

ever, in the range pH 10.38–8.85 covered in the present experiments the predominant effect as far as the mercaptide group is concerned is the conversion of  $\text{DMP}^{-2}$  to  $\text{DMPH}^-$ . This can be seen in Table II where the fraction of each of the protonated forms of DMP and cystine is given.

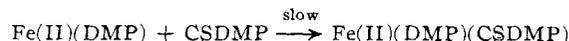
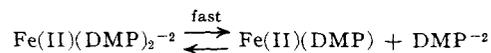
There are not sufficient data nor are the proton dissociation constants for cystine known with sufficient accuracy to warrant resolving the pH dependence of  $k'$  (i.e.,  $k_2$ ) into constants for all of the possible reactions between the various species. Since the values of  $k'$  increase as the pH decreases and since the concentrations of  $\text{DMP}^{-2}$  and  $\text{CSCC}^-$  profoundly decrease in this pH interval it seems unlikely that the path involving these species is important. Quite clearly the activated complexes are more or less protonated. Protonation would increase the reactivity both by decreasing the total negative charge of the activated complex and, through the inductive effect of the positive ammonium groups, increase the electrophilicity of cystine.

Some estimate of the maximum values of the individual rate constants can be obtained as follows. If at pH 8.85 the exchange proceeds only *via* reaction of the major species  $\text{DMPH}^-$  and  $\text{HCSSC}^-$ , the data would yield an absolute rate constant between these ions of about 0.04 l. mole<sup>-1</sup> sec.<sup>-1</sup>. On the other hand, if  $\text{DMP}^{-2}$  and  $\text{HCSSCH}$  were the only reactive species, the absolute value of the rate constant would be 17.6 l. mole<sup>-1</sup> sec.<sup>-1</sup>. The former of these rate constants is somewhat smaller than those reported<sup>22</sup> for thiol-disulfide exchange for unhindered, unstrained alkyl systems in methanol, while the latter is somewhat greater.

The second step of the consecutive  $\text{CSCC-Fe}(\text{DMP})_2^{-2}$  reaction involves two parallel Fe(II) dependent paths both of which display an inverse dependence on DMP. This observation suggests that predissociation of coordinated DMP is involved. The over-all hydrogen ion dependence of  $k''$  is also consistent with this provided  $\text{DMP}^{-2}$  is more basic than  $\text{CSDMP}^-$ . This seems to be likely since  $\text{DMP}^{-2}$  is

more basic than  $\text{CSCC}^-$ , and therefore  $\text{CSDMP}^-$  probably occupies an intermediate position.

The path first order in Fe(II) can be explained by reactions such as



The complex  $\text{Fe(II)(DMP)(CSDMP)}$  may then react rapidly with  $\text{Fe(II)(DMP)}_2^{-2}$  to give two Fe(III) in a two-electron transfer or may react in a one-electron transfer step to give a free radical.

The path second order in iron(II), which is the predominant path, shows the formation of a polynuclear activated complex. It is tempting to consider this activated complex to be analogous to the polynuclear intermediates formed in the oxidation of mercaptide by iron(III), with a two-electron transfer mediated by the complex.

The results can also be explained on the basis of the disulfide  $(\text{DMP})_2$  being the reactive intermediate instead of CSDMP. This would be the case if CSDMP reacted rapidly with DMP to give  $(\text{DMP})_2$ . Although it does not seem likely that the second molecule of DMP would react faster than the first, this possibility cannot be ruled out. For CSDMP to be the intermediate the results of the pre-equilibration experiments require that  $(\text{DMP})_2$  be appreciably less stable than  $\text{CSCC}$ . On the other hand, if  $(\text{DMP})_2$  were the intermediate, a statistical distribution of species would be consistent with the observations.

The increase in the disulfide reactivities in the order  $\text{CSCC} < \text{CSDMP}$  or  $(\text{DMP})_2 < \text{CSDMPDMPCS}$  is another interesting observation of this work. The difference in reactivities may arise to some extent from the abilities of these ligands to coordinate to Fe(II). The order of reactivities, at least with  $\text{CSCC}$  and  $\text{CSDMP}$  or  $(\text{DMP})_2$ , is in the same order as their coordination tendency.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

## The New Open-Chain Polyphosphines $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$ and $\text{CH}_3\text{P}\{\text{P}(\text{CF}_3)_2\}_2^1$

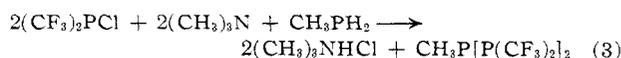
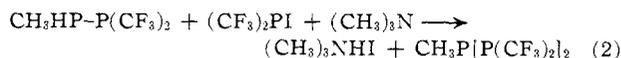
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The phosphine  $\text{CH}_3\text{PH}_2$  reacts with  $(\text{CF}_3)_2\text{PI}$  at  $-78^\circ$ , quantitatively forming  $\text{CH}_3\text{PH}_2\text{I}$  and the new diphosphine  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  (b.p. est.  $92^\circ$ ). This is decomposed by heat or light, quantitatively forming  $(\text{CF}_3)_2\text{PH}$  and material having the composition of the  $(\text{CH}_3\text{P})_n$  polymers. It is cleaved by HCl to make  $\text{CH}_3\text{PH}_2\text{Cl}$  and  $(\text{CF}_3)_2\text{PCl}$ ; or by reaction with  $(\text{CF}_3)_2\text{PI}$  and  $(\text{CH}_3)_3\text{N}$  it is almost wholly converted to the somewhat stabler new triphosphine  $\text{CH}_3\text{P}\{\text{P}(\text{CF}_3)_2\}_2$  (m.p.  $-66^\circ$ , b.p. est.  $151^\circ$ ). The same triphosphine is made almost quantitatively by the action of  $(\text{CF}_3)_2\text{PCl}$  upon a mixture of  $\text{CH}_3\text{PH}_2$  and  $(\text{CH}_3)_3\text{N}$  at  $-40^\circ$ . The ultraviolet absorption spectra of both new chain phosphines indicate delocalization of the lone-pair electrons, and their infrared spectra correspond to the expected structural components.

The P–P bond offers promise of many uniquely interesting compounds, each leading to a wide variety of new chemistry. The present work is concerned with two new types: the first of many possible trisubstituted diphosphines and the first fully substituted triphosphine. These were made by the virtually quantitative processes 1–3.

(1) This research was supported mostly by the United States Air Force through a subcontract under Contract AF 33(616)-6913 (terminated December 31, 1960), 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 are also grateful to the National Science Foundation for providing our department with a Beckman IR7 infrared spectrophotometer through Grant No. G-14465 and for permission to obtain the related cesium iodide optics through Grant No. GP-199.



The new triphosphine is stable enough to encourage the search for many other  $\text{P}_3\text{R}_5$  compounds, as well as a wide exploration of their chemical consequences. The formation of  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  by reaction 1 may be closely analogous to an intermediate stage of the  $\text{PH}_3-(\text{CF}_3)_2\text{PI}$  reaction to make  $(\text{CF}_3)_2\text{PH}$ ,<sup>2</sup> for the decompo-

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

sition  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2 \rightarrow (\text{CF}_3)_2\text{PH} + (\text{CH}_3\text{P})$  occurs easily and quantitatively. The  $(\text{CH}_3\text{P})$  part was not specifically identified, but may represent a new way to make the  $(\text{CH}_3\text{P})_n$  polymer series.<sup>3</sup> The formation of such material suggests an especial chemical availability of the  $\text{CH}_3\text{P}$  unit during the decomposition, and accordingly there were some attempts to utilize it by decomposing  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  in the presence of  $\text{CF}_3\text{I}$ . In just one experiment there was evidence for the reaction  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2 + \text{CF}_3\text{I} \rightarrow (\text{CF}_3)_2\text{PH} + \text{CH}_3\text{CF}_3\text{-PI}$ , but numerous repetitions of the experiment (including attempts by Dr. John F. Nixon) failed to confirm this result.

The following sections describe the experimental basis of our present knowledge of the new diphosphine and triphosphine. The work was done by quantitative high-vacuum methods, using a manifold with Stock-type mercury float valves when feasible. Mercury-sensitive substances were managed in a halocarbon-greased stopcock system, with a Pyrex glass spoon gage<sup>4</sup> serving as a null manometer.

### 1-Methyl-2,2-bis-(trifluoromethyl)-diphosphine

**Synthesis.**—Three experiments based upon eq. 1 are summarized by Table I. Each container was a sealed 15-ml. Pyrex tube, kept overnight at  $-78^\circ$  for completion of the reaction. For best results, initial mixing was important; and with larger reaction mixtures it was more difficult to approach quantitative yields.

TABLE I  
SYNTHESIS OF  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$

Expt.	—Reactants, mmoles—		$\text{CH}_3\text{HP-P}(\text{CF}_3)_2$ obtained	
	$(\text{CF}_3)_2\text{PI}$	$\text{CH}_3\text{PH}_2$	mmoles	Yield, %
1	7.49	15.84	7.12	95.1
2	13.29	26.55	12.26	92.3
3	1.059	2.196	1.058	99.9

The desired diphosphine was isolated by high-vacuum fractional condensation, passing a trap at  $-45^\circ$  and condensing at  $-63^\circ$ . The per cent yields were based upon  $(\text{CF}_3)_2\text{PI}$ .

**Proof of the Formula.**—The composition of the new diphosphine was determined by the quantitative stoichiometry of expt. 3. The recovery of 0.076 mmole of  $\text{CH}_3\text{PH}_2$  implied a reaction ratio of 2.002  $\text{CH}_3\text{PH}_2$  per  $(\text{CF}_3)_2\text{PI}$ . The salt  $\text{CH}_3\text{PH}_2\text{I}$  appeared as a slightly volatile yellow residue, which reacted with 1.061 mmoles (2.146 available) of  $(\text{C}_2\text{H}_5)_3\text{N}$ , leading to the recovery of 1.046 mmoles of  $\text{CH}_3\text{PH}_2$ : calcd. per eq. 1, 1.061 mmoles. The recovered  $\text{CH}_3\text{PH}_2$  was identified by its 28.4 mm. vapor tension at  $-78.5^\circ$  (calcd. 28.8) and mol. wt. 48.2 (calcd. 48.0). Thus all reactants and products agreed quantitatively with eq. 1, so that the results were equivalent to an elementary analysis of the diphosphine. The molecular weight was determined in the vapor phase (half-saturated at  $25^\circ$ ), as 215 (calcd. 216.0).

**Volatility.**—The vapor tension measurements shown in Table II were difficult to make on account of the instability of the diphosphine in a glass-mercury system, but fairly good results were obtained by repurifying the sample before each measurement. The equation gives the normal b.p. as  $91.6^\circ$  and the Trouton constant as 21.8 cal./deg. mole. Such a Trouton constant indicates good purity, although this could not be confirmed by the m.p., on account of glass formation.

TABLE II  
VAPOR TENSIONS OF  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$

	$\log P_{\text{mm}} = 6.1043 + 1.75 \log T - 0.00500T - 2146/T$						
t, °C.	-45.6	-37.3	-30.7	-23.3	0.00	12.0	18.2
$P_{\text{mm}}$ , obsd.	0.53	0.94	1.64	2.92	13.98	28.3	39.2
$P_{\text{mm}}$ , calcd.	0.46	0.99	1.64	2.90	14.00	28.1	39.3

(3) Such polymers were approached earlier by Ross I. Wagner, working in these laboratories in the year 1953, under a post-doctoral research grant from American Potash and Chemical Corporation. He had made the bisphosphine  $\text{CH}_3\text{HPCH}_2\text{PHCH}_3$  by the reaction between  $\text{H}_2\text{CCl}_2$  and  $2\text{Na-PHCH}_3$  in liquid ammonia and found that it decomposed below room temperature, quantitatively forming  $(\text{CH}_3)_2\text{PH}$  and solid material having the composition  $(\text{CH}_3\text{P})_n$ , volatile only at elevated temperatures. In more recent times, simpler approaches to (alkyl-P)<sub>n</sub> compounds have been found by K. Issleib and B. Mitscherling, *Z. Naturforsch.*, **15b**, 267 (1960), and by V. N. Kulakova, Yu. M. Zinoviev, and L. Z. Soborovskii, *Zh. Obshch. Khim.*, **29**, 3957 (1959) (*Eng. Trans.*, **29**, 3916).

(4) T. E. Phipps, M. L. Spealman, and T. G. Cooke, *J. Chem. Educ.*, **13**, 318 (1935).

**Decomposition.**—The diphosphine  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  proved to be fairly stable under normal laboratory conditions; indeed, two samples in sealed tubes were not quite all decomposed after 2.5 years, possibly be cause of solubility in a polymeric product. However, a sample exposed for 20 hr. to bright sunlight through Pyrex was 92% decomposed, and another was all decomposed during 6 hr. at  $160^\circ$ . In each case the decomposed material afforded a 99% yield of  $(\text{CF}_3)_2\text{PH}$ , which was identified by its mol. wt. (170, as calcd.), its 6.3 mm. vapor tension at  $-78.5^\circ$ ,<sup>5</sup> and agreement with the known infrared spectrum. Thus both decompositions indicated the equation  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2 \rightarrow (\text{CF}_3)_2\text{PH} + (\text{CH}_3\text{P})$ , with the  $\text{CH}_3\text{P}$  part appearing as a highly viscous liquid (colorless unless heated), not volatile at  $25^\circ$ . Catalysis by mercury or tertiary amines may cause a similar decomposition, but the products have not been explored.

**The Cleavage by Hydrogen Chloride.**—The reaction  $2\text{HCl} + \text{CH}_3\text{HP-P}(\text{CF}_3)_2 \rightarrow (\text{CF}_3)_2\text{PCL} + \text{CH}_3\text{PH}_2\text{Cl}$  occurred quantitatively during 20 hr. at  $-78^\circ$ , again confirming the formula of the diphosphine. In this experiment 1.121 mmoles of  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  consumed 2.27 mmoles (from 2.37) of HCl, forming 1.119 mmoles (99.8% yield) of  $(\text{CF}_3)_2\text{PCL}$  and 1.122 mmoles of  $\text{CH}_3\text{PH}_2\text{Cl}$  (100.1% yield). The  $(\text{CF}_3)_2\text{PCL}$  was identified by its infrared spectrum, mol. wt. (203 vs. calcd. 204.45), and characteristic vapor tensions. Upon evaporation, the  $\text{CH}_3\text{PH}_2\text{Cl}$  was completely dissociated to HCl and  $\text{CH}_3\text{PH}_2$ , showing an average mol. wt. value of 42.3 (calcd. 84.49/2); and after removal of the HCl the weight of  $\text{CH}_3\text{PH}_2$  represented 56.95% of the  $\text{CH}_3\text{PH}_2\text{Cl}$  (calcd. 56.84%).

At room temperature the HCl cleavage was accompanied by an equal amount of decomposition, for 1.664 mmoles of the diphosphine was wholly destroyed during 24 hr., but consumed only an equimolar portion of HCl (1.645 mmoles from 2.568 available). The yield of  $(\text{CF}_3)_2\text{PCL}$  was only 0.835 mmole (50.2%) and of  $\text{CH}_3\text{PH}_2\text{Cl}$  only 0.811 mmole (48.7%); and the decomposition product  $(\text{CF}_3)_2\text{PH}$  appeared in 50.2% yield (0.835 mmole). Thus the nonvolatile product corresponded to 0.853 mmole of  $\text{CH}_3\text{P}$  units.

Two attempts to cleave  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  by action of  $\text{B}_2\text{H}_6$  were unsuccessful: both components decomposed very slightly in normal daylight but were almost completely recovered after 16 hr. at room temperature. No  $\text{BH}_3$  adduct could be made by cooling the mixture to  $-116^\circ$ , evidently because neither of the phosphorus atoms would exert enough base strength.

### 2-Methyl-1,1,3,3-Tetrakis-(trifluoromethyl)-triphosphine

**Synthesis.**—The initial observation of the triphosphine  $\text{CH}_3\text{P-P}(\text{CF}_3)_2$  came during the first attempt to make the diphosphine  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  by the reaction of 2.93 mmoles each of  $(\text{CF}_3)_2\text{PCL}$ ,  $\text{CH}_3\text{PH}_2$ , and  $(\text{CH}_3)_3\text{N}$  in solution in 10 ml. of ether. After 16 hr. at  $-78^\circ$ , the phosphinolysis had gone well past the first stage, giving only a 16% yield of the diphosphine and much more triphosphine. Similarly, 4.4 mmoles each of the same reactants in 6 ml. of ether, again during 16 hr. at  $-78^\circ$ , gave a 9% yield of the diphosphine and almost a 50% yield of the triphosphine.

In the first approach toward a quantitative synthesis of the triphosphine, 0.659 mmole of  $\text{CH}_3\text{HP-P}(\text{CF}_3)_2$  and 0.662 mmole of  $(\text{CF}_3)_2\text{PI}$  were first allowed to stand together *in vacuo* without solvent at  $-78^\circ$ , producing no HI; and then  $(\text{CH}_3)_3\text{N}$  was added for the abstraction of HI, with the mixture now in a sealed tube. After warming up and remaining for 14 hr. at  $25^\circ$ , the mixture was subjected to high-vacuum fractional condensation, yielding a trace of material which passed a trap at  $-45^\circ$ , while the main volatile component very slowly passed a  $-30^\circ$  trap and condensed at  $-36^\circ$ . The recovery of this product was 234.2 mg., or 92.4% if it be interpreted as  $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$ ; and some loss could be ascribed to catalytic destruction by grease and mercury.

A slightly cleaner synthesis of the triphosphine was done in a 100-ml. vertical tube, attached to the high-vacuum manifold through a halocarbon greased stopcock. A mixture of 1.017 mmoles of  $(\text{CH}_3)_3\text{N}$  and 0.501 mmole of  $\text{CH}_3\text{PH}_2$ , in the reaction tube at  $-40^\circ$ , was treated with 1.086 mmoles of  $(\text{CF}_3)_2\text{PCL}$ , added slowly through the stopcock. Thus the dense vapor of the chlorophosphine could fall through the mixture, reacting rapidly to precipitate  $(\text{CH}_3)_3\text{NHCl}$  and finally the desired triphosphine on the tube wall. Under such conditions there was only a minimal chance of an undesired P-H to P-Cl exchange reaction; and in fact no  $(\text{CF}_3)_2\text{PH}$  could be detected as an immediate reaction product. For sure completion of the amine-induced phosphinolysis, the reaction mixture was distilled completely over into a second tube, where scarcely any further reaction was apparent after a brief period at  $25^\circ$ . Then 0.018 mmole of  $(\text{CH}_3)_3\text{N}$  and 0.089 mmole of  $(\text{CF}_3)_2\text{PCL}$  were recovered by fractional condensation through a trap at  $-78^\circ$ . The demonstrable yield of the triphosphine was 0.471 mmole, or 94% of that expected in terms of the equation  $2(\text{CH}_3)_3\text{N} + \text{CH}_3\text{PH}_2 + 2(\text{CF}_3)_2\text{-}$

(5) A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958).

$\text{PCl} \rightarrow 2(\text{CH}_3)_3\text{NHC}l + \text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$ . Again the deficiency of yield could be attributed to decomposition during handling in the high-vacuum system and in weighing.

**Chemical Behavior.**—The triphosphine  $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$  may well have long-range stability when stored in contact only with Pyrex glass at room temperature, for a trace of it was found in a sealed tube in which a sample of  $\text{CH}_3\text{HP}-\text{P}(\text{CF}_3)_2$  had decomposed almost completely during 2.5 years. However, the decomposition of a triphosphine sample was complete after 20 hr. in a sealed tube at  $160^\circ$ . It was possible to obtain good vapor-tension measurements by fast equilibrations up to  $60^\circ$ , and good mol. wt. measurements for the vapor at  $75^\circ$ , but a sample of the liquid triphosphine in contact only with Pyrex glass and mercury during 40 hr. at  $25^\circ$  was 3% decomposed according to the equation  $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2 \rightarrow (\text{CH}_3\text{P}) + \text{P}_2(\text{CF}_3)_4$ . Brief contact with Apiezon L grease produced  $\text{P}_2(\text{CF}_3)_4$  and  $(\text{CF}_3)_3\text{PH}$ . These products were separated easily by high-vacuum fractional condensation (traps at  $-60$ ,  $-78$ , and  $-196^\circ$ ) and identified by their unique patterns of infrared C-F stretching bands. These are listed in order of decreasing intensity; for  $(\text{CF}_3)_2\text{PH}$ , 1178 = 1129, 1125, 1144, 1139 = 1211  $\text{cm}^{-1}$ ; for  $\text{P}_2(\text{CF}_3)_4$ , 1169, 1140, 1193, 1120, and 1155  $\text{cm}^{-1}$ .

Attempts to cleave the triphosphine by either  $\text{CH}_3\text{PH}_2$  or  $\text{HCl}$ , to form  $\text{CH}_3\text{HP}-\text{P}(\text{CF}_3)_2$ , did not succeed. During 12 hr. at  $-78^\circ$  or 1 hr. at  $-40^\circ$  there was no reaction in either case, and during a 0.5 hr. at room temperature there was only slight decomposition to form  $\text{P}_2(\text{CF}_3)_4$  and  $(\text{CF}_3)_2\text{PH}$ .

**Physical Properties.**—The molecular weight of the triphosphine was determined for each of two separately-derived samples of the triphosphine, confirming the formula indicated by the virtually quantitative syntheses. The vapor-density measurements were at  $74^\circ$  and 42 mm. and at  $75^\circ$  and 29 mm., respectively. Both determinations gave the mol. wt. as 385 (calcd. 383.98), presumably with fortuitous accuracy due to a balance between van der Waals forces and slight decomposition.

When distilled rapidly to a trap at  $-196^\circ$ , the triphosphine condensed mostly as a glass, but a very slow process of condensation at  $-196^\circ$  often produced a solid melting sharply at  $-66^\circ$ .

The vapor tensions of a 0.4-mmole sample of the triphosphine were measured in an immersible tensimeter of 140-ml. volume, with rapid readjustments of the temperature between measurements. The results shown in Table III are  $\log P$  and  $1/T$

TABLE III

VAPOR TENSIONS OF $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$						
$\log P_{\text{mm}} = 7.5474 + 1.75 \log T - 0.006350T - 2786/T$						
$t, ^\circ\text{C}.$	0.00	11.7	22.6	30.6	39.6	50.6
$P_{\text{mm}}$ (obsd.)	.73	1.76	3.76	6.23	10.52	19.96
$P_{\text{mm}}$ (calcd.)	.75	1.79	3.75	6.18	10.48	20.02

averages of adjacent points. The equation gives the normal b.p. as  $151^\circ$  and the Trouton constant as 21.2 cal./deg. mole, suggesting acceptable purity.

### Absorption Spectra

**Ultraviolet.**—In any P-P bonded polyphosphine the lone-pair electrons of phosphorus must be at least slightly delocalized by interaction with adjacent P atom orbitals having mostly 3d character. In such compounds as  $\text{CH}_3\text{HP}-\text{P}(\text{CF}_3)_2$  and  $\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2$  the lone-pair electrons on the especially electronegative  $-\text{P}(\text{CF}_3)_2$  group should be more tightly bound to their P atom, and so a little less delocalized than those on the more strongly basic  $\text{CH}_3\text{P}=\text{P}$  group. Hence there should be some difference in the frequencies of maximum ultraviolet absorption by the different lone-pairs in each compound.

In the actual spectra (recorded by the Cary Model 14 ultraviolet spectrophotometer) the effect is recognizable only as an unusually high minimum (possibly covering a submerged peak) on the low wave-length side of the main peak for each compound. For the diphosphine the maximum is at  $2170 \text{ \AA}$ , with molar extinction coefficient  $\epsilon$  7804, while the fairly wide minimum is at  $2025 \text{ \AA}$ , with  $\epsilon$  6280. The triphosphine shows a flatter maximum at  $2200 \text{ \AA}$ . ( $\epsilon$  3980) and a very shallow minimum at  $2100 \text{ \AA}$ . ( $\epsilon$  3900).

**Infrared.**—The infrared spectra of the new diphosphine and triphosphine were recorded at fairly high resolution by the Beckman IR7 instrument, using NaCl and CsI optics. For the frequency range below  $650 \text{ cm}^{-1}$  the cell windows were 0.5 mm. thick rolled-sheet polyethylene, previously heated to the point of visible transparency to remove crystallinity. This material proved to be rigid enough that a 40-mm. disk would not collapse under vacuum when fixed to the cell-body by the O-ring method; and the empty-cell absorption was only about 15%, without specific bands or short-range deviations.

The instability of these phosphines required special care for recognition of the true spectra. Each sample was investigated after each run, and when impurities were found, their spectra

were recorded in order to determine what bands should be ascribed solely to them. Decomposition was minimal when the samples were wholly in the vapor phase, but usually was appreciable when liquid was present at the  $40^\circ$  temperature of the cell chamber—as when weak bands were sought in slow scans of the saturated vapor.

The frequencies of the diphosphine and triphosphine (Table IV) agree with the expected vibrational modes about as well as could be expected, considering that some bands should be very weak. Much experience has shown that C-H stretching bands for hydrocarbon-P-CF<sub>3</sub> compounds are especially weak and difficult to record, presumably because the C-H stretching does not vary the polarity much relative to the rest of the molecule. The present compounds offer no exception to this rule. Indeed, the triphosphine, having two relatively polar  $\text{P}(\text{CF}_3)_2$  groups, clearly showed only one C-H stretching band; some extremely weak absorption around 3015 and 3030  $\text{cm}^{-1}$  might have been due to impurities. On the other hand, the  $\text{CH}_3$  deformation modes showed clearly enough; and indeed these usually do appear well enough in many such compounds.

The assignment of the 2335  $\text{cm}^{-1}$  band to P-H stretching seems clear enough, although accurate estimates of the frequency and intensity were made difficult by the interference of a somewhat less intense record of the 2348  $\text{cm}^{-1}$  band of  $\text{CO}_2$ . The assignment of the 1000  $\text{cm}^{-1}$  band to P-H bending is based upon the absence of any such band for the triphosphine; and then the relatively low frequencies ascribed to  $\text{CH}_3$  rocking and wagging in the diphosphine would be ascribed to the large mass of the  $\text{P}(\text{CF}_3)_2$  group. However, a wagging frequency for  $\text{CH}_3$  in the triphosphine could not be found—possibly because it was covered by the  $\text{CF}_3$  symmetric deformation band at 743  $\text{cm}^{-1}$ .

Assuming that the P- $\text{CH}_3$  stretching bands are correctly assigned, the lower frequency for the triphosphine would be ascribed to the greater reduced mass of a  $\text{CH}_3\text{P}$  group carrying two  $\text{P}(\text{CF}_3)_2$  groups instead of one.

TABLE IV  
INFRARED SPECTRA OF TWO CHAIN PHOSPHINES<sup>a</sup>

Expected mode	$-\text{CH}_3\text{HP}-\text{P}(\text{CF}_3)_2-$		$-\text{CH}_3\text{P}[\text{P}(\text{CF}_3)_2]_2-$		
	Freq.	$k$	Freq.	$k$	
C-H stretching	2990	0.2	Uncertain		
	2936	0.7	2937	0.3	
	2841	0.15	..	..	
P-H stretching	2335 ± 5	2	..	..	
C-F stretching overtones	2304	0.3	2271	0.4	
	2253	0.5	2246	0.65	
$\text{CH}_3, \delta\text{-a}$	1432	1.0	1430	1.6	
	$\text{CH}_3, \delta\text{-e}$	1300	0.5	1298	1.1
C-F stretching		1280	0.6	..	..
	1190	45	1184	80	
	1187				
	1161	49	1159	72	
	1156				
	1134		44	1129	64
	1130	1124 sh			
		1115	35	..	..
	Uncertain	1026 sh	0.2	..	..
	P-H bending	1000	2.4	..	..
$\text{CH}_3$ rocking	895	1.2	894	5.6	
$\text{CH}_3$ wagging	781	0.8	..	..	
$\text{CF}_3, \delta\text{-e}$	746	1.5	743	3.1	
	742				
P- $\text{CH}_3$ stretching	707	0.3	676	0.1	
$\text{CF}_3, \delta\text{-a}$	560	0.6	559	1.8	
P- $\text{CF}_3$ stretching	476	1.1	476	1.2	
	445	1.8	441	4.6	
$\text{CF}_3$ rocking	..	..	331	0.8	

<sup>a</sup> Frequencies are given in  $\text{cm}^{-1}$ , and with one exception are accurate to about  $1 \text{ cm}^{-1}$ . Relative intensities were calcd. by the equation  $k = \frac{100}{P \times L} \log \frac{I_0}{I}$  for pressures  $P$  and path length  $L$  in cm., using the values for per cent transmission  $I$  at each observed band maximum. Abbreviations:  $\delta$  = deformation; a = asymmetric; e = symmetric; sh = shoulder.

The C-F stretching overtones and combinations are not well described in Table IV, for they actually appeared as a wide, ragged band with peaks and shoulders, especially in the spectrum of the triphosphine. It is interesting that three of the C-F stretching fundamentals for the diphosphine appeared as dou-

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  $\text{CF}_3$  rocking mode, the  $\text{CF}_3$  deformations, and the P- $\text{CF}_3$  stretching modes were recognized by analogy to the results of Nabi and Sheppard for the somewhat simpler S- $\text{CF}_3$  compounds.<sup>6</sup>

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

For the  $\text{CF}_3$   $\delta$ -e mode we agree also with the range found by Beg and Clark for the methyltrifluoromethylphosphines.<sup>7</sup>

No definite P-P stretching band could be recognized for either compound, although a weak and ragged absorption by the diphosphine in the range 532-540  $\text{cm}^{-1}$  (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 $\text{P}_3(\text{CF}_3)_5$ <sup>1</sup>

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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  $\text{CF}_3\text{PH}_2$  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  $\text{PCF}_3$ ; this process is strongly catalyzed by bases or mildly by mercury, and a hydrocarbon grease yields  $(\text{CF}_3)_2\text{PH}$ . 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  $\text{P}_2\text{H}_4$  very unstable, while higher  $\text{P}_n\text{H}_{n+2}$  compounds are unknown. Even a partial replacement of H by less labile groups can greatly improve  $\text{P}_n$ -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 study<sup>2</sup>; 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.<sup>3</sup> However, most  $\text{CF}_3$ -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.<sup>4</sup> 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  $\text{CF}_3\text{PI}_2$  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  $\text{CF}_3\text{PH}_2$ , 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  $\text{CF}_3\text{PH}_2$  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.

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(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  $\text{CF}_3\text{PI}_2$  were made by the usual process of heating iodine and red phosphorus with  $\text{CF}_3\text{I}$ ,<sup>5,6</sup> made from iodine and silver trifluoroacetate.<sup>7</sup> The chlorophosphine  $(\text{CF}_3)_2\text{PCL}$  was made by the very convenient reaction of  $(\text{CF}_3)_2\text{PI}$  with  $\text{HgCl}_2$ . The phosphine  $\text{CF}_3\text{PH}_2$  was made in 88% yield by the vigorous reaction of  $\text{CF}_3\text{PI}_2$  with  $2\text{PH}_3$ —a process analogous to the Harris method of making  $(\text{CF}_3)_2\text{PH}$ .<sup>8</sup> 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  $(\text{CF}_3)_2\text{PI}$ ,  $\text{CF}_3\text{PH}_2$ , 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  $\text{CF}_3\text{PH}_2$  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,  $(\text{CH}_3)_3\text{N} + (\text{CF}_3)_2\text{PI} + 43 n\text{-C}_5\text{H}_{12}$  formed a precipitate at -78° (redissolved on slight warming); this was assumed to be a 1:1 adduct susceptible to phosphinolysis. By bubbling  $\text{CF}_3\text{PH}_2$  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  $\text{CF}_3\text{PH}_2$  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  $\text{CF}_3$ -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  $\text{PCF}_3$  tetramer-pentamer mixture. With more accurate control of the introduction of the amine, the method might well become quantitative.

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