Synthesis and Characterization of Bis(trifluoromethyl)thiophosphinic Acid and Its Anhydride

A. A. Pinkerton and R. G. Cavell*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. Received May 3, 1971

Abstract: Bis(trifluoromethyl)thiophosphinic acid, $(CF_3)_2P(S)OH$, has been prepared by the reaction of concentrated sulfuric acid with salts of the acid. The new moderately strong ($K_a \sim 3.2 \times 10^{-3}$) monothio acid is stable in aqueous solution but yields 1 mol of CF_3H per mole of acid upon alkaline hydrolysis. The acid has been characterized by chemical and spectroscopic methods including gas-phase infrared spectra which suggest that the acid has the $(CF_3)_2P(S)OH$ structure. Dehydration of the acid with P_4O_{10} proceeds smoothly to give good yields of the anhydride, $[(CF_3)_2P(S)]_2O$, which is extremely inert toward electrophilic reagents such as hydrogen halides and hydrogen sulfide. The anhydride reacts with nucleophilic reagents such as dimethylamine to yield the aminophosphine $(CF_3)_2P(S)N(CH_3)_2$ and with halide ions in solution to yield the thiophosphoryl halides, $(CF_3)_2P(S)X$ (X = F, Cl, Br). The residual product in both systems was the $(CF_3)_2PSO^-$ ion as a salt or in solution. Neutral hydrolysis of the anhydride gave a solution of the parent acid, and alkaline hydrolysis liberated 2 mol of CF_3H per mole of anhydride to leave the $CF_3PO_2S^{2-}$ ion in solution. The infrared and nmr spectral properties of the acid and its anhydride are discussed.

$\mathbf{B}$is(trifluoromethyl)dithiophosphinic acid, $(CF_3)_2PS_2H$, has been recently prepared,[1,2] and bis(trifluoromethyl)phosphinic acid, $(CF_3)_2PO_2H$, has been known for many years.[3] Salts of the unknown monothio acid, $(CF_3)_2P(S)OH$, were obtained while attempting to prepare the ester $(CF_3)_2P(S)OCH_3$ from $(CF_3)_2P(S)Cl$, methanol, and trimethylamine.[4] We wish to report herein the synthesis of $(CF_3)_2P(S)OH$ from this salt and by other methods and also the preparation and characterization of the anhydride of the acid, $[(CF_3)_2P(S)]_2O$.

Results

Synthesis and Structure of Bis(trifluoromethyl)thiophosphinic Acid. The reaction of $(CF_3)_2P(S)Cl$ with methanol and trimethylamine yields a white, involatile solid which we formulate as a mixture of tri- and tetramethylammonium salts of Cl^- and $(CF_3)_2POS^-$ ions[4] (eq 1). Treatment of this mixture with concentrated

$$(CF_3)_2P(S)Cl + CH_3OH + 2(CH_3)_3N \longrightarrow$$
$$(CF_3)_2PSO^- + Cl^- + (CH_3)_4N^+ + (CH_3)_3NH^+ \quad (1)$$
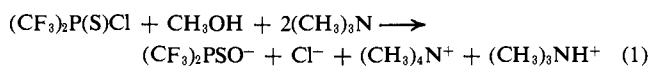
sulfuric acid under mild conditions (*i.e.*, allowing the mixture to warm slowly from $-196°$ to room temperature) results in a vigorous reaction which produces HCl and the new oxythio acid, $(CF_3)_2P(S)OH$, as a mixture of volatile products which may be easily separated by vacuum fractionation.

The acid has also been obtained by the careful oxidation of $(CF_3)_2PSH$ with a small excess of dry air, but a pure product was never obtained by this method. Attempts to prepare the monothio acid by sulfur oxidation of $(CF_3)_2POH$ following the method used[1] to prepare $(CF_3)_2PS_2H$ were unsuccessful owing to the combination of high temperatures required to induce reaction and the low thermal stability of the monothio acid (*vide infra*).

Salts of the monothio acid give stable aqueous solutions containing the same anions as solutions of the acid itself. The nmr spectra of salt solutions and aqueous acid solutions are identical, showing a simple doublet with a coupling constant[5] ($^2J_{PF}$) of 97.4 Hz and a chemical shift (ϕ) of 73.1 ppm (*vs.* CCl_3F). Although neutral hydrolysis of $(CF_3)_2P(S)Cl$ yields the monothio anion, neutralization with silver carbonate led to a desulfurization[6] and the formation of only $(CF_3)_2PO_2^-$ in the solution; hence, the monothio acid cannot be obtained by means of reactions analogous to those used to prepare $(CF_3)_2PO_2H$.[3] Alkaline hydrolysis of the monothio acid and its salts liberates 1 mol of fluoroform per mole of compound to leave the $CF_3PSO_2^{2-}$ ion[6] in solution, thus demonstrating the presence of a bis(trifluoromethyl)thiophosphoryl group.

The ^{19}F nmr spectrum of the acid shows a simple doublet ($^2J_{FP} = 120$ Hz, ϕ_F +72.2 ppm *vs.* CCl_3F) and the ^{31}P nmr spectrum a septet ($^2J_{FP} = 123$ Hz, δ_P +58.4 ppm *vs.* P_4O_6). These parameters are in agreement with those expected for a pentavalent bis(trifluoromethyl)thiophosphoryl group.[1] The single-proton nmr signal is relatively sharp at room temperatures, but the chemical shift varied between samples possibly because of concentration differences or the presence of impurities in this difficultly handled compound. Cooling of any one of the samples results in the broadening of the peak and a shift of the resonance to lower field; however, the signal remained unresolved even at $-100°$, indicating that the proton suffers rapid exchange between environments on the nmr time scale. In contrast, the proton spectrum of the dithio acid, $(CF_3)_2PS_2H$, which showed a single peak at ordinary temperatures, gave a doublet[1,7] at $-114°$ which was of the correct order of magnitude for a P–H coupling ($^2J_{PH}$) through sulfur, indicating that the exchange rate in this case could be sufficiently reduced by cooling to provide a lifetime of the proton in one environment which is sufficient for resolution of the coupling to

(1) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, 90, 2015 (1968).

(2) K. Gosling and A. B. Burg, *ibid.*, 90, 2011 (1968).

(3) H. J. Eméleus, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 563 (1965).

(4) R. G. Cavell and W. Sim, unpublished observations.

(5) The notation for coupling constants is due to J. I. Musher and E. J. Corey, *Tetrahedron*, 18, 791 (1962).

(6) A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 10, 2720 (1971).

(7) R. G. Cavell, unpublished observations.

phosphorus. It seems reasonable to expect more facile exchange in systems involving oxygen.
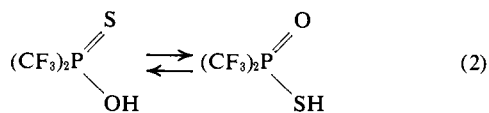
The KBr windows of infrared cells were rapidly etched by the acid, but the infrared spectrum could be recorded with windows protected by a film of paraffin wax. The spectrum shows strong bands in the CF_3 region with values typical of those for a $(CF_3)_2P$ compound. The band at 3615 cm^{-1} (2665 cm^{-1} in the deuterio compound) can be assigned to an OH stretch and the band at 1000 cm^{-1} to a POH bend. Using the ratio between the OH and OD stretching vibrations (1.35), the POD bend is predicted to be at 740 cm^{-1} (i.e., very close to the P=S stretching band in energy). The appearance of bands in the spectrum of the deuterio compound at 810 and 695 cm^{-1} and the absence of the expected band at 773 cm^{-1} ($\nu_{P=S}$) are attributed to Fermi resonance between POD bending and P=S stretching vibrations, because both vibrations transform as A' under C_s symmetry and are therefore subject to Fermi interaction if they are of similar energy.[8] The complete spectrum with assignments is given in Table I.

Table I. Infrared Spectra[a,b]

$(CF_3)_2$-P(S)OH	$(CF_3)_2$-P(S)OD	$[(CF_3)_2$-P(S)]_2O	Assignment
3615 (s)			ν_{OH}
	2665 (s)		ν_{OD}
1214 (vs)	1214 (vs)	1206 (vs) ⎫	
1188 (vs)	1188 (vs)	1182 (vs) ⎬	ν_{CF_3}
1145 (m)	1145 (m)	1153 (m, sh) ⎭	
1000 (s)			δ_{POH}
		980 (m) ⎫	
		929 (vs) ⎬	ν_{asym} POP
		903 (m) ⎭	
925 (s)	925 (s)	841 (s)	ν_{P-O} See text
	810 (s)[c]		
773 (m)		803 (m)	$\nu_{P=S}$
713 (m)	713 (m)	754 (w)	$\delta_{sym\ CF_3}$
		732 (m)	ν_{sym} POP
	695 (m, sh)[c]		See text
		636 (w)	
549 (m)	549 (m)	551 (m)	$\delta_{asym\ CF_3}$
497 (m)	497 (m)	495 (m)	ν_{PC}
		442 (w, sh)	
414 (w)	414 (w)	413 (m)	P=S bend

[a] All frequencies in cm^{-1}. [b] Abbreviations: ν, stretching; δ, deformation; s, strong; m, medium; w, weak; v, very, sh, shoulder. [c] P=S stretch and POD bend bands shifted from expected positions by Fermi resonance.

The infrared data are consistent with the $(CF_3)_2P$-(S)OH structure in the gas phase rather than the isomeric $(CF_3)_2P(O)SH$ structure. However, the marked variation of proton chemical shift with concentration and temperature suggests that an equilibrium of the type shown in eq 2 may be important in nonaqueous solvents.

$$(CF_3)_2P \overset{S}{\underset{OH}{\diagup\hspace{-0.3em}\diagdown}} \rightleftharpoons (CF_3)_2P \overset{O}{\underset{SH}{\diagup\hspace{-0.3em}\diagdown}} \qquad (2)$$

The mass spectrum of the acid has a strong parent ion and shows the expected fragmentation and rearrangement patterns in the mass spectrometer.[9] The complete spectrum is shown in Table II.

(8) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Wiley-Interscience, New York, N. Y., 1967, p 330.

(9) (a) R. G. Cavell and R. C. Dobbie, Inorg. Chem., 7, 101 (1968); (b) ibid., 7, 690 (1968).

Table II. Mass Spectra[a,b]

(a) $(CF_3)_2P(S)OH$			(b) $[(CF_3)_2P(S)]_2O$		
m/e	Rel int	Assignment	m/e	Rel int	Assignment
218[c]	20.9	C_2F_6PSOH	418[d]	11.1	$C_4F_{12}P_2S_2O$
198	0.5	C_2F_9PSO	349	4.1	$C_3F_9P_2S_2O$
186	1.8	C_2F_6POH	317	1.5	$C_3F_9P_2SO$
150	0.4	C_2F_5P	267	3.1	$C_2F_7P_2SO$
149	3.2	CF_3PSOH	230	0.5	$C_2F_5PS_2O$
128	2.7		217	4.5	C_2F_6PSO
127	1.2		201	0.6	C_2F_6PS
119	1.1	CF_4P, C_2F_5	185	1.1	C_2F_6PO
117	1.0	CF_3POH	167	1.9	CF_4POS
101	0.6	SPF_2	151	1.1	CF_4PS
100	0.6	CF_3P, C_2F_4	135	8.4	CF_4PO
99	4.2	$FPSOH$	129	0.9	CF_2PSO
85	0.5	F_2PO	119	4.5	C_2F_5, CF_4P
83	2.2	$FPSH$	113	0.7	CF_2PS
82	1.4	FPS	101	0.7	SPF_2
80	0.8	$PSOH$	100	0.8	CF_3P, C_2F_4
78	0.5	$CFPO$	81	2.0	CF_2P, C_2F_3
76	5.8	$CPSH$	80	0.5	S_2O
69	13.3	CF_3, PF_2	69	14.8	CF_3, PF_2
67	13.3	$FPOH$	64	4.2	S_2
66	0.4	FPO	63	19.1	PS
64	0.5	PSH	50	1.1	PF, CF_2
63	5.7	PS	47	4.2	PO
51	5.0	CF_2H	45	0.6	
50	1.7	CF_2, PF	43	0.5	
48	0.9	SO	32	4.0	S
47	3.8	PO	31	3.3	P, CF
44	1.4	CPH, C_2FH			
38	0.8	F_2			
36	1.0	HOF			
32	0.8	S			
31	1.8	P, CF			

[a] Intensities are expressed relative to the total ionization defined as Σ(intensity) for all ions with $m/e > 30$ whose intensity is greater than 2% of the base peak. [b] All species are positive ions and masses are calculated for the ^{32}S isotope unless otherwise indicated. [c] Identified by mass measurement: found, m/e 217.9395; required for C_2F_6PSOH, m/e 217.9390. [d] Identified by mass measurement: found, m/e 417.8672; required for $C_4F_{12}P_2S_2O$, m/e 417.8675.

Properties of Bis(trifluoromethyl)thiophosphinic Acid.

The acid was found to be thermally unstable; heating at 150° for 4 days led to dehydration, condensation, and rearrangements giving the anhydride and the dithio acid as major volatile products. The failure of others[10] to prepare the monothiodifluoro acid, $F_2P(S)OH$, is perhaps not surprising in view of the low thermal stability of the CF_3 analog.

Typical acid behavior was demonstrated by the formation of 1:1 salts in the reactions of the acid with anhydrous dimethylamine or with aqueous solutions of sodium bicarbonate. These acid salts do not react with anhydrous HCl, suggesting that the acid is a reasonably strong one. Potentiometric titration of an aqueous solution of the acid prepared from the anhydride gave $K_a \sim 3.2 \times 10^{-3}$.

Attempts to form sulfur-bridged dimers of the acid anion by reaction of the salts with halogens (cf. the synthesis of $F_2P(S)S_2(S)PF_2$[11] and $(CF_3)_2P(S)S_2(S)P(CF_3)_2$[12]) led to the formation of thiophosphoryl halides and no other volatile products were obtained. The $(CF_3)_2PO_2^-$ ion was found in the residual products of

(10) C. B. Colburn, W. E. Hill, and D. W. A. Sharp, J. Chem. Soc. A, 2221 (1970).

(11) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, Inorg. Chem., 9, 831 (1970).

(12) A. A. Pinkerton and R. G. Cavell, J. Amer. Chem. Soc., 93, 2384 (1971).

both chlorine and bromine oxidations, indication that the reactions are complex. Steps similar to eq 6 (vide infra) involving halide attack on the anhydride may be involved.

The acid reacted smoothly at 70° to cleave the P–N bond in dimethylaminobis(trifluoromethyl)phosphine sulfide and form the anhydride according to

$$(CF_3)_2P(S)-N(CH_3)_2 + 2(CF_3)_2P(S)OH \longrightarrow$$
$$(CF_3)_2P(S)-O-P(S)(CF_3)_2 + (CH_3)_2NH_2^+(CF_3)_2PSO^- \quad (3)$$
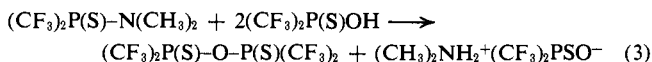
A reaction of the acid with dimethylaminobis(trifluoromethyl)phosphine did not give the expected mixed-valence compound $(CF_3)_2P(S)-O-P(CF_3)_2$, in contrast to the ready preparation[12] of $(CF_3)_2P(S)-S-P(CF_3)_2$ by a similar reaction; instead the anhydride, $[(CF_3)_2P(S)]_2O$, and the known[13,14] sulfur-bridged diphosphine, $[(CF_3)_2P]_2S$, were obtained as the only volatile products, plus a mixture of the amine salts of the $(CF_3)_2PSO^-$ and $(CF_3)_2PO_2^-$ ions.[3,6] This appears to be a very complex system which involves oxygen–sulfur exchange and mutual oxidation–reduction reactions.

Although the dithio acid is rapidly reduced by hydrogen iodide,[12] the monothio acid was found to be resistant to reduction even in the presence of mercury. Metallic mercury alone did not react with the monothio acid. The acid was also not oxidized by air at room temperature.

Synthesis and Structure of Bis(trifluoromethyl)thiophosphinic Anhydride. Dehydration of $(CF_3)_2P(S)OH$ with P_4O_{10} at 70° gave good yields of the anhydride, $(CF_3)_2P(S)-O-P(S)(CF_3)_2$. Low yields of the same compound were also obtained from the Al_2Cl_6-catalyzed addition of sulfur to $(CF_3)_2P-O-P(CF_3)_2$ at 100°. Elevated temperatures led to inseparable mixtures of products. Also, $(CF_3)_2P(S)I$ reacted rapidly with a stoichiometric amount of silver carbonate to give good yields of the anhydride, a reaction which is similar to the preparation[15] of $(CF_3)_2P-O-P(CF_3)_2$; however, the product was contaminated with a small amount of $(CF_3)_2P-S-P(CF_3)_2$ which could not readily be removed. Reaction of $(CF_3)_2PS_2H$ with $(CF_3)_2P-(O)-N(CH_3)_2$ proceeded smoothly at 70°, but instead of giving the unsymmetrical compound $(CF_3)_2P(O)-S-P(S)(CF_3)_2$ which might have been expected, the reaction gave only the anhydride, $[(CF_3)_2P(S)]_2O$, contaminated with traces of starting materials which could not be removed by vacuum distillation. Similar results were obtained using $(CF_3)_2P(S)OH$ and $(CF_3)_2-P(S)-N(CH_3)_2$, indicating that the oxygen bridge is more readily formed. Previous studies on the fluorophosphorus system[16] gave similar results; the oxygen bridge was readily formed and the unsymmetrical isomers could only be made with difficulty.

The compound is a true anhydride and may be dissolved in water to give acidic solutions which can be titrated with standard alkali to give a molecular weight of 412 (418 required for $(CF_3)_4P_2S_2O$). The anion obtained by neutral hydrolysis was shown to be $(CF_3)_2P-SO^-$ by nmr spectroscopy.[6] Alkaline hydrolysis yields 2 mol of fluoroform per mole of compound, and the $CF_3PSO_2^{2-}$ ion[6] may be identified as the only fluorine-containing species present in the hydrolysate;

(13) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964).
(14) A. B. Burg and K. Gosling, *J. Amer. Chem. Soc.*, 87, 2113 (1965).
(15) J. E. Griffiths and A. B. Burg, *ibid.*, 84, 3442 (1962).
(16) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 9, 379 (1970).

this is consistent with the presence of two bis(trifluoromethyl)thiophosphoryl groups in the molecule.[6]

The ^{19}F nmr spectrum is second order, showing a sharp doublet due to $|^2J_{FP} + {}^4J_{FP}|$ with a separation of 129 Hz, with less intense lines on either side of the two major lines. The pattern is characteristic of the ^{19}F nmr spectra of $X_6AA'X_6'$ systems such as[7,12] $(CF_3)_2-P-P(CF_3)_2$, $(CF_3)_2P-O-P(CF_3)_2$, $(CF_3)_2P-S-P(CF_3)_2$, and $(CF_3)_2P(S)-S-S-P(S)(CF_3)_2$ and supports the symmetric formula. The ^{31}P nmr spectrum shows the same major spacing, 129 Hz, with the major septet having further structure due to the second-order effects. Complete analysis of the spectrum is not possible at this time, but both the ^{19}F and ^{31}P chemical shift parameters (ϕ_F +70.7 ppm vs. CCl_3F and δ_P +72.8 ppm vs. P_4O_6) are compatible with the existence of equivalent pentavalent phosphorus atoms.

The infrared spectrum shows the expected strong bands in the CF_3 region, with values expected for a $(CF_3)_2P$ compound. Three bands centered at 930 cm^{-1} may be assigned to the P—O—P structure[15] and the band at 802 cm^{-1} to a P=S stretching vibration. The complete spectrum is shown in Table I.

The mass spectrum shows the expected fragmentation and rearrangement patterns[9] and a strong parent ion. The complete spectrum is shown in Table II.

Properties of Bis(trifluoromethyl)thiophosphinic Anhydride. The anhydride was thermally stable to 160° and was not oxidized by dry air at room temperature. Heating with mercury to 100° for 7 days led to no compound formation nor to any desulfurization.

In general, the compound was inert toward electrophilic reagents in the gas phase except at elevated temperatures. The products obtained from the high-temperature reactions with HX may be explained if initial reaction occurs according to eq 4, followed by thermal decomposition of the monothio acid to give the observed products. In the case of HI, the reaction is further complicated by the reactions[12] of HI with

$$(CF_3)_2P(S)-O-P(S)(CF_3)_2 + HX \longrightarrow$$
$$(CF_3)_2P(S)OH + CF_3)_2P(S)X \quad (4)$$
$$(X = Cl, Br, I, SH)$$
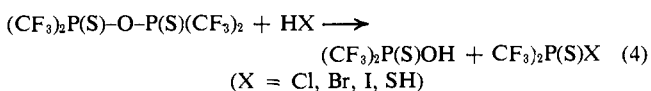
$(CF_3)_2P(S)I$ and with $(CF_3)_2PS_2H$ (formed by the thermal decomposition of $(CF_3)_2P(S)OH$) to give $(CF_3)_2-PSH$ in both cases.

Nucleophilic attack by halide ions in acetonitrile solution is rapid, as in the case of the fluoro analog,[10] giving good yields of the expected thiophosphoryl halides and the thiophosphinate anion according to

$$(CF_3)_2P(S)-O-P(S)(CF_3)_2 + X^- \longrightarrow$$
$$(CF_3)_2PSO^- + (CF_3)_2P(S)X \quad (5)$$
$$(X = F, Cl, Br)$$
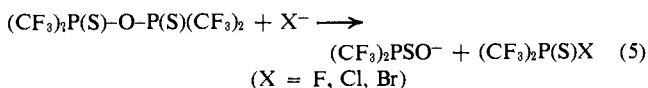
No reaction occurred when the same system was used in an attempt to prepare $[(CF_3)_2P(S)]_2S$, using, as X^-, the $(CF_3)_2PS_2^-$ ion.

Rapid nucleophilic attack by dimethylamine takes place at low temperatures according to

$$(CF_3)_2P(S)-O-P(S)(CF_3)_2 + 2(CH_3)_2NH \longrightarrow$$
$$(CF_3)_2P(S)-N(CH_3)_2 + (CH_3)_2NH_2^+(CF_3)_2PSO^- \quad (6)$$
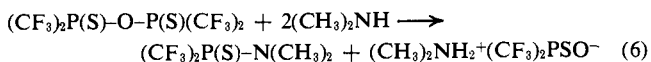
Discussion

The symmetrical structure of the anhydride was expected from work on analogous fluoro systems[10,16]

and is clearly demonstrated by the pattern shown by the ^{19}F nmr spectrum[7,12] and from the products obtained from the rapid attack of a variety of nucleophiles. Its marked resistance to electrophilic attack is notable and may perhaps be explained in terms of the low availability of the lone pairs on sulfur due to the action of the highly electronegative bridging atom combined with that of the CF₃ substituents. This same proposal may explain the resistance of the monothio acid toward reduction by hydrogen iodide in contrast to the extremely rapid reduction of the dithio acid, $(CF_3)_2PS_2H$, by hydrogen iodide[12] under similar conditions. If one assumes that the reaction proceeds by initial attack on the sulfur by the proton in HI, then the increased electronegativity of the substituents accompanying substitution of oxygen for a sulfur in $(CF_3)_2P(S)OH$ probably leads to a marked reduction in the availability of lone pairs on the sulfur (and hence its nucleophilicity) and a marked reduction in reactivity. Further support for this interpretation comes from the knowledge that difluorodithiophosphinic acid, F_2PS_2H, with its highly electronegative fluorine substituents, is only slowly reduced[17] by HI even on warming to 65°.

Experimental Part

Standard vacuum techniques were used throughout. The system was constructed from Pyrex glass with stopcocks lubricated with Apiezon grease. Routine infrared spectra for purposes of identification were recorded on a Perkin-Elmer 337 spectrometer. Spectra of new compounds were recorded on Perkin-Elmer 421 dual-interchange or Beckman IR11 instruments. Fluorine nmr spectra were recorded on Varian A-56/60A and HA-100 spectrometers operating at 56.4 and 94.1 MHz, respectively, using approximately 15% solutions in CCl₃F for volatile compounds and similar concentrations in H₂O or CD₃CN for involatile salts. Proton spectra were recorded on the same instruments operating at 60 and 100 MHz, respectively, using the same solutions. Phosphorus spectra were recorded on neat samples at 40.5 MHz with the Varian HA-100 spectrometer, a signal-averaging computer being used in the case of $(CF_3)_2P_2S_2O$ to obtain a good spectrum. Fluorine chemical shifts were measured to relative to CCl₃F as solvent or in a capillary, proton shifts relative to external TMS, and phosphorus shifts relative to an external P₄O₆ capillary.[18] Mass spectra were recorded on an AEI MS9 instrument operating at an ionizing voltage of 70 eV with samples introduced as gases with a heated inlet system. Starting materials were prepared by indicated literature methods. Reagent grade chemicals were used as supplied. Reagent gases were vacuum distilled before use. Methanol was redistilled from sodium methoxide. All reactions were carried out in sealed Pyrex glass tubes except where otherwise noted.

Preparation of Bis(trifluoromethyl)thiophosphinic Acid. (1) From $(CF_3)_2P(S)Cl$. Bis(trifluoromethyl)thiophosphoryl chloride[1,2] (0.7317 g, 3.10 mmol), methanol (~3.8 mmol) freshly distilled from sodium methoxide, and trimethylamine (~6.3 mmol) reacted below room temperature to produce a white solid. The volatile products (only excess methanol and trimethylamine) were removed to leave a solid which was then allowed to react with concentrated sulfuric acid while warming slowly from −196° to room temperature. Vacuum fractionation of the volatile products gave $(CF_3)_2P(S)OH$ (0.3495 g, 1.60 mmol, 51% yield) which was trapped at −63°.

(2) From $(CF_3)_2PSH$ and Dry Air. Bis(trifluoromethyl)mercaptophosphine[13] (0.049 g, 0.242 mmol) was allowed to react with air (dried by passage through a series of −196° traps) containing 0.13 mmol of oxygen for 24 hr at room temperature. Vacuum fractionation gave $(CF_3)_2P(S)OH$ (0.0204 g, 0.094 mmol) which contained a trace of $(CF_3)_2PS_2H$, trapped at −63°.

Preparation of the Deuterium-Enriched Acid. A sample of $(CF_3)_2P(S)OH$ was allowed to react with several fresh samples of DCl until an enrichment of ~60% was achieved.

Preparation of Bis(trifluoromethyl)thiophosphinic Anhydride. (1) From $(CF_3)_2P(S)OH$ and P_4O_{10}. Bis(trifluoromethyl)thiophosphinic acid (0.3495 g, 1.60 mmol) and excess P_4O_{10} (1 g) were allowed to react for 2 days at 70°. Vacuum fractionation gave $(CF_3)_4P_2S_2O$ (0.268 g, 0.642 mmol) in 80% yield, which was collected at −84°, as the only volatile product.

(2) From $(CF_3)_2P-O-P(CF_3)_2$. Tetrakis(trifluoromethyl)diphosphoxane[15] (0.0373 g, 0.105 mmol) was combined with resublimed sulfur (0.5 g) in the presence of a trace of resublimed Al₂Cl₆ and heated to 100° for 3 days. Vacuum fractionation of the volatile products gave $(CF_3)_4P_2S_2O$ (0.0153 g, 0.037 mmol) in 35% yield. A more volatile fraction contained $(CF_3)_2PCl$ and $(CF_3)_2P(S)Cl$. Reaction in the absence of Al₂Cl₆ did not proceed below 180°, and at this temperature led to an inseparable mixture of products.

(3) From $(CF_3)_2P(S)I$ and Ag_2CO_3. Iodobis(trifluoromethyl)phosphine sulfide[1] (0.0110 g, 0.335 mmol) and silver carbonate (0.0484 g, 0.175 mmol) were allowed to react for 15 hr at room temperature. The reaction actually began well below room temperature. Vacuum fractionation gave $(CF_3)_4P_2S_2O$ (0.0624 g) which contained about 7% of $(CF_3)_2P-S-P(CF_3)_2$ impurity.

(4) From $(CF_3)_2PS_2H$ and $(CF_3)_2P(O)-N(CH_3)_2$. Bis(trifluoromethyl)dithiophosphinic acid[1,2] (0.0721 g, 0.308 mmol) and dimethylaminobis(trifluoromethyl)phosphine oxide[19] (0.0378 g, 0.165 mmol) did not react during 4 days at room temperature. A further 2 days at 70° gave $(CF_3)_4P_2S_2O$ (0.0478 g, 0.114 mmol) contaminated with about 4% (molar basis) of $(CF_3)_2PS_2H$. An involatile oil remained in the reaction tube.

(5) From $(CF_3)_2P(S)OH$ and $(CF_3)_2P(S)-N(CH_3)_2$. Bis(trifluoromethyl)thiophosphinic acid (0.0864 g, 0.396 mmol) and dimethylaminobis(trifluoromethyl)phosphine sulfide[1,2] (0.0406 g, 0.166 mmol) were combined and allowed to warm slowly from −78° to room temperature, and the mixture was then allowed to stand for 4 days at room temperature. Vacuum fractionation gave $(CF_3)_4P_2S_2O$ (0.0430 g, 0.103 mmol) contaminated with 8.0% of $(CF_3)_2P(S)-N(CH_3)_2$. The solid which remained in the reaction tube was identified as $(CH_3)_2NH_2^+(CF_3)_2PSO^-$.

Vapor Pressure of Bis(trifluoromethyl)thiophosphinic Acid. The variation of the vapor pressure with temperature was examined in a Pyrex spiral-gauge microtensimeter. The data (temperature, °C; pressure, mm), 4.0 (7.5), 10.0 (10.2), 14.5 (12.7), 20.3 (16.4), 24.8 (20.8), 31.6 (30.2), 35.3 (36.6), 40.3 (47.1), 44.5 (57.4), and 50.1 (74.8), obey the linear equation $\log P = -1954/T + 7.90$, which gives a calculated ΔH_{vap} of 8940 cal mol⁻¹, an extrapolated boiling point of 116°, and a Trouton constant of 23.0 eu.

Vapor Pressure of Bis(trifluoromethyl)thiophosphinic Anhydride, $[(CF_3)_2P(S)]_2O$. The vapor pressure data for the anhydride (obtained with a grease-free mercury-in-glass microtensimeter) (temperature °C; pressure, mm), 8.1 (8.5), 10.7 (9.0), 13.5 (10.2), 15.5 (11.2), 17.5 (12.7), 20.0 (14.1), 22.3 (15.8), 24.2 (17.9), 25.6 (19.5), 27.5 (21.3), 30.1 (23.8), 33.4 (28.1), 36.3 (31.8), 39.4 (37.7), 42.3 (42.7), 45.1 (49.0), 48.4 (56.6), 52.4 (67.6), 56.9 (82.6), and 59.9 (91.9), obey the linear equation $\log P = -1941/T + 7.78$, giving a calculated heat of vaporization of 8880 cal mol⁻¹, an extrapolated boiling point of 122.6°, and a Trouton constant of 22.4 eu.

Reactions of Bis(trifluoromethyl)thiophosphinic Acid. (1) With Heat. A sample of the acid (0.1196 g, 0.550 mmol) heated at 150° for 4 days decomposed and rearranged to give 0.0914 g of volatile products which were found to be unreacted $(CF_3)_2P(S)OH$, $(CF_3)_2PS_2H$, and $(CF_3)_4P_2S_2O$ in the molar ratio 3.0:4.9:2.1 by nmr. No involatile material was observed.

(2) With Water. No fluorocarbon-containing volatile products were formed when $(CF_3)_2P(S)OH$ (0.0317 g, 0.145 mmol) reacted with ~0.5 ml of degassed distilled water for 24 hr. The resultant aqueous solution was quite stable and had the same nmr parameters as aqueous solutions of salts of the acid. The acid was quite volatile in water vapor, and the aqueous solution could be distilled to leave no residue.

(3) With Aqueous Alkali. Room-temperature reaction of $(CF_3)_2P(S)OH$ (0.0632 g, 0.290 mmol) with ~5.0 ml of 10% NaOH solution for 24 hr gave CF₃H (0.0204 g, 0.291 mmol) as the only volatile product. The aqueous alkaline solution contained $CF_3PSO_2^{2-}$ ions[6] (analyzed by nmr). A sodium nitroprusside test[20] indicated the absence of S²⁻ ions.

(4) Preparation of Salts. (a) $Na^+(CF_3)_2PSO^-$. Sodium bicarbonate (0.0206 g, 0.245 mmol) was dissolved in ~1.0 ml

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(20) W. J. Criddle and G. P. Ellis, "Qualitative Organic Chemical Analysis," Butterworths, Washington, D. C., 1967, p 2.

of water and allowed to react with $(CF_3)_2P(S)OH$ (0.0586 g, 0.269 mmol). When the reaction had ceased, CO_2 and the solvent were removed under vacuum to leave a white solid, the ir spectrum of which suggested a hydrate. *Anal.* Calcd for $H_2O_2C_2$-F_6PSNa: H, 0.74. Found: H, 0.79. Treatment of the solid with concentrated sulfuric acid gave a small amount of $(CF_3)_2P$-$(S)OH$. The nmr spectrum of an aqueous solution of the salt showed the same species as solutions of the acid.

(b) $(CH_3)_2NH_2^+(CF_3)_2PSO^-$. When $(CF_3)_2P(S)OH$ (0.1146 g, 0.525 mmol) and dimethylamine (0.0266 g, 0.590 mmol) were warmed together, a rapid reaction occurred below room temperature to produce a white solid. After 18 hr only a trace of $(CH_3)_2NH$ was recovered. The solid dissolved in water to produce a stable solution with nmr parameters which compared well with those recorded[6] for the $(CF_3)_2PSO^-$ ion.

(5) With $(CF_3)_2P-N(CH_3)_2$. Dimethylaminobis(trifluoromethyl)-phosphine[21] (0.0426 g, 0.200 mmol) and $(CF_3)_2P(S)OH$ (0.0900 g, 0.413 mmol) were combined and allowed to warm slowly from $-78°$ to room temperature over a period of 3 days. Vacuum fractionation gave 0.0662 g of a mixture which contained $[(CF_3)_2P]_2S^{13,14}$ and $[(CF_3)_2P(S)]_2O$ in the ratio 1.15:1. A white solid remained which was identified as a mixture of amine salts of the $(CF_3)_2PSO^-$ and $(CF_3)_2PO_2^{-3,6}$ ions in the ratio 1.65:1. A minor amount of an involatile oil which reacted with the air also remained in the reaction tube.

(6) With Hg. No reaction occurred when a sample of $(CF_3)_2$-$P(S)OH$ (0.0727 g, 0.334 mmol) was maintained in contact with excess mercury for 7 days at room temperature. Only unchanged $(CF_3)_2P(S)OH$ (0.0662 g, 0.304 mmol) was recovered.

(7) With HI. (a) In the Absence of Hg. No reaction occurred when $(CF_3)_2P(S)OH$ (0.0747 g, 0.343 mmol) was treated with hydrogen iodide ($\sim$3.5 mmol) at room temperature for 5 days. Vacuum fractionation gave $(CF_3)_2P(S)OH$ (0.0608 g, 0.279 mmol after iodine contamination had been removed with mercury). Difficulty was experienced in separating all of the unreacted acid from the HI.

(b) In the Presence of Hg. A similar reaction involving $(CF_3)_2$-$P(S)OH$ (0.0750 g, 0.344 mmol), hydrogen iodide ($\sim$3.4 mmol), and excess mercury gave unchanged acid (0.0655 g, 0.300 mmol) and large amounts of hydrogen on vacuum fractionation.

(8) With Dry Air. Unchanged $(CF_3)_2P(S)OH$ (0.0745 g, 0.342 mmol) was recovered after 4 days of room-temperature reaction of the acid (0.0817 g, 0.374 mmol) with air (dried by passage through several $-196°$ traps) containing $\sim$0.4 mmol of O_2.

Reactions of the Bis(trifluoromethyl)thiophosphinate Anion. (1) With HCl. No reaction occurred when a sample of $(CH_3)_2$-$NH_2^+(CF_3)_2PSO^-$ was treated with excess HCl at room temperature for 24 hr.

(2) With Cl_2 and Br_2. When $(CH_3)_2NH_2^+(CF_3)_2PSO^-$ (0.0698 g, 0.266 mmol) was combined with chlorine (0.0110 g, 0.155 mmol) and warmed slowly from $-78°$ to room temperature, the only volatile product obtained was $(CF_3)_2P(S)Cl^{1,2}$ (0.0244 g, 0.103 mmol). A similar reaction between $(CH_3)_2NH_2^+(CF_3)_2PSO^-$ (0.73 mmol) and bromine (0.42 mmol) produced only $(CF_3)_2P(S)Br^{1,2}$ (0.36 mmol). The solid products of the chlorination reaction contained, according to ^{19}F nmr data,[6] the $(CF_3)_2PO_2^-$ ion as well as unreacted $(CF_3)_2POS^-$. Residues from the bromination reaction contained only $(CF_3)_2PO_2^-$ and no other fluorocarbon phosphorus species.

Reactions of Bis(trifluoromethyl)thiophosphinic Anhydride. (1) With Heat. A sample of $(CF_3)_4P_2S_2O$ (0.0581 g, 0.139 mmol) heated to 160° for 3 days showed no observable change and was almost quantitatively recovered (0.0570 g, 0.136 mmol).

(2) With Dry Air. Air, dried by passage through several $-196°$ traps, containing $\sim$0.2 mmol of oxygen, was allowed to react with $(CF_3)_4P_2S_2O$ (0.0454 g, 0.108 mmoles) at room temperature for 3 days. Almost quantitative recovery of unchanged $(CF_3)_4P_2S_2O$ (0.0446 g) was achieved on vacuum fractionation.

(3) With Water. No volatile fluorocarbon products were obtained when $(CF_3)_4P_2S_2O$ (0.1726 g, 0.413 mmol) was treated with

(21) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

10.0 ml of degassed, distilled water. The aqueous solution contained $(CF_3)_2PSO^-$ ions (demonstrated by nmr).[6] The solution was diluted to $\sim$90 ml and titrated against 0.100 *M* NaOH under an atmosphere of nitrogen. The endpoint was detected potentiometrically at 8.39 ml corresponding to a molecular weight of 412. The pH at the half-neutralization point was 2.49.

(4) Aqueous Alkali. The reaction of $(CF_3)_4P_2S_2O$ (0.0636 g, 0.152 mmol) with 5.0 ml of degassed 10% NaOH solution for 24 hr at room temperature gave CF_3H (0.0207 g, 0.296 mmol) as the only volatile product. The aqueous alkaline solution contained $CF_3PSO_2^{2-}$ ions[6] (identified by nmr).

(5) With Hydrogen Sulfide. No reaction occurred when $(CF_3)_4$-P_2S_2O (0.0440 g, 0.105 mmol) was heated for 5 days at 100° with hydrogen sulfide ($\sim$1.1 mmol). After heating for a further 5 days at 170°, 0.0386 g of a mixture of $(CF_3)_2PS_2H$,[1,2] $(CF_3)_2P(S)OH$, and $(CF_3)_4P_2S_2O$ in the ratio 6.8:1.6:1.6 (analyzed by nmr) was trapped at $-132°$. A trace of sulfur remained in the reaction tube and a small amount of noncondensable gas (O_2?) was also obtained.

(6) With HCl and HBr. A sample of $(CF_3)_4P_2S_2O$ (0.0386 g, 0.092 mmol) failed to react with hydrogen chloride ($\sim$1.0 mmol) during 4 days at 100°. Heating at 160° for a further 5 days produced 0.0318 g of a mixture of $(CF_3)_2P(S)Cl$,[1,2] $(CF_3)_2PS_2H$,[1,2] and $(CF_3)_4P_2S_2O$ in the ratio 6.9:2.1:1.0 (analyzed by nmr) trapped at $-132°$.

A similar reaction involving $(CF_3)_4P_2S_2O$ (0.0468 g, 0.112 mmol) and hydrogen bromide ($\sim$1.1 mmol) did not proceed during 6 days at 100°. A further 5 days at 150° yielded 0.0486 g of a mixture trapped at $-132°$ of $(CF_3)_2PS_2H$,[1,2] $(CF_3)_2P(S)Br$,[1,2] and $(CF_3)_2P$-$(S)OH$ in the ratio 1.4:7.2:1.4.

(7) With HI. (a) In the Absence of Hg. Very little reaction took place when $(CF_3)_4P_2S_2O$ (0.0893 g, 0.214 mmol) and hydrogen iodide ($\sim$2.1 mmol) were heated for 5 days at 100°. A further 5 days at 150° led to $\sim$50% reaction to give a mixture of products analyzed (by nmr) as starting material, $(CF_3)_2P(S)OH$, $(CF_3)_2PS_2H$, $(CF_3)_2PI$, $(CF_3)_2PSH$, and much iodine.

(b) In the Presence of Hg. No reaction occurred between $(CF_3)_4$-P_2S_2O (0.0482 g, 0.115 mmol) and hydrogen iodide ($\sim$1.1 mmol) in the presence of excess mercury during 2 days at room temperature. Vacuum fractionation recovered unchanged $(CF_3)_4P_2S_2O$ (0.0483 g, 0.115 mmol). Hydrogen gas was produced.

(8) With $(CH_3)_2NH$. A sample of $(CF_3)_4P_2S_2O$ (0.0340 g, 0.081 mmol) reacted rapidly below room temperature with excess dimethylamine ($\sim$0.8 mmol). Vacuum fractionation after 17 hr at room temperature gave $(CF_3)_2P(S)-N(CH_3)_2$[1,2] (0.0176 g, 0.072 mmol). The white salt remaining in the reaction tube was identified as $(CH_3)_2NH_2^+(CF_3)_2PSO^-$.

(9) With Sodium Halides. Reactions were carried out by condensing the anhydride onto a frozen solution of the halide in 0.3 ml of acetonitrile. The reaction was allowed to proceed at 70° until there was only one liquid layer (the anhydride is immiscible with acetonitrile), which in general required about 24 hr. The solvent was removed from the products by vacuum fractionation. In reaction c, total separation proved to be impossible.

(a) Sodium fluoride (0.0132 g, 0.315 mmol) reacted with $[(CF_3)_2$-$P(S)]_2O$ (0.1134 g, 0.271 mmol) to give $(CF_3)_2P(S)F^1$ (0.0543 g, 0.247 mmol) and a residue containing $(CF_3)_2PSO^-$ ions (identified by nmr).[6]

(b) Sodium chloride (0.0214 g, 0.366 mmol) reacted with $[(CF_3)_2$-$P(S)]_2O$ (0.1364 g, 0.326 mmol) to give $(CF_3)_2P(S)Cl^{1,2}$ (0.0737 g, 0.312 mmol) and a residue containing $(CF_3)_2PSO^-$ ions (identified by nmr).[6]

(c) Sodium bromide (0.0323 g, 0.314 mmol) reacted with $[(CF_3)_2$-$P(S)]_2O$ (0.1110 g, 0.265 mmol) to give $(CF_3)_2P(S)Br^{1,2}$ and a residue containing $(CF_3)_2PSO^-$ ions (identified by nmr).[6]

(10) With Hg. No reaction occurred when $[(CF_3)_2P(S)]_2O$ was heated for 7 days at 100° with excess mercury.