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PREPARATION AND CHARACTERIZATION OF SOME PHOSPHORUS COMPOUNDS CONTAINING THE HEXAFLUOROISOPROPOXY GROUP

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SUMMARY

A series of phosphorus(V) compounds, $X_2P[OCH(CF_3)_2]_3$ ($X = F, Cl, Br, OCH(CF_3)_2$; $X_2 = O, S$) have been synthesized and characterized by their ^{31}P, ^{19}F, and ^{1}H n.m.r. spectra; by mass spectrometry; and by elemental analysis. New covalent chloro- and bromo-phosphoranes were obtained by direct halogenation of the phosphite, $P[OCH(CF_3)_2]_3$, whereas the first pure acyclic penta-alkoxyphosphorane was obtained from the reaction of $Cl_2P[OCH(CF_3)_2]_3$ with the lithium salt, $Li[OCH(CF_3)_2]$.

INTRODUCTION

Following on from our investigations of cyclic perfluoropinacolyl derivatives of phosphorus halides [1-4], we have begun a study of phosphorus compounds containing the acyclic hexafluoroisopropoxy group in order to compare stability and reactivity of cyclic and acyclic derivatives of alcohols containing electronegative groups. Considering the stability of acyclic fluorophosphoranes [5,6], $[C_4F_9O]_nPF_{5-n}$ (n = 1,2) and $[C_6F_5O]_nPF_{5-n}$ (n = 1,2,3) the $(CF_3)_2CHO$ group was expected to give stable halophosphoranes.

Until recently only a few phosphorus compounds with one or two $(CF_3)_2CHO$ substituents have been reported [7-16].

Furthermore, only few penta-alkoxy and -phenoxy phosphoranes were known [17-18], and of these only the penta-phenoxy derivative [17] has been isolated as a pure compound. Most of the syntheses described here involve nucleophilic displacement of halogen using the lithium salt, $Li[OCH(CF_3)_2]$ which avoids the difficulties of separating mixtures which are encountered when alcohol/base/phosphorus halide/solvent systems are used.

RESULTS AND DISCUSSION

The phosphite with three hexafluoroisopropoxy groups, $P[OCH(CF_3)_2]_3$, is easily prepared in good yield by reaction of the lithium salt [19], $Li[OCH(CF_3)_2]$ with PCl_3 or by adding PCl_3 to an ether solution of $(CF_3)_2CHOH$, using triethylamine as the base,

$$\begin{array}{llr} PCl_3 + 3Li[OCH(CF_3)_2] \xrightarrow{-3LiCl} & & (1a) \\ & P[OCH(CF_3)_2]_3 \quad \underset{=}{1} & \\ PCl_3 + 3(CF_3)_2CHOH \xrightarrow[-3Et_3NHCl]{3Et_3N} & & (1b) \end{array}$$

Compound 1, a colourless volatile liquid of b.p. 130°C, adds one mole of chlorine or bromine (2) forming covalent dihalophosphoranes, $X_2P[OCH(CF_3)_2]_3$,

$$1 + X_2 \rightarrow X_2P[OCH(CF_3)_2]_3 \qquad (2)$$

$$2: X = Cl \qquad 3: X = Br$$

At room temperature no ^{31}P n.m.r. spectroscopic evidence for equilibria such as $X_2P[OCH(CF_3)_2]_3 \rightleftharpoons X^-[P\{OCH(CF_3)_2\}_3X]^+$ has been found. The electronegativity of the alkoxy group apparently prevents an Arbuzov type rearrangement,

$$X_2P[OCH(CF_3)_2]_3 \nrightarrow XP(O)[OCH(CF_3)_2]_2 + (CF_3)_2CHX \qquad (3)$$

Both compounds, **1** and **2**, are very sensitive to moisture, the hydrolysis product in each case being the phosphoric acid ester, $OP[OCH(CF_3)_2]_3$, **4**. Compound **4** and the thio analogue, **5**, are obtained from reaction (4),

$$EPCl_3 + 3Li[OCH(CF_3)_2] \rightarrow EP[OCH(CF_3)_2]_3 + 3LiCl \qquad (4)$$

4: E = O ; **5**: E = S

Compound **4** is also obtained by reaction of $(CF_3)_2CHOH$ with $OPCl_3$ in the presence of triethylamine in ether solution. The reactivity of **2** enabled substitution of chlorine by the $(CF_3)_2CHO$ group,

$$Cl_2P[OCH(CF_3)_2]_3 + 2Li[OCH(CF_3)_2] \rightarrow \underset{\mathbf{6}}{P[OCH(CF_3)_2]_5} + 2LiCl \qquad (5)$$

Reaction (5) occurs smoothly, yielding the first pure penta-alkoxyphosphorane, **6**, as colourless crystals of m.p. 25-28°. Compound **6** is also fairly reactive towards moisture, again yielding **4** as a hydrolysis product.

$$\mathbf{6} + H_2O \rightarrow \mathbf{4} + 2(CF_3)_2CHOH \qquad (6)$$

Fluorination of **2** using antimony trifluoride gives a mixture of fluorophosphoranes* from which can be separated $F_2P[OCH(CF_3)_2]_3$, **7**, and $F_3P[OCH(CF_3)_2]_2$, **8**. Apparently antimony trifluoride causes an exchange of the $(CF_3)_2CHO$ group by fluorine. Efforts were made to prepare $F_4P[OCH(CF_3)_2]$ by reacting $Me_3Si[OCH(CF_3)_2]$ and $Li[OCH(CF_3)_2]$, respectively, with PF_5. Even a large excess of PF_5 does not yield $F_4P[OCH(CF_3)_2]$; instead a mixture of compounds **7** and **8** is formed in each case.

Possibly, the reaction rate of PF_5 with $Me_3Si[OCH(CF_3)_2]$ and $Li[OCH(CF_3)_2]$ is slow, while reaction of the intermediate

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* There is some ^{19}F n.m.r. evidence suggesting formation of mixed halogen species such as $FClP[OCH(CF_3)_2]_3$, $FCl_2P[OCH(CF_3)_2]_2$ but such species could not be unequivocably identified.

$F_4P[OCH(CF_3)_2]$ with $Me_3Si[OCH(CF_3)_2]$ and $Li[OCH(CF_3)_2]$ is fast. Such a situation has been proposed for the case of the reaction of PF_5 with KOC_6F_5 and $Me_3SiOC_6F_5$ [6]. Furthermore, it seems possible that the rearrangement process of $F_4P[OCH(CF_3)_2]$ to form $F_3P[OCH(CF_3)_2]_2$ and PF_5 is fast.

Compound **8** is a colourless thermally stable liquid and **7** is a colourless crystalline solid. Both **7** and **8** are covalent and their ^{19}F n.m.r. spectra do not show any evidence of scrambling which might yield ionic products e.g.

$$2F_3P[OCH(CF_3)_2]_2 \nrightarrow P[OCH(CF_3)_2]_4{}^+[PF_6]^- \qquad (7)$$

Compound characterization

Mass spectra: In the cases of compounds **1**, **4**, **5** molecular ions, M^+ were formed in their 70 eV mass spectra. None of the phosphoranes **2**, **3**, **6**, **7**, **8** gave molecular ions [20,21] and for compound **2** only the fragments due to the hydrolysis product, **4**, were observed, despite several attempts to work in a rigorously dried ion source. Compound **3** loses bromine to give $[M-Br]^+$ while compounds **6**, **7**, **8** each lose fluorine to give $[M-F]^+$ as peaks of highest mass number. It is particularly interesting to note that compound **6** has the ion fragment $[P[OCH(CF_3)_2]_4]^+$ as the base peak. This may be compared to observations on fluorophosphoranes, PF_5 and RPF_4 (R = aliphatic group) which invariably do not exhibit a fragment due to the parent molecule while the group PF_4 is the base peak [23].

N.m.r. spectra: N.m.r. data were recorded at ambient temperature and are in all cases in agreement with the formulations presented in table 1.

In the ^1H n.m.r. spectra of compounds **3**, **4**, and **7** a broad signal for the CH protons is seen which might result from overlapping signals due to slightly different $(CF_3)_2CHO$ groups. For each of the compounds **1**, **2**, **5**, **8** the ^1H n.m.r. spectra could be resolved into a septet of doublets, enabling $^3J_{PH}$ and $^3J_{FH}$ coupling constants to be measured.

TABLE 1

^{1}H, ^{19}F, and ^{31}P n.m.r. data for compounds **1** to **8** [a]

Compound	δ_H [b]	δ_{CF_3} [c]	δ_P [d]	$^{3}J_{PH}$	$^{3}J_{FH}$
1	-4.8	76.0	-141	9.7	5.3
2	-5.9	77.3	+76	21.0	6.0
3	-5.7	73.0	+80	-	-
4	-5.4	75.5	+3	-	-
5	-5.5	76.4	-73	16.5	6.0
6	-5.2	73.0	+84	10.5	-
7	-5.5	79.0 [e]	+82	-	-
8	-5.2	76.0 [f]	+79	7.0	6.5

a. δ in p.p.m.; J in Hz; values obtained at ambient temperature

b. δ relative to TMS; negative values downfield

c. δ relative to $CFCl_3$

d. δ relative to 85% H_3PO_4; positive values upfield

e. $\delta_{P\underline{F}}$ +57.0; J_{FP} 790

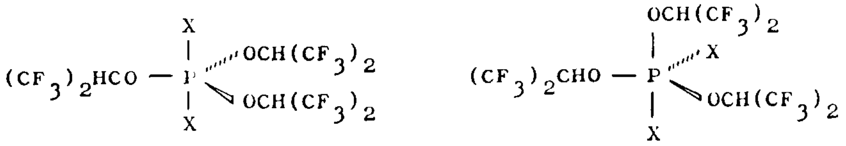
f. $\delta_{P\underline{F}}$ +65.0; J_{FP} 845

Signals in the ^{19}F n.m.r. spectra confirm the presence of the $(CF_3)_2CHO$ group. No fine structure due to H-F coupling could be observed in the ^{19}F n.m.r. spectra.

Doublets are found in the ^{19}F n.m.r. spectra of compounds **7** and **8** whereas the ^{31}P n.m.r. spectra of these compounds showed a triplet (centered at +82 p.p.m.) and a quartet (centered at +79 p.p.m.), respectively. Both compounds **7** and **8** have rather large F-P coupling constants. The ^{31}P n.m.r. spectra of the phosphoranes show no resonances attributable to either four-coordinate or six-coordinate phosphorus. Shift values are all in the region considered typical of covalent phosphoranes [24].

The ^{19}F n.m.r. spectra of compounds 2 and 7 did not show any evidence for non-equivalent [15,16] hexafluoroisopropoxy groups for a trigonal bipyramidal structure at temperatures down to -90° (at which temperature the compounds crystallized from pentane/$CFCl_3$ solution). The low solubility of compounds 3 and 6 precluded a low temperature n.m.r. study.

Considering the electronegativity of the halogen atoms, it seems most likely that 2, 3, 6, and 7 have a trigonal bipyramidal structure A (figure 1) although structure B cannot be definitely excluded. Furthermore, even traces of free HX (X = F, Cl, Br) and hexafluoroisopropanol would cause rapid rearrangement of the ligands about the phosphorus atom and this could also cause equivalence of the two $(CF_3)_2CHO$ groups. Both structures A and B seem equally likely for 6.



[X = F, Cl, Br, $(CF_3)_2CHO$]

Structure A

Structure B

FIGURE 1

EXPERIMENTAL

General. The appropriate precautions in handling moisture-sensitive compounds were observed. Solvents were dried by standard techniques and standard high vacuum procedures were used throughout.

Hydrogen-1, ^{19}F and ^{31}P n.m.r. spectra were recorded on a JEOL 60 JNMC instrument at 60.0, 56.4, and 24.3 MHz, respectively. An external H_2O lock system with generation of 4000 Hz side bands was used to locate resonances accurately. Mass spectra were recorded on an AEI MS9 (direct inlet or reservoir system) instrument. Elemental analyses were carried out by Beller Laboratories, Göttingen.

Reagents. Chlorine, after establishing the absence of hydrogen chloride, was used without further treatment. Bromine was dried over concentrated sulphuric acid and purified by trap to trap condensation. $Li[OCH(CF_3)_2]$ was prepared by a literature method [19].

Preparation of Tris-(1,1,1,3,3,3-hexafluoropropoxy)-phosphine (1)

Phosphorus trichloride (1.4 g; 10.0 mmol) was condensed into a thick-walled glass tube fitted with a teflon tap and containing $Li[OCH(CF_3)_2]$ (6.1 g; 35.0 mmol). The reaction mixture was allowed to warm to room temperature over a period of one hour, and the product, 1, was condensed into a second glass tube at -196°.

Alternatively, 1 was prepared by reaction of 1,1,1,3,3,3-hexafluoropropanol-(2) (5.9 g; 35.0 mmol) with phosphorus trichloride (1.4 g; 10.0 mmol) in ether solution (150 ml) in the presence of triethylamine (3.6 g; 35.0 mmol). After filtration of the amine hydrochloride and removal of the solvent, the colourless product 1 was distilled.

b.p. 130° (760 mm). Yield 4.9 g (92%, based on PCl_3)
Anal. calculated for $C_9H_3O_3PF_{18}$ (mol. wt. 532.09): C, 20.3; H, 0.6; F, 64.3%. Found: C, 20.5; H, 0.6; F, 64.4%.
MS: 532 (M^+, 22%), 69 (CF_3^+, 100%).

Dichloro-tris(1,1,1,3,3,3-hexafluoropropoxy)phosphorane (2)

Chlorine (0.7 g; 10.0 mmol) was condensed into a glass tube at -196° containing 1 (5.3 g; 10.0 mmol). The reaction mixture was allowed to warm to room temperature over two hours and was then briefly opened to a vacuum system and excess chlorine pumped away. The colourless product, 2, was then condensed into a trap at -196°.

b.p. 48° (0.01 mm); yield 5.0 g (83%, based on 1)

Anal. calculated for $C_9H_3O_3PF_{18}Cl_2$ (mol. wt. 602.99): C, 17.9; H, 0.5; F, 56.7; Cl, 11.8%. Found: C, 17.8; H, 0.5; F, 56.0; Cl, 13.5%.

Dibromo-tris-(1,1,1,3,3,3-hexafluoropropoxy)phosphorane (3)

Bromine (1.6 g; 10.0 mmol) was condensed into a tube at -196° containing 1 (5.3 g; 10.0 mmol). The tube was allowed to warm to room temperature over two hours. Excess bromine was pumped away by brief exposure to a vacuum system. The colourless solid product, 3, was sublimed into another trap at -196°.

M.p. 12°. Yield 5.4 g (78%, based on 1).
Anal. calculated for $C_9H_3O_3PF_{18}Br_2$ (mol.wt. 691.89): C, 15.6; H, 0.1; F, 49.4%. Found: C, 16.8; H, 0.4; F, 51.9%.
MS: 611($[M-Br]^+$, 3%), 69 (CF_3^+, 100%).

Difluoro-tris-(1,1,1,3,3,3-hexafluoropropoxy)phosphorane (7)

Attempts to fluorinate 2 using sodium fluoride in the absence of a solvent were unsuccessful and produced no new products even when the mixture was held at 100° for two hours. 2 (0.8 g; 15.0 mmol) was condensed into a tube containing antimony trifluoride (1.8 g; 10.0 mmol) and allowed to remain at room temperature for three hours, producing a mixture of fluorinated products which were separated by trap to trap condensation using traps held at -5°, -80°, and -196°. The trap at -5° contained colourless crystals of 7.

Compound 7 was also prepared by condensing phosphorus pentafluoride (2.5 g; 20.0 mmol) into a trap containing $Me_3Si[OCH(CF_3)_2]$ [22] (1.2 g; 5.0 mmol) and allowing the reaction mixture to warm to room temperature over three hours. Again a mixture of products was obtained and was separated by trap to trap condensation as before.

M.p. 28-32°. Yield 1.5 g (52%, based on $Me_3Si[OCH(CF_3)_2]$).

Anal. calculated for $C_9H_3O_3PF_{20}$ (mol.wt. 570.09): C, 19.9; H, 0.5; F, 66.7%. Found: C, 18.8; H, 0.6; F, 66.7%. MS: 551 ($[M-F]^+$, 73%), 403 ($[M-OCH(CF_3)_2]^+$, 100%).

Trifluoro-bis-(1,1,1,3,3,3-hexafluoropropoxy)phosphorane (8)

Compound 8 was prepared and separated as described for 7. The trap at -80° contained the colourless liquid 8.

B.p. 38°. Yield 1.0 g (21%, based on $Me_3Si[OCH(CF_3)_2]$). Anal. calculated for $C_6H_2O_2PF_{15}$ (mol.wt. 422.06): C, 17.1; H, 0.5%. Found: C, 17.6; H, 0.9%.
MS: 403 ($[M-F]^+$, 95%), 255 ($[M-OCH(CF_3)_2]^+$, 100%).

Pentakis-(1,1,1,3,3,3-hexafluoropropoxy)phosphorane (6)

2 (1.8 g; 3.0 mmol) was condensed into a tube at -196° containing $Li[OCH(CF_3)_2]$ (1.1 g; 6.0 mmol). The reaction mixture was then heated at 50° for three hours. Subsequently, the tube was kept in a water bath at 40° and the colourless crystalline product, 6, was sublimed into another tube, held at -196°.

M.p. 25-28°. Yield 1.9 g (73%, based on 2).
Anal. calculated for $C_{15}H_5O_5PF_{30}$ (mol.wt. 866.15): C, 20.8; H, 0.6; F, 65.8%. Found: C, 20.8; H, 0.6; F, 65.5%.
MS: 847 ($[M-F]^+$, 20%), 699 ($[M-OCH(CF_3)_2]^+$, 100%).

Tris-(1,1,1,3,3,3-hexafluoropropoxy)phosphate (4)

A mixture of $POCl_3$ (1.5 g; 10.0 mmol in 50 ml ether) and $Li[OCH(CF_3)_2]$ (5.3 g; 30.0 mmol) in 100 ml ether was refluxed for two hours. Ether was removed under vacuum and the solid product, 4, was vacuum-condensed into a tube at -196°.

M.p. 23°. Yield 4.9 g (90%, based on $POCl_3$)
Anal. calculated for $C_9H_3O_4PF_{18}$ (mol.wt. 548.09): C, 19.7; H, 0.6; F, 62.4%. Found: C, 19.8; H, 0.5; F, 62.9%.
MS: 548 (M^+, 0.5%), 43 (100%).

Tris-(1,1,1,3,3,3-hexafluoropropoxy)thiophosphate (5)

The preparation was as for compound 4 but using $PSCl_3$. The liquid product, 5, was condensed into a trap at -196°.

B.p. 170-175° (760 mm). Yield 4.1 g (73%, based on PSCl
Anal. calculated for $C_9H_3O_3PF_{18}S$ (mol.wt. 564.15): C, 19.2; H, 0.5; F, 60.6%. Found: C, 19.1; H, 0.6; F, 60.4%.
MS: 564 (M^+, 77%), 69 (CF_3^+, 100%).

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