. The formation and n.m.r. spectra of $PO(OPF_2)_2Ph$ and $PO(OPF_2)Ph_2$ are also reported.

The reactions of $Se(PF_2)_2$ and $S(PF_2)_2$ with hydroxy-compounds have been shown to provide a convenient and versatile method for the synthesis of compounds containing the OPF_2 group,[1] equation (1). This type of reaction has been applied to the preparation of derivatives of carbon and phosphorus,[1] and we have extended it to silicon, sulphur, selenium, and tellurium.[2]

$$S(PF_2)_2 + ROH \longrightarrow ROPF_2 + PF_2(S)H \quad (1)$$

In this paper we describe the reactions of $S(PF_2)_2$ with hydroxy-derivatives of phosphorus(v) to give compounds of the types $PO(OPF_2)R_2$, $PO(OPF_2)_2R$, and $PO(OPF_2)_3$, which are potentially mono-, bi-, and tri-dentate ligands respectively.

Results and Discussion

The reaction of $S(PF_2)_2$ with phosphorus acids [equation (2)]

$$PO(OH)_nR_{3-n} + nS(PF_2)_2 \longrightarrow PO(OPF_2)_nR_{3-n} + nPF_2(S)H \quad (2)$$
$$n = 3;\ n = 2,\ R = F \text{ or } Ph;\ n = 1,\ R = Ph$$

proceeded rapidly and in high yield at room temperature, for all values of n and substituents, R, studied. In all cases, excess of $S(PF_2)_2$ was used to remove any traces of moisture present.

The new compounds $PO(OPF_2)_3$, $PFO(OPF_2)_2$, $PO(OPF_2)_2Ph$, and $PO(OPF_2)Ph_2$ were characterised by ^{19}F and ^{31}P n.m.r. spectroscopy. The first two of these compounds were isolated using standard high-vacuum techniques, and vibrational and mass spectra were also obtained. No attempt was made to isolate $PO(OPF_2)Ph_2$, and $PO(OPF_2)_2Ph$ was obtained by simply evaporating the more volatile $PF_2(S)H$ and $S(PF_2)_2$ from the reaction mixture.

$PO(OPF_2)_3$.—The identity of $PO(OPF_2)_3$ was first established by its ^{31}P and ^{19}F n.m.r. spectra. The ^{31}P spectrum has two sets of resonances, one of which is essentially a wide triplet of doublets, and may be assigned to the phosphorus nuclei of the difluorophosphino-groups. The other has 16 lines visible and has been analysed as a first-order quartet [^2J(PP')] of septets [^3J(P'F)], with one coupling three times the magnitude of the other, and is assigned to the phosphorus(v) nucleus. At high resolution each line of the phosphino-resonance splits further, as shown in Figure (*a*): the whole pattern is centrosymmetric, consistent with an $[A[MX_2]_3]$ spin system. This pattern has not been analysed, but the small splittings must arise from significant (*ca.* 2 Hz) four- and five-bond PP and PF couplings. Similarly, the ^{19}F spectrum is second order [Figure (*b*)], although at low resolution it appears to be a simple doublet [^1J(PF)] of doublets [^3J(P'F)]. Measured n.m.r. parameters are listed in Table 1.

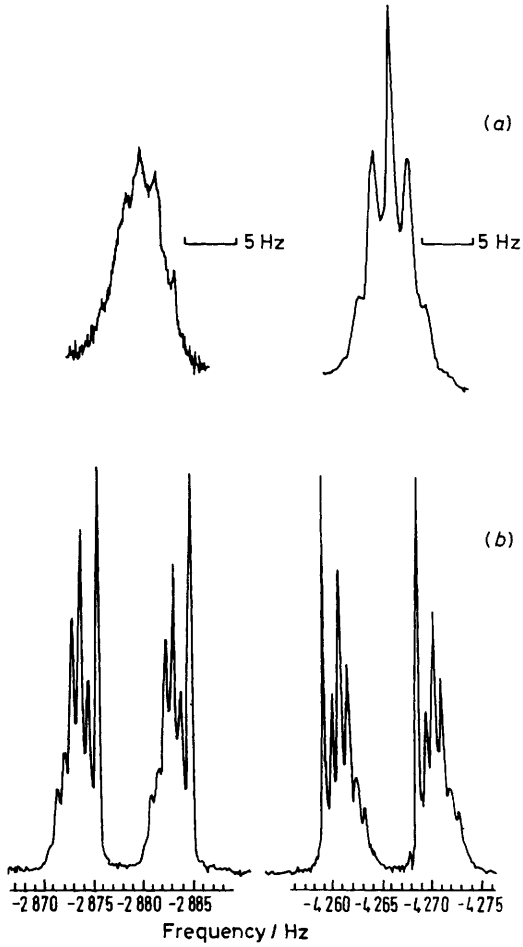


Figure. N.m.r. spectra of $PO(OPF_2)_3$: (*a*) high-resolution ^{31}P spectrum, showing one of the high-frequency doublets and one of the central doublets of resonances due to the difluorophosphino-groups; (*b*) high-resolution ^{19}F spectrum

Details of the i.r. spectra of $PO(OPF_2)_3$ in gas, liquid, and solid (amorphous and annealed) phases, and of Raman spectra of liquid and solid phases, are given in Table 2. Analysis of these spectra is difficult, first because the orientations of the OPF_2 groups are not known, so that the molecule may belong to point groups C_{3v}, C_3, C_s, or C_1, or there may be several

† *Non-S.I. units employed*: mmHg ≈ 134 Pa, eV ≈ 1.60×10^{-19} J.

Table 1. N.m.r. parameters [a]

	$P'O(OPF_2)_3$	$P'F'O(OPF_2)_2$	$P'O(OPF_2)_2Ph$	$P'O(OPF_2)Ph_2$
$\delta(^{31}P)$/p.p.m.	107.9	106.8	110.7	113.7
$\delta(^{31}P')$/p.p.m.	−40.8	−37.5	1.4	30.4
$\delta(^{19}F)$/p.p.m.	−37.5	−37.2 [b]	−38.6 [c]	−39.7
$\delta(^{19}F')$/p.p.m.		−66.2		
$^1J(^{31}P^{19}F)$/Hz	1 385	1 390	1 363	1 358
$^1J(^{31}P'^{19}F')$/Hz		1 025		
$^2J(^{31}P^{31}P')$/Hz	28.9	32.5	17.8	n.o.
$^2J(^{19}F^{19}F)$/Hz		21	19	
$^3J(^{31}P^{19}F')$/Hz		n.o.		
$^3J(^{31}P'^{19}F)$/Hz	9.5	9.4	7.5	n.o.
$^4J(^{19}F^{19}F')$/Hz		n.o.		

[a] Spectra were recorded for solutions in CCl_3D or CCl_2D_2. Chemical shifts are to high frequency of external CCl_3F or 85% H_3PO_4. [b] Mean value: difference of chemical shifts of geminal fluorine nuclei, 0.17 p.p.m. [c] Mean value: difference of chemical shifts of geminal fluorine nuclei, 0.46 p.p.m.

Table 2. Vibrational spectra (cm^{-1}) of $PO(OPF_2)_3$

Gas	Liquid		Amorphous solid		Crystalline solid		
I.r.	I.r.	Raman	I.r.	Raman	I.r.	Raman	Assignment
1 345m	1 321s	1 314m,p	1 298m	1 295w	1 258s	1 255s	ν(P=O)
1 042(sh),w			1 050(sh)		1 057s		ν_{asym}(POP)
988vs	977br,s		990br,s		1 021s		
867vs	843br,s	860vs,p		870s	877m		
		841s,dp	835br,s		844s	853s	ν(PF_2)
				820s	825s		
					808vs	808s	
	746(sh),m	735m,dp	743w		743w		
					734m		ν_{sym}(POP)
728m	710m		716w	725m	726m	728m	
		661s,p	670(sh),w	665vs			
					616m		
					611m	613s	
529m			535m		507m	505m	
					499s		
	509m		515w				
469(sh),w	474(sh),w		457w		487m		
		415m,dp	410w	410w	414w	416m	Deformations
399vw					406m		
			370vw		359w	359m	
					324vw	325m	
					296vw	296m	
						264m	
		220m,dp					

Abbreviations used: w = weak, m = medium, s = strong, v = very, br = broad, sh = shoulder, p = polarised, and dp = depolarised.

conformers present. Secondly, the molecule has 14 atoms, and so has 36 normal modes. Finally, the atoms are all of comparable mass, so mixing of vibrations will occur, making the concept of group frequencies less helpful than normal. Nevertheless, there are bands in the region (800—900 cm^{-1}) associated with PF stretches of PF_2 groups, and bands at around 1 000 and 700 cm^{-1} may, by comparison with $O(PF_2)_2$,[3] be assigned to modes that involve symmetric or antisymmetric stretching of P–O–P units. No attempt has been made to assign the numerous low-frequency deformation modes, but the sole remaining high-frequency band must clearly be due to the P=O stretching mode. The frequency of this band depends strikingly on the phase of the sample, decreasing progressively on condensing from gas through liquid to solid, and decreasing further on annealing the solid. The overall change is 90 cm^{-1}, suggesting that there is some intermolecular interaction involving the phosphoryl group. This idea is supported by observations of a high melting point [254 K compared to 165 K for $P(OPF_2)_3$ [2]], a low vapour pressure [1 mmHg at 273 K compared to 20 mmHg for $P(OPF_2)_3$], and the formation of long rod-like crystals, suggesting unbranched chains of molecules. Unfortunately, this behaviour made it impossible to grow a crystal suitable for *X*-ray crystallography, and we have been unable to determine the structure of the compound in the solid phase. However, it should be noted that the melting points of phosphoryl halides, POX_3, are about 100 K higher than those of the corresponding phosphorus trihalides,[4] and that $POCl_3$ and $POBr_3$ form rod-like crystals in which the molecules interact to form chains linked by the oxygen atoms of the phosphoryl group and one halogen atom of each molecule.[5] It is therefore probable that there are interactions between phosphoryl oxygen and an atom (probably phosphorus) of a PF_2 group of a neighbouring molecule as in (I).

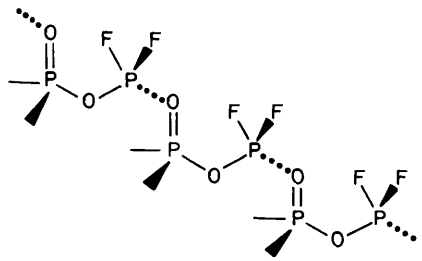
Details of the mass spectrum of $PO(OPF_2)_3$ are given in Table 3. The spectrum supports the suggested formulation, and shows that fragmentation of the molecular ion occurs primarily by loss of PF_2O. The second stages, loss of PFO to

Table 3. Mass spectrum of $PO(OPF_2)_3$

m/e	Relative abundance	Assignment
302	3	$[PO(OPF_2)_3]^+$
217	24	$[PO(OPF_2)_2]^+$
154	16	$[O(PF_2)_2]^+$
151	12	$[P_2F_3O_2]^+$
150	4	$[P_2F_3]^+$
148	4	$[P_2F_2O_4]^+$
135	8	$[P_2F_3O]^+$
129	10	$[P_2FO_3]^+$
88	10	$[PF_3]^+$
85	4	$[PF_2O]^+$
69	100	$[PF_2]^+$
66	4	$[PFO]^+$
50	8	$[PF]^+$
47	24	$[PO]^+$

Metastable ions

m/e	Assignment
155.9	$[PO(OPF_2)_3]^+ \longrightarrow PF_2O + [PO(OPF_2)_2]^+$
105.1	$[PO(OPF_2)_2]^+ \longrightarrow PFO + [P_2F_3O_2]^+$
76.7	$[PO(OPF_2)_2]^+ \longrightarrow PF_3 + [P_2FO_3]^+$
31.5	$[P_2F_3O_2]^+ \longrightarrow PFO_2 + [PF_2]^+$
16.4	$[P_2F_3O]^+ \longrightarrow PF_3 + [PO]^+$



(I)

give an ion with formula $[P_2F_3O_2]^+$, or elimination of PF_3, must involve migration of a fluorine atom.

$PFO(OPF_2)_2$.—The ^{19}F and ^{31}P n.m.r. spectra of $PFO(OPF_2)_2$ are complex, but provide unequivocal identification of the compound. In this molecule the two fluorine nuclei of each PF_2 group are chemically non-equivalent, by virtue of the prochirality of the phosphoryl phosphorus atom, and so there are two chemically distinct types of phosphorus and three types of fluorine. Moreover, the two PF_2 groups are magnetically non-equivalent, and should give second-order spectra. However, the couplings [^4J(PP) and ^5J(PF)] must be substantially smaller than in $PO(OPF_2)_3$, and these effects were not observed.

The ^{31}P spectrum of $P'F'O(OPF_2)_2$ was therefore effectively first order, and contained a wide doublet [^1J(P'F')] of triplets [^2J(PP')] of quintets [^3J(P'F)], and a wide triplet [^1J(PF)] of doublets [^2J(PP')]. The ^{19}F spectrum was second order, with a wide doublet [^1J(PF)] of doublets [^3J(P'F)] of [AB] sub-spectra, arising from the inequivalent pairs of fluorine nuclei in the PF_2 groups, and a simplet doublet, assigned to the unique fluorine nucleus. The parameters are all listed in Table 1, and are consistent with the proposed formulation. It is interesting to note that ^2J(PP') and ^3J(P'F) are observed both for $PFO(OPF_2)_2$ and for $PO(OPF_2)_3$, whereas in $PF_2O(OPF_2)$ neither coupling was observed.[6] It is probable that in the latter case there is a rapid intermolecular exchange, possibly catalysed by solid decomposition products which were also present. The equivalent couplings were also absent from the spectra of $PO(OPF_2)Ph_2$.

Samples of $PFO(OPF_2)_2$ were always contaminated with small amounts of $PO(OPF_2)_3$, arising from orthophosphoric acid in the commercial fluorophosphoric acid, and so a full study of its vibrational spectra was not undertaken. Details of the most prominent bands in the i.r. spectrum of the gas phase are given in Table 4. The spectrum is broadly similar to that of $PO(OPF_2)_3$, with an extra band at 930 cm^{-1}, assigned to the phosphorus(v)–fluorine stretching mode.

Table 4. I.r. spectrum of gaseous $PFO(OPF_2)_2$ recorded in the range 4 000—400 cm^{-1}

Band	Assignment
1 365s	ν(P=O)
1 005vs	ν_{asym}(POP)
930vs	$\nu(P^{V}F)$
865vs	$\nu(P^{III}F)$
725s	ν_{sym}(POP)
530m	δ(PF_2)

Table 5. Mass spectrum of $PFO(OPF_2)_2$

m/e	Relative abundance	Assignment
236	9	$[PFO(OPF_2)_2]^+$
217	3	$[PO(OPF_2)_2]^+$
170	7	$[P_2F_4O_2]^+$
154	10	$[O(PF_2)_2]^+$
151	78	$[P_2F_3O_2]^+$
135	4	$[P_2F_3O]^+$
132	4	$[P_2F_2O_2]^+$
129	5	$[P_2FO_3]^+$
88	5	$[PF_3]^+$
85	8	$[PF_2O]^+$
79	3	$[PO_3]^+$
69	100	$[PF_2]^+$
66	7	$[PFO]^+$
50	5	$[PF]^+$
47	15	$[PO]^+$

Metastable ions

m/e	Assignment
96.6	$[PFO(OPF_2)_2]^+ \longrightarrow PF_2O + [P_2F_3O_2]^+$
76.7	$[PO(OPF_2)_2]^+ \longrightarrow PF_3 + [P_2FO_3]^+$

Samples of $PO(OPF_2)_2Ph$.—A sample of $PO(OPF_2)_2Ph$ was prepared by direct reaction of $PO(OH)_2Ph$ and $S(PF_2)_2$. The volatile products were then removed and solvent was added to the product before n.m.r. spectra were recorded. This procedure, although crude, resulted in a fairly pure product, with only very small amounts of $PF_2(S)H$ present.

The ^{31}P n.m.r. spectrum of $P'O(OPF_2)_2Ph$ showed two sets of resonances, a triplet of quintets, assigned to P', and a wide triplet of doublets, assigned to the phosphorus nuclei of the difluorophosphino-groups. The ^{19}F spectrum was more complicated, as there is a prochiral centre on the central phosphorus atom, making the two fluorine nuclei of each PF_2 group non-equivalent. The spectrum therefore consisted of a doublet [^1J(PF)] of doublets [^3J(P'F)] of [AB] sub-spectra. Analysis of the spectra gave the parameters listed in Table 1.

As with $PFO(OPF_2)_2$, no four- or five-bond couplings between the PF_2 groups were observed.

$PO(OPF_2)Ph_2$.—The reaction of $PO(OH)Ph_2$ and $S(PF_2)_2$ was carried out in a sealed n.m.r. tube, and no attempt was made to isolate the products, which were $PF_2(S)H$ and $PO(OPF_2)Ph_2$. The ^{31}P n.m.r. spectrum of the latter showed two types of phosphorus to be present, but no coupling between them, and similarly the ^{19}F spectrum was simply a doublet. The n.m.r. parameters (included in Table 1) are entirely consistent with the proposed formulation. The absence of PP and three-bond PF couplings suggests that there is some exchange process occurring, and this is further supported by the observation that the ^{31}P resonances broadened on warming the sample from 200 to 300 K, with the phosphorus(v) line then having a half-width of *ca.* 50 Hz.

Reaction of $PO(OPF_2)_3$ *with* B_2H_6.—This reaction was carried out in a sealed n.m.r. tube, using a large excess of diborane, and was monitored by ^{19}F and ^{31}P n.m.r. spectroscopy. Good spectra were difficult to obtain, due to the complexity and overlapping of the spectra of the individual species formed, and so only the signals due to free PF_2 groups of mono- and bis-borane adducts could be clearly resolved. The signals due to the $PF_2{\cdot}BH_3$ groups of mono-, bis-, and tris-borane adducts overlapped and were broad due to coupling with boron, and the resonances of the phosphorus(v) nuclei all overlapped.

After an hour at room temperature the signals due to $PO(OPF_2)_3$ had greatly diminished in intensity, and a new species with δ(P) 106.8 p.p.m., $^1J(PF)$ 1 396 Hz, and $^2J(PP')$ 23 Hz had appeared. These resonances were assigned to the uncomplexed PF_2 groups of $PO(OPF_2)_3{\cdot}BH_3$. On standing, these resonances decreased, and after 20 h the major component had δ(P) 105.9 p.p.m., $^1J(PF)$ 1 406 Hz, and $^2J(PP')$ 40 Hz: this was assigned to $PO(OPF_2)_3{\cdot}2BH_3$. It was hoped that on further standing the reaction would go to give entirely $PO(OPF_2)_3{\cdot}3BH_3$, but over several days a solid was formed and n.m.r. spectra showed that the major species in solution was now $PF_2H{\cdot}BH_3$. The white solid was pyrophoric, and may be a derivative of a higher boron hydride, but it was not characterised further.

Experimental

Manipulations of volatile materials were carried out on a Pyrex glass vacuum line, fitted with Sovirel greaseless taps. Bis(difluorophosphino) sulphide was prepared by reaction of bromodifluorophosphine with bis(tributylstannyl) sulphide.[7] Other reagents were obtained commercially or prepared by standard methods.

N.m.r. spectra were obtained using Varian XL100 (^{31}P and ^{19}F) and JEOL FX60Q (^{31}P) spectrometers, and mass spectra were recorded on an A.E.I., MS902 spectrometer, with an ionising voltage of 70 eV. Vibrational spectra were recorded on a Cary 83 Raman spectrometer, with 488-nm argon-ion laser excitation, and a Perkin-Elmer 557 spectrometer. Using cells equipped with KBr or CsI windows, i.r. spectra were recorded down to 400 or 200 cm^{-1}.

Samples for study by n.m.r. spectroscopy were obtained by distilling measured amounts (typically 0.2 mmol) of volatile compounds into 5-mm n.m.r. tubes containing *ca.* 0.5 cm^3 of solvent. The tubes were then sealed.

Preparations.—$PO(OPF_2)_3$. The compound $S(PF_2)_2$ (16.5 mmol) was condensed into a glass ampoule (250 cm^3) containing 100% H_3PO_4 (4.5 mmol). On warming to room temperature, the solid material disappeared and effervescence was noted. After 30 min the volatile products were removed, and separated by fractional condensation *in vacuo*. Tris(difluorophosphino) phosphate (4.3 mmol, 95%) was obtained as the fraction volatile at 228 K but involatile at 177 K.

$PFO(OPF_2)_2$. The compound $S(PF_2)_2$ (5 mmol) was condensed into a glass ampoule (40 cm^3) containing $PFO(OH)_2$ (1.5 mmol). After warming the reagents to room temperature for 20 min the volatile products were removed and separated by fractional condensation. Bis(difluorophosphino) monofluorophosphate (1.3 mmol, 87%) was obtained as the fraction passing a trap at 228 K, but retained at 195 K.

$PO(OPF_2)_2Ph$. The compound $S(PF_2)_2$ (0.5 mmol) was condensed into a glass ampoule (20 cm^3) containing $PO(OH)_2Ph$ (0.2 mmol), and the reagents were warmed to room temperature for 15 min. The volatile products were then removed, and CCl_3D was added to the involatile product, $PO(OPF_2)_2Ph$, which was then poured into an n.m.r. tube.

Acknowledgements

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