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New Preparations and Properties of Tetrafluorophosphoranes

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The reactions between dimethylaminotetrafluorophosphorane and anhydrous hydrogen halides have been investigated. By means of these reactions, it has been possible to prepare tetrafluorochlorophosphorane and the previously unknown tetrafluorobromophosphorane. These compounds have been characterized by molecular weight and ^{19}F, ^{31}P, mass, and infrared spectral measurements. In contrast to the behavior of hydrogen chloride and hydrogen bromide, hydrogen iodide gives only PF_3 and I_2 as volatile products.

Introduction

The ease with which halodifluorophosphines may be formed from dialkylaminodifluorophosphine[1-3] and the ease with which halodifluorophosphoryl and halodifluorothiophosphoryl compounds may be obtained from corresponding dialkylaminodifluorophosphoryls and dialkylaminodifluorothiophosphoryls[4,5] has prompted us to investigate the action of anhydrous hydrogen chloride and hydrogen bromide upon dimethylaminotetrafluorophosphorane.[6-9] The results obtained indicate that these reactions do result in the formation of PF_4Cl, prepared previously by Carter and Holmes,[10] and the previously unknown PF_4Br. The reaction of hydrogen iodide results in the formation of PF_3 and I_2 as volatile products.

Experimental Section

Standard high-vacuum techniques were used throughout. Dimethylaminotetrafluorophosphorane was prepared as described previously.[8] The identity of the phosphorane was established by comparison of its infrared spectrum with the previously reported spectrum[8] and by a vapor pressure of 43.0 mm at 0° (lit.[8] pressure 44.0 mm). The proton nmr and glpc suggested that the material was more than 95% pure. Anhydrous HCl (Matheson) was distilled just prior to use. Anhydrous HBr and HI were made from bromine and iodine, respectively, with 1,2,3,4-tetrahydronaphthalene.[11]

The infrared spectra were obtained on a Perkin-Elmer 237B grating spectrophotometer. For the region below 600 cm^{-1}, a Perkin-Elmer 301 spectrophotometer was employed. For volatile materials a gas cell with a 7.5-cm path length and CsI windows was used.

Proton nmr spectra were observed on a Varian Model A-60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Fluorine nmr spectra were obtained on a Varian Model 56/60 nuclear magnetic spectrometer operating at 56.4 Mc. For the proton spectra, tetramethylsilane and methylene chloride were used as external standards. For fluorine magnetic resonances, fluorotrichloromethane was used as an external reference, by the tube-interchange technique. Whenever possible, samples were run as neat liquids. Phosphorus nmr absorptions were obtained on a Varian Model HA 100 spectrometer. Phosphoric acid (85%) was used as a reference.

All mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103C spectrometer operating with an ionizing voltage of 56 V.

A F & M research chromatograph was used for glpc, with helium as the carrier gas and a flame ionization detector. Glpc of the products was performed on a 0.125 in. × 20 ft stainless steel column packed with 20% silicon gum rubber SE 30 on Chromosorb W. The column was operated at 70°.

The Reaction of Dimethylaminotetrafluorophosphorane with Anhydrous Hydrogen Chloride.—Because of difficulties encountered when this reaction was allowed to proceed in a condensed state, the reaction between $(CH_3)_2NPF_4$ and HCl was carried out entirely in the gas phase using a system previously described by Treichel, Goodrich, and Pierce.[12] Two bulbs of about 1-l. capacity and about 250-ml capacity were connected together with an intervening stopcock. In a typical reaction, a 6.28-mmol sample of HCl was condensed *in vacuo* at −196° into the smaller bulb. A 3.51-mmol sample of $(CH_3)_2NPF_4$ was condensed *in vacuo* into the larger bulb at −196°. Both reactants were allowed to warm to 23°. No liquid $(CH_3)_2NPF_4$ was observed. When the stopcock between the two bulbs was opened, the HCl expanded into the larger bulb. An immediate reaction was observed by the formation of a fine white solid. The volatile products of this reaction were condensed in a −196° trap on the vacuum system and then fractionated through traps held at 0, −78, and −196°. The −78° fraction contained 0.30 mmol of unreacted $(CH_3)_2NPF_4$, identified by its gas-phase ir spectrum. The −196° trap contained 3.12 mmol of PF_4Cl. The PF_4Cl was identified by its gas-phase ir spectrum. This spectrum was identical with the previously reported spectrum of PF_4Cl[13] except those bands which were attributed to POF_3[13] are of lower intensity. PF_4Cl was also identified by a gas-phase molecular weight of 141.1 (theoretical 142.4) and its ^{19}F nmr at −60° which exhibited a doublet pattern at 24.3 ppm (lit.[10] 23.5 ppm) from CCl_3F. The coupling constant (J_{PF}) was 1000 ± 10 cps (lit.[10] 1000 cps). The nmr spectrum exhibited no peaks which can be attributed to POF_3 or PF_3Cl_2 but did exhibit peaks which can be attributed to minor amounts of PF_5 at +68 ppm with J_{PF} of 930 cps (lit. δ +72.5 ppm;[14] J_{PF} = 916 cps[15]).

Mass spectra obtained at 56 V also supported the formulation of PF_4Cl. Peaks attributed to the following species (with mass number and relative abundance, respectively) were observed: PF_4^+, 107, 18; $PF_3{}^{37}Cl^+$, 106, 2; $PF_2{}^{35}Cl^+$ and POF_3^+, 104, 22; PF_3^+, 88, 18; $PF^{37}Cl^+$, 87, 13; $PF^{35}Cl^+$ and POF_2^+, 85, 68; PF_2^+, 69, 62; POF^+, 66, 1; POF_3^{2+}, 57, 1; PF^+, 50, 10; PF_3^{2+}

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(?), 44, 80; $H^{37}Cl^+$, 38, 32; $^{37}Cl^+$, 37, 24; $H^{35}Cl^+$, 36, 100; $^{35}Cl^+$, 35, 72; POF_2^{2+}, 33, 4; O_2^+, 32, 12; P^+, 31, 7; N_2^+, 28, 57; PF^{2+}, 25, 5.

The Reaction of Dimethylaminotetrafluorophosphorane with Anhydrous Hydrogen Bromide.—This reaction was run in a manner identical with that previously described for the reaction involving HCl. In a typical reaction, a 7.22-mmol sample of HBr was allowed to interact with a 3.35-mmol sample of $(CH_3)_2NPF_4$. The reaction proceeded with the formation of a white powder. The volatile products were fractionated three times through traps held at 0, −126, and −196°. A 3.22-mmol sample of a gas, later identified as a mixture of about 80% PF_4Br and about 20% PF_5, was obtained from the −126° fraction. A 0.35-mmol sample of HBr, identified by its infrared spectrum, was recovered from the −196° trap. Characterization of PF_4Br is presented in subsequent portions of this article.

The infrared spectrum of the −126° fraction exhibited peaks attributed to PF_4Br, POF_3, and PF_5. The complete spectrum may be summarized by the following absorptions in cm^{-1} (with intensity and tentative assignments, respectively): 1760 (vw) ($2\nu_1 = 1770$); 1570 (mw) ($\nu_1 + \nu_2 = 1560$); 1405, 1415, 1426 (mw) (POF_3); 1365 (w) ($\nu_{10} + \nu_8 = 1370$); 1020, 1025, 1035 (s) (PF_5); 985, 990, 1000 (s) (POF_3); 955 (s) (POF_3); 945 (vs) (POF_3 or PF_5); 906, 915 (s) (ν_7, PF_2 str); 899 (vs) (ν_{10}, PF_2 str); 855 (vs) (ν_1, PF_2 str); 855, 865 (m) (POF_3); 725 (vw) (?); 675, 678 (s) (ν_2, PF_2 str); 617 (mw) (?); 573, 584 (ms) (?); 532, 542 (vs) (ν_{11}, PF_2Br out-of-plane bend); 522 (ms) (PF_5); 461, 470 480 (s) (ν_8 and ν_3, PF_2 in-plane bend and PF_2Br in-plane bend); 387 (w) (ν_4, PBr str).

A mass spectrum of the −126° fraction exhibited peaks attributed to the following species (with mass number and relative abundance, respectively): $PF^{81}Br_2^+$, 212, 1; $PF^{79}Br^{81}Br^+$, 210, 2; $PF^{79}Br_2^+$, 208, 1; $P^{81}Br_2^+$, 193, 2; $P^{79}Br^{81}Br^+$, 191, 4; $P^{79}Br_2^+$, 189, 2; $PF_2{}^{81}Br^+$, 150, 4; $PF_2{}^{79}Br^+$, 148, 4; $PF^{81}Br^+$, 131, 2; $PF^{79}Br^+$, 129, 2; PF_4^+, 107, 58; POF_3^+ or SiF_4^+, 104, 38; ?, 91, 10; PF_3^+, 88, 23; POF_2^+ or SiF_3^+, 85, 46; $H^{81}Br^+$, 82, 100; $^{81}Br^+$, 81, 86; $H^{79}Br$, 80, 100; $^{79}Br^+$, 79, 86; PF_2^+, 69, 40; PF^+, 50, 12; PF_3^{2+} (?), 44, 19; $H^{81}Br^{2+}$, 41, 14; $^{81}Br^{2+}$, 40.5, 12; $H^{79}Br^{2+}$, 40, 14; $^{79}Br^{2+}$, 39.5, 12; O_2^+ (?), 32, 11; P^+, 31, 11; N_2^+, 28, 54 (also appears as intense background peak); PF^{2+}, 25, 7.

The large amount of HBr which appears is apparently formed by hydrolysis of PF_4Br at the injection part of the mass spectrometer. No bands which could be attributed to HBr were observed in the infrared spectrum of PF_4Br at 50 mm pressure.

The gas-phase molecular weight of the −126° fraction was 178.5 (theoretical for PF_4Br, 186.9).

The Reaction of Dimethylaminotetrafluorophosphorane with Anhydrous HI.—The reaction was run in a manner identical with those previously described. The −196° trap contained PF_3, identified by its gas-phase infrared spectrum and a gas-phase molecular weight of 88.3 (theoretical 88.0). The solids remaining in the reaction bulb were deep purple. A portion of these solids could be dissolved in CCl_4. The visible spectrum of this solution was identical with that of a solution of elemental iodine dissolved in CCl_4. The amount of I_2 produced in this reaction was determined using standard techniques.[16] The experimental stoichiometry for the over-all reaction is

$$1.00(CH_3)_2NPF_4 + 1.99HI \longrightarrow 0.94PF_3 + 0.92I_2 + \text{solid}$$

The solid remaining in the reaction flask may be identified, on the basis of these data, as $(CH_3)_2NH_2{}^+F^-$.

Discussion

Anhydrous hydrogen bromide or hydrogen chloride react with dialkylaminotetrafluorophosphorane to yield tetrafluorobromophosphorane and tetrafluorochlorophosphorane according to the equation

$$(CH_3)_2NPF_4 + 2HX \longrightarrow PF_4X + [(CH_3)_2NH_2]^+X^-$$

In contrast to this behavior, hydrogen iodide reacts with $(CH_3)_2NPF_4$ according to the equation

$$(CH_3)_2NPF_4 + 2HI \longrightarrow PF_3 + I_2 + [(CH_3)_2NH_2]^+F^-$$

Cavell and Charlton[17] have shown that hydrophosphoryl difluoride, OPF_2H, is formed when $(CH_3)_2NPOF_2$ is allowed to interact with HI. The fact that PF_4H is not produced from the interaction of $(CH_3)_2NPF_4$ and HI may be a result of the inability of PF_4H to exist in the presence of reducing agents such as HI.

Of the two tetrafluorohalophosphoranes prepared by this method, PF_4Cl is much more stable and easier to isolate and characterize. It has been previously reported[10] that a sample of PF_4Cl could be stored in the gaseous state for 4 days before deposition of a white solid on the walls of the storage container could be observed. This observation was also noted in these laboratories. In contrast to this behavior, when a sample of PF_4Br was stored in the gaseous state (in a glass ampoule), it was observed that a yellow-red solid was deposited on the walls of the ampoule within 15 min. A liquid sample of water white PF_4Br deposits a deep red solid in less than 1 min at room temperature. On the other hand, no change was observed where a liquid, water white sample of PF_4Cl was held at room temperature for 30 min. The thermal instability of PF_4Br suggests that the compound decomposed when allowed to strike the warm tubing between the cold traps on the vacuum system. That this is the case is also suggested by the fact that attempts to purify PF_4Br by recycling *in vacuo* the partially purified material four times through traps held at −78, −126, and −196° did not result in a tensiometrically homogeneous sample. In spite of the fact that PF_4Br could not be obtained in a state of high purity, physical measurements, presented below, strongly suggest that PF_4Br in about 80% yield is obtained from the interaction of $(CH_3)_2NPF_4$ and HBr.

First, the ^{19}F nmr spectrum of a sample presumed to be PF_4Br consisted at −60° of a simple doublet pattern (P–F coupling at +9.6 ppm). The coupling constant was 1085 ± 10 cps. The chemical shift and J_{PF} coupling constant for PF_4Br is intermediate between the values for PF_5 and PF_3Br_2.[18] The ^{19}F nmr spectrum also exhibited absorptions which can be attributed to PF_5 at +66.7 ppm with $J_{PF} = 940 \pm 10$ cps (lit.[14,15] δ +72.5 ppm; $J_{PF} = 916$ cps). On the basis of the area under the peaks, the sample contained about 20% PF_5. No absorptions attributed to PF_3Br_2 were observed. These data are consistent with molecular weight determinations which always yielded values lower than the theoretical values. As mentioned previously, we were unable to remove the PF_5 by fractional distillation *in vacuo*. At the lowest temperature obtainable on our nmr spectrometer, −60°, no line broadening was observed, suggesting that the molecule was exchanging intramolecularly at a rate faster than could be observed by nmr techniques at −60°.

Second, the ^{31}P nmr spectrum of this same sample at

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(17) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

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−70° consisted of a simple quintet of 1:4:6:4:1 at +72.6 ppm with J_{PF} = 1075 ± 15 cps. No other absorptions were observed.[19] This observation can only be rationalized by the existence of a tetrafluorophosphorus group.

Third, the formula PF_4Br is also supported by the infrared data. Several assignments may be made on the basis of assignments carried out for PF_4Cl,[13] if it is assumed that PF_4Br and PF_4Cl are of C_{2v} symmetry. In the P–F stretching region of the PF_4Br spectrum, the very intense bands at 885, 899, and 915 cm^{-1} are associated with the PF stretching modes. In PF_4Cl these are found[13] at 895, 903, and 921 cm^{-1}. The PF_2 symmetric axial stretch has been assigned[13] to bands at 691 cm^{-1} in PF_4Cl and is probably observed at 675 cm^{-1} in PF_4Br. An out-of-plane bending motion appears at 560 cm^{-1} in PF_4Cl[13] and is probably associated with the intense bands at 532 and 542 cm^{-1} in PF_4Br. An intense band centered at 470 cm^{-1} in PF_4Br and at 490 cm^{-1} in PF_4Cl may be assigned to either a PF_2 in-plane bending motion or a PF_2X in-plane bending motion. Medium-weak bands in PF_4Cl which are easily ascribed to PCl stretching vibration appear at 427 and 434 cm^{-1} in PF_4Cl. These are, of course, absent in the spectrum of PF_4Br. However, a band at 387 cm^{-1} in PF_4Br may be associated with a PBr stretching motion. Other bands in the infrared absorption spectra of PF_4Br may be ascribed to impurities.

Fourth, mass spectra obtained at 56 V of PF_4Cl and PF_4Br are quite similar, as expected. The parent ions were not detected. This is consistent with other phosphorane results.[12] Intense peaks appear at *m/e* corresponding to PF_4^+, PF_3^+, PF_2^+, and X^+. The similarity of the mass spectra of PF_4Cl and PF_4Br further augment the formulation as PF_4Br. The presence of molecular ions containing two bromine atoms in the spectrum of PF_4Br suggests that small amounts of PF_3Br_2 are formed when PF_4Br decomposes, as expected.[10] The PF_3Br_2 thus formed appears to be, on the basis of the ^{19}F nmr data, substantially removed upon distillation *in vacuo*.

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[19] Because of the low magnetogyric ratio of phosphorus, the signal is about 10 times less intense than that of fluorine. This lack of sensitivity accounts for the fact that the expected septet due to PF_6 was not observed.

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The Preparation and Properties of Iodothiophosphoryl Difluoride, SPF_2I[1]

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Iodothiophosphoryl difluoride has been prepared from hydrothiophosphoryl difluoride by reaction with (a) N-iodosuccinimide, (b) sulfur and iodine, or (c) sulfur and hydrogen iodide. The reactions of iodothiophosphoryl difluoride with dimethylamine, methanol, methyl mercaptan, hydrogen chloride, and hydrogen bromide yielded the appropriate substituted thiophosphoryl difluoride. Hydrogen iodide rapidly reduced the iodo compound to the hydride. Dimethylphosphine yielded methyl-substituted thiophosphoryl fluorides and dimethylarsine yielded dimethyliodoarsine in complicated reactions with iodothiophosphoryl difluoride. Physical data and spectroscopic properties of iodothiophosphoryl difluoride and its new methoxy and methylthio derivatives are reported.

Introduction

We recently suggested that the novel synthesis of hydrophosphoryl difluoride and hydrothiophosphoryl difluoride from the reaction of dimethylaminophosphoryl difluoride or dimethylaminothiophosphoryl difluoride with hydrogen fluoride proceeded through the unknown phosphoryl or thiophosphoryl iodofluoride EPF_2I (where E = O or S).[2] Although a number of organophosphoryl iodides are known,[3] no mixed phosphoryl or thiophosphoryl halogenides containing both iodine and another halogen have been reported. We now wish to report the successful synthesis of iodothiophosphoryl difluoride and a description of some of its properties including reduction to hydrothiophosphoryl difluoride by hydrogen iodide.

Experimental Section

Standard vacuum techniques using Pyrex-glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon N grease. Infrared spectra were measured with a Beckman IR-12 (4000–300 cm^{-1}) instrument, mass spectra with an AEI MS-9 double-focusing mass spectrometer, and nuclear magnetic resonance spectra with Varian A-56/60 or DP60 instruments. All fluorine spectra were measured at 56.4 MHz rela-

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[1] Presented in part at the 51st Conference of the Chemical Institute of Canada, Vancouver, B. C., June 3–5, 1968.

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