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# Reactions of Tetrafluorohydrazine with Di- and Triphenylphosphine. A New Method for Preparation of Fluorophosphoranes

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In view of the current interest in compounds containing phosphorus–fluorine bonds, we wish to report a new method for the preparation of fluorophosphoranes.[2] The method is illustrated by the ready fluorination of di- or triphenylphosphine with tetrafluorohydrazine. These reactions were carried out at or

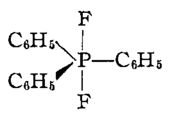
$$2(C_6H_5)_3P + N_2F_4 \longrightarrow 2(C_6H_5)_3PF_2 + N_2 \qquad (1)$$

$$(C_6H_5)_2PH + N_2F_4 \longrightarrow (C_6H_5)_2PF_3 \qquad (2)$$

below ambient temperature by condensing or diffusing the desired amount of tetrafluorohydrazine into an evacuated Pyrex glass reactor which contained the arylphosphine, generally in solution.

When triphenylphosphine was treated with tetrafluorohydrazine under these conditions, the amount of nitrogen which formed was in agreement with the stoichiometry indicated by eq. 1. A solid product was also formed. Its identification as difluorotriphenylphosphorane is based upon elemental analyses, hydrolysis of the compound to triphenylphosphine oxide and fluoride ion, and an $F^{19}$ n.m.r. spectrum which was consistent with a P–F compound.

On the other hand, infrared spectra of this compound in mulls or in a potassium bromide pellet were unusual. In neither case was a strong band observed in the usual P–F region.[3,4] However, P–F stretching absorptions were recently reported[5] to occur at unusually long wave lengths for compounds of the type $R_3PF_2$ and $Ar_3PF_2$. These absorptions were attributed to the axial positions of the fluorine atoms as shown in I. In agreement with these results the infrared spectrum of the solid product from the reaction of triphenylphosphine and tetrafluorohydrazine has a strong band at 670 cm.$^{-1}$, which is in addition to the two expected bands at 728 and 689 cm.$^{-1}$ characteristic of a monosubstituted benzene.[6] The band at 670 cm.$^{-1}$ is therefore assigned to the $PF_2$ asymmetric stretching vibration in structure I. The reader is referred to the paper by Muetterties and co-workers for a discussion of the stereochemistry of phosphorus(V) fluorides.



I

A sample of difluorotriphenylphosphorane was synthesized for comparison by the reaction of triphenylphosphine with sulfur tetrafluoride.[7] The conditions used were milder than those reported and were comparable with those used for the reaction of triphenylphosphine with tetrafluorohydrazine. The products from the two reactions had identical infrared spectra and similar melting points.[8]

The trifluorodiphenylphosphorane which was obtained from the reaction of tetrafluorohydrazine with diphenylphosphine (eq. 2) and a sample which we prepared by the reaction of diphenylphosphinic acid and sulfur tetrafluoride[7] were identical. Their $F^{19}$ n.m.r. spectra were in agreement with the spectrum reported by Muetterties and co-workers.[5]

The reaction of tetrafluorohydrazine with several other phosphines was briefly explored, although rigorous characterization of the products was not carried out. Fluorophosphoranes appeared to be formed from the following compounds: $(n\text{-}C_4H_9)_3P$, $(CH_3)_3P$, $(n\text{-}C_4H_9)_2PH$, $(C_6H_5)_2PBr$. An unidentified material containing P–F bonds was formed in the reaction of phenylphosphine with tetrafluorohydrazine.

## Experimental

Vacuum line and drybox techniques were used, and the reactions were carried out in Pyrex glass tubes. Gas pressures of 100–700 mm. were generally used. Joints and stopcocks were lubricated with Kel-F No. 90 grease.

*Caution.*—Although the reactions described below were carried out without incident, there is a possibility of explosion when tetrafluorohydrazine reacts with organic materials. Adequate safeguards[9] are advised.

**Reactions of Tetrafluorohydrazine with Triphenylphosphine.**—A dry 216-ml. reactor was charged in a drybox with 1.77 g. of triphenylphosphine (6.77 mmoles). The reactor was evacuated and *ca.* 10 ml. of chlorobenzene was charged by vacuum transfer into the reactor from a bulb containing phosphorus pentoxide. The reactor was cooled with liquid nitrogen and 8.4 mmoles of 90% pure tetrafluorohydrazine[10] (7.55 mmoles) was added by vacuum transfer. The reaction mixture was allowed to warm to room temperature and was then stirred magnetically. Bubbles of gas could at first be seen to form in the solution. After 2 hr. no further gas evolution was observed, and a white product had separated from solution. The quantity of gas was essentially unchanged, but contained 3.4 mmoles of nitrogen (the theoretical amount), identified by mass spectrometry. After the excess tetrafluorohydrazine was removed, the solid product was filtered and washed with dry ethyl ether. Transfer of the solid to a polyethylene vial and vacuum drying gave a 45% yield (0.92 g.) of difluorotriphenylphosphorane; duplicate melting points[8] were 158–159° and 160–162°; $\lambda_{\max}^{\text{mineral oil}}$ (strongest peaks): 1430, 1112, 762, 746, 728, 689, and 670 cm.$^{-1}$; $\lambda_{\max}^{\text{KBr}}$ (strongest

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(1) This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract No. NOrd 18728.

(2) For a recent review of known methods for preparing fluorophosphoranes see R. Schmutzler, *Chem. Ind.* (London), 1868 (1962).

(3) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951), ascribe bands in the 840–980 cm.$^{-1}$ region to P–F absorptions.

(4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 311, gives 810–885 cm.$^{-1}$ as the usual region.

(5) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(6) L. J. Bellamy, ref. 4, p. 65.

(7) W. C. Smith, *J. Am. Chem. Soc.*, **82**, 6176 (1960).

(8) The melting points were obtained in sealed capillary tubes which contained an atmosphere of dry air or prepurified nitrogen. The observed melting points (see Experimental section) were higher than the reported[7] value of 136–140°.

(9) C. L. Knapp, *Ind. Eng. Chem.*, **55**, No. 2, 25 (1963).

(10) The impurities were fluorocarbons.

peaks): 1447, 1111, 762, 746, 730, 696, and 679 cm.$^{-1}$. The F$^{19}$ n.m.r. spectrum was obtained on a benzene solution of the solid. In spite of low solubility and low fluorine content, satisfactory spectra were obtained by carefully optimizing the radio-frequency field, receiver gain, and sweep rate settings. A doublet with a chemical shift of −39.2 p.p.m. (from trifluoroacetic acid as external reference) and a $J_{PF}$ of 667 c.p.s. was observed (lit.[5] −39 p.p.m. and 695 c.p.s. for the neat liquid).

*Anal.* Calcd. for $C_{18}H_{15}F_2P$: C, 71.99; H, 5.03; F, 12.65; P, 10.32. Found: C, 71.90; H, 5.33; F, 12.0; P, 10.25.

The same product was formed in a similar reaction in which anhydrous ethyl ether was substituted for chlorobenzene and when triphenylphosphine was heated at 91° with excess tetrafluorohydrazine. However, the product from the latter reaction showed additional weak bands at 878 and 785 cm.$^{-1}$ in its infrared spectrum and had a lower melting point (141–150°) than the products prepared in solution.

**Reaction of Triphenylphosphine with Sulfur Tetrafluoride.**—An approximately 550-ml. Pyrex glass reactor was charged with 1.87 g. (7.1 mmoles) of triphenylphosphine. The reactor was evacuated and 10 ml. of chlorobenzene was charged by vacuum transfer from a bulb containing phosphorus pentoxide into the reactor. Excess sulfur tetrafluoride (*ca.* 20 mmoles) was condensed into the reactor with a liquid nitrogen bath. The reactor was closed and the bath was removed. After 10 min. magnetic stirring was started and continued for 0.5 hr. The volatiles were then removed, leaving a solid residue. The infrared spectrum (mineral oil mull) of the solid and the corresponding spectrum of the product from tetrafluorohydrazine were identical.

The solid was washed out of the reactor with anhydrous benzene, filtered, washed with anhydrous ethyl ether, and dried. The yield of pale yellow solid was 1.1 g. (3.7 mmoles, 52%); m.p. 154–158°.[8]

Some of the solid was recrystallized from hot benzene using polypropylene centrifuge tubes to carry out the recrystallization. The hot solution was decanted from a small amount of yellow, insoluble material (presumably sulfur). The recrystallized material was treated with reagent grade methanol and dried; m.p. 159.6–160.6°.[8] The treatment with methanol removed an impurity, absorbing weakly at 1145 cm.$^{-1}$, in the benzene-recrystallized product.

**Hydrolysis of Difluorotriphenylphosphorane.**—Difluorotriphenylphosphorane was stirred overnight with an excess of a 10% solution of sodium hydroxide in 1:1 ethanol–water. The solvents were largely distilled and the solid product was filtered and washed with water to give a 67% yield of triphenylphosphine oxide, identified by its m.p. of 156–156.4° (lit.[11a] 152–153°; lit.[11b] 156°) and its infrared spectrum.[12] A fluoride determination on the filtrate found 0.62 mequiv. (86%).

In another experiment difluorotriphenylphosphorane in a polyethylene container was dissolved in 96% sulfuric acid (fumes of presumed hydrogen fluoride were evolved) and the solution was poured into water. The insoluble solid which formed was triphenylphosphine oxide.

**Reaction of Tetrafluorohydrazine with Diphenylphosphine.**—Tetrafluorohydrazine (7.7 mmoles, 87% pure,[10] 6.7 mmoles of $N_2F_4$) was allowed to diffuse over a stirred solution of diphenylphosphine (1.1 g., 6.1 mmoles) in 30 ml. of 1,2,3-trichloropentafluoropropane. Nitrogen gas was removed periodically by cooling most of the system in liquid nitrogen and pumping off the noncondensables. After 24 hr., 3.5 mmoles of nitrogen (identified by mass spectrometry) had been evolved. The solvent was distilled at 25° from an amber oil, which was then distilled bulb-to-bulb to give 0.8 g. (54%) of trifluorodiphenylphosphorane.

The infrared and F$^{19}$ n.m.r. spectra of the phosphorane were essentially the same as those of a sample which we prepared by the published method of Smith.[7,13] The infrared spectrum showed the presence of P–F absorption at 870 cm.$^{-1}$ but no P–H absorption at 2380 cm.$^{-1}$. The F$^{19}$ n.m.r. spectrum of the neat liquid showed a doublet of doublets of chemical shift −43.68 p.p.m. and a doublet of triplets of chemical shift +1.15 p.p.m. (from trifluoroacetic acid as an external standard). The reported values are −44 and +1.2 p.p.m., respectively.[5]

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[11] (a) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **64**, 2982 (1942); (b) M. R. Sauvage, *Compt. rend.*, **139**, 674 (1904).

[12] We wish to thank Dr. A. K. Hoffmann for the sample of triphenylphosphine oxide which was used for comparison.

[13] The assistance of Mr. S. W. Grant in this preparation is gratefully acknowledged.

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# Kinetics of the Reduction of Halopentaamminecobalt(III) Complexes by Chromium(II)

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Earlier attempts[1] to measure the rates of reduction of the halopentaamminecobalt(III) complexes by chromium(II)

$$(NH_3)_5CoX^{2+} + Cr^{2+}(aq) + 5H_3O^+ \longrightarrow Co^{2+}(aq) + (H_2O)_5CrX^{2+} + 5NH_4^+$$

(where X = F, Cl, Br, I) were unsuccessful because the reactions were too fast for the stopped-flow procedure employed. By modifying the procedure, we have now succeeded in measuring these rates, which are reported in the present paper.

The essential features of the experimental method, the stopped-flow apparatus, and the preparation of materials have all been described earlier.[1] The present modification consisted of substituting a Beckman deuterium lamp for the tungsten lamp of the stopped-flow apparatus, thus making it possible to use the ultraviolet absorption bands of the halopentaamminecobalt(III) ions ($\lambda_{max}$ ranging from 210 m$\mu$ for $(NH_3)_5CoF^{2+}$ to 287 m$\mu$ for $(NH_3)_5CoI^{2+}$), in place of the visible bands, to follow their disappearance. Because of the much higher extinction coefficients ($\sim 2 \times 10^4$) of these bands, the reactant concentrations could be lowered sufficiently to bring the rate measurement into the range of the stopped-flow apparatus ($t_{1/2} > 5 \times 10^{-3}$ sec.). The initial reactant concentrations were, typically, $[(NH_3)_5CoX^{2+}] \sim 5 \times 10^{-6}$ *M*, $[Cr^{2+}]$ ranging from $2 \times 10^{-5}$ to $1.2 \times 10^{-4}$ *M*. The kinetic data fitted the second-order rate law, $k[Cr^{2+}][(NH_3)_5CoX^{2+}]$,

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[1] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).