$-70°$ consisted of a simple quintet of 1:4:6:4:1 at +72.6 ppm with $J_{PF} = 1075 \pm 15$ 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*.

Acknowledgment.—Generous support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. It is also a pleasure to thank Dr. J. Heeschen of the Dow Chemical Co., Midland, Mich., for help in obtaining the ^{19}F nmr spectra, and to thank Dr. R. W. Parry and Mr. F. Parker of the University of Michigan, Ann Arbor, Mich., for help in obtaining the ^{31}P nmr spectra.

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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]

BY T. L. CHARLTON AND R. G. CAVELL

Received May 20, 1968

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.

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

[3] B. Miller, "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., 1965, p 133.

tive to CCl_3F and hydrogen spectra were measured at 60 MHz relative to tetramethylsilane (τ 10.0). In some cases hydrogen spectra were measured at 100 MHz with a Varian HA100 instrument. Phosphorus spectra were measured at 24.1 MHz relative to P_4O_6.[4]

Materials.—Hydrothiophosphoryl difluoride was prepared as described previously.[2] Dimethylphosphine and dimethylarsine were prepared by literature methods.[5] Gaseous HCl, HBr, $(CH_3)_2NH$, and CH_3SH (Matheson) were used as obtained. Hydrogen iodide (Matheson) was purified before use by fractional distillation under vacuum. N-Iodosuccinimide (NIS) was obtained from the Arapahoe Chemical Co. and used without further purification. All other chemicals were of reagent grade and used without further purification.

Preparation of Iodothiophosphoryl Difluoride. (a) From SPF_2H and N-Iodosuccinimide (NIS).—Hydrothiophosphoryl difluoride (0.64 g, 6.3 mmol) was condensed onto an excess of NIS contained in a 75-cm^3 reaction tube. A moderately exothermic reaction occurred immediately on warming the tube and its contents to room temperature, forming a colorless liquid, and turning the NIS to a light reddish color. After 1 hr, the volatile products were fractionated in the vacuum system to give iodothiophosphoryl difluoride, SPF_2I (1.25 g, 5.5 mmol), in 95% yield condensed at −81°. A trace of unreacted SPF_2H was collected at −196° (0.04 g, 0.4 mmol). Also obtained, at −95°, were traces of a compound which was later identified as $(SPF_2)_2O$.[6] Although the amount of $(SPF_2)_2O$ produced could be reduced by pumping on the NIS for several hours prior to reaction with SPF_2H, the oxide was never eliminated by this method. Yields of SPF_2I decreased if the reaction time was allowed to exceed 3–4 hr, and the use of a large excess of NIS did not produce complete conversion of SPF_2H to SPF_2I. Lower yields also resulted if the temperature of the reaction vessel was allowed to increase much above room temperature.

(b) From SPF_2H, Sulfur, and Iodine.—Hydrothiophosphoryl difluoride (0.092 g, 0.90 mmol) was condensed into a tube containing sulfur and iodine in excess. The reaction was allowed to proceed for 8 hr at 65°. Fractionation of the volatile products gave SPF_2I (0.15 g, 0.7 mmol), a trace of unreacted SPF_2H (0.02 g, 0.2 mmol), and hydrogen sulfide (0.011 g, 0.33 mmol).

(c) From SPF_2H, Sulfur, and Hydrogen Iodide.—Equimolar quantities of SPF_2H (0.18 g, 1.85 mmol) and HI (0.27 g, 2.10 mmol) were condensed into a tube with an excess of sulfur. Immediately on warming the tube to room temperature, a reaction occurred with the formation of a dark brown solid. After 72 hr, fractionation of the volatile products gave SPF_2I (0.11 g, 0.48 mmol), SPF_2H (0.10 g, 0.98 mmol), and H_2S (0.05 g, 1.49 mmol). No HI was found in the products. Molecular iodine was observed in the residues. In a separate experiment sulfur was found to react with HI under the above conditions to yield H_2S and iodine.

Characterization of SPF_2I—Iodothiophosphoryl difluoride is a colorless, volatile liquid. It was characterized by vapor density molecular weight (calcd for SPF_2I: 227.8; found: 228.5), mass spectroscopy, including accurate mass measurement of the parent ion (calcd for $^{32}SPF_2I$: *m/e* 227.8473; found: *m/e* 227.8473), and elemental analysis. *Anal.* Calcd for SPF_2I: S, 14.0; P, 13.6; I, 55.7. Found: S, 14.4; P, 13.35; I, 55.5. SPF_2I was found to suffer less than 5% decomposition after 4 days at 150°. The products of the decomposition were molecular iodine and an unidentified involatile material. Exposed to normal illumination in a Pyrex tube at room temperature for several days, SPF_2I slowly turned red and fractionation of the colored solution left minute traces of molecular iodine. The vapor pressure of SPF_2I was measured in an all-glass Bourdon spiral gauge microtensimeter with both ascending and descending temperatures. The results are given in Table I.

Reactions of SPF_2I. (a) With Water.—Iodothiophosphoryl difluoride and water in a 2:1 molar ratio were sealed in a 10-cm^3 reaction tube. The two were initially immiscible but reacted on shaking to give a solution which gradually turned from light yellow to dark red. A viscous liquid separated from the solution. The volatile products were fractionated after 72 hr with recovery of half of the original SPF_2I and an inseparable mixture of SiF_4, SPF_2H, PF_3, SPF_3, and H_2S, all identical spectroscopically.[2,7,8] Molecular iodine and an unidentified colorless hygroscopic liquid remained as residues in the reaction tube. No excess H_2O was recovered.

In another reaction, SPF_2I (0.16 g, 0.68 mmol) and H_2O (0.011 g, 0.60 mmol) were sealed together in a tube and allowed to react for 4 hr. The volatile products were then fractionated to give SPF_2I (0.01 g, 0.06 mmol) and an inseparable mixture of SIF_4, SPF_3, PF_3, and H_2S (0.02 g). Residues of the reaction were similar to those found previously.

(b) With Anhydrous Hydrogen Iodide.—Iodothiophosphoryl difluoride (0.11 g, 0.48 mmol) and hydrogen iodide (0.08 g, 0.65 mmol) were sealed together in a 75-cm^3 reaction tube. Immediately on warming to room temperature, the colorless liquid turned light yellow and then rapidly changed to dark red. After 1 hr, a crystalline solid started to form. The volatile products were fractionated to give SPF_2H (0.05 g, 0.45 mmol) and excess HI. Molecular iodine remained as a residue. A separate experiment conducted under the same conditions but including a large excess of mercury in the reaction mixture gave a quantitative yield of SPF_2H and a mixture of mercury and mercurous and mercuric iodides in the residue.

(c) With Anhydrous Hydrogen Bromide.—Iodothiophosphoryl difluoride (0.22 g, 0.96 mmol) and hydrogen bromide (0.08 g, 1.02 mmol) were sealed together in a 75-cm^3 reaction tube. On warming to room temperature, the liquid turned pink and then rapidly darkened. The volatile products were fractionated after 48 hr to give SPF_2H (0.03 g, 0.29 mmol), SPF_2Br (0.07 g, 0.41 mmol), unreacted SPF_2I (0.04 g, 0.19 mmol), and an inseparable mixture containing HBr, H_2S, and PF_2Br identified spectroscopically.[7,9] Molecular iodine remained as a residue.

(d) With Anhydrous Hydrogen Chloride.—Iodothiophosphoryl difluoride (0.36 g, 1.57 mmol) and hydrogen chloride (0.06 g, 1.64 mmol) were sealed in a 75-cm^3 reaction tube. When no reaction was observed after several hours, the tube was placed in the oven at 65°. After 18 days, the volatiles were fractionated to give SPF_2H (0.16 g, 0.16 mmol), SPF_2Cl (0.55 g, 0.40 mmol), unreacted SPF_2I (0.19 g, 0.82 mmol), and an inseparable mixture of HCl, H_2S, and PF_2Cl (0.06 g) identified spectroscopically.[7,10] Molecular iodine remained as a residue. A separate reaction carried out at 150° for a shorter period of time gave similar results.

(e) With Dimethylamine.—Iodothiophosphoryl difluoride (0.10 g, 0.44 mmol) and dimethylamine (0.04 g, 0.90 mmol) were sealed in a 25-cm^3 reaction tube. Immediately on warming to room temperature a reaction occurred producing a white solid material. After 1 hr, the volatiles were fractionated to give only $SPF_2N(CH_3)_2$ (0.06 g, 0.40 mmol) identified by comparison with an authentic sample.[11] The solid residue was not examined.

(f) With Dimethylphosphine.—Iodothiophosphoryl difluoride (0.18 g, 0.81 mmol) and dimethylphosphine (0.05 g, 0.87 mmol) were sealed in a 25-cm^3 reaction tube. Immediately on warming to room temperature, a reaction occurred forming a light yellow

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(4) A. C. Chapman, J. Homer, D. J. Mowthorpe, and R. T. Jones, *Chem. Commun.*, 121 (1965).

(5) Dimethylphosphine was prepared by $LiAlH_4$ reduction of tetramethyldiphosphine disulfide following the procedure of K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 704 (1959). Dimethylarsine was made by hydrochloric acid reduction of dimethylarsonic acid with a zinc–mercury amalgam followed by vacuum distillation.

(6) R. G. Cavell and T. L. Charlton, unpublished observations.

(7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

(8) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, **46**, 3057 (1967); R. G. Cavell, *Spectrochim. Acta*, **23A**, 249 (1967); H. G. Horn, A. Muller, and O. Glemser, *Z. Naturforsch.*, **20a**, 746 (1965).

(9) A. Muller, E. Niecke, and O. Glemser, *Z. Anorg. Allgem. Chem.*, **350**, 256 (1967).

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TABLE I

VAPOR PRESSURE DATA FOR IODOTHIOPHOSPHORYL DIFLUORIDE AND ITS DERIVATIVES

SPF_2I

Temp, °C	−37.2	−36.9[b]	−27.0	−22.2[b]	−14.0[b]	−7.1	2.6	8.0[b]	12.6	14.2[b]	21.6	25.6
Pressure, mm												
Obsd	3.3	3.4	6.6	8.3	14.3	20.5	34.2	45.6	56.8	60.0	86.2	100.5
Calcd[a]	3.3	3.4	6.5	8.7	14.1	20.7	34.4	44.9	55.9	60.3	84.3	100.8

SPF_2OCH_3

Temp, °C	−36.8	−32.9[b]	−27.8	−18.2	−8.1	16.9[b]	22.0	24.6
Pressure, mm								
Obsd	10.3	13.6	19.3	33.4	58.8	187.3	233.3	259.5
Calcd[a]	10.7	13.7	18.9	33.1	57.2	187.8	233.6	260.3

SPF_2SCH_3

Temp, °C	−20.0	−14.6[b]	−9.7	0.0	5.1[b]	10.1	19.7	24.8
Pressure, mm								
Obsd	2.9	4.4	5.9	11.1	15.1	20.3	35.8	45.5
Calcd[a]	3.0	4.3	6.0	11.2	15.3	20.4	34.8	45.5

[a] Pressures calculated from the linear equation $\log P_{mm} = A - (B/T)$ according to the parameters given in Table II. [b] Measured with temperature descending from the highest value reached. All other points measured with ascending temperatures.

solid and a liquid of low volatility. After a few minutes, the solid turned orange. The volatile products were fractionated after 7 days to give dimethylthiophosphoryl fluoride, $SPF(CH_3)_2$ (0.06 g, 0.52 mmol), a small amount of CH_3PSF_2,[12] and an inseparable mixture of SiF_4 and PF_3. The orange residue which remained was not identified.

(g) **With Dimethylphosphine and Trimethylamine.**—Iodothiophosphoryl difluoride (0.49 g, 2.16 mmol), dimethylphosphine (0.12 g, 1.89 mmol), and trimethylamine (0.12 g, 1.97 mmol) were sealed together in a 75-cm^3 reaction tube. Immediately on warming to room temperature, a reaction occurred producing a white solid product which turned dark orange after 1 hr. No condensable material remained at this point. The reaction tube was heated to 150° for 2 days. The resulting volatile products were fractionated to give $SPF(CH_3)_2$ (0.16 g, 1.43 mmol), PF_3, and a trace of SPF_3 (0.07 g). A dark orange residue remained which was not identified.

(h) **With Dimethylarsine.**—Iodothiophosphoryl difluoride (0.16 g, 0.71 mmol) and dimethylarsine (0.08 g, 0.72 mmol) reacted at room temperature in a 25-cm^3 vessel to yield a yellow solution and a small amount of yellow solid. Separation of volatiles after 3 weeks gave a small amount of dimethyliodoarsine (0.06 g, 0.02 mmol) and an inseparable mixture of SPF_2H, PF_3, and H_2S (0.06 g). An unidentified light orange residue remained.

(i) **With Methanol.**—Iodothiophosphoryl difluoride (0.20 g, 0.86 mmol) and methanol (0.03 g, 0.86 mmol) reacted in a 25-cm^3 vessel immediately on warming to room temperature to form a red solution. Separation of the volatiles after 30 min gave SPF_2H (0.04 g, 0.37 mmol), SPF_2OCH_3 (0.05 g, 0.34 mmol) (identified by mass spectra including accurate mass measurement of the parent peak: found: *m/e* 131.9602; calcd for $^{32}SPF_2OCH_3$: 131.9610, infrared and nmr spectra), unreacted SPF_2I (0.02 g, 0.08 mmol), and unreacted CH_3OH. Molecular iodine remained as a residue.

(j) **With Methyl Mercaptan.**—Iodothiophosphoryl difluoride (0.35 g, 1.55 mmol) reacted with methyl mercaptan (0.05 g, 1.05 mmol) in a sealed 75-cm^3 vessel converting the original colorless liquids to dark red. Separation of the volatiles after 7 days at 65° gave SPF_2H (0.05 g, 0.51 mmol), SPF_2SCH_3 (0.07 g, 0.48 mmol) (identified by mass spectroscopy including accurate mass measurement of the parent peak: found: *m/e* 147.9382; calcd for $^{32}S_2PF_2CH_3$: 147.9382, infrared and nmr spectra), unreacted SPF_2I (0.09 g, 0.40 mmol), and unreacted methyl mercaptan (0.02 g, 0.35 mmol). Molecular iodine remained as a residue.

(k) **With Mercuric Chloride.**—Iodothiophosphoryl difluoride (0.20 g, 0.87 mmol) and an excess of $HgCl_2$ were sealed in a 25-cm^3 reaction tube. Fractionation of the volatiles after 1 month at 65° quantitatively yielded chlorothiophosphoryl difluoride (0.12 g, 0.87 mmol).

(l) **With Silver Chloride.**—Iodothiophosphoryl difluoride was heated with an excess of AgCl for 12 days at 65°. Fractionation of the volatile materials yielded only a trace of chlorothiophosphoryl difluoride; most of the original SPF_2I was recovered unchanged. The surface of the AgCl turned bright yellow during the reaction.

(m) **With Mercury and Other Reactive Metals.**—Iodothiophosphoryl difluoride (0.36 g, 1.56 mmol) was sealed in a 75-cm^3 reaction tube with excess mercury. Immediately on warming to room temperature, a reaction occurred producing a greenish solid. After 4 days no volatile products could be recovered. HCl (0.06 g, 1.56 mmol) was condensed onto the mixture of green residue and excess mercury, and the reaction tube was resealed. After 10 days, the volatile products were fractionated to give $SPF_2(SH)$[6] (0.02 g, 0.18 mmol) and HCl (0.04 g, 1.09 mmol). The residue was again resealed in the reaction tube with excess HCl. After 2 weeks at 150° all HCl was recovered. The residue was not identified. Copper, antimony, and magnesium also consumed the iodo compound, yielding only variable amounts of PF_3, OPF_3, and SPF_3 as volatile products plus intractable residues.

Reaction of SPF_2H and HCl.—Hydrothiophosphoryl difluoride (0.26 g, 2.56 mmol) and HCl (0.10 g, 2.78 mmol) were sealed in a 75-cm^3 reaction tube and allowed to react at 110° for 1 month. The volatiles were then fractionated to give SPF_2H (0.11 g, 1.04 mmol) and an inseparable mixture (0.19 g) of HCl, PF_3, PF_2Cl, H_2S, and a trace of SiF_4, all identified spectroscopically.[7,10] A yellow residue remained that was not identified.

Infrared Spectra.—Bands were observed in the following positions (the abbreviations have the usual meanings): SPF_2I: 1821 (vw), 1787 (vw), 1635 (vw), 1427 (vw), 1422 (wv), 1081 (vw), 1021 (w, PQR), 929 (w, sh), 923 (vs, PF_2 sym str), 898.5 (s, PQQ'R, PF_2 antisym str), 828 (vw), 796 (vw), 713 (vs, PR, P=S str), 606 (vw), 476 (w, sh), 453 (s, PQR), 412.5 (w, PQR), 375.5 (m, PQR, PF_2 def), and 287 (vw), cm^{-1}. SPF_2OCH_3: 3032 (vw), 2974 (w), 2930 (vw), 2871 (w), 1948 (vw), 1738 (vw), 1461 (w), 1265 (vw), 1190 (w, br, PQR), 1084 (vs, br, P–O–C str), 942 (vs, PQR, PF_2 sym str), 915 (vw, sh), 875 (s, PR, PF_2 asym str), 654 (w, PQR, P=S str), 458 (w, PQR), and 394 (w, PQR, PF_2 def) cm^{-1}. SPF_2SCH_3: 3031 (vw), 2948 (w), 2860 (vw), 1442 (w, PQR), 1329 (w, PQR), 1038 (vw), 975 (w, PQR), 919 (vs, PQR, PF_2 sym str), 896 (vw, sh), 887 (s, PF_2 antisym str), 874 (vw, sh), 733 (vs, PQR, P=S str), 524 (m, PQR), 402 (w), 395 (vw, sh), 372 (w, PQR), 344 (w), 315 (vw), and 305 (vw) cm^{-1}.

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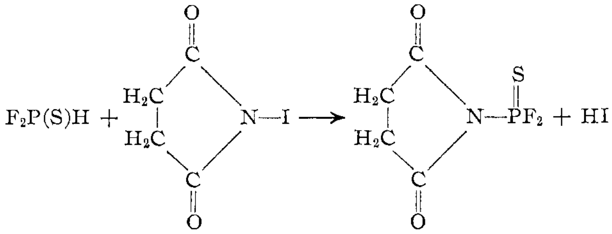
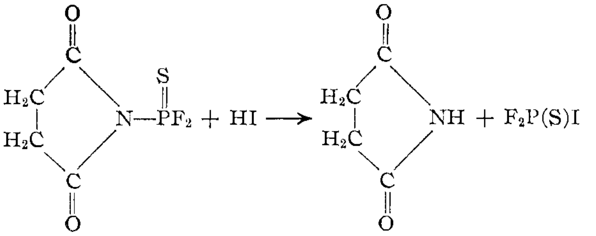
(12) Methylthiophosphoryl difluoride was also obtained from the reaction of SPF_2Cl with dimethylammonium iodide. Complete characterization of the methylthiophosphoryl fluorides will be reported in the near future.

Results and Discussion

A. Preparation of Iodothiophosphoryl Difluoride and Its Reduction to the Hydride.—Iodothiophosphoryl difluoride was obtained in good yield from the reaction of hydrothiophosphoryl difluoride with N-iodosuccinimide (NIS). The reaction is analogous to the conversion of dialkyl phosphonates $(RO)_2P(O)H$, to the appropriate dialkyl phosphorohaloidates by the action of N-chloro- or N-bromosuccinimide,[13] which appear to act as sources of "positive halogen." Recent studies suggest[14] that the reactions involve the formation of the N-phosphorylated intermediate so it seems reasonable to suggest that the present reaction proceeds through initial reaction of N-iodosuccinimide with the P–H link to form a neutral N-phosphorylated derivative (or perhaps an analogous phosphonium salt containing a P–N link), *e.g.*


(1)

followed by cleavage of the P–N link with hydrogen iodide to form the iodophosphorus compound and probably (although it was not specifically identified) succinimide


(2)

The acidic nature of succinimide[15] precludes the formation of a salt with hydrogen iodide or the attack on the P–F bonds analogous to the typical behavior of secondary amines.[16] Both of these secondary reactions would prevent the isolation of good yields of $F_2P(S)I$.

Iodothiophosphoryl difluoride was also obtained from the reaction of hydrothiophosphoryl difluoride with sulfur and iodine or with sulfur and hydrogen iodide. Neither of these alternative methods was as effective as the NIS method. It seems reasonable to propose that these latter reactions involve attack of iodine on SPF_2H to form hydrogen iodide and the iodo compound

$$SPF_2H + I_2 \rightleftharpoons SPF_2I + HI \qquad (3)$$

The equation is probably best written as an equilibrium, which under ordinary circumstances favors the formation of SPF_2H, since the hydride is normally prepared in the presence of molecular iodine.[2] We have also shown in a separate experiment that hydrogen iodide rapidly converts iodothiophosphoryl difluoride to hydrothiophosphoryl difluoride and iodine. If, however hydrogen iodide is removed from the system by reaction with sulfur

$$S + HI \longrightarrow H_2S + I_2 \qquad (4)$$

(a reaction which was found to proceed readily under the experimental conditions used), the equilibrium expressed by eq 3 is displaced in favor of SPF_2I formation. The synthesis of SPF_2I involving hydrogen iodide and sulfur probably proceeds through the initial production of iodine by reaction and thence through the equilibrium (eq 3). By appropriate choice of reagents and conditions, either iodo- or hydrothiophosphoryl compounds can be obtained.

It is interesting to note that mercury or other active metals were not required in the synthesis of hydrothiophosphoryl difluoride from hydrogen iodide and the iodo compound, whereas in previously reported reductions of phosphorus, arsenic, and carbon iodides with HI, mercury was found to be essential or at least desirable for a good yield of the hydride.[17–19] The function of the mercury in these cases appears to be the removal of iodine in the form of mercury iodide, with consequent displacement of an equilibrium similar to that of eq 3 toward the formation of the hydride.

The results of the present study strongly suggest that the synthesis of hydrothiophosphoryl difluoride according to[2]

$$(CH_3)_2NP(S)F_2 + 3HI \longrightarrow SPF_2H + I_2 + (CH_3)_2NH_2^+I^- \qquad (5)$$

proceeds first through the formation of the predicted iodofluoride

$$(CH_3)_2NP(S)F_2 + 2HI \longrightarrow SPF_2I + (CH_3)_2NH_2^+I^- \qquad (6)$$

following the general hydrogen halide cleavage of P–N bonds demonstrated elsewhere.[20] This relatively slow reaction is followed by fast reduction of the iodofluoride to the hydride by hydrogen iodide again according to eq 3.

B. Reactions of Iodothiophosphoryl Difluoride with Compounds Containing Active Hydrogen.—Of the three phosphorus–halogen bonds in iodothiophosphoryl difluoride, the phosphorus–iodine link is the most reactive and by using limited quantities of reagent the P–I bond can react preferentially leading to the formation of substituted thiophosphoryl difluoride derivatives. For example, dimethylamine gave a nearly quantitative yield of the dimethylamido compound

$$SPF_2I + 2(CH_3)_2NH \longrightarrow (CH_3)_2NP(S)F_2 + (CH_3)_2NH_2^+I^- \qquad (7)$$

Methanol and methyl mercaptan reacted with iodothiophosphoryl difluoride to form the oxygen or sulfur

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[13] G. W. Kenner, A. R. Todd, and F. J. Weymouth, *J. Chem. Soc.*, 3675 (1952).

[14] See ref 3, p 149.

[15] L. F. Fieser and M. Fieser, "Textbook of Organic Chemistry," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1956, pp 242, 243.

[16] See ref 11; R. G. Cavell, *Can. J. Chem.*, **45**, 1309, (1967); A. Mullers H. G. Horn, and O. Glemser, *Z. Naturforsch.*, **21b**, 1150 (1965), and reference, therein.

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[18] R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

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[20] R. G. Cavell, *J. Chem. Soc.*, 1992 (1964); R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, **5**, 1464 (1966); ref 9 and 16 and references therein.

methyl esters $F_2P(S)ECH_3$ (where E = O or S). Also obtained in the latter two reactions was a quantity of hydrothiophosphoryl difluoride approximately equal to the amount of ester formed. These reactions probably proceed through initial formation of the ester and hydrogen iodide

$$SPF_2I + CH_3EH \longrightarrow SPF_2 \cdot ECH_3 + HI \quad (E = O, S) \tag{8}$$

followed by immediate reduction of unreacted iodofluoride by the liberated hydrogen iodide according to eq 3. The over-all reaction

$$2SPF_2I + CH_3EH \longrightarrow SPF_2 \cdot ECH_3 + SPF_2H \tag{9}$$

which predicts the formation of equal proportions of ester and hydrofluoride as observed was not complete since not all of the iodofluoride was consumed.

In contrast to the straightforward behavior of dimethylamine, dimethylphosphine did not yield a compound containing a phosphorus–phosphorus bond as might have been anticipated. Instead dimethylphosphine consumed all of the available iodothiophosphoryl difluoride to give a 66% yield of dimethylthiophosphoryl fluoride, $(CH_3)_2P(S)F$, based on the initial quantity of SPF_2I and minor amounts of PF_3. Addition of an equimolar quantity of trimethylamine to the reaction mixture did not alter the proportion of $(CH_3)_2P(S)F$ obtained, although a solid intermediate was formed which yielded dimethylthiophosphoryl fluoride upon heating.

Dimethylarsine likewise did not yield a phosphorus–arsenic compound upon reaction with iodothiophosphoryl difluoride; instead a solid was formed and the volatile products of the reaction were SPF_2H, H_2S, PF_3, and a 5% yield of dimethyliodoarsine. The mechanism and intermediates of these reactions are not clear. Further studies are in progress which will hopefully illuminate the nature of these reactions. It is interesting however to note that these reactions did not yield diphosphorus or phosphorus–arsenic compounds in contrast to the facile synthesis of the phosphorus–nitrogen derivative by the straightforward reaction of dimethylamine with iodothiophosphoryl difluoride.

Iodothiophosphoryl difluoride reacted with hydrogen chloride and bromide to yield the hydride and the halogenothiophosphoryl difluoride. The reaction probably proceeds through attack of hydrogen halide on SPF_2I yielding hydrogen iodide and halogenothiophosphoryl difluoride

$$SPF_2I + HX \longrightarrow SPF_2X + HI \tag{10}$$

followed by fast reduction of SPF_2I by the hydrogen iodide according to eq 3, a sequence which also accounts for the formation of molecular iodine in the reaction products. Less hydrothiophosphoryl difluoride than expected from the above reaction sequence (which predicts an equimolar ratio of SPF_2H and SPF_2X) is obtained, however; the other products obtained were PF_2X and H_2S. The most reasonable explanation for these observations is that the hydrothiophosphoryl difluoride formed is decomposed in the presence of hydrogen halide under the reaction conditions employed. In a separate experiment, SPF_2H and HCl were heated in a sealed tube which resulted in the consumption of 60% of the SPF_2H and the formation of PF_2Cl, PF_3, and H_2S.

C. Properties of Iodothiophosphoryl Difluoride and Its Derivatives.—Iodothiophosphoryl difluoride and the methyl and methylthio esters $F_2P(S)ECH_3$ (E = O, S) are clear, colorless liquids of moderate volatility. The vapor pressures are given in Table I and the boiling point and volatility data derived from an equation of the type $\log P_{mm} = A - (B/T)$ are summarized in Table II. All of the compounds have typical first-order nmr spectra and the resultant coupling constant and chemical shift data are given in Table III.

TABLE II

VOLATILITY CONSTANTS FOR IODOTHIOPHOSPHORYL DIFLUORIDE AND ITS DERIVATIVES

Compound	*A*	*B*	Extrap bp, °C	Heat of vapn, cal/mol	Trouton const, eu
SPF_2I	7.580	1667	81.6	7628	21.5
SPF_2OCH_3	7.753	1590	53.2	7276	22.3
SPF_2SCH_3	8.367	1999	91.2	9148	25.1

TABLE III

NMR PARAMETERS FOR IODOTHIOPHOSPHORYL DIFLUORIDE AND ITS DERIVATIVES

Parameter	SPF_2I	SPF_2OCH_3	SPF_2SCH_3
Chemical Shifts, ppm			
$\tau(^1H)$ (*vs.* TMS)	...	5.95^c	7.41^c
$\phi(^{19}F)$ *vs.* $CFCl_3$)	$+11.2^a$	$+48.0^d$	$+26.7^d$
$\delta(^{31}P)$ (*vs.* P_4O_6)	183.5^b	...	...
Coupling Constants, cps			
J_{PF}	1271	1126	1207
J_{PH}	...	14.1	20.3
J_{HF}	...	0.7	1.3

[a] Simple doublet. [b] Triplet. [c] Doublet of triplets. [d] Doublet of quartets.

The mass spectra, given in Table IV, all show the molecular ion as the most intense ion in the spectrum, quite general behavior for thiophosphoryl halides and their derivatives.[6] Only one metastable peak was observed for each of the three compounds. A metastable peak at 44.8 amu (calcd, 44.7 amu) in the mass spectrum of iodothiophosphoryl difluoride demonstrated the expected loss of iodine from the molecular ion

$$SPF_2I^+ \longrightarrow SPF_2^+ + I \tag{11}$$

The methylthio ester decomposed according to the process

$$SPF_2 \cdot SCH_3^+ \longrightarrow SCH_3^+ + SPF_2 \tag{12}$$

as demonstrated by the metastable peak at 14.9 amu (calcd, 14.9 amu). The methoxy ester appears to rearrange with formation of CHO

$$SPF_2 \cdot OCH_3^+ \longrightarrow SPF_2H_2^+ + CHO \tag{13}$$

as indicated by the metastable peak at 80.4 amu (calcd, 80.4 amu).

Infrared spectra, listed above, show certain general

TABLE IV

MASS SPECTRA OF IODOTHIOPHOSPHORYL DIFLUORIDE AND SOME OF ITS DERIVATIVES

	Intensity[a]		
Ion	$X = I$[b]	$X = OCH_3$[c]	$X = SCH_3$[d]
$^{34}SPF_2X$	2.4	1.9	2.5
$^{33}SPF_2X$	0.5	0.9	0.9
$^{32}SPF_2X$	51.9[e]	34.1[e]	27.9[e]
$^{34}SPF_2$	1.4	...	...
$^{32}SPF_2$	24.0	6.7	3.3
$^{32}SPFX$	...	0.9	...
^{32}SPF	1.4	1.1	0.9
PF_2	8.9	15.6	11.7
PX	...	...	1.1
PF	1.4	1.1	1.3
^{32}SP	1.4	0.9	1.3
^{32}S	1.4	1.1	1.3
X	3.8	3.9[f]	7.5

[a] Intensities are expressed relative to the total ionization defined as Σ_n (intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. [b] Also observed: $^{32}SI^+$ (2.1%). [c] Also observed: $^{34}SPF_2H^+$ (0.9%), $^{32}SPF_2H_2^+$ (2.8%),[e] $^{32}SPF_2H^+$ (12.2%), $PF_2OCH_2^+$ (4.7%), OPF_2^+ (0.9%), PO^+ (5.8%). [d] Also observed: $^{32}S_2PF_2^+$ (1.5%), $^{32}SPF_3^+$ (0.7%), $^{32}SPF^+$ (1.5%), $^{34}SCH_2^+$ (1.2%), $^{32}SCH_2^+$ (23.0%), $^{32}SCH^+$ (8.8)%, $^{32}SC^+$ (0.7%). [e] Identity confirmed by exact mass measurement. [f] Possibly also contains P^+.

features. All compounds show strong P—F absorptions in the 850–950-cm^{-1} region. The P═S stretch appears to be best assigned to strong bands at 713 cm^{-1} in SPF_2I and 733 cm^{-1} in SPF_2SCH_3 and the weak band at 654 cm^{-1} in SPF_2OCH_3. The last compound does not show a strong band in the 1200–1500-cm^{-1} region; thus we can exclude the possibility of the methyl ester having the $F_2P(O)SCH_3$ isomeric structure.

D. Some Further Properties of Iodothiophosphoryl Difluoride.—The compound appears to possess appreciable thermal stability since less than 5% decomposition occurred after 4 days at 150°. Under ordinary illumination, samples appear to photolyze slightly liberating molecular iodine. The other product of the photolysis has not been identified but could possibly be the diphosphorus compound $F_2(S)P–P(S)F_2$. Attempts to synthesize this compound or its isomers by means of coupling reactions of the iodofluoride with active metals such as mercury, copper, antimony, etc., have not yet been successful in spite of the many well-established syntheses of diphosphorus compounds from reactions of the iodophosphorus compound with metals such as mercury.[21] The lack of success in the synthesis of diphosphorus compounds by either the coupling reactions or the reaction with dimethylphosphine might suggest that the diphosphorus compounds involving pentavalent phosphorus are much less stable than trivalent diphosphines, especially when the phosphorus atom carries highly electronegative substituents such as fluorine.

Replacement of iodine by chlorine can be effected with mercuric chloride[22] but silver chloride, which has often been used for this purpose,[21b] did not react appreciably with SPF_2I, possibly because of surface effects.

Hydrolysis of iodothiophosphoryl difluoride appears to involve all of the halogens and also the P═S bond. The reaction involves equimolar proportions of iodofluoride and water and yields SiF_4 (presumably from attack of the liberated HF on the glass vessel), SPF_2H (presumably arising from the formation of HI followed by reduction according to eq 3), and H_2S. The involatile residue is probably phosphorous acid $OPH(OH)_2$ or the thio analog $SPH(OH)_2$. The iodothiophosphoryl difluoride was apparently consumed initially with formation of SPF_2H which is also hydrolyzed[2] but apparently at a reduced rate. The course and stoichiometry of the reaction have not yet been completely determined.

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(21) See for example: (a) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966); (b) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953); (c) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

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Reactions of Triphenylphosphine with S_4N_3Cl

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Received June 17, 1968

It has been shown that S_4N_3Cl gives a complex series of reactions in which $[(C_6H_5)_3P{=}NP(C_6H_5)_3]Cl$ (I), $[(C_6H_5)_3PNH_2]Cl$ (II), and $[\{(C_6H_5)_3PN\}_3S]Cl_3$ (III) are produced. Compound III reacts with two molecules of triphenylphosphine giving $[\{(C_6H_5)_3PN\}_3S]Cl_3 \cdot 2P(C_6H_5)_3$ (IV), which crystallizes out of acetone with 2 moles of acetone. N-Chlorotriphenylphosphinimine is suggested as a probable intermediate in these reactions.

Introduction

We have been concerned with the chloramination of a variety of electron-donor species, more particularly amines, phosphines, and aminophosphines. We speculated that S_4N_3Cl, even though it has been shown to be principally ionic in character, might behave toward electron-donor molecules in a manner analogous to that of chloramine. The research reported below has