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PREPARATION AND CHARACTERIZATION OF SOME STABLE ACYCLIC OXYPHOSPHORANES

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SUMMARY

A series of phosphoranes containing the hexafluoroisopropoxy group has been synthesized and characterized by ^{1}H, ^{19}F, and ^{31}P n.m.r., and by mass spectrometry. Some variable temperature n.m.r. studies are reported and the results are discussed in terms of possible ground state structures of the phosphoranes.

Only few stable acyclic oxyphosphoranes have as yet been synthesized[1-6]. Oxyphosphoranes containing also fluorine bonded to five-coordinate phosphorus were generally found to be unstable with respect to their decomposition into phosphoryl compounds[7-9], as illustrated, for example, by alkoxytrifluorophosphoranes,

$$R^1PF_3OR^2 \longrightarrow R^1P(O)F_2 + R^2F$$

Such compounds can be stabilized by introducing electron-withdrawing substituents into the alkoxy group[1,4,10].

As a continuation of our previous investigations of phosphorus(III)[1,11] and phosphorus(V)[1] compounds containing the hexafluoroisopropoxy group, we now present a further series of phosphoranes containing this electronegative group. We have sought to study systematically the effects of various substituents upon the fluxionality and general stability of the phosphoranes. The ligand reorganization of oxyphosphoranes is of special interest because it may, and in some cases must, intervene in the hydrolysis of phosphate esters[2,3].

We also report some alkoxyphosphoranes which, though not isolated as pure compounds, have been unambigously characterized by their n.m.r. and mass spectra as well as by their transformation into known fluorophosphorane derivatives.

For the compound preparation use was again made of reactions employing the lithium salt, $Li[OCH(CF_3)_2]$[12], 1. (From hereon the hexafluoroisopropoxy group, $(CF_3)_2CHO-$, will be abbreviated to R_fO-). Reactions involving this salt offer attractive preparative routes leading to the formation of many phosphoranes which may otherwise be difficult or impossible to synthesize. Another advantage is that one of the products is the easily separated lithium chloride.

RESULTS AND DISCUSSION

Methyl-tetra(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane, 2, and phenyl-tetra(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane, 7, may easily be prepared in good yield according to equation (1).

$$RP(OR_f)_2 + 2\ LiOR_f \xrightarrow[-2\ LiCl]{Cl_2} RP(OR_f)_4 \qquad (1)$$

1

2: R = Me

7: R = Ph

For R = Me the probable intermediate, $MeCl_2P(OR_f)_2$, 3, could be obtained as colourless sublimable crystals*

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* Compound 3 may exist in equilibrium with several other species (e.g. $MePCl(OR_f)_3$, $MePCl_3(OR_f)$, or ionic compounds) and could not be unequivocably characterized by mass spectra or elemental analysis.

from the reaction between chlorine and methyl-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite. Further reaction of compound 3 with 1 produces the corresponding phosphorane, 2, in good yield. Fluorination of 3 with SbF_3 gave $MeF_2P(OR_f)_2$ [13], 5, and $MeP(OR_f)_4$, 2; this is further evidence that 3 exists mainly as $MeCl_2P(OR_f)_2$. Compound 5 has previously been prepared from the reaction between methyl tetrafluorophosphorane and $Me_3Si(OR_f)$ [13].

Dimethyl-tris(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane, 4, was prepared according to equation (2).

$$R_2P(OR_f) + 2\ Li(OR_f) \xrightarrow[-2\ LiCl]{Cl_2} R_2P(OR_f)_3 \qquad (2)$$

4: $R = CH_3$
6: $R = CF_3$

The phosphorane 4 could be prepared only by adding chlorine to a mixture of 1 and dimethyl(1,1,1,3,3,3-hexafluoroisopropyl)phosphite[14] at -196° and allowing the reaction mixture to warm very slowly to room temperature (over ca. 10 h). Warming the reaction mixture more quickly causes extensive decomposition and carbonization. Compound 4 is a stable, easily sublimable, colourless solid.

Bis(trifluoromethyl)tris(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane, 6, is a stable, colourless liquid which may be easily prepared according to equation (2).

All attempts at the preparation of trimethyl-bis-(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane by reacting mixtures of trimethyl phosphine and 1 with chlorine were unsuccessful. The probable intermediate, trimethyl dichlorophosphorane, is mostly ionic in nature[15], apparently rearranging too quickly to allow subsequent reaction with 1. However, several phosphorus-containing compounds were formed (δ_P -99, -64, -53, -33 p.p.m.)

but yields were small and none of the compounds could be identified.

Fluorophenyl-tris(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane, 8, can be prepared from phenyl-fluoro-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite according to equation (3),

$$C_6H_5FP(OR_f) \quad + \quad 2\ \underline{1} \quad \xrightarrow[-\ 2\ LiCl]{Cl_2} \quad \underset{\underline{8}}{C_6H_5FP(OR_f)_3} \qquad (3)$$

A mixture of 8 and difluorophenyl-bis(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane, 9, was obtained from the reaction of phenyldifluorophosphine with $Cl_2/LiOR_f$.

Compounds 8 and 9 could not be completely separated from one another but both compounds were unequivocably characterized by their mass and n.m.r. spectra.

Trifluorophenyl-bis(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane, 10, was prepared from the reaction between phenyl tetrafluorophosphorane and 1 . Reaction (4) yielded a mixture of the difluoro- and trifluorophosphoranes, 9 and 10.

$$C_6H_5PF_4 \quad \xrightarrow[-\ LiF]{LiOR_f} \quad \underset{\underline{10}}{C_6H_5F_3P(OR_f)}, \quad \underset{\underline{9}}{C_6H_5F_2P(OR_f)_2} \qquad (4)$$

Mass Spectra

Most of the compounds of the present series give a weak or nondetectable molecular ion. Loss of the R_fO group is usually more extensive than loss of either fluorine or other groups R attached to phosphorus. Compounds 2, 7, 8, and 9 all lose R_fO groups to give the corresponding four-coordinate phosphorus species in high abundance. Similar results have been reported for the mass spectra of phosphoranes containing slightly different alkoxy groups[4]. Compound 6 seems to lose CF_3 and R_fO with about equal ease whereas compound 4 appears to rearrange within the mass spectrometer* to give a spectrum similar in many respects to that observed for pentakis(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane[1].

N.M.R. Spectra

^{1}H, ^{19}F, ^{31}P n.m.r. data are given in Table 1. All compounds described in this paper are expected to have a trigonal bipyramidal structure. The tetraalkoxy phosphoranes, 2 and 7 (Fig. 1) should show rapid, almost unhindered, pseudorotation with the fifth ligand (methyl and phenyl, respectively) as a pivot, assuming a Berry pseudorotation mechanism[16]. As expected, compounds 5, 9 (Fig. 2), and 10 (Fig. 3) show no "freezing" of ligand exchange down to temperatures of -100° (solvent: toluene or $CFCl_3$/iso-pentane). For these three compounds it is likely that the fluorine atoms occupy axial positions at trigonal bipyramidal phosphorus[16].

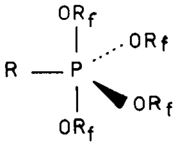

Fig. 1

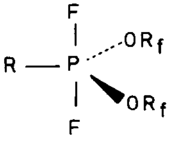

Fig. 2

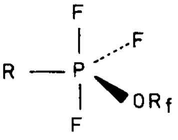

Fig. 3

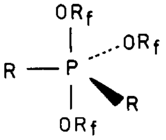

Fig. 4

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* The n.m.r. spectrum shows no change after three months storage at room temperature.

Table 1. Ambient temperature n.m.r. data for compounds <u>2</u>, <u>4</u> to <u>10</u> (δ in ppm, J in Hz)

Compound		δ_H [a]			δ_F [a]		δ_P [a]
		CH_3 ($^2J_{PH}$)	C_6H_5	$OCH(CF_3)_2$ ($^3J_{PH}$, $^3J_{FH}$)	$(CF_3)_2CHO$	PF ($^1J_{PF}$)	
$MeP[OR_f]_4$	<u>2</u>	-1.75 (18.0)		-4.10(ax)[b,c] -5.00(eq)[b,c] (13.5, 6.0)	75.3(ax)[c] 74.8(eq)[c]		+53.0
$Me_2P[OR_f]_3$	<u>4</u>	-1.82 (15.0)		-4.37(ax)[b,d] -5.52(eq)[b,d]	73.0(ax) 71.3(eq)		+20.3
$MeF_2P[OR_f]_2$	<u>5</u>	-1.70 (18.0)		-5.35[b]	73.0	35.5 (846)	+41.6
$(CF_3)_2P[OR_f]_3$	<u>6</u>			-5.30[b]	74.0[e]		+72.8
$PhP[OR_f]_4$	<u>7</u>		-7.50 to -8.00	-5.30[b]	72.5		+65.0
$PhFP[OR_f]_3$	<u>8</u>		-7.35 to -8.60	-5.30[b]	73.8	48.8 (860)	+58.1
$PhF_2P[OR_f]_2$	<u>9</u>		-7.30 to -8.35	-5.30[b]	75.0	45.0 (846)	+59.3
PhF_3POR_f	<u>10</u>		-7.00 to -8.10	-5.18	75.0	55.0 (945)	+56.4

a. Signals upfield from TMS, $CFCl_3$ and 85% H_3PO_4 are measured as positive. b. Broad signal, not resolved. c. Measured at 25°, at 40° $\delta_H[OC\underline{H}(CF_3)_2] = -4.55$ ($^3J_{PH} = 13.5$; $^3J_{FH} = 6.0$), $\delta_F = 75.0$; coalescence temperature +30°, d. Measured at 25°, at 80° $\delta_H[OC\underline{H}(CF_3)_2] = -4.95^b$ $\delta_F = 72.1$; coalescence

Surprisingly, compound 2 clearly shows two different $(CF_3)_2CHO$-groups below +30° in both ^1H and ^{19}F n.m.r. spectra (axial $(CF_3)_2CHO$-group: δ_F 75.30 p.p.m.; δ_H -4.10 p.p.m.; equatorial $(CF_3)_2CHO$-group: δ_F 74.80 p.p.m.; δ_H -5.00 p.p.m.). Both axial and equatorial $(CF_3)_2CHO$-groups have similar $^3J_{HF}$ values. The distinction between axial and equatorial groups can be made based on the results obtained for compound 4 (see below). Apparently steric effects cause this "freezing" of ligand distribution which has also been observed in the case of the compound methyl-tetrakis(2,6-dimethylphenoxy)phosphorane[17] where a coalescence temperature of -65° has been determined from the ^1H n.m.r. spectrum.

Compound 4, which has two methyl groups bonded to phosphorus (Fig. 4), has a higher barrier against pseudorotation than 2, indicated by a coalescence temperature in the ^{19}F n.m.r. spectrum of +60° (axial $(CF_3)_2CHO$ group: δ_F 73.00 p.p.m.; δ_H -5.52 p.p.m.; equatorial δ_F 71.30 p.p.m.; δ_H -4.37 p.p.m.). Compound 4 in the ground state must have the structure shown in figure 4. The integration values from the ^1H and ^{19}F n.m.r. spectra enable a clear identification of axial and equatorial groups and the structure shown in figure 4 is the only one possible. Dimethyl trifluorophosphorane also shows rigidity in its ^{19}F n.m.r. spectrum at room temperature[16].

The ^{19}F n.m.r. spectrum of compound 6, the perfluoro analog of 4, shows no temperature dependence down to -100° and therefore the ground state structure[18] could not be assigned with certainty.

EXPERIMENTAL

The usual precautions in handling moisture sensitive compounds were observed. Whenever possible, compounds were vacuum-condensed at pressure less than 10^{-3} mm. 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 with generation of 4000 Hz side bands was used to calibrate resonances accurately. Mass spectra were recorded on an AEI MS9 (direct inlet or reservoir system) instrument.

Dichloromethyl-bis(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (3)

Chlorine (0.75 g; 10 mmol) was condensed into a heavy wall glass tube at -196°, containing methyl-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite[14] (3.80 g; 10 mmol). The tube was allowed to warm to room temperature over 2 h and was briefly opened to a vacuum system and excess chlorine pumped away. The colourless crystalline product, 3, was condensed into another tube held at -196°.

M.p. = 38-43°. Yield 3.7 g (83%, based on methyl-bis(1,1,1,3,3,3-hexafluoroisopropyl)phosphite).

Methyl-tetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (2)

Compound 3 (4.50 g; 10 mmol) was condensed into a heavy-wall glass tube at -196° containing 1 (3.50 g; 20 mmol). The tube was allowed to warm to room temperature over 0.5 h and then left for 3 h. The colourless product, 2, was sublimed into another tube at -196°.

M.p. = 33-37°. Yield 6.1 g (85%, based on 3). $C_{13}H_7O_4PF_{24}$ (714.12).

Anal. found: C, 21.9; H, 1.1; F, 64,1%
calc.: C, 21,8; H, 1.0; F, 64.0

Mass spectrum: 714 (M^+, 1%); 699 (M^+ $-CH_3$, 4%); 695 (M^+ -F, 5%); 547 (M^+ $-R_fO$, 57%); 399 ($C_6H_2F_{13}O_2P^+$, 30%); 380 (M^+ $-2R_fO$, 8%); 377 ($C_7H_5F_{11}O_3P^+$, 12%);

209 ($C_4H_3O_2F_5P^+$, 23%); 137 ($C_3HF_5^+$, 46%); 101 ($C_2HF_4^+$ or $O_2PF_2^+$, 32%); 99 ($C_2H_2F_2O^+$, 87%); 79 (C_2HFO^+, 51%); 69 (CF_3^+, 96%); 59 (C_2FO^+, 40%); 51 (HFP^+ or CHF_2^+, 100%).

Dimethyl-tris(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (4)

Chlorine (0.75 g; 10mmol) was condensed into a tube at -196° containing a mixture of 1 (3.50 g; 20 mmol) and dimethyl-1,1,1,3,3,3-hexafluoroisopropyl-phosphite[14] (2.30 g; 10 mmol) and allowed to warm to room temperature over 10 h. The tube was briefly opened to a vacuum system and excess chlorine was pumped away. The colourless solid product, 4, was vacuum-sublimed (at room temperature) into another tube held at -196°.

M.p. = $46-49^{\circ}$. Yield 2.50 g (45%, based on dimethyl-1,1,1,3,3,3-hexafluoroisopropyl-phosphite). $C_{11}H_9F_{18}O_3P$ (562.13).

Anal. found: C, 23.2; H, 1.4; F, 60.1%
calc.: C, 23.5; H, 1.6; F, 60.9

Mass spectrum: 847 ($C_3H_5F_{29}O_5P^+$, 10%); 699 ($C_{12}H_4F_{24}O_4P^+$, 51%); 532 ($C_9H_3F_{18}O_3P^+$, 39%); 513 ($C_9H_3F_{17}O_3P^+$, 14%); 491 ($C_{10}H_7F_{15}O_3P^+$, 81%); 393 ($C_8H_{10}F_{12}O_2P^+$, 91%); 361 ($C_7H_8F_{10}O_3P^+$, 42%); 69 (CF_3^+, 100%); 51 (HFP^+ or CF_2H^+, 49%). The mass spectrum is in many ways similar to that for pentakis(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane[1]. Presumably the compound rearranges in the mass spectrometer.

Difluoromethyl-bis(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (5)

Compound 3 (2.20 g; 5 mmol) was condensed into a tube containing SbF_3 (1.80 g; 10 mmol) at -196°. The tube was allowed to warm to room temperature and was left for a further 72 h. Volatile products were then condensed into another tube held at -196°. ^{31}P n.m.r. showed a mixture of 2 and 5. The mixture was separated by trap to trap condensation using traps at -40°, -80° and -196°, the trap at -80° containing the pure liquid product, 5. Yield 0.80 g (19%, based on 3). This compound has previously been prepared from the reaction of methyl tetrafluorophosphorane and the trimethylsilyl compound, Me_3SiOR_f[13].

Bis-trifluoromethyl-tris(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane (6)

Chlorine (0.40 g; 5.6 mmol) was condensed into a tube at -196° containing a mixture of 1 (1.75 g; 10 mmol) and bis-(trifluoromethyl)-(1,1,1,3,3,3-hexafluoroisopropyl)-phosphite[11] (1.70 g; 5 mmol). The tube was allowed to warm to room temperature over 3 h and was then briefly opened to a vacuum system and excess chlorine pumped away. The colourless liquid 6 was distilled at 45°/10^{-2} mm. Yield 2.30 g (69%, based on bis-(trifluoromethyl)-1,1,1,3,3,3-hexafluoroisopropyl-phosphite).

Mass spectrum: 601 (M^+-CF_3, 100%); 551 ($C_9H_3F_{19}O_3P^+$, 15%) 503 ($C_8H_2F_{18}O_2P^+$, 90%); 453 ($C_7H_2F_{16}O_2P^+$, 22%); 69 (CF_3^+, 70%).

Phenyl-tetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (7)

Chlorine (0.75 g; 10 mmol) was condensed into a tube at -196° containing a mixture of 1 (3.50 g; 20 mmol) and phenyl-bis(1,1,1,3,3,3-hexafluoroisopropyl)phosphite[11] (4.40 g; 10 mmol). The tube was allowed to warm to room temperature over 3 h and was then briefly opened to a vacuum system and excess chlorine pumped away. The colourless solid 7 was sublimed at 50°/10^{-3} mm.

M.p. = 91°. Yield 5.60 g (72%, based on phenyl-bis-(1,1,1,3,3,3-hexafluoroisopropyl)phosphite).
$C_{18}H_9F_{24}O_4P$ (776.19)

Anal. found: C, 26.5; H, 1.4; F, 57.0%
calc.: C, 27.8; H, 1.2; F, 58.8

Mass spectrum: 757 (M^+-F, 6%); 609 (M^+-R_fO, 100%); 589 ($C_{15}H_8F_{17}O_3P^+$, 5%); 251 ($C_7H_6F_6OP^+$, 8%); 142 ($C_6H_5PFO^+$, 14%); 77 ($C_6H_5^+$, 20%); 69 (CF_3^+, 28%); 51 (HPF^+ or HCF_2^+, 14%).

Fluorophenyl-tris(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (8)

Chlorine (0.75 g; 10.5 mmol) was condensed into a tube at -196° containing 1 (3.50 g; 20 mmol) and phenyl difluorophosphine[19] (1.50 g; 10 mmol). The tube was allowed to warm to room temperature over 2 h und was then briefly opened to a vacuum system and excess chlorine pumped away. The liquid product was distilled at 50°/10^{-3} mm to give a mixture of 8 and 9 (as shown by ^{19}F and ^{31}P n.m.r.). All attempts at the separation of the two compounds were unsuccessful and resulted in a final product, 8 which is estimated to be about 90% pure (from ^{31}P n.m.r.), the other 10% being 9.

The mass spectrum contains the molecular ion M^+, 628 in small abundance. Also present are fragments representing loss of fluorine and the R_fO group, from the molecular ion. Relative abundances cannot be given because of the uncertain contribution resulting from the fragmentation of 9.

Difluorophenyl-bis(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (9)

Chlorine (0.75 g; 10.5 mmol) was condensed into a glass tube at -196° containing 1 (3.50 g; 20 mmol) and phenyl difluorophosphine[19] (1.50 g; 10 mmol). The tube was warmed to room temperature over 30 minutes, and then briefly opened to a vacuum system and excess chlorine pumped away. Distillation of the product at 50°/10^{-3} mm gave a mixture of 8 and 9, this time 9 being present in about 90% abundance (as evidenced from the ^{31}P n.m.r. spectrum).

Mass spectrum: 480 (M^+, 10%); 461 (M^+-F, 55%); 403 (M^+-C_6H_5, 25%); 313 (M^+-R_fO, 100%); 99 ($C_2H_2F_2O^+$, 10%); 79 (C_2HFO^+, 24%); 69 (CF_3^+, 22%).

Trifluorophenyl-(1,1,1,3,3,3-hexafluoroisopropoxy)-phosphorane (10)

Phenyl tetrafluorophosphorane[20] (2.70 g; 20 mmol) was condensed into a glass tube at -196° containing 1 (3.50 g; 20 mmol). The tube was then warmed to room temperature over 2 h. The resultant mixture contained the product, 10, as well as about 20% of 9 (identified from ^{19}F and ^{31}P n.m.r.) and was distilled at 45°/10^{-3} mm. Repeated distillation gave a product, 10, estimated as 90% pure (^{31}P n.m.r.).

The mass spectrum contains the molecular ion M^+, 332. Also present in high abundance are fragments representing loss of the R_fO-group and loss of a fluorine atom from the molecular ion.

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