

plets, each with the two peaks equally intense. Resolution of these doublets was possible only by operating the instrument with the slit as narrow as 0.6 mm., at a high amplifier gain, requiring slow response and low scan speed.

The CF_3 rocking mode, the CF_3 deformations, and the P- CF_3 stretching modes were recognized by analogy to the results of Nabi and Sheppard for the somewhat simpler S- CF_3 compounds.⁶

(6) S. N. Nabi and N. Sheppard, *J. Chem. Soc.*, 3439 (1959).

For the CF_3 δ -e mode we agree also with the range found by Beg and Clark for the methyltrifluoromethylphosphines.⁷

No definite P-P stretching band could be recognized for either compound, although a weak and ragged absorption by the disphosphine in the range 532-540 cm^{-1} (intensity 0.2) might represent this. A similar absorption appeared for $\text{P}_2(\text{CF}_3)_4$ but was uncertain for $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$.

(7) M. A. A. Beg and H. C. Clark, *Can. J. Research*, **40**, 395 (1962).

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The Open-Chain Triphosphine $\text{P}_3(\text{CF}_3)_5$ ¹

By ANTON B. BURG AND JOHN F. NIXON

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The new open-chain triphosphine $\text{P}_3(\text{CF}_3)_5$ (b.p. est. 140°) has been made by the $(\text{CH}_3)_3\text{N}$ -promoted reaction of CF_3PH_2 with $(\text{CF}_3)_2\text{PI}$ or $(\text{CF}_3)_2\text{PCL}$. A minor by-product probably was the hitherto unknown diphosphine $\text{CF}_3\text{HP}-\text{P}(\text{CF}_3)_2$ (volatility 61 mm. at 0°). The new triphosphine can be decomposed quantitatively to $\text{P}_2(\text{CF}_3)_4$ and the ring tetramer and pentamer of PCF_3 ; this process is strongly catalyzed by bases or mildly by mercury, and a hydrocarbon grease yields $(\text{CF}_3)_3\text{PH}$. The infrared spectrum of $\text{P}_3(\text{CF}_3)_5$ shows the expected fundamentals, and the strong ultraviolet absorption at 2210 Å. is like that of other P-P bonded polyphosphines.

The study of P-P open-chain polyphosphines must depend upon the synthesis of substitution derivatives, since the high lability of P-H bonds makes P_2H_4 very unstable, while higher P_nH_{n+2} compounds are unknown. Even a partial replacement of H by less labile groups can greatly improve P_n -chain stability, for both the diphosphine $(\text{HPCF}_3)_2$ and the triphosphine $\text{H}_2(\text{PCF}_3)_3$ are stable enough for convenient synthesis and study²; also the diphosphine $\text{CH}_3\text{HP}-\text{P}(\text{CF}_3)_2$ and the triphosphine $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$ proved to be fairly stable in the absence of catalysts.³ However, most CF_3 -P polyphosphines are catalytically affected by bases; for example, the diphosphine $(\text{CH}_3)_2\text{P}-\text{P}(\text{CF}_3)_2$ is unstable because it contains a moderately basic phosphorus atom.⁴ Also noticeable is catalysis by stopcock greases or mercury; and indeed the latter catalysis doubtless accounts for the failure of earlier attempts to use mercury to convert a mixture of CF_3PI_2 and $(\text{CF}_3)_2\text{PI}$ to the first homosubstituted triphosphine, $\text{P}_3(\text{CF}_3)_5$.

We now have made $\text{P}_3(\text{CF}_3)_5$ by the reaction of either $(\text{CF}_3)_2\text{PI}$ or $(\text{CF}_3)_2\text{PCL}$ with CF_3PH_2 , using $(\text{CH}_3)_3\text{N}$ to promote the reaction by removing the hydrogen halide. This process can succeed only if the catalytic action of $(\text{CH}_3)_3\text{N}$ upon the triphosphine is minimized, as by work at low temperatures or by avoiding any local excess of amine. Thus the best yield was obtained by introducing the amine vapor slowly into the otherwise unreactive mixture of the vapors of CF_3PH_2 and $(\text{CF}_3)_2\text{PCL}$ at -40°. The amine immediately formed $(\text{CH}_3)_3\text{NHCl}$, which precipitated upon the walls of the chamber along with the desired triphosphine; thus there never was appreciable contact of the triphosphine with the amine.

Experimental

The experimental work here described was done by means of a Stock-type high-vacuum manifold, often with halocarbon-greased stopcocks instead of mercury float valves, since mercury or hydrocarbon greases affected the triphosphine, and the iodophosphines were known to be very reactive toward mercury.

(1) This research was supported mostly by the United States Air Force through a subcontract (terminated December 31, 1962) under Contract AF 33(616)-7810, monitored by the Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Certain refinements were accomplished through support by Grant No. GP-199 from the National Science Foundation. We thank the National Science Foundation also for making available a Beckman IR7 infrared spectrophotometer with NaCl and CsI optics, through Grant No. G-14465 and Grant No. GP-199.

(2) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(3) A. B. Burg and K. K. Joshi, *ibid.*, **86**, 353 (1964).

(4) L. R. Grant and A. B. Burg, *ibid.*, **84**, 1834 (1962).

For purification of the triphosphine by high-vacuum fractional condensation methods, the mercury system could be employed, and mercury manometers could be used for molecular weight and vapor tension measurements, under conditions of minimum duration of contact with mercury.

Synthesis of Reactants.—The iodophosphines $(\text{CF}_3)_2\text{PI}$ and CF_3PI_2 were made by the usual process of heating iodine and red phosphorus with CF_3I ,^{5,6} made from iodine and silver trifluoroacetate.⁷ The chlorophosphine $(\text{CF}_3)_2\text{PCL}$ was made by the very convenient reaction of $(\text{CF}_3)_2\text{PI}$ with HgCl_2 . The phosphine CF_3PH_2 was made in 88% yield by the vigorous reaction of CF_3PI_2 with 2PH_3 —a process analogous to the Harris method of making $(\text{CF}_3)_2\text{PH}$.⁸ Its identity was confirmed by its mol. wt. (101 vs. calcd. 102), its 45.0 mm. vapor tension at -78.5°, and its characteristic infrared spectrum.

Exploratory Syntheses of the Triphosphine.—Equimolar amounts of $(\text{CF}_3)_2\text{PI}$, CF_3PH_2 , and $(\text{CH}_3)_3\text{N}$ in a closed tube at -78° rapidly formed a white solid tending to sequester the last of the reactants. Only half of the CF_3PH_2 was consumed, suggesting that $\text{CF}_3\text{PH}_2 + 2(\text{CF}_3)_2\text{PI} + 2(\text{CH}_3)_3\text{N} \rightarrow 2(\text{CH}_3)_3\text{NHI} + \text{P}_3(\text{CF}_3)_5$; however, the yields of $\text{P}_3(\text{CF}_3)_5$ did not exceed 30% and its decomposition products $(\text{PCF}_3)_4$, $(\text{PCF}_3)_5$, and $\text{P}_2(\text{CF}_3)_4$ were abundant. In another type of experiment, $(\text{CH}_3)_3\text{N} + (\text{CF}_3)_2\text{PI} + 43 n\text{-C}_8\text{H}_{12}$ formed a precipitate at -78° (redissolved on slight warming); this was assumed to be a 1:1 adduct susceptible to phosphinolysis. By bubbling CF_3PH_2 repeatedly through the mixture and isolating the product at intermediate stages, a 44% yield of $\text{P}_3(\text{CF}_3)_5$ was obtained.

It was considered that better yields of $\text{P}_3(\text{CF}_3)_5$ might come from using $(\text{CF}_3)_2\text{PCL}$ instead of $(\text{CF}_3)_2\text{PI}$, which tends to lose iodine and form $\text{P}_2(\text{CF}_3)_4$ —a reaction possibly promoted by the amine. However, a mixture proportioned as $\text{CF}_3\text{PH}_2 + 2(\text{CF}_3)_2\text{PCL} + 2(\text{CH}_3)_3\text{N}$ reacted in a simple closed tube to give only a 29% yield of $\text{P}_3(\text{CF}_3)_5$ and a 51% yield of $\text{P}_2(\text{CF}_3)_4$. It seemed that high yields of $\text{P}_3(\text{CF}_3)_5$ could be obtained only by more delicate use of the catalytically destructive amine.

Efficient Synthesis of the Triphosphine.—A cylindrical chamber (5 cm. diameter and 16 cm. high), connected to the high-vacuum manifold through a stopcock by way of a concentric inner-sealed tube reaching nearly to the bottom, was filled with 0.388 mmole of CF_3PH_2 and 0.775 mmole of $(\text{CF}_3)_2\text{PCL}$, which did not react during 2 days at 25°. The chamber was cooled to -40° (reactants not quite condensed) and the central entrance tube was cleared by introduction of just enough dry nitrogen. Now a measured sample of $(\text{CH}_3)_3\text{N}$ was allowed to flow in, encountering the denser CF_3 -phosphine mixture at the bottom of the chamber. When 0.805 mmole of amine had entered (with immediate reaction) the components volatile at -40° were removed for slight further reaction elsewhere. The yield of purified $\text{P}_3(\text{CF}_3)_5$ was 0.317 mmole, or 83% in terms of the equation $\text{CF}_3\text{PH}_2 + 2(\text{CF}_3)_2\text{PCL} + 2(\text{CH}_3)_3\text{N} \rightarrow 2(\text{CH}_3)_3\text{NHCl} + \text{P}_3(\text{CF}_3)_5$. The yield deficiency could be explained by the recovery of traces of $\text{P}_2(\text{CF}_3)_4$ and the PCF_3 tetramer-pentamer mixture. With more accurate control of the introduction of the amine, the method might well become quantitative.

(5) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1568 (1953).

(6) A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber, and D. L. Herring, *J. Am. Chem. Soc.*, **79**, 247 (1957).

(7) A. L. Henne and W. G. Finnegan, *ibid.*, **72**, 3806 (1950).

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

Proof of the Triphosphine Formula.—The vapor densities of three samples of the presumed P₃(CF₃)₅ were measured in the usual mercury-containing immersible tensimeter⁹ at 35, 43, and 51°, with no difficulty when the immersion was done suddenly and the readings taken quickly. The resulting mol. wt. values were 438, 441, and 443 (calcd. 438.0).

Elementary analyses were performed by decomposition of the triphosphine to known CF₃-phosphines, which were isolated, identified, and measured as vapors or weighed. A 29.0-mg. sample (0.0662 mmole) gave 0.197 mg.-atom of P (calcd. 0.199) and 0.329 mmole of CF₃ groups (calcd. 0.331). A 50.5-mg. sample (0.115 mmole) gave 0.115 mmole of PCF₃ units as tetramer and pentamer and 0.230 mmole of P(CF₃)₂ units as P₂(CF₃)₄, quite in accord with the formula P₃(CF₃)₅.

Volatility of the Triphosphine.—The colorless liquid triphosphine P₃(CF₃)₅ could be separated easily from the less volatile PCF₃ tetramer and pentamer by passage slowly under high vacuum through a trap at -35°, and P₂(CF₃)₄ was removed by repeated passage through a trap at -50°. The vapor-tension values shown in Table I were obtained partly with the sample in a small vertical tube with adjacent wide-bore mercury manometer, and partly by means of the immersible tensimeter, with re-purification before each elevated-temperature reading, and with fast establishment of the temperature. The equation was determined partly by assuming a normal Trouton constant of 21.0 cal./deg. mole, and fits the data as well as could be expected in view of the difficulty of the measurements. It indicates the normal b.p. as 140 ± 5°.

The m.p. of P₃(CF₃)₅ could not be observed because it never formed crystals—only a glass or viscous liquid.

TABLE I

VAPOR TENSIONS OF P₃(CF₃)₅

log P _{mm} = 7.1080 + 1.75 log T - 0.00600T - 2616/T							
t, °C.	0.00	8.4	14.6	19.3	23.9	46.1	71.3
P _{mm} (obsd.)	1.43	2.63	3.87	5.34	7.01	24.2	77.2
P _{mm} (calcd.)	1.43	2.60	3.92	5.30	7.03	24.0	77.1

Spectroscopy.—The ultraviolet spectrum of P₃(CF₃)₅ showed a strong maximum at 2210 Å. Such absorption seems to be characteristic of all P-P bonded polyphosphines.

The infrared spectrum of P₃(CF₃)₅ was recorded for the vapor at pressures no higher than 17 mm. (saturated vapor at the 40° constant temperature of the Beckman IR7 instrument), in cells with 100-mm. path length. After each run the sample was investigated for decomposition products, and in order to allow for their possible effects, the spectra of these—namely, P₂(CF₃)₄ and the mixture of PCF₃ tetramer and pentamer—were recorded

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

separately. For most of the pertinent range the cell windows were potassium bromide, but for the lowest frequencies the windows were of polyethylene, as described elsewhere.³

The fundamental frequencies (cm.⁻¹) for P₃(CF₃)₅ and its immediate decomposition products are listed with the probable assignments in Table II. The relative intensities were calculated by the equation $k = (100/P \times L) \log I_0/I$ for pressures and path length in cm., using the values for per cent transmission I at each observed band maximum. The frequencies were corrected by calibration of the instrument at the frequencies of known bands, and are believed to be accurate to 1 cm.⁻¹. Table II omits some ragged and uncertain absorption in the range 530–545 cm.⁻¹ ($k = 0.3$ or less), for both P₃(CF₃)₅ and P₂(CF₃)₄, but not found for the PCF₃ tetramer-pentamer mixture. However, the pressures of the vapor of that mixture never were very high, and the effect might have been missed.

TABLE II

INFRARED SPECTRA OF P₃(CF₃)₅ AND ITS DECOMPOSITION PRODUCTS^a

Probable assignment	—P ₃ (CF ₃) ₅ —		—P ₂ (CF ₃) ₄ —		—(PCF ₃) _{4,5} —	
	Freq.	k	Freq.	k	Freq.	k
C-F stretching	1194	82	1193	74
	1172	113	1169	151	1173	13
	1152	114	1154	64	1154	60
	1133.5	70	1141	84	1135	26
	1119	90	1120	70
CF ₃ , δ-e	747	4.7	749	5.5	742	4
CF ₃ , δ-a	562	1.0	560	1.2	553	0.3
P-C stretching	480	0.16
	455	2.0
	443	2.1	442	6.7	434	1.4
CF ₃ rocking	388	1.2	363	0.4	353?	?
	350	1.5	342	0.6

^a Abbreviations: δ = deformation; e = symmetric; a = asymmetric.

A Probable New Diphosphine.—The initial syntheses of P₃(CF₃)₅ usually gave small yields (e.g., 10%) of a by-product which was not fully characterized but probably was the new diphosphine CF₃HP-P(CF₃)₂. Its vapor tension at 0° was 61 mm. and its vapor-phase mol. wt. was 269.6 vs. calcd. 270.0. Its infrared spectrum did not distinctly show P-H stretching, possibly because the ragged group of C-F stretching overtones covered the expected sharp peak. However, a medium-strong band at 1070 cm.⁻¹ seems assignable to P-H bending. The compound seemed unstable, for repeated high-vacuum fractional condensation always yielded small amounts of the expected decomposition products (CF₃)₂PH and the PCF₃ tetramer and pentamer.

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Synthesis and Chemistry of SF₅Cl

BY C. W. TULLOCK, D. D. COFFMAN, AND E. L. MUETTERTIES

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Sulfur chloride pentafluoride, SF₅Cl, has been prepared in high yield from the reaction of sulfur tetrafluoride, chlorine, and cesium fluoride. Evidence is presented for the intermediate formation of CsSF₅ in this synthesis. Through the ultraviolet light-catalyzed addition of SF₅Cl to nitriles and subsequent substitution or replacement reactions, a wide range of novel SF₅N< derivatives has been prepared.

Synthesis of SF₅Cl.—Sulfur chloride pentafluoride has been prepared by electrolysis of sulfur dichloride-hydrogen fluoride mixtures,¹ by chlorination of disulfur decafluoride,² by reaction of sulfur dichloride and fluorine,³ and by addition of chlorine fluoride to sulfur tetrafluoride.⁴ Only the last method has given good conversions to SF₅Cl.

We have now found a simple, high-yield synthesis of SF₅Cl in a novel chlorofluorination of sulfur tetrafluoride.



- (1) E. L. Muetterties, U. S. Patent 2,937,123 (1960).
- (2) J. W. George and F. A. Cotton, *Proc. Chem. Soc.*, 317 (1959).
- (3) H. L. Roberts and N. H. Ray, *J. Chem. Soc.*, 665 (1960).
- (4) F. Nyman and H. L. Roberts, *ibid.*, 3180 (1962).

Other metal fluorides, e.g., potassium fluoride and silver(I) fluoride, have been successfully substituted for cesium fluoride. However, the conversions to SF₅Cl were substantially lower, 5–22% as compared to 70–80% with cesium fluoride.

We have demonstrated that cesium fluoride absorbs sulfur tetrafluoride beginning at about 110° in a sealed reactor to yield the cesium salt of the novel SF₅⁻ anion



This anion presumably is isostructural with bromine pentafluoride and iodine pentafluoride. Since this salt is significantly dissociated at about 150°, it is necessary to maintain a high sulfur tetrafluoride pressure in