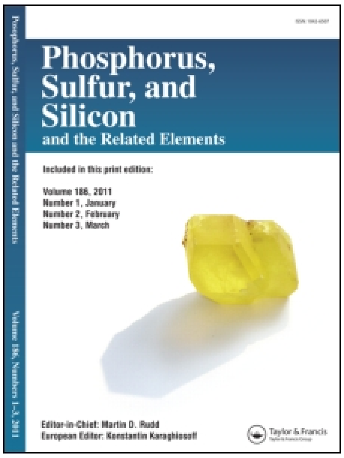

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ATTEMPTED PREPARATIONS OF PHOSPHORANES CONTAINING PERFLUOROPHENYL GROUPS

Donald B. Denney[a]; Dorothy Z. Denney[a]; Lun-Tsu Liu[a]
[a] Contribution from the Department of Chemistry, Rutgers-The State University of New Jersey, New Brunswick, New Jersey

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ATTEMPTED PREPARATIONS OF PHOSPHORANES CONTAINING PERFLUOROPHENYL GROUPS

DONALD B. DENNEY,* DOROTHY Z. DENNEY and LUN-TSU LIU

Contribution from the Department of Chemistry, Rutgers-The State University of New Jersey, New Brunswick, New Jersey 08903

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The reaction of perfluorophenol with phosphorus pentachloride in the presence of triethylamine or γ-collidine yielded perfluoropentaphenoxyphosphorane, **5**, along with perfluorotriphenylphosphate, **6**, and perfluorodiphenyl ether, **7**. Attempts to prepare penta(perfluorobenzyloxy)phosphorane, **12**, by a number of methods failed. Similarly attempts to prepare perfluorothiophenylphosphorane, **19**, always resulted in perfluorothiophenyl phosphite, **20**, and perfluorodiphenyl disulfide, **21**.

The chemistry of phosphoranes has received much attention over the past two decades. There exists a considerable amount of information concerning the structures of these substances and their intramolecular and intermolecular ligand reorganization processes.[1] Despite all of this work, there remain many interesting questions concerning these molecules. One general question is, what are the activation energies for the intramolecular ligand reorganizations of simple pentaalkoxyphosphoranes? Variable temperature NMR studies of a number of these molecules have not led to an answer to this question.[2]

Another potentially interesting question is why have no acyclic pentathioalkyl or pentathioarylphosphoranes been reported? A few cyclic materials have been made.[3]

In general electronegative ligands stabilize phosphoranes and thus one finds many examples of fluorine containing phosphoranes and phosphoranes containing fluorinated ligands. Another advantage that fluorine containing ligands provide is the ability to study these materials by ^{19}F NMR. ^{19}F NMR is advantageous because of the sensitivity of fluorine and because of the rather large chemical shift differences that are possible between nonequivalent nuclei. It was the purpose of this work to attempt to prepare phosphoranes containing perfluorinated benzene rings. It was hoped that some answers to the questions posed above might be provided, and to some extent this has been accomplished.

RESULTS AND DISCUSSION

Condensation of perfluorophenol, **1**, with phosphorus pentachloride, **2**, in the presence of either triethylamine, **3**, or γ-collidine, **4**, led to mixtures of perfluoropentaphenoxyphosphorane, **5**, perfluorophenyl phosphate, **6**, and perfluorodiphenyl ether, **7**. These substances were separated and **5** was found to be relatively stable.

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* Author to whom all correspondence should be addressed.

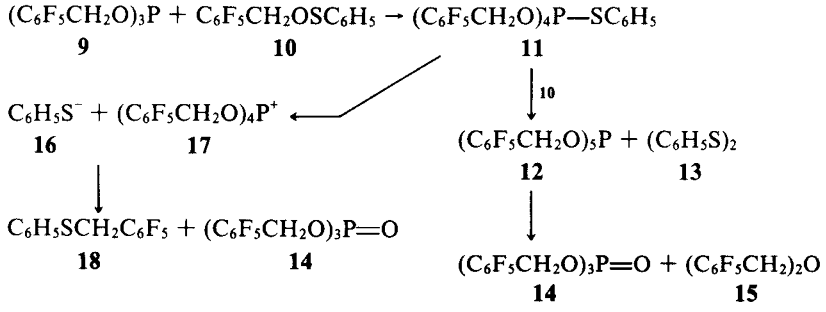
See Table I for all spectral data. The room temperature

$$\underset{2}{PCl_5} + \underset{1}{C_6F_5OH} \xrightarrow{3\text{ or }4} \underset{5}{(C_6F_5O)_5P} + \underset{6}{(C_6F_5O)_3P{=}O} + \underset{7}{(C_6F_5)_2O}$$

^{19}F NMR spectrum of **5** has three multiplets for equivalent ortho, meta and para fluorines. The ^{19}F NMR spectra from −70°C to +90°C showed no change. Although it is possible that there is accidental equivalence of the various nuclei, it seems more likely that intramolecular ligand reorganization is still rapid on the NMR scale. This finding is in accord with other results found with simple acyclic phosphoranes.[2]

The formation of **6** and **7** during the preparation of **5** undoubtedly occurs by attack of perfluorophenol or the anion on **5**. Treatment of **5** with the sodium salt of **1** led to the formation of phosphate **6**. Similarly treatment of PCl_5 with the sodium salt of **1** yielded only **6** and **7**.

Perfluorobenzyl alcohol, **8**, was considered to be another potential ligand for phosphorane formation. When it was allowed to react with phosphorus pentachloride in the presence of γ-collidine only the phosphate, $(C_6F_5CH_2O)_3P{=}O$, **14**, was formed. Attempts to prepare the phosphorane **12**, by reaction of the phosphite, **9**, with two moles of the sulfenate **10**, yielded phosphate, **14**, the fluorobenzyl ether, **15**, and diphenyl disulfide, **13**. These products can arise if **12** was formed but then underwent rapid decomposition to give **14** and **15**. When 1 mole of **10** was allowed to react with **9**, **14** was again formed but under these conditions **18** was produced. A sequence involving dissociation of **11** to **16** and **17** followed by S_N2 decomposition satisfactorily accounts for the products. It is somewhat surprising that **12** is so unstable as compared to pentatrifluoroethoxyphosphorane[2b] or even pentabenzyloxyphosphorane.[2a]



$$\begin{tikzcd}
\underset{9}{(C_6F_5CH_2O)_3P} + \underset{10}{C_6F_5CH_2OSC_6H_5} \arrow[r] & \underset{11}{(C_6F_5CH_2O)_4P{-}SC_6H_5} \arrow[dl] \arrow[d, "10"] \\
\underset{16}{C_6H_5S^-} + \underset{17}{(C_6F_5CH_2O)_4P^+} \arrow[d] & \underset{12}{(C_6F_5CH_2O)_5P} + \underset{13}{(C_6H_5S)_2} \arrow[d] \\
\underset{18}{C_6H_5SCH_2C_6F_5} + \underset{14}{(C_6F_5CH_2O)_3P{=}O} & \underset{14}{(C_6F_5CH_2O)_3P{=}O} + \underset{15}{(C_6F_5CH_2)_2O}
\end{tikzcd}$$

An attempt to prepare pentathiophenylphosphorane from phosphorus pentachloride and thiophenol in the presence of base yielded trithiophenylphosphite and diphenyl disulfide.[4] The phosphorane probably was formed but then lost the elements of diphenyl disulfide. This kind of reaction is apparently quite common with a wide variety of organometalloids.[5] Very little work has been done on the mechanism of this reaction. In two cases it appears to involve direct formation of the sulfur-sulfur bond by a concerted process.[5a,5b]

It was hoped that perfluorothiophenol might provide perfluorothiophenylphosphorane, **19**. When bis- (perfluoro-phenylthio)lead, **22**, was allowed to react with phosphorus pentachloride only the thiophosphite **20** and the disulfide **21**

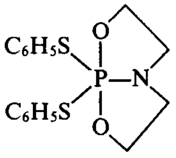
$$\underset{22}{(C_6F_5S)Pb} + PCl_5 \rightarrow \underset{19}{[(C_6F_5S)_5P]} \rightarrow \underset{20}{(C_6F_5S)_3P} + \underset{21}{(C_6F_5S)_2}$$

TABLE I[a]

No.	Structure	^{31}P	^{19}F			^{1}H			
			ortho	meta	para				
5	$(C_6F_5O)_5P$	−86	−158.0 m	−167.0 m	−164.3 d of t $^3J = 26.3$ $^6J = 3.7$				
6	$(C_6F_5O)_3PO$	−13	−170.7 d of d $^3J = 18.3$ $^4J = 6.9$	−172.9 t $^3J = 18.7$	−180.1 t of t $^3J = 21.8$ $^4J = 6.9$				
7	$C_6F_5OC_6F_5$		−162.3 d $^3J = 20.0$	−165.2 t $^3J = 20.0$	−167.6 t $^3J = 20.0$				
9	$(C_6F_5CH_2O)_3P$	142	−149.1 d of t $^3J = 22.1$ $^4J = 7.7$	−167.9 d of t $^3J = 20.6$ $^4J = 7.5$	−157.0 t $^3J = 22.0$		4.95 d of t $^3J = 7.6$	$^4J = 1.4$	
10	$C_6F_5CH_2OSC_6H_5$		−148.0 d of d $^3J = 22.0$ $^4J = 9.4$	−168.1 d of t $^3J = 21.0$ $^4J = 7.1$	−158.6 t $^3J = 21$	4.88 2H t $^4J = 1.0$		7.4 5H m	
15	$C_6F_5CH_2OCH_2C_6F_5$		−146.7 d of d $^3J = 22.4$ $J = 8.5$	−164.2 d of t $^3J = 18.0$ $J = 7.4$	−156.4 t $^3J = 18$	4.81 t $^4J = 1.7$			
14	$(C_6F_5CH_2O)_3PO$	−3	−148.5 d $^3J = 20.3$	−167.6 d of t $^3J = 20.5$ $^4J = 7.1$	−157.6 t $^3J = 20.4$	5.23 d of t $^3J = 8.8$ $^4J = 1.5$			
18	$C_6F_5CH_2SC_6H_5$		−148.8 d of d $^3J = 21.0$ $^4J = 8.1$	−168.4 d of t $^3J = 21.0$ $^4J = 7.1$	−158.6 t $^3J = 20.7$	4.06 2H t $^4J = 1.0$			7.33 5H m
21	$C_6F_5SSC_6F_5$		−137.4 d $^3J = 13.1$	−165.5 m	−153.8 m				

[a] See Experimental for details of NMR Experiments. Solvent is $CDCl_3$.

were found. Evidently **19** was formed but decomposed to **20** and **21**. Interestingly there appears to be only one known phosphorane which contains two exocyclic thiophenyl groups and it is **23**.[6] This substance is quite stable.



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EXPERIMENTAL SECTION

^1H NMR spectra were recorded with Varian Models T-60 and A-60A spectrometers. Chemical shift values are reported in parts per million relative to internal tetramethylsilane. ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded with a Varian Model FT-80 spectrometer equipped with a variable-temperature broadband probe. In all cases nuclei which are deshielded relative to their respective standard are assigned a positive chemical shift. ^{13}C NMR spectra were obtained by using full proton decoupling, a 45° flip angle, and a 2-s repetition rate with no pulse delay. All ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{19}F NMR spectra were acquired using a 45° flip angle, a 2-s repetition rate with no pulse delay and with full proton coupling. Chemical shifts are reported relative to external trichlorofluoromethane. ^{31}P NMR spectra were acquired using a 45° flip angle, a 1-s repetition rate with no pulse delay and with full proton decoupling. Chemical shifts are reported relative to external phosphoric acid (85%).

Reaction of Perfluorophenol **1** *with Phosphorus Pentachloride* **2** *in the Presence of Triethylamine.*

To a solution of triethylamine (2.02 g, 0.02 mol) in dry benzene (25 mL), cooled to 5°C, was added with stirring and under nitrogen phosphorus pentachloride (0.83 g, 0.004 mol). To this was then added perfluorophenol (3.85 g, 0.02 mol) in dry benzene (10 mL). The resulting mixture was stirred for an additional hr at 5°C. After removing the solid by filtration under nitrogen, the filtrate was concentrated and the ^{31}P NMR spectrum was run immediately. It showed absorptions at δ ($CDCl_3$) −15.5 and −86.1. Addition of hexane to this oil and cooling to −10°C yielded a white solid; ^{31}P ($CDCl_3$) δ −86.1. The filtrate was concentrated at reduced pressures and then molecularly distilled (70°C, 0.02 mm) to yield a liquid and a solid. The liquid was found to have identical spectral properties to the phosphate, **6**, whose synthesis is described below. The solid was identical to the ether **7** in all respects.

Reaction of Perfluorophenol **1** *with Phosphorus Pentachloride* **2** *in the Presence of γ-Collidine.*

Phosphorus pentachloride (0.624 g, 0.003 mol) was added, in small portions, to a solution of γ-collidine (1.82 g, 0.015 mol) in dry hexane (25 mL) at 0°C. To this was slowly added, under a nitrogen atmosphere, perfluorophenol (2.76 g, 0.015 mol) in dry hexane (10 mL). The reaction mixture was stirred at 0°C for 3 hr. and then the solid was removed by filtration. After concentrating the filtrate, there was formed a solid which had two absorptions in its ^{31}P NMR spectrum; δ (hexane) −15.9 and −87.1. From this solid there could be obtained, by low temperature crystallization from hexane, a material **5** m.p. 155–156°. The ^{19}F NMR spectrum of this compound showed no change from −70° to +90°C.

Perfluorotriphenyl Phosphate **6**.

To a suspension of potassium perfluorophenoxide (2.38 g, 0.011 mol) in acetone (30 mL) at 10°C, was added with stirring phosphorus oxychloride (0.55 g, 0.0036 mol). After stirring for 12 hr at room temperature, a solid formed; the solid was removed by filtration. The filtrate was concentrated and the residue was distilled, b.p. 140°C (0.1 mm) (lit.[7] 164–8, 1 mm).

Bis(perfluorophenyl)ether **7**.

This was synthesized by the method of L. A. Wall *et al.*,[8] m.p. 70–71° (lit.[8] 67–69°).

Reaction of **5** *with Sodium Perfluorophenoxide.*

To perfluoropentaphenyloxyphosphorane (1.42 g, 0.0015 mol) in benzene (2 mL) at 10° and under nitrogen was added a solution of sodium perfluorophenoxide (0.645 g, 0.003 mol) and 18-crown-6-ether (0.792 g, 0.003 mol) in benzene (2 mL). After 15 min the ^{31}P NMR spectrum of this sample showed one absorption at δ −16 (C_6H_6).

Reaction of Phosphorus Pentachloride with Sodium Perfluorophenoxide.

To a solution of sodium perfluorophenoxide (1.50 g, 0.0075 mol) in acetonitrile (20 mL) at 0°, was added with stirring phosphorus pentachloride (0.312 g, 0.0015 mol) in acetonitrile (10 mL). After warming to room temperature, the reaction mixture was stirred for two hrs. The ^{31}P NMR spectrum of this mixture showed one absorption at δ −14 (CH_3CN). The sodium chloride was removed by filtration and the filtrate was concentrated. Molecular distillation of the residual oil afforded two fractions; a liquid and a solid. The liquid had a ^{31}P NMR absorption at δ −13.2 ($CDCl_3$). The solid was recrystallized from pentane, to yield a material (m.p. 69–70°) which was identical in all respects to the ether. **7**.

Reaction of Phosphorus Pentachloride with Perfluorobenzyl Alcohol **8**.

Phosphorus pentachloride (1.25 g, 0.006 mol) was added, in small portions, to a solution of γ-collidine (3.63 g, 0.03 mol) in dry pentane (40 mL) at 0°C. To this mixture was added, with stirring, perfluorobenzyl alcohol (5.94 g, 0.03 mol) in benzene (10 mL). The reaction mixture was allowed to warm to room temperature and it was stirred for an additional two hours. After removing the solid by filtration, the filtrate was concentrated at reduced pressure. The residual oil was triturated with pentane (10 mL) to yield a solid which could be recrystallized from dichloromethane, m.p. 77–78°, ^{31}P NMR δ −2.87 (CD_2Cl_2). The pentane extracts were concentrated and molecularly distilled (70°, 0.025 mm). This was identical to the ether **15**.

Synthesis of Bis-perfluorobenzyl Ether, **15**.

A solution of perfluorobenzyl bromide (1.0 g, 0.0038 mol), perfluorobenzyl alcohol (0.758 g, 0.0038 mol) and triethylamine (0.38 g, 0.0038 mol) in dimethylformamide (30 mL) was heated under reflux for 24 hr. The solid was removed by filtration and the filtrate was concentrated. The residual oil was molecularly distilled (65°, 0.01 mm) to yield **15**.

Synthesis of Tris(perfluorobenzyl)Phosphite, **9**.

To a solution of perfluorobenzyl alcohol (5.7 g, 0.03 mol) and triethylamine (3.03 g, 0.03 mol) in dry ether (50 mL) at −10°, was added with stirring phosphorus trichloride (1.37 g, 0.01 mol) in dry ether (20 mL). After the addition was completed, the reaction mixture was stirred for 30 min at −10° and it was then allowed to warm to room temperature. The solid was removed by filtration and the resulting liquid was concentrated at reduced pressure. All attempts to further purify this material failed. The ^{31}P NMR spectrum showed the major absorption at δ 141.8 ($CDCl_3$).

Synthesis of Perfluorobenzyl Benzenesulfenate, **10**.

To a solution of perfluorobenzyl alcohol (1.78 g, 0.009 mol) and triethylamine (0.91 g, 0.009 mol) in tetrahydrofuran (30 mL) at −20° was added benzenesulfenyl chloride (1.30 g, 0.009 mol) in tetrahydrofuran (10 mL). The reaction mixture was allowed to warm to room temperature and then the solid, which had formed, was removed by filtration. The filtrate was concentrated under reduced pressure. The resulting material was recrystallized from pentane, m.p. 80–81°.

Reaction of Tris(perfluorobenzyl)Phosphite, **9**, *with One Equivalent of Perfluorobenzyl Benzenesulfenate* **10**.

To a solution of **9** (3.64 g, 0.0058 mol) in pentane (15 mL) cooled to −78°, under an atmosphere of nitrogen, was added **10** (1.79 g, 0.0058 mol) dissolved in a mixture of pentane (10 mL) and tetrahydrofuran (10 mL). The reaction mixture was allowed to warm to room temperature slowly. After concentrating the mixture there remained an oil which could be molecularly distilled (60°, 0.05 mm Hg). The distillate solidified upon standing (m.p. 58–60°). It was identical in all respects to **18**. The residue after the molecular distillation was recrystallized from dichloromethane (m.p. 78°). It proved to be tri-perfluorobenzyl phosphate, **14**.

Anal. Calcd. for $C_{21}H_6F_{15}O_4P$: C, 39.50; H, 0.94. Found: C, 39.65; H, 1.18.

Synthesis of **18**.

A solution of perfluorobenzyl bromide (1.0 g, 0.0038 mol), thiophenol (0.44 g, 0.004 mol) and triethylamine (0.4 g, 0.004 mol) in tetrahydrofuran (40 mL) was heated under reflux for 12 hrs. After removing the solid by filtration the solvent was removed. There remained a solid which could be recrystallized from petroleum ether (m.p. 61–62°).

Anal. Calcd. for $C_{13}H_7F_5S$: C, 53.79; H, 2.42. Found: C, 53.71; H, 2.60.

*Reaction of Tris(perfluorobenzyl)*Phosphite, **9**, *with Two Equivalents of Perfluorobenzyl Benzenesulfenate* **10.**

To a solution of **10**, (0.93 g, 0.0036 mol) in pentane (10 mL) at −20°C and under nitrogen, was added the phosphite **9** (1.12 g, 0.0018 mol) in pentane (10 mL). The mixture was allowed to warm to room temperature slowly. Low temperature filtration (−20°) led to separation of most of the diphenyldisulfide (m.p. 58–60°). The filtrate was concentrated at reduced pressure. The ^{31}P NMR spectrum of this material showed a single absorption at δ −3.48 (toluene-d_8). This material was washed with pentane to give a solid which could be recrystallized from dichloromethane (m.p. 78°). This material was determined to be the phosphate **14** by analysis of its NMR spectra as well as the presence of a strong absorption at 1200 cm^{-1} in the I.R. (P=O stretch). The pentane solution was concentrated and the residue was molecularly distilled (70°C, 0.025 mm Hg). The product was identical, in all respects, to the ether **15**.

Preparation of Bis(perfluorophenylthio)lead **22**, *and Bis(perfluoro-phenyl)disulfide* **21**.

To plumbic oxide (2.87 g, 0.012 mol) in water (50 mL) was added perfluorothiophenol (10.0 g, 0.05 mol). This mixture was stirred at room temperature for 30 min. A yellow solid was separated by filtration. This solid was washed with ether and dried to yield 6.38 g (83%) of **22**; m.p. 255° (lit.[9] 256°). After having concentrated the ether washings there remained a solid which could be recrystallized from ether, m.p. 50–51° (lit.[10] 51°). This was identical in all respects to the disulfide **21**.

Reaction of Bis(perfluoro-phenylthio)lead **22** *with Phosphorus Pentachloride* **2**.

To a suspension of bis(perfluoro-phenylthio)lead (7.17 g, 0.012 mol) in pentane (30 mL) at 0°C, was added phosphorus pentachloride (1.0 g, 0.0048 mol). The reaction mixture was allowed to warm to room temperature. The white solid, plumbous chloride, was separated by filtration and the remaining solution was concentrated at reduced pressure. Upon cooling this pentane solution to −40°C a white solid formed. This solid was separated by filtration and it was recrystallized from ether to yield 1.5 g (78%) of **21**, m.p. 50° (lit.[10] 51°).

After concentrating the filtrate there remained a solid which could be recrystallized from hexane to yield 1.1 g (36.5%) of **20**, m.p. 61–63° (lit.[11] 63–64°).

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