$B_2(SH)_4$, would result from the treatment of B_2Cl_4 with hydrogen sulfide. This view was borne out. Nevertheless, hydrogen sulfide did react with B_2Cl_4. At low temperatures, simple Lewis adducts were obtained; and at room temperature and above, extensive cleavage of the boron–boron bond occurred. That hydrogen sulfide is far more effective than water in cleaving the boron–boron bond may be seen from the following comparisons. B_2Cl_4 and water (the latter in slight excess) produced no hydrogen over a period of 24 hr. at room temperature, while 57% of the theoretical quantity of hydrogen was released in 15 hr. when hydrogen sulfide was employed under similar conditions. Under conditions where hydrogen sulfide caused quantitative boron–boron bond cleavage (90° for 72 hr.), the use of water released only 6.8% of the theoretical quantity of hydrogen.

In view of the fact that four different boron-containing substances (BCl_3, B_2S_3, BCl_2SH and $B_3S_3Cl_3$) resulted from the quantitative destruction of B_2Cl_4 by hydrogen sulfide, no simple interpretation of the reaction seems feasible. However, since trichloroborane and boron sulfide were the major products, it is likely that BCl_2SH and $B_3S_3Cl_3$ were formed through secondary reaction. Since a mixture of boron sulfide, trichloroborane and hydrogen sulfide was shown to yield BCl_2SH, it is possible that the latter results from exchange between thioboric acid and trichloroborane.

$$2B(SH)_3 + 4BCl_3 \xrightleftharpoons{90^\circ} 6BCl_2SH$$

The thioboric acid might result from the action of hydrogen sulfide on boron sulfide.

$$B_2S_3 + 3H_2S \xrightleftharpoons{90^\circ} 2B(SH)_3$$

Of particular interest is the fact that BCl_2SH is capable of existence at all, in view of the fact that the oxygen analog, BCl_2OH, has not been prepared.

The Lewis adducts, $B_2Cl_4\cdot SMe_2$ and $B_2Cl_4\cdot 2SMe_2$, appear to be more stable than their oxygen analogs. While $B_2Cl_4\cdot 2OMe_2$ decomposes readily to yield $B_2Cl_4\cdot OMe_2$ and dimethyl ether at room temperature,[5] no dimethyl sulfide was recoverable from $B_2Cl_4\cdot 2SMe_2$ at 25° The increased stability of the alkyl sulfide addition compounds over that of the corresponding etherates is not unexpected, in view of the fact that similar trichloroborane–sulfide complexes (using diethyl sulfide and di-*n*-butyl sulfide) are more stable to cleavage and dissociation than the analogous trichloroborane–ether complexes.[18]

Acknowledgment.—The authors are grateful to the Callery Chemical Company for their financial support of this work.

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(18) Lappert, *J. Chem. Soc.*, 2784 (1953).

UNIVERSITY PARK, PENNA.

[CONTRIBUTION FROM THE PENNSYLVANIA STATE UNIVERSITY, COLLEGE OF CHEMISTRY AND PHYSICS, DEPARTMENT OF CHEMISTRY]

The Reaction of Cyanogen with Diboron Tetrachloride and with Boron Halides[1]

BY E. F. APPLE AND THOMAS WARTIK

RECEIVED JULY 7, 1958

The reactions of cyanogen with diboron tetrachloride and with boron trihalides did not yield volatile products. With diboron tetrachloride, a brown solid with the empirical composition $B_2Cl_4\cdot 1.5(CN)_2$ resulted. This material was decomposed by air and by water and absorbed 2 moles of trimethylamine per mole of $B_2Cl_4\cdot 1.5(CN)_2$. On heating to 400°, it released one mole of BCl_3 per mole of $B_2Cl_4\cdot 1.5(CN)_2$. The structures of $B_2Cl_4\cdot 1.5(CN)_2$ and the material obtained through its pyrolysis ($BCl(CN)_3$) are discussed. Cyanogen was found not to react with trifluoroborane, but the adducts $BCl_3\cdot(CN)_2$, $(BCl_3)_2\cdot(CN)_2$, $BBr_3\cdot(CN)_2$ and $(BBr_3)_2\cdot(CN)_2$ were prepared

In view of the previously observed reactivities of chlorine and bromine with B_2Cl_4,[2] the possibility of preparing compounds containing boron–cyanide linkages through similar reactions involving the pseudohalogen, cyanogen, suggested itself. Although these studies did not result in the isolation of simple compounds containing the desired boron–cyanide bond, several materials with interesting properties were produced.

With an excess of cyanogen, diboron tetrachloride reacted to form a dark brown material with the empirical composition $B_2Cl_4\cdot 1.5(CN)_2$. This material was soluble in water and in methanol, and, in each case, a brown solution resulted. It was not soluble in carbon tetrachloride nor in chloroform. $B_2Cl_4\cdot 1.5(CN)_2$ was not stable in air; on exposure to the atmosphere for 12 hr. it became completely white.

On heating, $B_2Cl_4\cdot 1.5(CN)_2$ was converted to a black solid with the empirical composition $BCl(CN)_3$, and trichloroborane was released.

$$B_2Cl_4\cdot 1.5(CN)_2 \xrightarrow{400^\circ} BCl_3 + BCl(CN)_3$$

The product of this reaction was considerably more stable than $B_2Cl_4\cdot 1.5(CN)_2$. No change in color was noticed on exposure to air for a two day period. Heating in air at 500° caused its color to lighten gradually, and at 800° the product was quickly converted to boric oxide.

One mole of $B_2Cl_4\cdot 1.5(CN)_2$ was observed to absorb 2 moles of trimethylamine without the release of cyanogen or any other volatile material.

As an aid in interpreting the cyanogen experiments, the behavior of this pseudohalogen with

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(1) Presented before the 131st meeting of the American Chemical Society in Miami, Florida, April, 1957.

(2) E. F. Apple and T. Wartik, THIS JOURNAL, **80**, 6153 (1958).

BF_3, BCl_3 and BBr_3 was studied. The first was found not to react at room temperature, the second to react only incompletely (to give the yellow-orange adduct $(CN)_2{\cdot}2BCl_3$) and the last to react rapidly at −22.9°, to form the dark brown solid $(CN)_2{\cdot}BBr_3$.

Experimental

Apparatus.—Standard vacuum apparatus was employed in these investigations

Preparation and Purification of Reagents.—Diboron tetrachloride was prepared by the method of Wartik, Moore and Schlesinger.[3] It exhibited a vapor pressure of 44 mm. at 0°.

Cyanogen was prepared by the method of Cook and Robinson.[4] The gas was purified by fractional condensation, using a series of U-tubes held at −78.5, −111.9 and −196°, respectively. The fraction retained at −111.9° had a vapor pressure of 704.0 mm. at −22.9°, compared with a reported value[5] of 701.6 mm.

Trimethylamine (Matheson Chemical Co.) was purified by fractional condensation. It exhibited a vapor pressure of 680.6 mm. at 0.0°, compared to the reported value[6] of 682.0 mm.

Trifluoroborane (Matheson Chemical Co.) was prepared by the action of aluminum chloride on the diethyl etherate of trifluoroborane. After purification by fractional condensation, the product exhibited a vapor pressure of 308.0 mm. at −111.9°, compared with a reported value[7] of 304.0 mm.

Trichloroborane (Matheson Chemical Co.) was purified by fractional condensation, after which it exhibited a vapor pressure of 478.0 mm. at 0° compared with a reported value[8] of 477.0 mm.

Tribromoborane was obtained from Professor H. I. Schlesinger at the University of Chicago. After purification by fractional condensation, it exhibited a vapor pressure of 19.0 mm. at 0°, compared with a reported value[9] of 18.0 mm.

Behavior of B_2Cl_4 with Cyanogen.—A number of experiments were carried out to determine the reaction ratio of B_2Cl_4 and cyanogen, using the following procedure. A mixture of B_2Cl_4 and cyanogen, in excess, was sealed off in a glass tube and allowed to warm to −78.5°, at which temperature the formation of a light brown solid was observed. (In an experiment which was interrupted at this stage, the molar reaction ratio of cyanogen to B_2Cl_4 was found to be 1.33 to 1.00.) On warming to −45.2°, the solid became dark brown. After the reaction tube had been allowed to remain at room temperature for ten days, its volatile contents were transferred to the vacuum system and found to consist exclusively of unchanged cyanogen. The reaction ratio of of cyanogen to B_2Cl_4 was found to be 1.48 to 1.00 (average of five experiments). This ratio was not changed by allowing as much as one month for the reaction. However, when the reaction was stopped after one day at room temperature, the ratio was less than that observed after ten days. The reaction product, which has the empirical formula $B_2Cl_4{\cdot}1.5(CN)_2$, is a dark brown solid which turns white on prolonged exposure to air. It is soluble in water and in methanol, yielding, in each case, a brown solution. It showed limited solubility in ethyl alcohol, ethyl ether, 1,2-dimethoxyethane, acetone, carbon disulfide and benzene and appeared to be insoluble in chloroform and carbon tetrachloride. Its chemical behavior will be described below.

Behavior of Trifluoroborane with Cyanogen.—An equimolar mixture of trifluoroborane and cyanogen, after having been allowed to remain at room temperature for 16 hr., was completely separable into its original components. Heating for 24 hr. at 100° in a sealed tube caused no reaction, nor did prolonged standing at room temperature.

Behavior of Trichloroborane with Cyanogen.—A mixture of trichloroborane (2.039 mmoles) and cyanogen (2.016 mmoles) was allowed to warm from −196° to room temperature in a sealed tube. A small quantity of white solid formed, whose amount was increased by repeatedly cooling to −196° and warming to room temperature. The volatile contents of the tube (3.106 mmoles) were recovered and shown to exhibit an apparent molecular weight (by vapor density) of 85.4. (Separation by fractional condensation was not attempted, owing to the tendency for further reaction to occur during manipulation.) This value corresponds to that calculated for an equimolar mixture of trichloroborane and cyanogen (84.7). This being the case, the white solid reaction product must necessarily have the composition $BCl_3{\cdot}(CN)_2$.

In the presence of an excess of trichloroborane, an adduct richer in the boron compound was prepared. Trichloroborane (23.90 mmoles) and cyanogen (1.913 mmoles) were allowed to stand in a sealed tube at room temperature for 12 hr. At the end of this time, an orange-yellow solid had formed, and it was found possible to recover only trichloroborane (20.12 mmoles, vapor pressure at 0° = 484.0 mm.; reported value[8] = 477 mm.) from the reaction mixture. The amounts of trichloroborane and cyanogen consumed indicated a reaction ratio of 1.98 moles of trichloroborane to 1.00 moles of cyanogen. The orange adduct therefore has the composition $(BCl_3)_2{\cdot}(CN)_2$. This adduct was completely soluble, with reaction, in water, methanol and dilute nitric acid, forming, in all cases, pale yellow solutions. It was sparingly soluble in carbon disulfide and benzene and apparently insoluble in carbon tetrachloride and chloroform. $(BCl_3)_2{\cdot}(CN)_2$, on being heated to 350° *in vacuo*, released trichloroborane and cyanogen (in relatively small amounts) and left behind a non-volatile, black residue. The color of the latter gradually changed to brown on exposure to air for several months.

With Tribromoborane.—When a mixture of tribromoborane (7.57 mmoles) and cyanogen (9.20 mmoles) was allowed to warm to −22.9°, a dark brown solid was produced. Only cyanogen (1.802 mmoles, molecular weight by vapor density = 51.94; calculated value = 52) was recovered on warming to room temperature. The quantities involved indicate that tribromoborane reacted with cyanogen in the molar ratio of 1.02 to 1.00, to produce an adduct of the composition $BBr_3{\cdot}(CN)_2$. The latter was very soluble in 1,2-dimethoxyethane and in methanol (with reaction). It was sparingly soluble in carbon disulfide, benzene and ether, producing brown solutions in all cases. Attempts to measure its molecular weight in benzene solution failed, since its solubility seemed to decrease with time. On warming to over 100°, BBr_3 $(CN)_2$ began to release bromine irreversibly.

After an excess of tribromoborane (3.178 mmoles) had been treated with cyanogen (1.374 mmoles) in a sealed tube at 130° for five days, a dark brown solid, similar in appearance to $BBr_3{\cdot}(CN)_2$, was observed. Tribromoborane (0.3568 mmole, molecular weight by vapor density = 256.1; calculated value = 250.7) was recovered in such amount as to indicate a molar reaction ratio between tribromoborane and cyanogen of 2.05 to 1.00. This ratio is in satisfactory agreement with the composition $(BBr_3)_2{\cdot}(CN)_2$. Attempts to carry out the preparation at lower temperatures resulted in lower reacting ratios. Like $BBr_3{\cdot}(CN)_2$, $(BBr_3)_2{\cdot}(CN)_2$ releases bromine slowly at elevated temperatures, and small amounts of the element result from its preparation.

Properties of $B_2Cl_4{\cdot}1.5(CN)_2$.—On standing in contact with liquid water for 12 hr. at 100°, $B_2Cl_4{\cdot}1.5(CN)_2$ reacted to produce an oily brown precipitate which proved to be soluble in concentrated nitric acid but which was not examined further. No hydrogen whatever was produced on hydrolysis, which strongly suggests that the boron-to-boron bonds in B_2Cl_4 had been cleaved.

On heating a sample of 2.396 mmoles of $B_2Cl_4{\cdot}1.5(CN)_2$ slowly to 400°, the release of 2.494 mmoles of BCl_3 (vapor pressure = 480.0 mm. at 0°, a reported value[8] = 477.0 mm.; molecular weight by vapor density = 116.1, calculated = 117.3), most of which came off below 250°, was observed. Trace quantities of a more volatile substance, probably cyanogen, also were released. Evolution of gas stopped completely when the temperature reached 400°. The number of moles of trichloroborane released corresponded approximately to the number of moles of $B_2Cl_4{\cdot}1.5(CN)_2$ in the adduct, implying a composition $BCl(CN)_3$ for the non-volatile residue.

This residue, which was jet black, appeared not to decompose on exposure to air and was insoluble in methanol, carbon

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(3) T. Wartik, R. Moore and H. Schlesinger, THIS JOURNAL, **71**, 3265 (1949).

(4) R. Cook and P. Robinson, *J. Chem. Soc.*, 1001 (1935).

(5) J. Peery and D. Bardwell, THIS JOURNAL, **47**, 2629 (1925).

(6) J. Aston, M. Sagenkahn, G. Szasz, G. Moessen and H. Zuhr, *ibid.*, **66**, 1171 (1944).

(7) E. Pohland and W. Harlos, *Z. anorg. Chem.*, **207**, 242 (1932).

(8) A. Stock and K. Priess, *Ber.*, **47**, 3117 (1914).

(9) A. Stock and E. Kuss, *ibid.*, **56B**, 1463 (1923).

tetrachloride, chloroform, water and cold dilute nitric acid. It dissolved completely in hot concentrated nitric acid to yield a brown solution. A sample (0.0921 g.) of the black solid was subjected to oxidation by fuming nitric acid at 350° in a heavy-walled bomb tube and yielded 2.356 mmoles of carbon dioxide and 0.756 mmole of boric acid. These values correspond to boron and carbon contents of 8.87 and 30.7%, respectively. The calculated values for $BCl(CN)_3$ are 8.67 and 29.0%.

On heating another sample of $BCl(CN)_3$ in a Vycor tube *in vacuo*, a gradual evolution of gas commenced at 550°. The temperature was raised to 800° and maintained at this value until gas evolution ceased. On cooling, the weight of the sample was found to have been reduced by about 50%. The gases evolved appeared to be cyanogen and hydrogen chloride. It is possible that the latter resulted from the action of water, desorbed from the apparatus at the high temperatures employed, on the black solid.

When a sample of $BCl(CN)_3$ was heated in contact with air in a Vycor tube, no evidence of decomposition was noted until about 500°, at which temperature a gradual whitening of the sample occurred. At 800°, almost complete and relatively rapid conversion to boric oxide, B_2O_3, was observed.

After a mixture of 1.071 mmoles of $B_2Cl_4 \cdot 1.5(CN)_2$ and 4.46 mmoles of trimethylamine had been allowed to remain in a sealed tube at room temperature for eight days, it was found possible to recover 2.432 mmoles of an apparently pure material with a vapor pressure exactly equal to that of the trimethylamine sample used (680.6 mm. at 0.0°) and a molecular weight, by vapor density, of 57.5 (the calculated value for trimethylamine is 59.1). These data correspond to a trimethylamine absorption of 1.90 moles per mole of $B_2Cl_4 \cdot 1.5(CN)_2$, or approximately one trimethylamine per boron atom. No volatile matter other than excess trimethylamine was observed, and the appearance of the solid did not change as the result of its having absorbed the amine.

Discussion

As described in the Experimental section, cyanogen reacts readily with tribromoborane, slowly with trichloroborane and not at all with trifluoroborane. This diminishing trend in reactivity is consistent with previous observations. Hydrogen sulfide, for instance, is not affected by trichloroborane at 250°, but it reacts with tribromoborane at 50°.[10]

The tendency for cyanogen to undergo polymerization in the various adducts under consideration has not been directly established but may perhaps be inferred from some of their properties. Since excess cyanogen is recovered in the unpolymerized condition, it seems likely that any polymerization which occurs takes place after, not before, reaction with the boron halides.

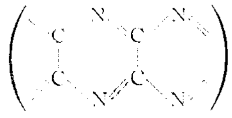
The colors of $BCl_3 \cdot (CN)_2$ (white) and $(BCl_3)_2 \cdot (CN)_2$ (orange-yellow) are not such as to indicate extensive polymerization of the cyanogen. $BBr_3 \cdot (CN)_2$, $(BBr_3) \cdot (CN)_2$ and $B_2Cl_4 \cdot 1.5(CN)_2$, on the other hand, all appear very similar to polymerized cyanogen (paracyanogen) in color. The observation that the solubility of $BBr_3 \cdot (CN)_2$ in benzene decreases with time may mean that cyanogen polymerization occurs, at least in this case, after formation of the simple, unpolymerized adduct

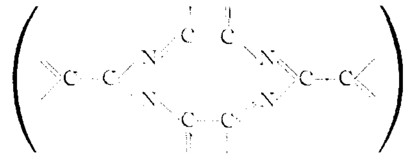
$$BBr_3 + (CN)_2 \xrightarrow{\text{fast}} BBr_3 \cdot (CN)_2$$

$$xBBr_3 \cdot (CN)_2 \xrightarrow{\text{slow}} (BBr_3 \cdot (CN)_2)_x$$

In the case of $B_2Cl_4 \cdot 1.5(CN)_2$, its low solubility, complete lack of volatility and very intense coloration strongly suggest that the adduct involves a polymerized form of cyanogen, probably paracyanogen. There is as yet uncertainty concerning the structure of paracyanogen. Infrared data[11] seem to be consistent with any of the structures

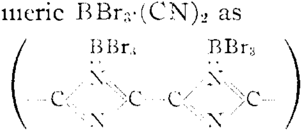

I


II

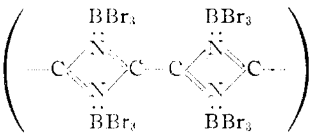

III

All of these structures are suited to the admittedly speculative interpretations which follow. However, since structure I is the simplest, it will be used for purposes of discussion. No implication as to its preference over structures II and III is intended.

Using structure I, one might indicate the structure of polymeric $BBr_3 \cdot (CN)_2$ as


(IV)

and of polymeric $(BBr_3)_2 \cdot (CN)_2$ as

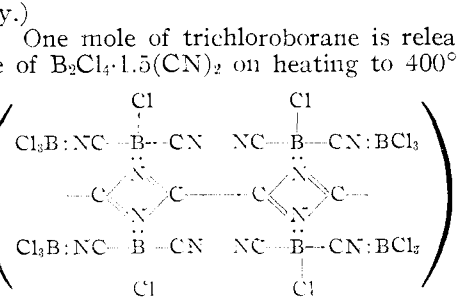

(V)

The structure of the material resulting from the action of cyanogen on B_2Cl_4 ($B_2Cl_4 \cdot 1.5(CN)_2$) is certainly more complex. Chemical behavior bearing on its structure may be summarized as follows:

1. No hydrogen at all was released on heating $B_2Cl_4 \cdot 1.5(CN)_2$ with a large excess of water at 100° for 12 hr. Since B_2Cl_4 itself would have released measurable amounts of hydrogen under these conditions, this behavior may indicate the absence of boron–boron bonds in $B_2Cl_4 \cdot 1.5(CN)_2$.

2. Two moles of trimethylamine are absorbed per mole of $B_2Cl_4 \cdot 1.5(CN)_2$. If it is assumed that all of the boron is now coördinated to trimethylamine, the inference might be drawn that the latter has replaced the weaker base, cyanogen. (The absorption of trimethylamine might also be explained by the existence of tricovalent boron atoms in $B_2Cl_4 \cdot 1.5(CN)_2$, but this does not seem very likely.)

3. One mole of trichloroborane is released per mole of $B_2Cl_4 \cdot 1.5(CN)_2$ on heating to 400°. This


(VI)

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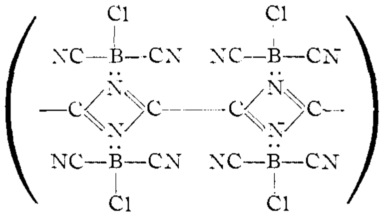
[10] A. Stock and O. Poppenburg, *Ber.*, **34**, 399 (1901).

[11] L. Bircumshaw, F. Taylor and D. Whiffen, *J. Chem. Soc.*, 931 (1954).


(VII)

may mean (but does not necessarily require) that a BCl_3 adduct is involved in $B_2Cl_4\cdot1.5(CN)_2$ itself.

In view of the above, it is perhaps not unreasonable to postulate for $B_2Cl_4\cdot1.5(CN)_2$ the structure (VI). On heating, this compound (VI) might release trichloroborane and leave (VII). The reaction of trimethylamine with $B_2Cl_4\cdot1.5(CN)_2$ might be explained in terms of the formation of $BCl_3\cdot NMe_3$, $BCl(CN)_2\cdot NMe_3$ and $(CN)_n$ (paracyanogen).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Cyclopolyphosphines $(CF_3P)_4$ and $(CF_3P)_5$, and Related Chemistry[1]

BY WALTER MAHLER AND ANTON B. BURG

RECEIVED JUNE 23, 1958

The ring polymers $(CF_3P)_4$ and $(CF_3P)_5$ (m.p. 66.4 and −33°, b.p. 145 and 190°, respectively) are made quantitatively by the room temperature reaction of CF_3PI_2 with Hg, or formed with higher CF_3P polymers by pyrolysis of either $P_2(CF_3)_4$ or $(CF_3)_2PH$ at 350°. Iodine converts $(CF_3P)_n$ to nCF_3PI_2; and chlorine reacts to form nCF_3PCl_4 (m.p. −52°; b.p. est. 104°), which mercury reduces to nCF_3PCl_2. The pentamer $(CF_3P)_5$ is largely converted to the stabler tetramer by heating. In a fluorocarbon solvent the tetramer reacts smoothly with O_2 to form $(CF_3PO_2)_x$ polymers, which hydrolyze rapidly to $CF_3PO(OH)_2$ and intermediate polyphosphonic acids. The neutral-water hydrolysis of $(CF_3P)_4$ at 140° gives $HPO(OH)_2$, HCF_3, CF_3PH_2 (synthesis method) and the new biphosphine $(CF_3PH)_2$ (b.p. est. 69.5°), which decomposes at 225° to HCF_3, CF_3PH_2, $(CF_3)_2PH$ and CF_3P polymers with probable cross-linking. Hydrolysis of $(CF_3P)_5$ in a polyether solvent gives CF_3PH_2, $(CF_3PH)_2$ and the new triphosphine $H_2(CF_3P)_3$ (v.t. 3.7 mm. at 0°). This is decomposed on active nickel to CF_3PH_2 and $(CF_3P)_n$. By basic hydrolysis, $(CF_3P)_4$, $(CF_3P)_5$ and $(CF_3PH)_2$ give just half of their CF_3 groups as HCF_3; but $H_2(CF_3P)_3$ gives only one HCF_3. Some of the new compounds were characterized by infrared spectra, which supported the presumed structures. The ultraviolet spectra of the polyphosphines would accord with the idea that phosphorus lone-pair electrons are delocalized, supplementing the sigma bonding.

The chemistry of phosphorus compounds is extensive, but much is yet to be learned about the P–P bond. A number of P–P compounds with CF_3 groups are volatile enough for convenient study by quantitative high-vacuum methods and stable enough for extensive investigations of their chemical properties as well as the physical nature of P–P bonding. The four-membered phosphorus ring compound $(CF_3P)_4$ was the subject of an earlier publication,[2] wherein it was suggested that Michaelis' "Phosphobenzol" actually has a polymeric ring structure. This was confirmed almost simultaneously.[3]

The phosphorus(III)-ring compounds may be designated as cyclopolyphosphines, by extension from biphosphine for P_2H_4. Thus $(CF_3P)_4$ becomes tetrakis-(trifluoromethyl)-cyclotetraphosphine and $(CF_3P)_5$ is pentakis-(trifluoromethyl)-cyclopentaphosphine. For convenience we shall refer to these compounds as the tetramer and pentamer of CF_3P, or directly by formulas.

Formation of the Ring Polyphosphines.—The room-temperature reaction of CF_3PI_2 with mercury gives mercury iodides and a 100% yield of the CF_3P unit as tetramer (60%) and pentamer (40%). Higher CF_3P polymers are formed (with useful yields of the tetramer and pentamer) when $P_2(CF_3)_4$ or $(CF_3)_2PH$ is heated at 350°. Both the tetramer and the pentamer are unstable at this temperature and so must be removed from the reaction zone almost as soon as they are formed. The possibility that $(CF_3)_2P$ and CF_3P groups might combine to give a straight-chain triphosphine, $P_3(CF_3)_5$, did not materialize: no open-chain polyphosphine of any kind could be recognized as a product of these experiments.

The reaction $P_2(CF_3)_4 \rightarrow (CF_3)_2P + CF_3P$ is detectable at 300° but is more conveniently carried on at a higher temperature. The CF_3P appears 30% as the tetramer, 7% as the pentamer and the rest as higher polymer. Higher polymers are favored by a lower pressure of the starting material. The reaction $(CF_3)_2PH \rightarrow HCF_3 + CF_3P$ requires at least 350° for reasonable speed and seems to be quantitative during the first two-thirds of the process, when 54% of the CF_3P groups appear as the tetramer, 6% as the pentamer and the rest as the higher polymer. Toward the end of the reaction, however, one observes the formation of P_4 and $(CF_3)_3P$ at the expense of the CF_3P polymers.

Thermal Stability of the Tetramer and Pentamer.—As might be inferred from the relative yields, the tetramer of CF_3P is considerably stabler than the pentamer, which undergoes thermal rearrangement at 255°. A major product (56%) is the tetramer, which is stable up to 300°. Not quite 5% of the phosphorus appears as $(CF_3)_3P$ and $P_2(CF_3)_4$; but the appearance of any of the latter means that its decomposition to form CF_3P polymers is appreciably reversible. The non-volatile

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[1] This research was supported by the United States Air Force under Contracts AF 33(616)-2743 and AF 33(616)-5435, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] W. Mahler and A. B. Burg, THIS JOURNAL, **79**, 251 (1957).

[3] W. Kuchen and H. Buchwald, *Angew. Chem.*, **68**, 791 (1956).