iodine and selenium. We also thank Mr. D. Venerable for his assistance with some of the glass transition determinations. The financial assistance of the office of Naval Research is gratefully acknowledged.

Stable Thiotrifluoromethylphosphines[1]

Anton B. Burg and Keith Gosling

Contribution from the Department of Chemistry, University, of Southern California, Los Angeles, California 90007. Received December 28, 1964

Thiophosphines can be stable if CF_3 is attached to phosphorus, preventing isomerization to phosphine sulfides in the Arbuzov manner. The new volatile compounds $(CF_3)_2PSP(CF_3)_2$ (m.p. $-33°$; b.p. est. $112°$), $HSP(CF_3)_2$ (m.p. $-100°$; b.p. est. $55°$), $CH_3SP(CF_3)_2$ (m.p. $-58°$; b.p. est. $92°$), $t\text{-}C_4H_9SP(CF_3)_2$ (m.p. $-18°$; b.p. est. $144°$), and $(CH_3S)_2PCF_3$ (m.p. $-65°$; b.p. est. $168°$) undergo no such conversion, whereas a slow catalytic isomerization of $ROP(CF_3)_2$ is possible. The syntheses were accomplished mostly by $(CH_3)_3N$-assisted thiolyses of $CF_3\text{-}P$ halides, except that $HSP(CF_3)_2$ came from cleavage of $(CF_3)_2PSP(CF_3)_2$ by H_2S or HCl. The H_2S cleavage is slightly reversible: whereas $(CF_3)_2POH$ is stable, $HSP(CF_3)_2$ forms some H_2S and $(CF_3)_2PSP(CF_3)_2$. The HCl cleavage of $(CF_3)_2PSP(CF_3)_2$ occurs at both P–S bonds, forming more $(CF_3)_2PCl$ than $HSP(CF_3)_2$. Accurate infrared spectra of the five new thiophosphines are compared.

The recent isolation and study of the new oxyphosphines $(CF_3)_2POP(CF_3)_2$,[2] $(CF_3)_2POH$,[2] and the ester types $ROP(CF_3)_2$[2,3] and $(RO)_2PCF_3$[4] led to the question whether the analogous thiophosphines would show any very different chemical behavior. In fact, the new compounds $(CF_3)_2PSP(CF_3)_2$, $HSP(CF_3)_2$, $CH_3SP(CF_3)_2$, $t\text{-}C_4H_9SP(CF_3)_2$, and $(CH_3S)_2PCF_3$ proved to be fairly similar to the corresponding oxyphosphines, but with some significant differences.

One difference is the appreciably greater resistance of the $RSP(CF_3)_2$ type to isomerization in the Arbuzov manner: *i.e.*, conversion to the $R(CF_3)_2PS$ type. For example, neither $CH_3SP(CF_3)_2$ nor $t\text{-}C_4H_9SP(CF_3)_2$ could be even slightly converted to the corresponding tertiary phosphine sulfide by the aid of CH_3I during a week at $100°$, whereas $t\text{-}C_4H_9OP(CF_3)_2$ with CH_3I was mostly converted to the phosphine oxide $t\text{-}C_4H_9(CF_3)_2PO$ during 2 hr. below $80°$ and $CH_3OP(CF_3)_2$ could be partially isomerized at higher temperatures and pressures.[2] One reason for the difference might relate to the sometimes observed higher fission-resistance of alkyl–sulfur *vs.* alkyl–oxygen bonding. However, such a kinetic stability of S–C bonding does not prevent the rapid spontaneous isomerization of $RSP(C_6H_5)_2$ compounds.[5]

The thiobisphosphine $(CF_3)_2PSP(CF_3)_2$ proved to be almost as stable as the corresponding diphosphoxane, for only 17% decomposed during 6 days at $200°$, forming $(CF_3)_3P$ and other products not identified. Unlike the analogous thiobisarsine, which loses sulfur on contact with mercury at $25°$, producing $(CF_3)_2As\text{–}As(CF_3)_2$,[6] this P–S–P compound is inert to mercury up to $150°$ (16 hr., slight action). It is not surprising that the P–S–P chain is more stable than As–S–As in the same situation, for phosphorus bonding orbitals are at deeper energy levels than the corresponding arsenic orbitals; also the node in the arsenic $4d_\pi$ orbital would be unfavorable to $S_{3p}\text{–}As_{4d}$ π-bonding.

The thiophosphinous acid $HSP(CF_3)_2$ seems to resist a protonic rearrangement quite as well as $(CF_3)_2POH$ does, but is less stable on account of a tendency to undergo condensation, forming $(CF_3)_2PSP(CF_3)_2$ and H_2S. The difference may be explained by assuming that $S_{3p}\text{–}P_{3d}$ π-bonding is intrinsically less effective than $O_{2p}\text{–}P_{3d}$ π-bonding. Thus if we write

$$2(CF_3)_2POH \rightleftarrows (CF_3)_2POP(CF_3)_2 + H_2O$$

$$2(CF_3)_2PSH \rightleftarrows (CF_3)_2PSP(CF_3)_2 + H_2S$$

it can be argued that two molecules of a left-hand component develop more π-bonding energy than is afforded by the corresponding right-hand components; hence the forward reaction would be suppressed more for the system in which the π-bonding is intrinsically stronger. In fact, the forward reaction has not been detected for $(CF_3)_2POH$, whereas for the thio compound it is easily observable. Even.so, this condensation is not extensive, for an efficient synthesis of $HSP(CF_3)_2$ is based upon the reverse process of cleaving $(CF_3)_2PSP(CF_3)_2$ by H_2S.

The same condensation offers one way to account for the unequal cleavage of $(CF_3)_2PSP(CF_3)_2$ by HCl, yielding more than one $(CF_3)_2PCl$ and less than one $HSP(CF_3)_2$. Condensation of the latter would form H_2S and $(CF_3)_2PSP(CF_3)_2$ for further cleavage, thus affording a secondary process equivalent to direct cleavage of $HSP(CF_3)_2$ by HCl. The analogous direct cleavage of $CH_3SP(CF_3)_2$ gave one $(CF_3)_2PCl$ per HCl consumed, but could not be forced to completion: even with HCl at 10 atm. pressure (5.5 days, $100°$) forward progress beyond 15% was not achieved. No such cleavage of $(CF_3)_2POH$ has been noticed: HCl cleaves $(CF_3)_2POP(CF_3)_2$ cleanly, with no secondary effect.[2]

(1) Supported by Grant No. GP-199 from the National Science Foundation, which contributed also through Grant No. G-14665 toward the purchase of the Beckman IR7 instrument.

(2) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, 82, 1507 (1960).

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(5) A. E. Arbuzov and K. V. Nikoronov, *Zh. Obshch. Khim.*, 18, 2008 (1948).

(6) W. R. Cullen, *Can. J. Chem.*, 41, 2424 (1963).

Experimental

The experimental work here described was performed by means of a high-vacuum manifold, including a series of U-traps and mercury float valves for quantitative high-vacuum fractional condensation and various ground-joint connected devices such as a micro-scale high-vacuum reflux column.[7] Stopcocks were employed only in such a manner as not to affect quantitative manipulation of the volatile products.

Syntheses. The new P-S-P, RS-P, and RS-P-SR compounds all could be made efficiently by the use of trimethylamine to remove protons and halide from mixtures of appropriate H-S and P-X compounds. The thiobisphosphine could be made also quite effectively by the action of a $(CF_3)_2P$ halide upon Ag_2S. The cleavage of the thiobisphosphine by either H_2S or HCl offered two alternative methods for $HSP(CF_3)_2$. In the following experiments, the quantities were determined by gas volume measurements where feasible; otherwise by weight.

For $(CF_3)_2PSP(CF_3)_2$, 5.2 mmoles of H_2S and 10.4 mmoles each of $(CF_3)_2PCl$ and $(CH_3)_3N$ were warmed together from $-196°$ in a sealed tube, reacting suddenly and exothermally in the range -40 to $-35°$. The volatile product was high-vacuum distilled from the solid $(CH_3)_3NHCl$ and purified by a reflux column operating *in vacuo* at $-30°$.[7] The yield of the pure product was 1.71 g. (4.62 mmoles, or 89%). It had been shown that no reaction would occur in the absence of the amine.[8]

Alternatively, 1 g. (4 mmoles) of Ag_2S (freshly precipitated from $AgNO_3$ solution, washed well with water and acetone, and dried by vacuum) was exposed to 3.9 mmoles of $(CF_3)_2PCl$ in a sealed tube. The reaction failed to progress at 25°, but during 5 days at 105° it consumed 2.4 mmoles of the $(CF_3)_2PCl$ to produce 350 mg. (0.95 mmole, or 79% yield) of $(CF_3)_2$-$PSP(CF_3)_2$. Similarly, 2.5 g. (10 mmoles) of Ag_2S and 1.55 g. (5.15 mmoles) of $(CF_3)_2PI$, heated for 19 days in a sealed tube at 100°, gave 0.79 g. (2.14 mmoles, or 83% yield) of pure $(CF_3)_2PSP(CF_3)_2$.

For $HSP(CF_3)_2$, 1.14 g. (3.1 mmoles) of $(CF_3)_2$-$PSP(CF_3)_2$ and 43 mmoles of H_2S were heated in a sealed 85-ml. glass tube for 6 days at 100°. Considering the recovery of 0.43 mmole of the P-S-P compound, the final isolation of 1.05 g. (5.2 mmoles) of pure $HSP(CF_3)_2$ meant a 97% yield. Less efficient was the HCl cleavage of the P-S-P compound: from a mixture of 2.81 mmoles of each component, held at 100° for 14 days, 1.45 mmoles of HCl and 1.7 mmoles of the P-S-P compound were recovered; thus only 1.11 mmoles (40%) of the P-S-P compound had been consumed, but it yielded 1.3 mmoles of $(CF_3)_2$-PCl and only 0.81 mmole of $HSP(CF_3)_2$ instead of the expected equimolar proportions of these products. Hydrogen sulfide was identified as a product, but was not quantitatively determined.

The roughly isolated product of the H_2S cleavage process seemed inconveniently unstable, tending to revert to H_2S and the thiobisphosphine; however, after purification in the vacuum-reflux column at $-78°$ it was sufficiently stable for convenient study of its

(7) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1140 (1963). The diagram there represents the actual size.
(8) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

Table I. Volatility of $(CF_3)_2PSP(CF_3)_2$
($\text{Log } P = 6.4206 + 1.75 \log T - 0.00525T - 2329/T$)
($t_{760} = 112.4°$; Trouton constant = 21.9 e.u.)

Temp., °C.	0.00	4.2	20.0	41.8	56.5
P_{obsd}, mm.	5.33	6.97	18.04	55.5	107.6
P_{calcd}, mm.	5.30	6.96	17.97	55.5	107.6

Table II. Volatility of $HSP(CF_3)_2$
($\text{Log } P = 5.6685 + 1.75 \log T - 0.004798T - 1844/T$)
($t_{760} = 55.4°$; Trouton constant = 21.0 e.u.)

Temp., °C.	−55.4	−39.0	−29.0	−13.3	0.00	6.1
P_{obsd}, mm.	1.82	6.50	13.3	35.6	74.2	101.4
P_{calcd}, mm.	1.77	6.56	13.3	35.6	74.3	101.4

Table III. Volatility of $CH_3SP(CF_3)_2$
($\text{Log } P = 6.6245 + 1.75 \log T - 0.00596T - 2210/T$)
($t_{760} = 92.0°$; Trouton constant = 21.2 e.u.)

Temp., °C.	−24.6	−17.1	0.00	21.0	40.5
P_{obsd}, mm.	2.77	4.84	14.8	47.8	119.7
P_{calcd}, mm.	2.78	4.81	14.8	47.7	119.7

Table IV. Volatility of $t\text{-}C_4H_9SP(CF_3)_2$
($\text{Log } P = 6.9016 + 1.75 \log T - 0.00570T - 2595/T$)
($t_{760} = 143.6°$; Trouton constant = 21.0 e.u.)

Temp., °C.	0.00	23.7	38.2	50.0	59.1
P_{obsd}, mm.	1.28	6.22	14.4	26.4	40.6
P_{calcd}, mm.	1.28	6.24	14.3	26.4	40.7

Table V. Volatility of $(CH_3S)_2PCF_3$
($\text{Log } P = 5.7827 + 1.75 \log T - 0.00400T - 2545/T$)
($t_{760} = 168.4°$; Trouton constant = 21.4 e.u.)

Temp., °C.	18.9	49.8	72.2	76.5	90.8	93.0
P_{obsd}, mm.	1.64	10.02	29.6	36.1	65.7	71.5
P_{calcd}, mm.	1.64	10.04	29.8	36.1	65.5	71.5

physical properties and infrared spectrum. In relation to the latter, it may be mentioned that the repeat-scan mechanism of the Beckman IR7 instrument was employed for an 11-hr. monitoring of a sample of $HSP(CF_3)_2$ in the vapor phase at 40° and 47 mm. pressure. At the end of the run, the characteristic 834 and 863 cm.$^{-1}$ had not appreciably lost intensity, meaning that no more than 2% decomposition could have occurred. At 100°, however, a 1.15-mmole pure sample of $HSP(CF_3)_2$ underwent 10% condensation during 6 days in an 8-ml. sealed tube, yielding 0.055 mmole each of H_2S (10-mm. vapor tension at $-116°$) and $(CF_3)_2PSP(CF_3)_2$ (5 mm. vapor tension at 0°; accurate infrared agreement).

For $CH_3SP(CF_3)_2$, 2.21 mmoles each of CH_3SH, $(CF_3)_2PCl$, and $(CH_3)_3N$ were warmed from $-196°$ in a sealed glass tube, reacting suddenly at $-40°$. The volatile product was isolated by high-vacuum fractional condensation and purified by the vacuum reflux column at $-55°$. The yield of pure CH_3SP-$(CF_3)_2$ was 463 mg. (2.15 mmoles), or 97%.

For $t\text{-}C_4H_9SP(CF_3)_2$, the same method gave a good yield which was not accurately measured. It was purified by the vacuum reflux column, operating at -25 to $-20°$.

For $(CH_3S)_2PCF_3$, 1.051 g. (2.97 mmoles) of CF_3PI_2, in a sealed tube with 5.98 mmoles each of CH_3SH

Table VI. Data Confirming Molecular Formulas

Formula	Mol. wt. Obsd.	Calcd.	HCF₃ per mole Obsd.	Calcd.	Sulfur per mole	Obsd.	Calcd.
[(CF₃)₂P]₂S	372	370	3.99	4.00	H₂S	0.98	1.00
HSP(CF₃)₂	200	202	2.03	2.00	H₂S	1.00	1.00
CH₃SP(CF₃)₂	217	216	2.04	2.00	CH₃SH	1.01₅	1.00
C₄H₉SP(CF₃)₂	263	258	2.02	2.00	C₄H₉SH	1.00	1.00
(CH₃S)₂PCF₃	195	194	1.00	1.00₄	CH₃SH	1.93	2.00

Table VII. Fundamental Infrared Peaks of CF₃–P–S Phosphines[a]

Expected mode	[(CF₃)₂P]₂S	HSP(CF₃)₂	CH₃SP(CF₃)₂	t-C₄H₉SP(CF₃)₂	(CH₃S)₂PCF₃
C–H or S–H, ν	...	2595 (0.36)	3019 (0.23)	2978m (11)	
		2573R (0.16)	2952R (1.3)	2953 (5.7)	
		2566Q (0.44)	2948Q (1.8)	2937 (4.2)	2942 (3.1)
		2560P (0.16)	2944P (1.2)	2912 (4.5)	
			2857 (0.27)	2877 (2.5)	2851 (0.5)
CH₃, δ–a	...	...	1443 (1.0)	1477 (2.5)	1439 (1.5)
			1439 (1.0)	1464 (4.5)	1436 (1.5)
CH₃, δ–?	...	...		1401 (1.3)	...
CH₃, δ–e	...	...	1330 (0.9)	1376sh (7)	1324 (1.0)
			1325 (1.0)	1373 (8.9)	
C–F, ν	1203 (70)	1198 (15)	1204 (26)	1202 (48)	1202 (0.8)
	1174 (132)	1172 (25)	1193 (22)	1194d (50)	
	1142 (114)		1168 (46)	1164 (106)	1150 (27)
	1130 (64)	1135 (25)	1159 (35)	1128d (73)	1134 (35)
	1110 (7.1)		1132 (46)		
			1104 (33)		
CH₃, ρ	...	...	971 (0.58)	1029? (0.4)	965 (1.0)
S–H bend	...	863 (0.6)	...	...	...
		836R (0.23)			
		834Q (0.26)			
		830P (0.24)			
CF₃, δ–e	749 (3.3)	752R (0.9)	749 (0.9)	747 (1.2)	742 (0.45)
		749Q (1.3)	745sh (0.8)		
		746P (1.0)	730sh (0.2)		
S–CH₃, ν	...	...	697d (0.3)	...	696 (0.45)
CF₃, δ–a	557 (2.3)	556 (1.3)	559 (2.2)	562d (4.9)	548 (1.5)
P–S, ν	508.5 (11)	522? (1.1)	523 (2.1)	530 (1.8)	515 (2.6)
		508 (2.1)			
P–CF₃, ν	461 (2.2)	456sh (1.2)			481 (0.9)
	445 (7.7)	445 (2.5)	449 (5.5)	451d (5.8)	439 (1.0)
				379? (5.6)	
CF₃, ρ or P–S bend?	335 (1.1)	...	335 (0.11)	...	...
			313 (0.09)		
CF₃ wag	...	...	244 (0.22)	...	...
			227.5 (0.3)		

[a] Abbreviations: ν = stretching; δ = deformation; a = asymmetric; e = symmetric; ρ = rocking; m = multiplet spanning 10 cm.⁻¹; sh = shoulder; d = closely spaced doublet.

and (CH₃)₃N, reacted well below room temperature, yielding 527 mg. (2.72 mmoles; 92%) of the product, after purification by vacuum reflux at −15°.

Physical Properties. The melting ranges of the five new thiophosphines were observed visually, using vapor-tension thermometers. Results: (CF₃)₂PSP(CF₃)₂, −34 to −33°; HSP(CF₃)₂, −100 to −99.5°; CH₃SP-(CF₃)₂, −59 to −58°; t-C₄H₉SP(CF₃)₂, −18.5 to −17.5°; (CH₃S)₂PCF₃, −65.3 to −64.7°, all sharp enough to imply reasonable purity. Representative equilibrium vapor pressures are shown in Tables I–V, with equations, derived normal boiling points, and Trouton constants. High purity again is suggested by good conformity to principle.

The ultraviolet spectrum of (CF₃)₂PSP(CF₃)₂ showed a strong absorption maximum at 2095 Å. (molar absorption coefficient ε 5367) and a deep minimum at 1965 Å. (ε 89).

Confirmation of Formulas. For final confirmation of the molecular formulas, beyond the clear evidence from the quantitatively monitored syntheses and chemical reactions, the data of Table VI were developed. The molecular weights all were determined in the vapor phase far from the condensation pressure–temperature conditions. Analyses for CF₃ were done by basic hydrolysis, with identification of HCF₃ by its molecular weight and infrared spectrum. For determination of sulfur as H₂S or CH₃SH, acid hydrolysis was employed, but required far more drastic conditions than expected in view of the usually very easy hydrolysis of other P–S compounds. For liberation of H₂S, the samples were heated with 50% aqueous CF₃COOH (sealed tubes for 9 hr. at 150°); then the H₂S was isolated by conversion to NH₄HS (nonvolatile at −78°; HCF₃ pumped off), reliberated by dilute CF₃COOH, and identified by its molecular weight and volatility (10

mm. at $-116°$). The CH$_3$S–P compounds were attacked by constant-boiling hydrochloric acid (sealed tubes, 12 hr. at 160°), quantitatively liberating CH$_3$SH. This was isolated directly in the high-vacuum system and identified by its volatility (10 mm. at $-67°$) and infrared spectrum.

For t-C$_4$H$_9$SP(CF$_3$)$_2$ the HCl hydrolysis was not feasible because the P–S bond would not cleave except at temperatures high enough to convert t-C$_4$H$_9$SH to t-C$_4$H$_9$Cl, as proved in a separate experiment. However, the basic hydrolysis (10% KOH; 90–95°, 12 hr.) directly liberated both HCF$_3$ and t-C$_4$H$_9$SH. These were isolated by high-vacuum fractional condensation, passing through U-traps at -130 and $-45°$, respectively, and measured as gases. The pure HCF$_3$ was identified as before, with further confirmation by volatility (30 mm. at $-124°$). The pure t-C$_4$H$_9$SH was identified by its melting point ($+1°$, agreeing with various handbooks), comparison of volatility with the original reagent (17.5 mm. at $-20°$), and an infrared spectrum agreeing with the literature.[9] The quantitative recovery of this mercaptan proved that the t-C$_4$H$_9$SP(CF$_3$)$_2$ had not undergone an Arbuzov isomerization—nor could this be forced by long heating with CH$_3$I at 100°.

Infrared Spectra

The observed infrared fundamental bands for the five thiophosphines are listed in Table VII. They were recorded for vaporized samples by the Beckman IR7 instrument, using NaCl or CsI optics and windows of NaCl, KBr, or high-density polyethylene as appropriate, and paths ranging from 1.15 to 11.5 cm. The frequencies were corrected by calibrations based upon well-known fine structures: those below 2000 cm.$^{-1}$ should be accurate within 1 cm.$^{-1}$. The relative intensity of each feature (peak or shoulder) is shown in parentheses after the frequency (cm.$^{-1}$), having been calculated by the arbitrary definition $k = (100/PL) \log I/I_0$ for pressure P (at 25°) and path L, both in cm.

(9) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 481 (1946).

The transmissions I_0 and I were taken literally, so that any band overlap would mean an overestimate of the intrinsic k values.

The assignments are based upon our consistent records of scores of CF$_3$–P compounds, leaving no appreciable doubts except as indicated by question marks. Not tabulated are many weak bands, increasing in number with higher pressures, and presumed to represent overtones and combinations difficult to assign or compare. Those observed are listed as follows, in cm.$^{-1}$ with k values in parentheses.

(CF$_3$)$_2$PSP(CF$_3$)$_2$: 2256(0.7), 1905(0.14), 1879(0.24), 1290(1.2), 1275(1.2), 1027(0.3), and 723(0.24).

HSP(CF$_3$)$_2$: 2371(0.13), 2340(0.16), 2313(0.20), 2281 (0.5), 2260(0.4), 1945(0.04), 1905(0.09), 1880(0.20), 1690(0.05), 1600(0.02), 1574(0.03), 1480(0.04), 1390 (0.1), 1294(0.76), 1260(1.1), 1060(0.19), 1036(0.20), and 723(0.17).

CH$_3$SP(CF$_3$)$_2$: 2310(0.13), 2254(0.34), 1902(0.09), 1875(0.13), and 1265(0.6).

t-C$_4$H$_9$SP(CF$_3$)$_2$: 2304(0.2), 2245(0.3), 1900(0.2), and 1869(0.1). Modes characteristic of the (CH$_3$)$_3$C group seemed recognizable as follows: skeletal, 1273(0.9), 1252(0.8); CH$_3$ groups, 809(0.1), 773(0.1); CC$_3$ deformation, 482.5(0.3).

(CH$_3$S)$_2$PCF$_3$: none at the low pressures employed.

Also omitted from Table VII is a peak at 546(0.8) for HSP(CF$_3$)$_2$. Geminal CF$_3$ groups on P often show such a peak on the low-frequency side of a fairly strong band assigned to CF$_3$-asymmetric deformation; thus the 556- and 546-cm.$^{-1}$ peaks here probably represent in-phase and out-of-phase δ–a. For the other P(CF$_3$)$_2$ compounds here described, the weaker low-frequency peak failed to appear; and as yet no rule for predicting it has emerged.

The region below 400 cm.$^{-1}$ was not thoroughly investigated for any of the present compounds except CH$_3$SP(CF$_3$)$_2$; thus HSP(CF$_3$)$_2$ with path 11 cm. and pressure 10 mm. failed to absorb in that range, and (CH$_3$S)$_2$PCF$_3$ was equally blank at 5 mm. pressure; but higher-pressure scans were not attempted.