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Chemistry of Sulfur Tetrafluoride. VIII. Synthesis of Phenylfluorophosphoranes and Phenylarsenic(V) Fluorides[1]

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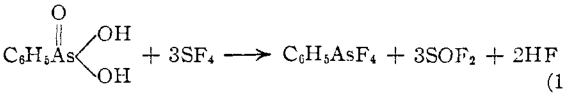
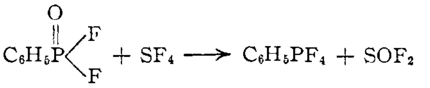
Sulfur tetrafluoride (SF_4) has been found to be a useful reagent for the replacement of oxygen doubly bonded to phosphorus or to arsenic with fluorine atoms. This type of fluorination reaction, similar to that involving the replacement of carbonyl oxygen atoms,[7] has been used to convert phenylarsonic acid to phenylarsenic tetrafluoride. In the same manner $C_6H_5PF_4$, $(C_6H_5)_2PF_3$ and $(C_6H_5)_3PF_2$ have been synthesized by the replacement of oxygen in the appropriate phenylphosphorus(V) compounds. The ability of SF_4 to function as an oxidative fluorinating agent has been demonstrated by the conversion of triphenylphosphine and -arsine to $(C_6H_5)_3PF_2$ and $(C_6H_5)_3AsF_2$, respectively. Some physical and chemical properties of these compounds are described.

Organophosphorus polychlorides of the types $RPCl_4$, R_2PCl_3 and R_3PCl_2 are well known.[3] These classes of compounds generally have poor thermal stability and, in many ways, resemble phosphorus pentachloride in appearance and behavior. In the past few years, syntheses for certain fluoro analogs of these compounds have been developed. A method for the preparation of alkyltetrafluorophosphoranes based on alkylphosphonous dichlorides, aluminum chloride and hydrogen fluoride was reported in 1955,[4] while more recently the synthesis of phenyltetrafluorophosphorane by the oxidative fluorination of phenylphosphonous dichloride with antimony trifluoride–antimony pentachloride mixtures was described.[5] Organoarsenic(V) fluorides have not been reported previously, although many chloro derivatives of this type have been prepared.[6]

Sulfur tetrafluoride has been found to be a useful reagent for the replacement of oxygen doubly bonded to phosphorus or to arsenic with two fluorine atoms. Any hydroxyl groups bonded to the metalloid will also be replaced by fluorine atoms, and it has been shown that this latter type of replacement reaction takes place at a somewhat lower temperature than that required for the replacement of the doubly bonded oxygen atom. Examples of these replacement reactions are



$$C_6H_5\overset{\overset{O}{\|}}{As}\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} + 3SF_4 \longrightarrow C_6H_5AsF_4 + 3SOF_2 + 2HF \qquad (1)$$



$$C_6H_5\overset{\overset{O}{\|}}{P}\begin{matrix}\diagup F\\ \diagdown F\end{matrix} + SF_4 \longrightarrow C_6H_5PF_4 + SOF_2 \qquad (2)$$

$$(C_6H_5)_3P{=}O + SF_4 \longrightarrow (C_6H_5)_3PF_2 + SOF_2 \qquad (3)$$

Phenyltetrafluorophosphorane and its arsenic analog are distillable liquids which fume vigorously on exposure to the atmosphere. It was found that $C_6H_5PF_4$ possesses unexpected thermal stability; it was recovered unchanged after being heated at 350° for 8 hours.

Sulfur tetrafluoride acts as an oxidative fluorinating agent toward triarylphosphines and -arsines. Triphenylphosphine was converted to difluorotriphenylphosphorane by this method at 150°, and the corresponding arsenic compound was prepared in a similar manner. The reactions are represented by the general equation

$$2R_3M + SF_4 \longrightarrow R_3MF_2 + S$$

and are carried out most conveniently in a medium such as benzene in order to avoid undesirable side reactions. The products are colorless, crystalline solids that have considerable solubility in non-polar organic solvents and undergo hydrolysis readily when exposed to the atmosphere. The physical properties of the arylfluorophosphoranes and their arsenic analogs indicate that these compounds, like the parent phosphorus and arsenic pentafluorides, are largely covalent in character.

Characterization studies of the products obtained included the determination of their infrared spectra. Bands at 3.17–3.26 μ in these products were ascribed to $=$CH groupings, those in the region 6.25–6.94 μ to aromatic —C=C— linkages and those at 13.45–14.47 μ to monosubstituted aromatic groups. A band at 13.30 μ observed for $(C_6H_5)_3PF_2$ may be due to a P–F linkage, and another at 6.95 μ may be associated with a phosphorus atom linked to a benzene nucleus. Nuclear magnetic resonance results were consistent with products in which only phenyl groups and fluorine atoms are bonded to the metalloid. The data obtained are not sufficient, however, to permit a unique determination of any structural features of the products.

Experimental

Reactions were carried out in 145-ml. shaker vessels lined with Hastelloy or stainless steel. In each instance the phosphorus or arsenic derivative (or its benzene solution) was charged into the reactor under a blanket of nitrogen and the vessel was cooled in an acetone–solid carbon dioxide-bath The vessel was then evacuated to about 1 mm., placed on a balance, and the desired amount of SF_4 weighed in. Volatile products, if retained, were collected in stainless-steel cylinders, and the solid or liquid products were transferred under a blanket of nitrogen to polyethylene bottles or containers fabricated of Teflon polytetrafluoroethylene.

Phenyltetrafluorophosphorane. (1) **From Phenylphosphonic Acid and SF_4.**—A shaker vessel charged with 39.5 g. (0.25 mole) of phenylphosphonic acid and 108 g. (1.00 mole) of SF_4 was heated at 100° for 2 hr., 120° for 4 hr. and finally at 150° for 10 hr. The volatile reaction products

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(1) Paper VII, C. W. Tullock, R. A. Carboni, R. J. Harder, W. R. Hasek, W. C. Smith and D. D. Coffman, THIS JOURNAL, **82**, 5107 (1960).

(2) Paper II, W. R. Hasek, W. C. Smith and V. A. Engelhardt, THIS JOURNAL, **82**, 543 (1960).

(3) G. K. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 70.

(4) H. Coates and P. Carter, British Patent 734,187 (1955).

(5) W. C. Smith, U. S. Patent 2,904,588, September 15, 1956.

(6) E. Kraus and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen," Edward Brothers, Inc., Ann Arbor, Mich., 1943.

were vented from the reactor.[7] The light-brown, liquid product (41.8 g.) was treated with 20 g. of anhydrous granular NaF suspended in 100 ml. of petroleum ether (b.p. 30–60°) to remove hydrogen fluoride and the insoluble solid (22.5 g.) separated by filtration under a nitrogen blanket. The filtrate was distilled at atmospheric pressure in a Vigreux column to give 27.0 g. (58%) of $C_6H_5PF_4$, b.p. 133–134° (760 mm.). The product was characterized by infrared, nuclear magnetic resonance, and elemental analyses.

Anal. Calcd. for $C_6H_5F_4P$: C, 39.15; H, 2.74; F, 41.29; P, 16.84. Found: C, 38.71; H, 2.96; F, 40.96; P, 17.13.

(2) From **Phenylphosphonic Difluoride and SF_4.**—Phenylphosphonic difluoride was prepared by the drop-wise addition of phenylphosphonic dichloride (97.5 g.) to a slurry of sodium fluoride (63 g.) suspended in tetramethylene sulfone (125 ml.) followed by heating of the slurry with stirring at 100° for 2.5 hr.[8,9] The product (58.5 g., 72%) was separated by distillation at reduced pressure, b.p. 55° (2 mm.). It was redistilled before use, b.p. 187–188° (760 mm.). *Anal.* Calcd. for $C_6H_5F_2OP$: F, 23.45. Found: F, 23.24.

A shaker vessel charged with 24.3 g. (0.15 mole) of phenylphosphonic difluoride and 33 g. (0.30 mole) of SF_4 was heated at 100° for 2 hr. and then at 150° for 10 hr. The volatile product, weighing 30 g., was shown by mass spectrometric analysis to consist solely of SOF_2 and unreacted SF_4. The liquid product, weighing 23.0 g., was distilled directly to give 17.2 g. (62%) of $C_6H_5PF_4$, b.p. 134–135° (760 mm.).

Trifluorodiphenylphosphorane.—A shaker vessel charged with 10.9 g. (0.05 mole) of diphenylphosphinic acid[10] and 27 g. (0.25 mole) of SF_4 was heated at 50° for 2 hr., 80° for 2 hr., 100° for 1 hr., 120° for 4 hr. and finally at 150° for 5 hr. The volatile product was discarded; a light-brown liquid weighing 9.9 g. was recovered from the bomb. The crude product was treated with 10 g. of sodium fluoride powder suspended in 50 ml. of dry petroleum ether (b.p. 30–60°). The petroleum ether solution was distilled to give 5.2 g. (42%) of $(C_6H_5)_2PF_3$, b.p. 106–107° (2 mm.). The fact that the product was the fluorophosphorane was confirmed by nuclear magnetic resonance analysis; the results are consistent with a bipyramidal structure in which the three fluorine atoms are in the equatorial plane, but do not uniquely establish the structure.

Anal. Calcd. for $C_{12}H_{10}F_3P$: C, 59.51; H, 4.16; F, 23.54; P, 12.79. Found: C, 59.57; H, 4.16; F, 23.65; P, 12.73.

Difluorotriphenylphosphorane. (1) From **Triphenylphosphine Oxide.**—A shaker vessel charged with a solution of 13.9 g. (0.05 mole) of triphenylphosphine oxide in 75 g. of benzene and with 66 g. (0.65 mole) of SF_4 was heated at 50° for 4 hr., 100° for 4 hr. and finally at 150° for 6 hr. The shaker vessel was bled slowly to atmospheric pressure and a colorless crystalline solid together with a pale yellow liquid (100.6 g.) was recovered. The solid product was separated by filtration under nitrogen and washed with two 20-ml. portions of anhydrous diethyl ether. The product was freed of diethyl ether in a vacuum desiccator and shown by infrared, nuclear magnetic and elemental analyses to be pure difluorotriphenylphosphorane, m.p. 136–140°.[11] The n.m.r. results are consistent with a trigonal bipyramidal structure in which the two fluorine atoms are at the apices, but do not uniquely determine it. The yield was 10.1 g. (67%). An additional quantity of $(C_6H_5)_3PF_2$ contaminated with unreacted $(C_6H_5)_3PO$ was recovered from the mother liquor by evaporation of the latter to dryness.

Difluorotriphenylphosphorane is moderately soluble in chloroform and benzene and insoluble in diethyl ether.

Anal. Calcd. for $C_{18}H_{15}F_2P$: C, 71.99; H, 5.04; F, 12.65; P, 10.32. Found: C, 73.21; H, 5.32; F, 12.25; P, 10.74.

(2) From **Triphenylphosphine.**—A shaker vessel charged with a solution of 13.2 g. (0.050 mole) of triphenylphosphine in 50 g. of benzene and with 66 g. (0.65 mole) of SF_4 was heated at 50° for 4 hr., 100° for 4 hr. and finally at 150° for 6 hr. The volatile product (66 g.), which was collected in a stainless-steel cylinder cooled in liquid nitrogen, was shown by mass spectrometric analysis in the liquid phase to contain unreacted SF_4 (92 mole %), SOF_2 (6 mole %) and benzene (2 mole %). A colorless solid and a light-yellow liquid with a combined wt. of 57.2 g. were recovered from the reactor. The solid was separated by filtration and washed on the filter with three 25-ml. portions of benzene. This product (8.1 g.) was shown by elemental analysis to be pure difluorotriphenylphosphorane. The benzene washes were evaporated to dryness and the crude solid obtained was treated with three 20-ml. portions of diethyl ether. The ether-insoluble solid (2.2 g.) was brought to constant weight at room temperature in a vacuum desiccator[11] and shown to be $(C_6H_5)_3PF_2$. The combined yield was 10.3 g. (69%). No attempt was made to recover additional product from the relatively small amount (2.7 g.) of yellow solid recovered on evaporation of the benzene mother liquor to dryness. The phosphorane was characterized by infrared, nuclear magnetic resonance and elemental analyses, and was identical with that synthesized from triphenylphosphine oxide.

Phenylarsenic Tetrafluoride.—A shaker vessel charged with 30.3 g. (0.15 mole) of phenylarsonic acid and 66 g. (0.60 mole) of SF_4 was heated at 70° for 10 hr. The liquid product (35.9 g.), which fumed on exposure to the atmosphere, was treated with 20 g. of anhydrous granular NaF suspended in 150 ml. of dry petroleum ether (b.p. 30–60°) and the solution separated by filtration under nitrogen. The petroleum ether was removed from the filtrate under reduced pressure and the residue distilled to give 15.5 g. (45% yield) of phenylarsenic tetrafluoride, b.p. 52–53° (2 mm.). The identity of the product was established by nuclear magnetic resonance and infrared studies.

Anal. Calcd. for $C_6H_5AsF_4$: C, 31.60; H, 2.21; As, 32.85; F, 33.33. Found: C, 31.91, 31.53; H, 2.57, 2.40; As, 32.45, 32.37; F, 33.31, 33.46.

Triphenylarsenic Difluoride.—A shaker vessel charged with a solution of 30.6 g. (0.10 mole) of triphenylarsine in 50 g. of benzene and with 44 g. (0.41 mole) of SF_4 was heated at 50° for 4 hr., 100° for 4 hr. and then at 130° for 6 hr. The reactor was then bled slowly to atmospheric pressure and the volatile material discarded. A colorless solid and a light-yellow solution (77 g.) were recovered from the reactor. The solid was separated by filtration under a blanket of nitrogen and washed successively on the filter with three 25-ml. portions of dry benzene. The solid product (7.8 g.) was characterized by infrared, nuclear magnetic resonance and elemental analyses.

Additional product was recovered by evaporation of the benzene washes to dryness at room temperature under a stream of nitrogen. The crude solid recovered in this way was treated with 25 ml. of diethyl ether and the ether-insoluble product after separation by filtration under nitrogen was washed on the filter with two additional 25-ml. portions of diethyl ether. An additional 8.0 g. of pure $(C_6H_5)_3AsF_2$ was recovered by bringing the solid to constant weight at room temperature in a vacuum desiccator. The yield of pure $(C_6H_5)_3AsF_2$ (m.p. 135–137°) isolated in the reaction was 15.8 g. (45.8%).[11] Evaporation of the benzene mother liquor to dryness yielded an additional 16.6 g. of crystalline light-yellow solid; this was shown by infrared analysis to contain an appreciable amount of $(C_6H_5)_3AsF_2$, but isolation of additional product was not attempted.

Anal. Calcd. for $C_{18}H_{15}F_2As$: C, 62.62; H, 4.37; F, 11.01; As, 21.69. Found: C, 62.14; H, 4.82; F, 10.81; As, 21.66.

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(7) In another run the volatile products were collected and shown by mass spectrometric analysis to consist of SOF_2, HF and unreacted SF_4.

(8) The author is indebted to Dr. C. W. Tullock for the procedure employed in this synthesis.

(9) The reaction of phenylphosphonic acid and SF_4 at 80° gave the difluoride in good yield, but purification difficulties made this procedure less desirable.

(10) L. Horner, H. Hoffman and H. Wippel, *Chem. Ber.*, **91**, 64 (1958).

(11) The product can be recrystallized from benzene, but extreme care is necessary because of the hygroscopicity of the material. The method described gives an essentially pure product directly. The product did not melt sharply even when recrystallized.