joints were greased with Fluorube "W" grease. A small uncovered iron magnetic follower was included in the reaction vessel for agitation during the second stage of the preparation.

Diselenium dichloride (80 g) was cooled in an ice-salt bath. This was found to be very important to prevent ignition at the commencement of fluorination. The apparatus was flushed with nitrogen at a rate of 5 l/hr. Fluorine, from an electrolytic cell and freed from hydrogen fluoride contamination, was then passed into the reaction vessel; the initial rate was 4 l/hr, but this was increased to 6 l/hr after 30 min. This rate of fluorination was continued until all sign of the red diselenium dichloride had disappeared; at this point the reaction vessel contained mostly a pale yellow solid together with a small quantity of colourless liquid.

The fluorine supply was then increased to 8 l/hr, the nitrogen supply turned off and the magnetic stirrer set in motion. The fluorination was continued until only a colourless liquid remained. The fluorine generator was then switched off and the apparatus was flushed with dry nitrogen for 20 min. The product was then purified by trap to trap distillation *in vacuo*.

The yield with respect to selenium was 73 per cent (79 g) and with respect to fluorine 41 per cent.

Analysis for selenium was carried out gravimetrically by reduction to the element with  $SO_2$ -saturated hydrochloric acid (% Se found 51.0; 50.8. Theory requires 51.0). Analysis for fluorine in the presence of selenium was found to be difficult. The method which was found to be most satisfactory was to hydrolyse a sample of selenium tetrafluoride and measure its total acidity by conductometric titration with standard alkali. The acid equivalent weight of hydrolysed selenium tetrafluoride is one sixth of its Mol. wt. (i.e., 25.83).

# $SeF_4 + 3H_2O \rightarrow H_2SeO_3 + 4HF$

The value obtained was 26.8 corresponding to a fluoride content of 47.5% (calculated value for SeF<sub>4</sub> is 49.0%).

Further confirmation of the product was obtained by Raman spectroscopy. The spectra were found to be identical with those published by ROLFE, WOODWARD and LONG.<sup>(5)</sup>

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<sup>(5)</sup> J. A. ROLFE, L. A. WOODWARD and D. A. LONG, Trans. Faraday Soc. 49, 1388 (1953).

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# Pentafluorophenyl-phosphorus chemistry-I. Tris(pentafluorophenyl)phosphine sulphide and tris(pentafluorophenyl)dichlorophosphorane

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PENTAFLUOROPHENYL derivatives of phosphorous have been described by several workers<sup>(1,2)</sup> and it has been reported that tris(pentafluorophenyl)phosphine sulphide does not form in the reaction of triphosphoryl chloride with the Grignard reagent,  $C_6F_8MgBr$ .<sup>(3)</sup> We have found that the reaction of

<sup>(1)</sup> L. A. WALL, R. E. DONADIO and W. J. PUMMER, J. Amer. Chem. Soc. 82, 4846 (1960).

<sup>(2)</sup> G. TESI, D. D. MAGNELLI and W. E. MCQUISTION, Abstr. of 148th Meeting of A.C.S. Chicago, p. 19K. Sept. 1964.

<sup>(3)</sup> M. TILD, D. GLEMSER and G. CHRISTOPH, Angew. Chem. (Int. Eng. Ed.) 3, 801 (1964).

elemental sulphur with tris(pentafluorophenyl)phosphine for 6 days at 160° yielded tris(pentafluorophenyl)phosphine sulphide,  $(C_6F_5)_3PS$ .

$$(C_6F_5)_{3}P + S \xrightarrow{160^{\circ}} (C_6F_5)_{3}PS$$

However, sulphur did not react with tris(pentafluorophenyl)phosphine on refluxing in benzene.

Tris(pentafluorophenyl)phosphine sulphide is a white solid, melting after purification at 170–172°. A strong band appears in its infra-red spectrum at  $684 \text{ cm}^{-1}$ , which is not present in tris(pentafluorophenyl)phosphine or phosphine oxide, (in which the PO stretch is the band at  $1235 \text{ cm}^{-1}$ ). This band is therefore assigned to the PS stretch. This compares with values of 718 and 800 cm<sup>-1</sup> for the PS stretching frequencies of thiophosphoryl bromide<sup>(4)</sup> and tris(trifluoromethyl) phosphine sulphide.<sup>(5)</sup> From the spectra recorded by KUCHEN and BUCHWALD<sup>(6)</sup> assignments of the PO and PS stretching frequencies can be made at 1188 and  $638 \text{ cm}^{-1}$  respectively for triphenylphosphine oxide and triphenylphosphine sulphide. Thus, in their respective pentafluorophenyl compounds, the PO and PS stretches appear 47 and 46 cm<sup>-1</sup> to higher frequency than in their phenyl analogues. This is to be expected because of the greater electronegativity of fluorine substituted aromatic rings.

The mass spectrum of the phosphine sulphide showed, as the parent peak, the expected molecular ion at mass 564 (7.5%). Fragmentation began by loss of sulphur, to give  $(C_6F_5)_3P^+$  (mass 532, 75%). Tris(pentafluorophenyl)phosphine oxide has, on the other hand, a much more abundant parent peak at mass 548 (36.5%), and rather than undergoing cleavage of the PO bond, it lost either a fluorine atom from one of the rings (mass 529,  $(C_6F_5)_3POC_6F_4^+$ , 2.9%), a pentafluorophenyl group (peak at mass 381,  $(C_6F_5)_2PO^+$ , 17.8%), or both the oxygen and one of the rings, (mass 365,  $(C_6F_5)_3P^+$ , 92%). This difference in modes of fragmentation is presumably due to PS bonds being weaker than PO bonds and also to the greater stability of sulphur radicals.

Tris(pentafluorophenyl)phosphine sulphide was oxidized to the corresponding phosphine oxide by reflux in a potassium dichromate/acetic acid/sulphuric acid solution, but not by gaseous oxygen bubbled through a solution of the phosphine sulphide in chloroform.

Solid ( $C_6F_5$ )<sub>3</sub>PS reacted slowly with gaseous chlorine at room temperature to give tris(penta-fluorophenyl)dichlorophosphorane, ( $C_6F_5$ ) $P_3Cl_2$ , and sulphur dichloride.

$$(C_6F_5)_3PS + 2Cl_2 \rightarrow (C_6F_5)_3PCl_2 + SCl_2$$

One mole of gaseous chlorine similarly reacts in a 1:1 ratio with solid tris(pentafluorophenyl)phosphine to give tris(pentafluorophenyl)dichlorophosphorane.

$$(C_6F_5)_3P + Cl_2 \rightarrow (C_6F_5)_3PCl_2$$

Unlike triphenylphosphine which reacts violently with chlorine, the fluorinated analogue reacted slowly over a period of a day.

Tris(pentafluorophenyl)dichlorophosphine is a white, moisture sensitive solid, which, after sublimation, melted over the range of 209–234°, with some decomposition. It has an infra-red spectrum characteristic of pentafluorophenyl derivatives, with a strong band at 362 cm<sup>-1</sup> which can be assigned to the PCl stretch. The mass spectrum of this compound indicated that complete rupture of the PCl bonds occurred in the source, with the evolution of molecular chlorine, since the parent peak was at mass 532, (72%, (C<sub>8</sub>F<sub>5</sub>)<sub>8</sub>P<sup>+</sup>). Hydrolysis of the dichlorophosphorane yields tris(pentafluorophenyl)phosphine oxide.

In Table 1 phosphorus-31 nmr chemical shifts for some pentafluorophenyl-phosphorus compounds and their phenyl analogues are listed. Only in the case of tris(pentafluorophenyl)phosphine is any splitting resolved. A septet is observed, for which  $J_{P-F} = 36$  cps (intensity ratio approximately 1:6:15:20:15:6:1), which is due to coupling of the six equivalent ortho fluorine atoms of the ring to

<sup>(4)</sup> M. L. DELWAULLE and F. FRANCOIS, C.R. Acad. Sci., Paris 226, 896 (1948).

<sup>(5)</sup> R. G. CAVELL and H. J. EMELÉUS, J. Chem. Soc. 5896 (1964).

<sup>&</sup>lt;sup>(6)</sup> W. KUCHEN and H. BUCHWALD, Chem. Ber. 91, 2871 (1958) and Documentation of Molecular Spectroscopy, Butterworths, London, Cards 3668 and 3669.

the phosphorus atom. For the other pentafluorophenyl-phosphorus compounds only line broadening was observed, line widths being about 23 cps at 16.2 Mc/s. As was expected, a large shift to high field was observed for the pentavalent phosphorus derivative,  $(C_6F_5)_8PCl_2$ . This result served as a further confirmation of its structure. Pentafluorophenyl groups seem to shield the phosphorus atom to a much greater extent than do the phenyl groups in analogous compounds. It also appears that when highly shielded by pentafluorophenyl groups, the phosphorus-31 chemical shift is virtually unaffected by substitution of sulphur for oxygen, again unlike their phenyl analogues.

Compound	δ ppm*	Solvent	Reference
Pentafluorophenyl- derivatives			
(C <sub>6</sub> F <sub>5</sub> ) <sub>8</sub> P	77.9	CHCl <sub>8</sub>	This work
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> PO	8.2	CHCl <sub>3</sub>	This work
(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> PS	8.6	CHCl <sub>8</sub>	This work
$(C_6F_5)_8PCl_2$	104.7	$C_6H_6$	This work
Phenyl derivatives			
(C <sub>6</sub> H <sub>5</sub> ) <sub>8</sub> P	8.0	Et <sub>2</sub> O	7
(C <sub>6</sub> H <sub>5</sub> ) <sub>8</sub> PO	-27·0	CHCl <sub>3</sub>	8
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PS	-42.6	CHCl <sub>8</sub>	8

TABLE 1.—PHOSPHORUS-31 NMR DATA

\* Chemical shifts are measured relative to 85% phosphoric acid as an external standard.

# **EXPERIMENTAL**

#### a. Tris(pentafluorophenyl)phosphine sulphide

In a typical reaction, tris(pentafluorophenyl)phosphine (5.32 g, 10 mmoles; prepared from  $C_6F_5MgCl$  and  $PBr_3)^{(1)}$  and sulphur (0.32 g, 10 mmoles) were sealed together in an evacuated tube and heated at 160° for a week. The crude, pale brown solid was recrystallized twice from 40–60 pet. ether-chloroform solution and then sublimed at 140–150°, giving a yield of 4.1 g of  $(C_6F_5)_3PS$ , as identified by molecular weight (M, 565 osmometrically in  $CH_2Cl_2$ ; calc. for  $(C_6F_5)_3PS$  M, 564), infra-red and mass spectra, and elemental analysis. (Found; C, 38.2; P, 5.1; S, 5.3: Calc. for  $(C_6F_5)_3PS$ ; C, 38.4; P, 5.5; S, 5.7). The ultra-violet spectrum in methanol solution showed maxima at 218 and 275 m $\mu$  ( $\varepsilon$ : 8240; 26,500).

 $(C_6F_5)_sP$  and sulphur were refluxed together for 2 days in benzene without reacting, the PS stretching frequency in the infra-red at 684 cm<sup>-1</sup> being used as a qualitative test for the formation of phosphine sulphide. Similarly the PO stretch at 1235 cm<sup>-1</sup> was used to test for oxidation of tris(penta-fluorophenyl)phosphorus derivatives to the phosphine oxide.  $(C_6F_5)_sPS$  (0·2 g) was refluxed for 2 hr in a solution containing 1 g of potassium dichromate, 2 ml of water, 1 ml of concentrated sulphuric acid and 3 ml of glacial acetic acid. After neutralization with sodium bicarbonate, and extraction with chloroform 0·1 g of white solid was recovered, identified by its infra-red spectrum as  $(C_6F_5)_sPS$ .

<sup>(8)</sup> K. MOEDRITZER, L. MAIER and L. C. D. GROENWEGHE, J. Chem. Engng. Data 7, 307 (1962).

<sup>&</sup>lt;sup>(7)</sup> J. R. VAN WAZER, C. F. CALLIS, J. M. SHOOLERY and R. C. JONES, J. Amer. Chem. Soc. 78, 5715 (1956).

## b. Tris(pentafluorophenyl)dichlorophosphorane

Tris(pentafluorophenyl)phosphine sulphide (0.397 g, 0.704 mmoles )was placed in a bulb and chlorine (2.06 mmoles) was condensed onto the solid. Reaction was allowed to proceed at 22° for 20 hr at which time the volatile components were pumped out and fractionated. Trapped at  $-96^{\circ}$  was SCl<sub>2</sub> (Found; M, 101.4, IR  $\nu_{max}$  525 cm<sup>-1</sup>; Calc. for SCl<sub>2</sub>; M, 102.9,  $\nu_{max}$  527 cm<sup>-1</sup>). Passing  $-96^{\circ}$  was chlorine (Found; M, 70.1, 0.704 mmoles; Calc. for Cl<sub>2</sub>; M, 70.9), 1.36 mmoles of chlorine was consumed compared to the calculated requirements of 1.41 mmoles.

In a similar reaction, tris(pentafluorophenyl)phosphine (2.00 g, 3.76 mmoles) was weighed out into the bulb and chlorine (10.0 mmoles) was condensed onto the solid. The reaction was allowed to proceed at room temperature aided by occasionally condensing the chlorine down onto the solid. After 20 hr 6.28 mmoles of chlorine remained unreacted, and after 40 hr 6.20 mmoles of chlorine remained, corresponding to a consumption of 3.80 mmoles, the theoretical being 3.76.

The white solids from the above two reactions had identical infrared spectra ( $\nu$  PCl<sub>2</sub>, 362 cm<sup>-1</sup>). The crude solid melted over the range 187–217°. After careful sublimation at 180–190° the solid was found to melt between 209 and 234° with some decomposition. (Found; C, 35·8; P, 4·92; Cl, 11·0; M, 602, osmometrically in CH<sub>2</sub>Cl<sub>2</sub>: Calc. for (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>PCl<sub>2</sub>; C, 35·8; P, 5·15; Cl, 11·8; and M, 603.) The solid (0·1164 g, 0·193 mmoles) after being shaken with water and chloroform, extracted and dried, yielded (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>PO (0·1076 g, calc. 0·1060 g).

## Spectra

Infra-red spectra were recorded over the range of 4000-250 cm<sup>-1</sup> using a Perkin-Elmer Model 521 grating infra-red spectrometer. Samples were prepared as nujol mulls between CsBr plates or as pressed KBr disks.

Phosphorus-31 NMR spectra were obtained at 16.2 Mc/s using a Varian V4300B NMR spectrometer with samples contained in 10 mm o.d. non spinning tubes. Calibration was by means of normal side band techniques. Solutions were made at their maximum possible concentrations at room temperature because of the low sensitivity of P-31 nmr.

Mass spectra were obtained on an A.E.I. MS9 spectrometer employing a heated inlet system.

Note added in proof: The following (Table 2) are some <sup>19</sup>F nmr data on (pentafluorophenyl)phosphorus compounds. From  $(C_6F_5)_8P$  the ortho-fluorine phosphorous coupling constant was found to be 39.4  $\pm$  2 cps, compared to approximately 36 cps obtained from the <sup>31</sup>P nmr.

	<sup>19</sup> F Chemical Shifts ppm Upfield of CCl <sub>3</sub> F			F-F Splitting in cps	
	$\delta_{ m ortho}$	$\delta_{ ext{para}}$	$\delta_{ extsf{meta}}$	$J_{m-p}$	$\mathbf{J}_{0-\mathbf{p}}$
$(C_{6}F_{5})_{3}P$	130.9	149.0	160.7	20.5	2.8
$(C_6F_5)_3OP$	131-9	142.7	158.4	20.2	2.8
$(C_6F_5)_3PS$	132-1	144.7	158.8	19.3	
$(C_6F_5)_3PCl_2$	128.9	146-3	158-9		

TABLE 2.

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