ing region[7,17] and is similar to the spectrum of diisopropoxyborane, but attempts to isolate this compound from this reaction mixture by conventional high-vacuum techniques, to date, have been unsuccessful. This may be due to the subsequent reaction of the alkoxyborane with morpholine, a by-product of the ketone reduction. Numerous reactions of amines with borate esters have been reported,[18-22] and we have found that diisopropoxyborane does, in fact, react with morpholine in acetone solution to produce a hygroscopic white solid and slowly evolve hydrogen. This product is being investigated further.

Acknowledgment. We wish to acknowledge the T.C.U. Research Foundation for support of this work which included a research fellowship for S. S. W. Also we wish to thank a referee whose discussion led to a study of the rate of the morpholine–borane–2-propanol reaction.

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Bis(trifluoromethyl)dithiophosphinic Acid and Related Derivatives[1]

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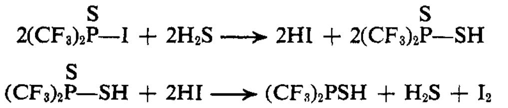
Abstract: The readily volatile new dithiophosphinic acid $(CF_3)_2PS_2H$ (mp 14°; bp estd 105°; monomeric, unlike the analogous oxygen compound) has been made by the H_2S cleavage of the nonvolatile $[(CF_3)_2PS]_2S$ (presumed), obtained by heating $[(CF_3)_2P]_2S$ with sulfur. Another process, in which $(CF_3)_2P(S)I$ is attacked by H_2S, depends upon a novel reduction process, liberating iodine. The spontaneous loss of iodine from $(CF_3)_2P(S)I$ was pushed forward by mercury, giving a 66% yield of $[(CF_3)_2P]_2S$; probably the reaction involves an anti-Arbuzov type of rearrangement. Other new derivatives of the dithiophosphinic acid include the chloride, the methyl ester, and two amides. Also reported are the thiophosphonic dichloride $CF_3P(S)Cl_2$ and the corresponding bis(dimethylamide). All of these have been fully characterized in regard to melting point, volatility, and infrared spectra, with P=S stretching and bending frequencies demonstrating a theoretically interesting trend of bond order.

The $(CF_3)_2P$ phosphines and phosphinic acid derivatives differ enough from the analogous R_2P compounds (R = ordinary alkyl or aryl) to suggest that the chemistry of the compounds of type $(CF_3)_2P(S)X$ (X = SH, SR, Cl, I, or an amido group) may not be fully predictable. Accordingly, we have made and studied such thiophosphinic compounds, as well as two examples of the thiophosphonic type $CF_3P(S)X_2$.

The new dithiophosphinic acid $(CF_3)_2PS_2H$ was obtained by two methods: addition of sulfur to $[(CF_3)_2P]_2S$[2,3] at 150° to form a nonvolatile liquid assumed to be $[(CF_3)_2PS]_2S$, which is cleaved by hydrogen sulfide at 100°; or by photochemical formation of the iodide $(CF_3)_2P(S)I$ from $[(CF_3)_2P]_2S$ and I_2, followed by an interesting reaction with H_2S, whereby half of the phosphinic material is reduced to the phosphinous state.

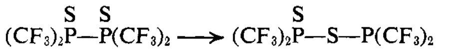


$$2(CF_3)_2\overset{S}{P}{-}I + 2H_2S \longrightarrow 2HI + 2(CF_3)_2\overset{S}{P}{-}SH$$

$$(CF_3)_2\overset{S}{P}{-}SH + 2HI \longrightarrow (CF_3)_2PSH + H_2S + I_2$$

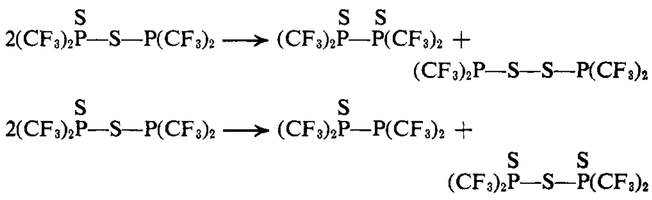
Apparently the reduction is the driving force for this result, for the analogous reaction of $(CF_3)_2P(S)Cl$ does not occur.

Although obtainable almost quantitatively as a colorless liquid, the iodide $(CF_3)_2P(S)I$ easily loses iodine, with interesting chemical results. Using mercury to remove the iodine, one might expect to obtain the diphosphine disulfide, but this would have good reason to undergo an anti-Arbuzov type of rearrangement[4]



$$(CF_3)_2\overset{S}{P}{-}\overset{S}{P}(CF_3)_2 \longrightarrow (CF_3)_2\overset{S}{P}{-}S{-}P(CF_3)_2$$

after which the resulting P-S-P compound would be expected to exchange groups in at least two ways.



$$2(CF_3)_2\overset{S}{P}{-}S{-}P(CF_3)_2 \longrightarrow (CF_3)_2\overset{S}{P}{-}\overset{S}{P}(CF_3)_2 + (CF_3)_2P{-}S{-}S{-}P(CF_3)_2$$

$$2(CF_3)_2\overset{S}{P}{-}S{-}P(CF_3)_2 \longrightarrow (CF_3)_2\overset{S}{P}{-}P(CF_3)_2 + (CF_3)_2\overset{S}{P}{-}S{-}\overset{S}{P}(CF_3)_2$$

Then the anti-Arbuzov rearrangement of the diphosphine monosulfide would produce $(CF_3)_2PSP(CF_3)_2$, which would come also from the action of mercury upon the P-S-S-P compound, and the diphosphine disulfide would go through the whole process again. If the two group exchanges should occur in equal

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[1] Supported by Grants GP-199, GP-3812, and GP-6751X from the National Science Foundation, which assisted also toward providing the instruments required for some parts of this research.

(2) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964).

(3) A. B. Burg and K. Gosling, *J. Am. Chem. Soc.*, **87**, 2113 (1965).

(4) J. E. Griffiths and A. B. Burg, *Proc. Chem. Soc.*, 12 (1961).

amount, this recycle of the diphosphine disulfide would imply an infinite series summing up to a 64% yield of $(CF_3)_2PSP(CF_3)_2$; actually, the yield was 66.5% Most probably, another group exchange to form $P_2(CF_3)_4$ and $(CF_3)_2PS_4P(CF_3)_2$ was not significant, but the results could have been affected in some small degree by entrapment of P–I material in the nonvolatile products, or by some formation of Hg–S–P compounds.

The acid chloride $(CF_3)_2P(S)Cl$ was made quite easily by the action of chlorine on $(CF_3)_2PSP(CF_3)_2$, by heating $(CF_3)_2PCl_3$ with silver sulfide, or by the Al_2Cl_6-catalyzed direct addition of sulfur to $(CF_3)_2PCl$ at 100°. The direct addition of sulfur also converted CF_3PCl_2 to $CF_3P(S)Cl_2$, again with Al_2Cl_6.

The thioester $(CF_3)_2P(S)SCH_3$ could be made from CH_3SH and $(CF_3)_2P(S)Cl$ by using trimethylamine to remove HCl, but, when the acid $(CF_3)_2PS_2H$ was sought by the analogous reaction of H_2S, the product of interest seemed to be the salt $(CH_3)_3NH^+(CF_3)_2PS_2^-$, from which the very strong acid $(CF_3)_2PS_2H$ could not be liberated by hydrogen chloride.

The acid amides were made easily by the ammonolysis or aminolysis of the appropriate chlorides. Our attempts to make them by the direct addition of sulfur to the aminophosphines did not succeed at 150°: $(CF_3)_2PN(CH_3)_2$ failed to react, while $(CF_3)_2PNH_2$ (inert at lower temperatures) went primarily to nonvolatile products. However, we have been informed of experiments in which these aminophosphines added sulfur at 150 and 180°, respectively, to form the desired acid amides.[5] The discrepancy most probably relates to the presence or absence of catalytic impurities, such as ammonia. Indeed, our observation that $(CF_3)_2P(S)NH_2$ liberated HCF_3 on standing (contrary to ref 5) would be explained if our sample contained a faint trace of ammonia, less likely to be present in the product of the sulfur-addition process. Ammonia would act like NaOH in basic hydrolysis and be regenerated as the compound is destroyed. This seems more likely than any base action by the NH_2 group, for its poor base action is proved by the slow reaction of $(CF_3)_2P(S)NH_2$ with high-pressure HCl.

The basic hydrolysis of our $(CF_3)_2P(S)X$ compounds gave only one HCF_3 per mole, and $CF_3P(S)X_2$ gave none. Thus we confirm that such basic hydrolyses stop at the phosphonate stage.[6] Furthermore, the P=S bond also resists bases, for the basic solutions failed to liberate H_2S upon acidification. However, the strong-acid hydrolysis of $(CF_3)_2P(S)X$ compounds at 140° did produce H_2S and one HCF_3, meaning that hydrolysis under such conditions went to the $CF_3PO(OH)_2$ stage and no farther.[7]

Syntheses and Characterizations

The Dithiophosphinic Acid. For the synthesis of pure $(CF_3)_2PS_2H$, a sealed tube containing $(CF_3)_2PSP(CF_3)_2$ with an excess over 2 g-atoms of sulfur per mole was heated 46 hr at 160°; lower temperatures were ineffective. The yield of a nonvolatile liquid, presumed to be $(CF_3)_2PS_3P(CF_3)_2$, was nearly quantitative. It was heated with more than one H_2S per mole, in the same tube (resealed), for 4 hr at 100°; then the volatile product was almost exclusively $(CF_3)_2PS_2H$. The yield was not measured accurately, but certainly exceeded 85%.

The two-stage process seemed necessary, for the initial presence of H_2S in a single-stage run would have meant the conversion of much of the $(CF_3)_2PSP(CF_3)_2$ to $(CF_3)_2PSH$, more rapidly than S could be attached to the $(CF_3)_2P$ unit; and experiments on the direct addition of sulfur to $(CF_3)_2PSH$ always gave impure $(CF_3)_2PS_2H$, not purifiable by high-vacuum distillation methods. Also necessary was the use of excess sulfur for conversion of $(CF_3)_2PSP(CF_3)_2$ to the supposed $(CF_3)_2PS_3P(CF_3)_2$, for an experiment using only 1.993 mg-atoms of sulfur per 1.833 mmoles of $(CF_3)_2PSP(CF_3)_2$ (26 hr, 165°) gave very little of the nonvolatile liquid, but much of an unstable liquid which may have been $(CF_3)_2PS_2P(CF_3)_2$. Its vapor tension at 0° was near 1 mm, and it deposited a nonvolatile white solid (combustion of which in O_2 gave no SO_2) wherever it was condensed in the high-vacuum line. It reacted with H_2S during 1 hr at 50° to form $(CF_3)_2PSH$, $(CF_3)_2PSP(CF_3)_2$, and a $(CF_3)_2PS_2H$ fraction which could not be purified by distillation.

The Thiophosphinic Acid Chloride. A sealed tube with 11.6 mmoles of $(CF_3)_2PSP(CF_3)_2$ and 24.6 mmoles of Cl_2 was warmed from −196 to −50° during 7 hr. The unused Cl_2 was removed through a −78° trap under high vacuum; then the major part of the product $(CF_3)_2P(S)Cl$ was similarly distilled through a trap at −60°. The yields were 10.71 mmoles of $(CF_3)_2P(S)Cl$ (93%) and 11.3 mmoles of $(CF_3)_2PCl_3$ (98%). The separation of these was done by means of a micro-size reflux column at −25° (avoiding solid formation), with the reflux ratio controlled by a stopcock leading into the high-vacuum system.

Alternatively, 0.81 mmole of $(CF_3)_2PCl_3$ and 1.22 mmoles of dry Ag_2S were heated in a very small sealed tube (keeping a liquid phase) for 4.5 days at 100°. The yield of $(CF_3)_2P(S)Cl$ was 0.78 mmole (96%). Further heating with Ag_2S (5 days at 140°) had no effect: there was no formation of either a silver thiophosphinate or a sulfur analog of the phosphinic anhydride.

For the third synthesis, 3.89 mmoles of $(CF_3)_2PCl$ and the equivalent amount of powdered sulfur ("flowers"), in a sealed tube with 0.344 mmole of freshly sublimed Al_2Cl_6, showed no reaction at 25° but a 3-min heating at 100° initiated a process which very rapidly consumed the sulfur. The yield of $(CF_3)_2P(S)Cl$ was 3.79 mmoles, or 97.5%. Both this and the product of the silver sulfide method were purified by the micro-column under high vacuum with the reflux at −60°.

This acid chloride proved to be inert to $HSP(CF_3)_2$, and an attempt to cause the formation of $(CF_3)_2P(S)SP(CF_3)_2$ by using trimethylamine to remove HCl led only to the conversion of the $HSP(CF_3)_2$ to $(CF_3)_2PSP(CF_3)_2$, with $(CH_3)_3N\cdot H_2S$ as the probable by-product.

The Thiophosphinic Acid Iodide. The cleavage of 2.76 mmoles of $(CF_3)_2PSP(CF_3)_2$ by 2.76 mmoles of I_2 began slowly in the dark at 25°, but went very rapidly in sunlight (through a Pyrex wall), leading to almost complete disappearance of the iodine color. The product $(CF_3)_2PI$ (2.55 mmoles; 92.4% yield) passed

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[5] R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Am. Chem. Soc.*, **90**, 2015 (1968), kindly shown to us by Dr. Cavell prior to publication.

[6] R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5896 (1964).

[7] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *ibid.*, 3896 (1954).

through a high-vacuum trap at −60°, where the desired product $(CF_3)_2P(S)I$ (2.65 mmoles; 96% yield) was condensed. The slight iodine color of this product was removed by zinc dust at 25°. The compound melted at 30°, with decomposition affecting the observation.

On standing at 20°, the thiophosphinic iodide slowly liquefied with liberation of iodine, with a decrease of rate suggesting an approach toward equilibrium. Accordingly, the mixture was shaken with mercury for 1 hr at 25°. The volatile product of 0.382 mmole of $(CF_3)_2P(S)I$ was 0.127 mmole of $(CF_3)_2PSP(CF_3)_2$, representing 66.5% of the original $(CF_3)_2P$ units. The character of the nonvolatile material was not studied.

The action of H_2S (in excess) upon $(CF_3)_2P(S)I$ occurred readily below room temperature and led to a fraction somewhat less volatile and far lower melting than the pure $(CF_3)_2PS_2H$ which was obtained later by another method. However, the formation of this substance in major yield was proved by the characteristic infrared peaks—accurately the same as for the pure acid but showing also some impurities. It was not very difficult to eliminate the $(CF_3)_2PSH$ byproduct, but much harder to remove the condensation product of this, namely $(CF_3)_2PSP(CF_3)_2$.[3]

The Thiophosphinic Acid Amide. A 0.74-mmole sample of $(CF_3)_2P(S)Cl$ was added slowly through a stopcock to 2.48 mmoles of ammonia in an 1100-ml bulb, immediately precipitating ammonium chloride. The reflux column was used at −35° to remove the excess ammonia and a trace of HCF_3; then at −25° it delivered 0.425 mmole (57% yield) of apparently pure $(CF_3)_2P(S)NH_2$. The nonvolatile liquid remaining in the bulb could well have been mostly the condensation product $[(CF_3)_2PS]_2NH$, but it was not investigated further.

The Thiophosphinic Acid Dimethylamide. The reaction of 2.08 mmoles of $(CF_3)_2P(S)Cl$ with 4.17 mmoles of $(CH_3)_2NH$ occurred in a sealed tube during a slow warming toward 25°, but, in order to ensure participation by occluded reactants, the tube was heated for 10 hr at 60°. High-vacuum fractional condensation delivered 0.067 mmole of HCF_3 and 0.041 mmole of unused $(CF_3)_2P(S)Cl$. The yield of pure $(CF_3)_2P(S)N(CH_3)_2$, delivered from the high-vacuum reflux column at −25°, was 1.81 mmoles, representing 89% of the consumed $(CF_3)_2P(S)Cl$.

The HCl cleavage of this amide represented an elementary analysis, as shown by the following equation with millimole stoichiometry.

$$\begin{array}{ccccccc} (CF_3)_2P(S)N(CH_3)_2 & + & 2HCl & \longrightarrow & (CF_3)_2P(S)Cl & + & (CH_3)_2NH_2Cl \\ 0.173 & & 3.70 & & 0.116 & & \\ \underline{-0.053} & & \underline{-3.46} & & & & \\ 0.120 & & 0.24 & & & & \end{array}$$

This experiment was carried on in a tube so small as to develop 11 atm pressure of HCl, and went for 3 days at 100°. Apparently the conditions for complete cleavage of the amide would be far more stringent.

The Methyl Dithioester. A gaseous mixture of 2.03 mmoles each of CH_3SH and $(CH_3)_3N$ was slowly introduced into 2.03 mmoles of $(CF_3)_2P(S)Cl$, contained in a 1000-ml bulb at 25°. The precipitation of $(CH_3)_3NHCl$ was immediate. The volatile product was purified by the high-vacuum reflux column at −20°: 1.70 mmoles (83.7% yield) of $(CF_3)_2P(S)SCH_3$. This product failed to react with H_2S at 9 atm and 110°.

The Thiophosphonic Acid Dichloride. A sealed tube containing 6.35 mmoles of CF_3PCl_2, 6.25 mg-atoms of sulfur, and 0.20 mmole of vacuum-sublimed Al_2Cl_6 was heated to 100° to initiate a reaction which then proceeded vigorously. The reflux column was operated at −30° (to avoid formation of solids), delivering 5.90 mmoles of $CF_3P(S)Cl_2$ (93% yield).

Table I. Confirmation of Molecular Formulas

Formula	—Mol wt— Obsd	Calcd	HCF₃ per mole	S per mole	Cl per mole
$(CF_3)_2PS_2H$	227[a]	229	0.991[b]		...
$(CF_3)_2PS_2CH_3$	247	248	0.963[c]	0.985H_2S[c] 0.961CH_3SH	... ...
$(CF_3)_2P(S)Cl$	237	236.5	0.995[b] 1.007[d]	0.96[d]	1.017
$(CF_3)_2PCl_3$	275	275.5	0.994	...	3.000
$(CF_3)_2P(S)NH_2$	221	217	1.002[d]	0.97[d]	...
$(CF_3)_2P(S)N(CH_3)_2$	248	245	1.01[b]	0.95[c]	...
$CF_3P(S)Cl_2$	202	203	None	1.006[c]	2.00
$CF_3PS[N(CH_3)]_2$	226	220	None	0.997[c]	

[a] Equiv wt by titration, 230. [b] Basic hydrolysis. [c] By 6 *M* HCl at 140°. [d] By CF_3COOH at 140°.

Table II. Volatility Constants

Formula	Nernst constants *A*	*B*	*C*	Bp, °C	Trouton constant, eu
$(CF_3)_2PS_2H$	2184	0.00500	6.0330	105.3	21.2
$(CF_3)_2P(S)SCH_3$	2435	0.00530	6.4564	133.6	21.1
$(CF_3)_2P(S)Cl$	1849	0.00500	5.6678	61.0	21.3
$(CF_3)_2P(S)N(CH_3)_2$	2658	0.00593	7.1046	147.2	20.8
$CF_3P(S)Cl_2$	2026	0.00550	5.5578	85.7	20.6
$CF_3P(S)[N(CH_3)_2]_2$	3278	0.00580	7.7610	211.0	22.7

Table III. Volatility Data

$(CF_3)_2PS_2H$, solid: $\log P = 8.903 - 2188/T$; 7.81 mm at 0.0°, 14.94 mm at 10.0°, 17.48 mm at 12.5°, and 19.20 mm at 14.0°; calcd, 7.81, 14.98, 17.51, and 19.20; calcd mp 18°. Liquid:

Temp, °C	18.0	23.9	27.4	32.0	35.6	41.3
P_{obsd}, mm	24.40	33.30	39.82	49.80	59.79	76.90
P_{calcd}, mm	24.44	33.33	39.80	49.89	59.77	76.91

$(CF_3)_2P(S)SCH_3$:

Temp, °C	0.00	11.4	26.0	46.9	70.1
P_{obsd}, mm	2.28	4.85	11.6	34.2	95.5
P_{calcd}, mm	2.28	4.85	11.6	34.3	95.5

$(CF_3)_2P(S)Cl$, solid: $\log P = 8.778 - 1891/T$; 3.16 mm at −44.7°, 6.0 mm at −37.0°, and 17.6 mm at −22.1°; calcd 3.16, 5.9, and 17.6; calcd mp −21.4°. Liquid:

Temp, °C	−20.0	−12.0	−5.4	0.05	6.4	11.9
P_{obsd}, mm	20.2	32.5	47.0	62.5	86.6	112.9
P_{calcd}, mm	20.2	32.5	47.0	62.6	86.6	112.8

$(CF_3)_2P(S)N(CH_3)_2$:

Temp, °C	0.00	9.5	20.5	32.7	55.2	63.3
P_{obsd}, mm	1.04	2.07	4.21	8.92	29.7	42.8
P_{calcd}, mm	1.04	2.10	4.24	8.92	29.7	42.8

$CF_3P(S)Cl_2$:

Temp, °C	−21.2	−11.0	0.00	6.1	19.4	40.3
P_{obsd}, mm	6.37	12.37	23.7	33.0	64.7	162.0
P_{calcd}, mm	6.37	12.37	23.7	33.0	64.7	162.1

$CF_3PS[N(CH_3)_2]_2$:

Temp, °C	40.6	51.6	62.7	70.6
P_{obsd}, mm	0.73	1.51	3.01	4.68
P_{calcd}, mm	0.73	1.51	2.98	4.68

Table IV. Infrared Spectra of Seven SP^V Compounds

Expected mode	$(CF_3)_2\overset{S}{P}SH$	$(CF_3)_2\overset{S}{P}SCH_3$	$(CF_3)_2\overset{S}{P}Cl$	$(CF_3)_2\overset{S}{P}NH_2$	$(CF_3)_2\overset{S}{P}N(CH_3)_2$	$CF_3\overset{S}{P}Cl_2$	$CF_3\overset{S}{P}[N(CH_3)_2]_2$
N–H, C–H, or S–H, ν	2681 (1.2) 2566 (0.5)	2944 (1.5) 2845?	. . .	3515 (4.1) 3407 (4.4)	2952 (4.3) 2926 (2.4) 2877 (2.1) 2843 (1.0) 2825 (0.7)	. . .	2942 (3.3) 2910 (2.4) 2864 (1.8) 2823 (1.1)
CH_3 or NH_2, δ	. . .	1438 (0.8)	. . .	1538 (6.1)	1492 (0.76) 1464 (2.0) 1426 (0.24) 1301 (6.0)	. . .	1467 (2.1) 1296 (5.7) sh 1273 (4.8)
C–F, ν	1207 (52) 1174 (78)	1203 (69) 1186 (49) 1167 (45)	1204 (76) sh 1200 (71) 1174 (65)	1220 (38) 1191 (52) 1169 (51)	1207 (71) 1177 (82) 1165 (79)	1184 (102)	1192 (19) 1146 (24) 1128 (24)
C–N, ν	. . .	. . .	. . .	. . .	1124 (5.0)	. . .	?
CH_3, ρ	. . .	974 (0.3)	. . .	. . .	1074 (1.6)	. . .	1067 (3.8)
P–X, ν	524 (4.0)	518 (4.7)	532 (5.2)	963 (7.6)	993 (30)	539 (4.9) 534 (6.4) 525 (9.1)	993 (17) 964 (13)
NH_2, ρ	. . .	. . .	. . .	930 (5.7)	. . .	. . .	. . .
S–H bend	849 (5.2) 845 (5.0)	. . .	. . .	. . .	. . .	. . .	. . .
CH_3 wag	. . .	?	. . .	. . .	788 (27)	. . .	778 (12)
P=S, ν	731 (20)	732 (25)	796 (20)	705 (11)	674 (11)	790 (19)	622 (4.4)
CF_3, δ-e	761 (9)	773 (13)	741 (12)	761 (3.2)	750 (0.80)	748 (8.9)	734 (1.8)
S–CH_3, ν	. . .	697 (0.8)	. . .	. . .	. . .	. . .	. . .
CF_3, δ-a	574 (5.0)	572 (6.8)	576 (7.4)	547 (3.4)	548 (2.9)	572 (16)	540 (?)
P–CF_3, ν	476 (6.6)	482 (4.8)	484 (5.5)	492 (6.2)	488 (4.6)	?520 (12)	492 (1.3)
P=S bend	362 (1.5)	380 (0.9)	368 (1.5)	349 (1.3)	332 (0.8)	sh 390 (1.4) 385 (2.5)	Not seen
CF_3, ρ	?	?	?319 (0.1)	293 (1.2)	?	308 (0.24)	Not seen
CF_3, wag	274 (1?)	?	?275 (0.1) ?242 (0.16)	259 (1.1)	272 (0.4) ?248 (0.3)	?	?

The Thiophosphonic Bis(dimethylamide). A closed tube containing 1.34 mmoles of $CF_3P(S)Cl_2$ and 5.36 mmoles of $(CH_3)_2NH$ was warmed slowly from −196°, showing precipitation of $(CH_3)_2NH_2Cl$ well below room temperature. The yield of $CF_3PS[N(CH_3)_2]_2$, delivered from the reflux column at −10°, was 1.30 mmoles, or 97%.

Proofs of Molecular Formulas. The data confirming the molecular formulas of our seven fully isolated new compounds, with like results for the known $(CF_3)_2PCl_3$, appear in Table I. The molecular weights were determined in the vapor phase at temperatures and pressures far from the condensation points, in an immersible tensimeter.[8] For the unstable $(CF_3)_2P(S)NH_2$ this was accomplished by unusually fast work at 84°. As mentioned before, hydrolysis for CF_3 groups as HCF_3 always stopped at the CF_3 phosphonate stage. Sulfur usually was determined as H_2S, which was liberated by aqueous acid at 140–150° and isolated from HCF_3 by conversion to NH_4HS and back to H_2S by CF_3COOH. The chloride determinations by $AgNO_3$ titration were done on the solutions left after removal of H_2S.

Physical Properties. The constants derived from liquid-phase volatility data for six of the new compounds are listed in Table II. The constants A, B, and C refer to the Nernst approximation equation $\log P = C + 1.75 \log T - BT - A/T$, with A and B rounded off and the precision implied by C. The melting ranges of these compounds, in the order of listing in Table II, were observed as 14.0–14.5, −17.6 to −17.2, −21.7 to −21.5, −16.8 to −16.7, −28.7 to −28.5, and 10.3–10.4°. For the unstable $(CF_3)_2P(S)NH_2$ (melting range −27.8 to −27.5°), only two volatility measurements were obtained: 1.19 mm at 0° and 9.79 mm at 31.7°. From these, with the reasonable assumption that the Trouton constant might be 22.7 eu for a hydrogen-bonded compound, one can determine the Nernst constants as 2406, 0.005, and 6.6924, to estimate the boiling point as 137°.

For the six compounds in Table II, the observed and calculated vapor-tension values (including those for solids, with equations, when appropriate) are given in Table III.

Proton Magnetic Resonance. The proton resonance spectrum of $(CF_3)_2PS_2H$ (observed by means of the Varian A-60 instrument) showed a single sharp peak with chemical shift δ −3.11 from tetramethylsilane. The absence of splitting by phosphorus and fluorine would correlate with a rapidly exchangeable proton.

Infrared Spectra. The infrared spectra of seven of our new phosphorus(V) compounds as recorded by the Beckman IR7 instrument are shown in Table IV. The frequency of each peak or shoulder is followed by the relative intensity in parentheses. These intensities were calculated by the definition $k = (100/PL) \log I_0/I$, for path L and pressure P, both in cm. The table employs the usual abbreviations: sh = shoulder, ν = stretching, δ = deformation, ρ = rocking, a = asymmetric, e = symmetric; the question mark is used to indicate uncertain assignment, appearance, or intensity. The symbol X is used to designate a variable univalent group: Cl, SH, SCH_3, NH_2, or $N(CH_3)_2$. Omitted from this table are overtones and combinations for $(CF_3)_2P(S)Cl$ at 2390 (0.17), 2351 (0.16), 2343 (0.22), 1287 (0.47), 1268 (0.35), 1148 (0.49); for $(CF_3)_2PS_2H$ at 2394 (0.1), 2280 (0.1), 1430 (0.05), 1329 (0.26),

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[8] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937).

sh 1304 (0.7), 1279 (0.95); and for $CF_3P(S)Cl_2$ at 1384 (0.12), 1334 (0.12), 1313 (0.32), 1283 (0.28), sh 1276 (0.19), sh 1266 (0.12), sh 1151 (1.9), 1132 (0.73), 650 (0.1), 614 (0.1), and sh 590 (2) cm^{-1}. Among these, it is possible to recognize a Fermi-resonance enhanced overtone of CF_3 asymmetric deformation, found for $(CF_3)_2P(S)NH_2$ at 1133 (2.3) cm^{-1}. A peak at 406 (2.1) cm^{-1} for this compound might represent NH_2-group torsion. Not yet assigned are 538 (1.2) cm^{-1} for $(CF_3)_2P(S)SCH_3$, and for $(CF_3)_2P(S)N(CH_3)_2$ 450 (0.9) and 394 (0.23) cm^{-1}. The number of weak and difficultly assignable peaks and shoulders for any of these compounds doubtless could increase indefinitely with increasing pressure and path length. Inflections suggestive of P and R branches were especially noticeable for modes concerning the CF_3 groups, but often were detectable for other fundamental modes as well.

Probably the most significant trend in Table IV is that shown by the $P{=}S$ frequencies—especially the $P{=}S$ stretching mode. It is quite clear that these frequencies decrease with increasing π-donor bonding power of the adjacent groups X: least for chloride and most for the amides. It is a reasonable rule that the $P{=}S$ bond order decreases as the adjacent groups feed π electron density more effectively toward phosphorus, and the present results support such a rule.

Preparation and Properties of Bis(trifluoromethyl)dithiophosphinic Acid and Some Related Pentavalent Trifluoromethylphosphine Sulfides

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Abstract: The aminophosphine sulfides, $(CF_3)_2P(S)NR_2$, where R = H or CH_3, and the halophosphine sulfides, $(CF_3)_2P(S)X$, where X = F, Cl, Br, and I, are prepared by heating the corresponding phosphines with sulfur. The chloro and bromo compounds are best prepared by the action of the appropriate hydrogen halide on $(CF_3)_2P(S)NMe_2$, while the fluoride is conveniently obtained by the action of antimony trifluoride on $(CF_3)_2P(S)Br$. When the iodo compound is shaken with mercury, $(CF_3)_2PSP(CF_3)_2$ is formed, while with mercury and hydrogen iodide the product is $(CF_3)_2PSH$, formed by an anti-Arbuzov rearrangement. Bis(trifluoromethyl)dithiophosphinic acid, $(CF_3)_2P(S)SH$, is formed by heating sulfur with either $(CF_3)_2PH$ or $(CF_3)_2PSH$. Addition of sulfur to CF_3PFNMe_2 and PF_2NMe_2 also gives the corresponding sulfides. The nmr and mass spectra of the new compounds are discussed.

While the chemistry of trifluoromethyl compounds of trivalent phosphorus has been extensively studied,[2] work on the corresponding phosphorus(V) derivatives has been limited to the preparation of halo[3,4] and oxy compounds,[5-10] and of one sulfide, $(CF_3)_3P{=}S$.[11] This paper describes the preparation and properties of some compounds containing the $(CF_3)_2P(S)$ group.

Results and Discussion

Synthesis and Properties of the Phosphine Sulfides. Heating aminobis(trifluoromethyl)phosphine with sulfur in a sealed tube at 180° readily gave the pentavalent phosphine sulfide $(CF_3)_2P(S)NH_2$ in 85% yield based on the aminophosphine consumed. Likewise dimethylaminobis(trifluoromethyl)phosphine, $(CF_3)_2PN(CH_3)_2$, reacted with sulfur at 150° to give the sulfide, $(CF_3)_2P(S)N(CH_3)_2$, although the yields were considerably lower.

Alkaline hydrolysis of $(CF_3)_2P(S)NH_2$ gave only 1 mole of CF_3H. This behavior is readily attributed to the formation of a hydrolytically stable acid containing a CF_3P^V group in solution in common with the behavior of $(CF_3)_3PCl_2$,[5] $(CF_3)_3PO$,[7] and $(CF_3)_3PS$[11] which gave only 2 moles of CF_3H upon alkaline hydrolysis. The evolution of 1 mole of fluoroform less than the total number in the molecule was characteristic of the compounds described in this paper, and the yield of fluoroform upon alkaline hydrolysis was used for analysis.

The chloride and bromide, $(CF_3)_2P(S)X$ (X = Cl, Br), were best prepared by the nearly quantitative reaction of the dimethylamido compound with a large excess of hydrogen halide at high pressure in a sealed tube, *e.g.*

$$(CF_3)_2P(S)N(CH_3)_2 + 2HX \longrightarrow (CF_3)_2P(S)X + (CH_3)_2NH_2^+X^-$$

The reaction was very slow at low pressures of hydrogen halide, suggesting that $(CF_3)_2P(S)N(CH_3)_2$ is only weakly basic. The oxygen analog, $(CF_3)_2P(O)N(CH_3)_2$, exhibits parallel behavior toward acids.[10] The chloride

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