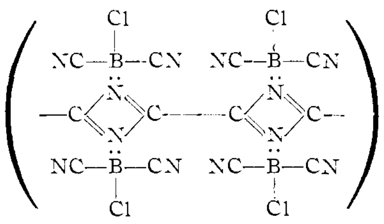
(VII)

may mean (but does not necessarily require) that a BCl_3 adduct is involved in $B_2Cl_4 \cdot 1.5(CN)_2$ itself.

In view of the above, it is perhaps not unreasonable to postulate for $B_2Cl_4 \cdot 1.5(CN)_2$ the structure (VI). On heating, this compound (VI) might release trichloroborane and leave (VII). The reaction of trimethylamine with $B_2Cl_4 \cdot 1.5(CN)_2$ 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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UNIVERSITY PARK, PENNSYLVANIA

[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

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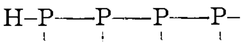
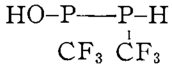
[1] This research was supported by the United States Air Force under Contracts AF 33(616)-2743 and AF 33(616)-5435, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

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

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

product includes P_4; and the possibility of fairly long open CF_3P chains with $(CF_3)_2P$ end-groups cannot be excluded.

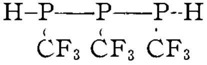
The Halogen Reactions.—The reaction of iodine with the CF_3P tetramer or pentamer gives quantitative reconversion to CF_3PI_2. This reaction, taken with the vapor-phase molecular weight determinations, served to demonstrate the formulas. Also to this purpose was the chlorine reaction, according to the equation $(CF_3P)_4 + 8Cl_2 \rightarrow 4CF_3PCl_4$. The pentamer also reacted quantitatively in this way; and a similar conversion proved especially convenient for demonstrating the character of the non-volatile higher polymers. The new compound CF_3PCl_4 was proved by the quantitative reaction-sequence $CF_3PCl_4 + 2Hg \rightarrow Hg_2Cl_2 + CF_3PCl_2$; $CF_3PCl_2 + HOH + 2OH^- \rightarrow HCF_3 + HPO(OH)_2 + 2Cl^-$, thus completing an independent proof of the polymer formulas.

Hydrolysis Reactions.—The tetramer $(CF_3P)_4$ reacts with aqueous alkali hydroxides to deliver exactly half of the CF_3 groups in the form of HCF_3. This result would be expected if the CF_3P units were equally and quantitatively converted to CF_3PH_2 and $CF_3PHO(OH)$, the former of which yields no HCF_3 while the latter produces one HCF_3.[4] Such a perfect dichotomy could be explained by a directive effect: the initially-formed open chain  $H-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-OH$ would go to CF_3PH_2, $CF_3PHO(OH)$ and  $HO-\underset{CF_3}{P}-\underset{CF_3}{P}-H$; then this last would form only the phosphine and phosphonous acid. But the pentamer $(CF_3P)_5$ yields just $2.5HCF_3$, opening the question whether CF_3PHOH is formed from the central CF_3P unit of an initially formed $H(CF_3P)_5OH$ chain, and then disproportionated before it can hydrolyze, or whether the central CF_3P unit is more directly hydrolyzed to equal proportions of the phosphine and phosphonous acid. The latter idea seems more tenable in view of the results of basic hydrolysis of the new biphosphine $(CF_3PH)_2$: the hypothetical CF_3PHOH seems to be a necessary intermediate, but the reaction produces one HCF_3 rather than half as much.

1,2-Bis-(trifluoromethyl)-biphosphine.—The new biphosphine $(CF_3PH)_2$ was obtained first by the plain-water hydrolysis of the tetramer $(CF_3P)_4$. This process could not be observed at room temperature, possibly because the reactants would not mix; and in the vapor phase the reaction was slow even at 140°—only two-thirds complete after 96 hours. A 21% yield of the primary phosphine CF_3PH_2 gave promise that this hydrolysis might become a convenient source of this rare substance. Both HCF_3 and $HPO(OH)_2$ were obtained in 24% yields, corresponding to a 24% yield of $CF_3PHO(OH)$, which is unstable above 100°.[5] The 20% yield of $(CF_3PH)_2$ requires a more nearly random sequence of P–P bond breaking than was considered for the basic hydrolysis of $(CF_3P)_4$; also, when the H–P–P–P–P–OH chain is broken at the central P–P bond, the end H and OH must exert long-range directive effects upon the entering H and OH groups.

The biphosphine $(CF_3PH)_2$ proved to be stable on heating nearly to 225°, at which the main reaction is a hydrogen-shift, $(CF_3PH)_2 \rightarrow CF_3PH_2 + CF_3P$, giving a 58% yield of $(CF_3P)_4$. This process seems to be nearly five time as prevalent as a parallel CF_3-group shift, $(CF_3PH)_2 \rightarrow (CF_3)_2PH + PH$. Since no PH_3 was observed, it seems that the PH units were incorporated into some kind of copolymer with CF_3P units; then the formation of a little HCF_3 would imply cross-links in the non-volatile CF_3P polymer.

The stoichiometry of the composite process demonstrates the composition CF_3PH and the vapor-phase molecular weight corresponds to the dimer formula. The strong ultraviolet absorption, at λ 2040 Å., would correspond to a P–P bond; and the infrared spectrum (see Table VI, with interpretation) suggests that the two CF_3 groups are not on the same phosphorus atom.

The biphosphine $(CF_3PH)_2$ was obtained also by the hydrolysis of $(CF_3P)_5$, of which a still more interesting product was the first triphosphine,  $H-\underset{CF_3}{P}-\underset{CF_3}{P}-\underset{CF_3}{P}-H$, as next described.

1,2,3-Tris-(trifluoromethyl)-triphosphine.—The plain-water hydrolysis of $(CF_3P)_5$ is even slower than that of $(CF_3P)_4$, giving only small yields of $(CF_3PH)_2$ and $H_2(CF_3P)_3$ after months at 140°. However, in a solvent such as β,β'-dimethoxydiethyl ether ("diglyme") the pentamer hydrolyzes quite readily at 50°, giving major yields of these phosphines. Analyses and molecular weight results demonstrate the formula of the triphosphine; further, the infrared spectrum is consistent with one CF_3 group on each P atom. The ultraviolet spectrum of the triphosphine suggests the extent of electronic delocalization which might be expected for a P_3 chain.

The formation of $H_2(CF_3P)_3$ in good yields, from $(CF_3P)_5$ with neutral water, ignores the basic-hydrolysis rule that the second group (H or OH) put on each P is the same as the first; but the rule holds for the basic hydrolysis of $H_2(CF_3P)_3$. Just one HCF_3 forms, presumably from $CF_3P(OH)_2$ made from the central CF_3P unit.

Oxygen Chemistry of the Tetramer.—The tetramer $(CF_3P)_4$ inflames spontaneously in air, giving degradation products such as carbonyl fluoride, phosphoryl fluoride and heterogeneous yellow to black non-volatile materials. A far cleaner oxidation occurs in a stirred solution of the tetramer in a fluorocarbon solvent. After a ten-minute induction period at room temperature, pure oxygen is absorbed rapidly up to one O atom per P; then a second O atom is absorbed at a fairly fast but measurable rate, approximately first order relative to the reacting solute. The end-point usually corresponds to the formula $(CF_3PO_2)_x$, but the oxygen content can be a little greater, in which case loss of oxygen occurs on heating of the product to 330°. The formation of a peroxyphosphorus compound would be a reasonable first

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[4] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954).

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

step in a chain reaction for which an induction period would be noted.

The oxidation product $(CF_3PO_2)_x$ evidently is a mixture of polymeric anhydrides of trifluoromethylphosphonic acid, $CF_3PO(OH)_2$, which is formed quantitatively by its complete hydrolysis. The mixed character of the anhydride is shown by heating it to 125°, with observation of a liquid which refluxes under high vacuum and a rigid foam which remains on the walls where evaporation of the solvent has left it. The more volatile part probably is a mixture of the cyclic polymers $(CF_3PO_2)_3$ and $(CF_3PO_2)_4$ having P–O–P ring structures analogous to the tri- and tetrametaphosphates.[6]

The reaction of $(CF_3PO_2)_x$ with water is nearly as vigorous as that of P_4O_{10}. Van Wazer and Holst have commented on the stability of the linear polyphosphates in water, in contrast to the water-sensitivity of branching points in cross-linked polyphosphates.[7] Since $(CF_3PO_2)_x$ cannot be cross-linked, our results suggest the broader rule that a phosphorus(V) atom having only one terminal oxygen, and three other electronegative groups, is susceptible to nucleophilic attack by water. A terminal oxygen on phosphorus not only has less electron-withdrawing power than a P–O–P oxygen, but also shares electrons with P-3d orbitals more exclusively; and replacement of a terminal oxygen by CF_3 certainly would release P-3d orbitals for the nucleophilic attack.

On this basis it is not surprising to find that the hydrolysis of $(CF_3PO_2)_x$ does not immediately give a 100% yield of $CF_3PO(OH)_2$, for the anion of the strong acid $CF_3\overset{O}{\underset{O_H}{P}}\text{–O–}\overset{O}{\underset{O_H}{P}}CF_3$ has two terminal oxygen atoms per phosphorus, offering considerable protection against the entry of water to phosphorus. Such an acid has been indicated by the titration curve of a 10-minute hydrolysate of $(CF_3PO_2)_x$: the weak acid aspect required only 0.38 as much base as the strong acid part of the curve, as though there were 0.62 equivalent of the two-proton-strong diphosphonic acid per 0.38 mole of the strong-and-weak diprotic acid $CF_3PO(OH)_2$. In terms of the theory, a triphosphonic acid (or longer-chain acid) would not have withstood hydrolysis, on account of the central CF_3PO_2 unit. Even the diphosphonic acid was unstable in a basic solution and was wholly converted by boiling. Titration then showed equal amounts of strong and weak acidity, conforming strictly to the titration curve given in the literature for $CF_3PO(OH)_2$.[4]

Theoretical Treatment of the Phosphorus Rings.—In our communication on the four-membered phosphorus ring[2] it was suggested that P–P sigma bonding may be supplemented by pi-type bonds involving phosphorus lone-pair electrons with neighboring P-3d orbitals. Support for such a view comes from the ultraviolet absorption spectra of the cyclopolyphosphines, shown in Fig. 1, with corroboration from the open-chain phosphines: $P_2(CF_3)_4$ has a single peak at 2160 Å., with molar extinction coefficient ϵ 7,800, and a minimum at 1960 Å. with ϵ 1,500; and $(CF_3PH)_2$ shows a single peak at 2040 Å. with ϵ 7,400. Also, $H_2(CF_3P)_3$ shows a peak at 2075 Å. (ϵ 7,600) and a shoulder at 2240 Å. (ϵ 5,500). By contrast, the monophosphines $(CF_3)_3P$ and CF_3PH_2 show no structure in the usual instrumental ultraviolet: for each, ϵ is near 500 at 2000 Å., increasing toward shorter wave lengths.

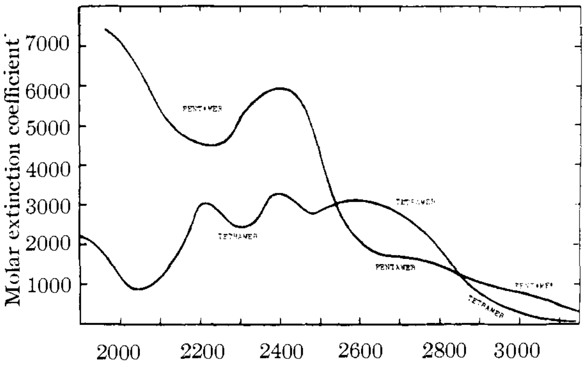

Fig. 1.—The ultraviolet absorption spectra of CF_3P tetramer and pentamer in the gas phase.

The strong absorption by the polyphosphines in the range 2000-2800 Å., might be understood in terms of a delocalization of the otherwise unshared electron pairs of phosphorus, to occupy molecular orbitals extending over the whole P–P bonded system. Then the absorption spectra would be attributed to relatively low-lying unoccupied energy levels to which electronic transitions would be possible. The free-electron molecular-orbital (FE MO) treatment[8,9] can be applied to the CF_3P-rings to test this idea.

For this purpose the valence electrons not involved in sigma bonding are considered to be in a box which for simplicity might be defined either as the one-dimensional perimeter of a circle or as the two-dimensional surface of a sphere, encompassing the phosphorus atoms. For the circular model the quantized energy levels are given by

$$W_n = \frac{n^2h^2}{8\pi^2 mR^2}$$

where n is a quantum number, h Planck's constant, m the mass of an electron and R the radius of the circle. Taking the normal P–P distance as 2.2 Å., R for the tetramer would be 1.55 Å. Then the energy difference from $n = 1$ to $n = 2$ is equivalent to $\lambda = 2600$ Å. This represents the lowest-energy transition, for of the eight electrons to be accommodated, two can reside in the $n = 0$ level while each (degenerate) higher level can hold as many as four; then in the ground state the $n = 2$ level is half empty. To account for the diamagnetic character of the tetramer, as well as its actual spectrum, the $n = 2$ level would have to be split, as might be expected from the less than circular symmetry of the ring.

The circular model for the pentamer $(CF_3P)_5$ accommodates ten electrons in the $n = 0$, $n = 1$,

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(6) J. R. Van Wazer and E. J. Griffith, THIS JOURNAL, **77**, 6140 (1955.)

(7) J. R. Van Wazer and K. H. Holst, *ibid.*, **72**, 639 (1950).

(8) N. S. Bayliss, *J. Chem. Phys.*, **16**, 287 (1948).

(9) W. T. Simpson, *ibid.*, **16**, 1124 (1948).

and $n = 2$ levels. The lowest-energy transition is $n = 2$ to the empty $n = 3$ level, and the difference is calculated to be equivalent to $\lambda = 2300$ Å., in reasonable agreement with the observed spectrum. However, the splitting is again quite noticeable, as expected if the P_5 ring is not planar.

A similar calculation for a P_6 ring would predict the center of the absorption band to be near 3140 Å. A splitting as large as that observed for the P_5 ring would extend the spectrum just into the visible region. Thus it would not be unreasonable to suppose that the observed yellow-green color of the CF_3P higher polymer is due to the presence of $(CF_3P)_6$.

The spherical model, having the energy equation

$$W_0 = \frac{l(l+1)h^2}{8\pi^2 mR^2}$$

is satisfactory for the tetramer, permitting a three-way splitting but not relating well to the radius of phosphorus. For the pentamer, however, this model is difficult to apply. It seems that intermediate models based upon the actual structural patterns would be more suitable; and the qualitative success of the simple models encourage the attempt to develop the delocalization theory more precisely.

Experimental Part

All compounds were manipulated by the usual high-vacuum methods, using Stock-type mercury float-valves for non-oxidizing materials. Substances reactive toward mercury (such as CF_3PI_2, CF_3PCl_4 and Cl_2) were managed in a stopcock system with a chlorofluorocarbon grease.(10) Pressures of these reactive materials were measured by means of a null-indicating glass spoon-gauge,(11) balanced by nitrogen.

Synthesis of the Trifluoromethylphosphorus(III) Polymers

The Mercury–Iodide Method.—A 61-g. sample of CF_3PI_2(2),(3) was shaken with 1 kg. of mercury in a closed 500-ml. flask at room temperature for 12 hr. The volatile products were brought into the high-vacuum system and condensed at −25° in the upper chamber of a magnetic-valved separatory apparatus.(4) The liquid $(CF_3P)_5$ ran into the lower chamber, leaving the solid $(CF_3P)_4$ on the walls of the upper chamber. Repetitions of the process brought the tetramer and pentamer fractions to 95% purity The yields were 10.7 g. of tetramer and 6.5 g. of pentamer; total CF_3P recovery, 17.2 g. (calcd., 17.23). Further purification of the pentamer was achieved by boiling off the dissolved tetramer at 100°, under 40 mm. pressure of nitrogen. The tetramer was freed from traces of pentamer by recrystallization from hexane: the saturated solution was cooled from room temperature to −10°

Pyrolysis of Tetrakis-(trifluoromethyl)-biphosphine.—In a preliminary experiment a 4.45 mmole sample of $P_2(CF_3)_4$(2) was heated in a sealed glass tube. There was no change after 48 hr. at 280° but after 7 hr. at 308° the sample had yielded 5.4 mmoles of $(CF_3)_3P$, 0.09 mmole of $(CF_3P)_4$ (8% yield), some white phosphorus and a non-volatile yellow oil. The formation of $(CF_3)_3P$ beyond a 1:1 ratio to the original sample, as well as the presence of some white phosphorus, indicated decomposition of $(CF_3P)_4$. In the next experiment this decomposition was minimized by using a pyrolysis chamber in the form of an inverted one-liter long-neck flask: the neck was extended and rounded off at one end, to serve as a hot reaction-zone; and a tube sealed on at the "north pole" led through a stopcock to a ground joint for connection to the vacuum system. Another tube, sealed on equatorially and bent downward to a round end, received the slightly volatile products as they were delivered by convection from the hot tube below and condensed upon the walls of the bulb.

With this apparatus a 3.98 mmole sample of $P_2(CF_3)_4$ was given a 5-hr. exposure to a furnace temperature of 350°; then a high-vacuum fractionation led to recovery of 1.88 mmoles of $P_2(CF_3)_4$; hence 2.1 mmoles had been used and the decomposition was 53% complete. The resulting $(CF_3)_3P$ was identified by its 3 mm. vapor tension at −78°, its mol. wt. (238, as calcd.), and its basic hydrolysis to give 3.0 volumes of HCF_3. The yield of $(CF_3)_3P$, 2.12 mmoles, corresponded so well to the used-up $P_2(CF_3)_4$ as to suggest that scarcely any destruction of CF_3P groups had occurred. The yield of $(CF_3P)_4$ and $(CF_3P)_5$ amounted to 1.05 mmoles of CF_3P groups, with the tetramer far in excess over the pentamer. The remaining 1.05 mmoles of CF_3P units must be ascribed to a higher polymer. This appeared as a yellow-green sublimate, not volatile at 25°.

The unused 1.88 mmoles of $P_2(CF_3)_4$, exposed further to heat in the same pyrolysis chamber (8 hr. at 350°), gave a further 1.81 mmole yield of $(CF_3)_3P$, but only 0.44 mmole of CF_3P units as a tetramer–pentamer mixture (average mol. wt. 419; identity checked by quantitative conversion to CF_3PI_2). Again the non-volatile remainder had the empirical formula $(CF_3P)_x$. Only 0.05 mmole of the $P_2(CF_3)_4$ escaped conversion.

Pyrolysis of Bis-(trifluoromethyl)-phosphine.—An exploratory sealed-tube experiment showed that $(CF_3)_2PH$(15) was unaffected by a 24 hr. exposure to 300°, but during 24 hr. at 350° the sample was almost all converted to HCF_3, a trace of $(CF_3)_3P$ and a black cinder. Hence again the special pyrolysis chamber was used to minimize decomposition of the CF_3P polymers. With the side-arm cooled to 0° and the furnace at 400° (cooler inside the tube, on account of convection), samples of $(CF_3)_2PH$ were exposed as shown in Table I. The resulting tetramer–pentamer mixture (average mol. wt. 410) was checked by quantitative conversion to CF_3PI_2. The $(CF_3P)_x$ product from expt. 2 was proved by treatment with excess chlorine, followed by mercury-reduction to give 2.3 mmoles of CF_3PCl_2. This and the HCF_3, $(CF_3)_3P$ and recovered $(CF_3)_2PH$ were identified by their molecular weights, vapor tensions and infrared spectra. The final stage of expt. 1 gave some white phosphorus, which was confirmed by chlorination to form phosphorus pentachloride.

TABLE I

PYROLYSIS OF $(CF_3)_2PH$ (FURNACE AT 400°)

Expt. no.	Heated sample (mmoles)	Time (min.)	Sample destroyed (mmoles)	Products (mmoles of monomers) HCF$_3$	$(CF_3P)_{4,5}$	$(CF_3P)_x$	$(CF_3)_3P$
1	7.6	10	2.1	2.1	1.4	0.7	..
	5.5	30	2.9	2.9	1.66	1.24	..
	2.6	200	2.25	2.25	0.175	?	0.51
2	7.5	240	5.0	5.0	2.7	2.3	..

Physical Properties of the Tetramer and Pentamer

Miscellaneous Properties.—The pure tetramer $(CF_3P)_4$ melted in the range 66.3–66.4°. The pentamer melted at −33°, but sometimes supercooled to very low temperatures. The molecular weights were determined by the vapor-density method, as 402 and 495, respectively (calcd., 400 and 500). The density of the solid tetramer was determined as 2.0 by X-ray methods.(16) The density of the liquid tetramer was measured as 1.54 at the m.p.; that of the liquid pentamer, 1.60 at 25°.

Volatility.—The measured vapor tensions of solid and liquid $(CF_3P)_4$ are shown in Table II. For the solid, they determine the equation $\log p_{\text{mm.}} = 11.7239 - 3384.6/T$; and for the liquid, $\log p_{\text{mm.}} = 8.3935 - 2251.6/T$. Thus the b.p. is calculated as 135° and the Trouton constant as 25.1—both unchanged by an alternative treatment of the data by the Nernst approximation equation. Such a high

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(10) "Halocarbon Stopcock Grease," from Halocarbon Products Corp., North Bergen, New Jersey.

(11) T. E. Phipps, M. L. Spealman and T. G. Cooke, *J. Chem. Ed.*, **12**, 321 (1935).

(12) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

(13) A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber and D. L. Herring, THIS JOURNAL, **79**, 247 (1957)

(14) R. I. Wagner and A. B. Burg, *ibid.*, **75**, 3870 (1953).

(15) Made by the method of A. B. Burg and W. Mahler, *ibid.*, **79**, 4242 (1957).

(16) J. Donohue and G. Palenik, structure determination in course of completion.

Trouton constant indicates that the b.p. from this extrapolation should be taken as tentative. The heat of fusion is calculated as 5.184 kcal./mole and the melting point as 66.9°, close to the observed range.

The vapor tensions of $(CF_3P)_5$ (Table III) are best correlated by the Nernst-type equation $\log p_{mm.} = 6.9302 - 0.004913T + 1.75 \log T - 2982.6/T$, according to which the normal b.p. would be 190° and the Trouton constant 21.5 cal./deg. mole.

TABLE II

VAPOR TENSIONS OF $(CF_3P)_4$

Solid			Liquid		
t (°C.)	p_{mm} (obsd.)	p_{mm} (calcd.)	t (°C.)	p_{mm} (obsd.)	p_{mm} (calcd.)
19.2	1.42	1.40	40.5[a]	16.4	16.4
24.6	2.28	2.28	47.8[a]	23.9	23.9
30.2	3.64	3.71	54.9[a]	34.2	33.9
33.4	4.88	4.86	66.3	57.7	57.7
41.6	9.35	9.47	71.0	71.3	71.1
51.0	19.3	19.1	74.8	83.7	83.8
60.2	38.2	38.1	83.6	121.0	121.0
65.6	56.1	55.3	88.5	147.8	147.3
			95.0	189.8	189.8
			101.9	244.8	246.0

[a] Values below 66° are for the supercooled liquid.

TABLE III

VAPOR TENSIONS OF LIQUID $(CF_3P)_5$

t (°C.)	p_{mm} (obsd.)	p_{mm} (calcd.)	t	p(obsd.)	p(calcd.)
46.6	2.63	2.59	101.9	43.8	43.8
60.0	5.60	5.70	110.0	61.0	61.0
70.3	9.98	9.94	120.3	90.6	90.8
78.0	14.71	14.68	129.1	125.6	125.3
92.0	28.5	28.4	162.4	363.6	364.2

Solubility.—The tetramer $(CF_3P)_4$ is not appreciably dissolved (nor even wet) by water at room temperature; but its solubility is at least 25% by weight in benzene, acetone, carbon tetrachloride, hexane, ether, acetic acid, trifluoroacetic acid or the liquid fluorocarbon oxide $C_8F_{16}O$,[17] all at 25°. The temperature coefficients all were high and positive; and in each case the undamaged tetramer could be recovered after evaporation of the solvent. The pentamer also proved to be quite insoluble in water but highly miscible with organic solvents.

The dissolution of the tetramer in methanol was followed by a fairly rapid reaction involving cleavage of the P–P bond. It also dissolved in liquid ammonia, with vigorous reaction.

Ultraviolet Spectra.—The ultraviolet absorption spectra of the tetramer and pentamer were recorded by means of a Cary Model 14 spectrophotometer. The performance of the instrument was demonstrated by its resolution of the vibrational structure of the ammonia spectrum[18] down to the 1939 Å. peak. All spectra were observed at room temperature, on vapors confined in vitreous silica cells (1 cm.[19] and 10 cm.), filled directly from the high-vacuum system. The filling process consisted of permitting the vapor in equilibrium with the condensed phase to enter the evacuated cell and closing it off by a stopcock. The pressure was calculated from the pertinent vapor tension equation on the basis of the known temperature of the condensed phase and checked by direct measurement to 0.02 mm. Thus the molar extinction coefficients measured at different pressures agreed within 5–10%; and in any one run they are mutually consistent within 3%. The maximum and minimum values, corresponding to the peaks and low points of Fig. 1 (and one shoulder) are given by Table IV.

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRA OF $(CF_3P)_4$ AND $(CF_3P)_5$

Tetramer			Pentamer		
λ (Å.)	Shape	Molar ext. coefficient	λ (Å.)	Shape	Molar ext. coefficient
2590	Max.	3080	2680	Shoulder	1730
2480	Min.	2800	2400	Max.	5970
2390	Max.	3250	2220	Min.	4480
2300	Min.	2450			
2210	Max.	3030			
2050	Min.	890			

Chemical Properties of the Tetramer and Pentamer

Thermal Stability and Interconversion.—A 0.089 mmole sample of $(CF_3P)_4$ was kept in a sealed glass tube for 24 hr. at 280° without change. After 24 hr. at 314° none of it could be recovered. The main volatile product was 0.073 mmole of almost pure $(CF_3)_3P$ (mol. wt. 243; calcd., 238; basic hydrolysis yielded 2.9 volumes of HCF_3). A white waxy portion of the inevaporable residue apparently was phosphorus: it reacted with iodine to give the red solid PI_3 (m.p. 58°; known value, 61°).

A 0.956 mmole sample of $(CF_3P)_5$ was unchanged after 12 hr. in a sealed tube at 200°. After 48 hr. at 255° about half of the sample had been used up; after 120 hr. virtually none was left. The volatile products were 0.13 mmole of $(CF_3)_3P$, 0.11 mmole of $P_2(CF_3)_4$ and 0.675 mmole (56% yield) of $(CF_3P)_4$ (mol. wt. 402; calcd., 400). The orange non-volatile residue contained a portion which vaporized under high vacuum at 100°; some of this was P_4, confirmed by conversion to PI_3.

Proofs of Formulas by Halogen Reactions.—A 99.2-mg. sample of $(CF_3P)_4$ (equivalent to 0.992 mmole of CF_3P units) was heated with excess iodine in a sealed tube for one hr. at 110°. The resulting brown volatile liquid, after distillation away from the excess iodine, weighed 359 mg., corresponding to 1.01 mmoles of CF_3PI_2. Its identity was checked by its 2 mm. vapor tension at 20° and by its nuclear magnetic resonance spectrum, showing the characteristic F^{19} chemical shift and F–P coupling constant.[20]

Under similar conditions 206.5 mg. of $(CF_3P)_5$ reacted with iodine to give 715 mg. of CF_3PI_2 (calcd., 731 mg.). In other experiments both the tetramer and the pentamer were completely converted to CF_3PI_2 during 48 hr. at room temperature.

A 251.0-mg. sample of $(CF_3P)_4$, with chlorine in excess, reacted while warming from −196° to room temperature. The excess chlorine was removed by fractional distillation in the halocarbon-greased stopcock system, leaving a uniform colorless liquid having the measured vapor tensions 3 mm. at 0° and 10 mm. at 20°; m.p. −52°; yield 606.9 mg. (calcd. for CF_3PCl_4, 607.0 mg.). The entire sample was shaken with mercury for 15 min., producing 2.48 mmoles of CF_3PCl_2 (calcd., 2.51). This was identified by its mol. wt. (172; calcd., 171) and its 157 mm. vapor tension at 0°. Also, another sample of CF_3PCl_2 was made for comparison, by reaction of AgCl with authentic CF_3PI_2.[12] Its vapor tension at 0° was 160 mm.; and the infrared spectra of both samples were identical. As a final check, the 2.48 mmole sample was hydrolyzed by 10% sodium hydroxide solution, giving 2.48 mmoles of HCF_3.

The new compound CF_3PCl_4 also was made more directly for purposes of comparison. A 2.08 mmole sample of CF_3PCl_2 was chlorinated to yield 500.9 mg. of the product, a weight which corresponds to 2.07 mmoles of CF_3PCl_4. This sample melted in the range −52.5 to −52.0° and showed the vapor tensions 3 mm. at 0°, 10 mm. at 20° and 12 mm. at 23°, in good agreement with the sample derived from $(CF_3P)_4$. These rough vapor tensions are correlated by the equation $\log p_{mm.} = 8.187 - 2106/T$; b.p. 104°; Trouton constant 24 cal./deg. mole.

The chlorination reaction to form CF_3PCl_4, and hence CF_3PCl_2 by mercury-reduction, was quantitative also for the pentamer $(CF_3P)_5$; and the same process was involved in the demonstration that the non-volatile $(CF_3)_2PH$-pyrolysis product was $(CF_3P)_x$ (expt. 2, Table I). The

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[17] Kindly supplied to us by Minnesota Mining & Manufacturing Company, as Fluorochemical O-75.

[18] E. Tannenbaum, E. M. Coffin and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

[19] We are grateful to the Explosive Dept. of E. I. du Pont de Nemours & Co. for the loan of a 1 cm. cell adaptable to high-vacuum techniques.

[20] W. Mahler, A. B. Burg, H. M. McConnell and P. Bromberg, paper in course of preparation, jointly with the California Institute of Technology.

action of chlorine on any of the CF_3P polymers proved to be highly exothermic; gentle treatment was needed to avoid some formation of PCl_5 and CF_3Cl. The reaction was clean when gaseous chlorine was allowed to flow slowly toward the CF_3P material or liquid chlorine allowed to react during very slow warming from −70° or lower. For analytical purposes it was not necessary to isolate the CF_3PCl_4; after the chlorine addition reaction, the product was simply shaken with mercury to form the easily-isolated CF_3PCl_2. The same method proved useful in the investigation of the products of pyrolysis of the new biphosphine $(CF_3PH)_2$.

The Action of Oxygen on the Tetramer.—In the exploratory experiment, a solution of 1.43 mmoles of $(CF_3P)_4$ in 4.4 g. of $C_8F_{16}O$[17] was stirred magnetically at 0° and exposed to oxygen at 100 mm. pressure; then the system was warmed to 22°. After 14 hr. the oxygen uptake amounted to 4.38 mmoles; then the oxygen pressure was increased to 480 mm. and after 14 hr. longer the total oxygen absorption amounted to 5.72 mmoles—just one O_2 per CF_3P unit.

In the second experiment 1.22 mmoles of $(CF_3P)_4$ in 4.4 g. of $C_8F_{16}O$, exposed to oxygen at 432 mm. at 22°, showed no action in the first 10 min., but within the next 2 min. the O_2 pressure dropped to 308 mm., corresponding to absorption of 2.10 mmoles of O_2. In the next 5 min. the pressure fell smoothly to 240 mm., and in another 5 min. to 211 mm. At the end of an hour the action had ceased; total oxygen absorption 5.22 mmoles, or 1.07 O_2 per CF_3P unit. The $C_8F_{16}O$ was distilled off and fractionated, with no evidence of any volatile reaction product. The reaction tube, containing the non-volatile white product, was sealed off and heated at the lower end to 125°, refluxing a liquid component. The whole tube was placed in an oven at 250° in such a way that there was a 5° thermal gradient from the bottom to the top; then after 12 hr. the solid component had sublimed to the top. After 36 hr. at 330°, the tube was opened and 0.40 mmole of O_2 pumped out—presumably a consequence of peroxide formation in the O_2-absorption process. Extensive decomposition of the $(CF_3PO_2)_x$ had occurred, producing COF_2 as the main volatile product; it was identified by its m.p., mol. wt., volatility and infrared spectrum.

Hydrolysis of the Polymeric Acid Anhydride.—The sample of $(CF_3PO_2)_x$ from the first controlled oxidation of $(CF_3P)_4$, amounting to 5.72 mmoles of CF_3PO_2 units, was slowly exposed to water, to form a clear aqueous solution. This was titrated no more than 10 min. after the initial exposure to water, using 0.872 *N* sodium hydroxide and a Beckman Model G *p*H meter to determine the curve. The first inflection point was reached by 5.6 mmoles of base, with indication of the value 1.0 for pK_1; then the second inflection point was established by 2.25 mmoles more base, giving pK_2 as 4.0; known values for $CF_3PO(OH)_2$ (trifluoromethylphosphonic acid), 1.16 and 3.93.[4] After standing 4 hr. at a *p*H of 12, the solution was acidified and now the titration from the first to the second inflection required 4.4 mmoles of base. After 15 min. at 100°, the solution was reacidified and now required 5.6 mmoles of base between the two inflection points. Such results are consistent with the slow break-down of a strong poly-acid, such as the diphosphonic acid $(CF_3POOH)_2O$, to the strong-and-weak $CF_3PO(OH)_2$.

Basic Hydrolysis of the Tetramer and Pentamer.—A 0.138 mmole sample of $(CF_3P)_4$ was placed with 1 ml. of 10% NaOH solution. The resulting gas, evolved at room temperature, was isolated by distillation and identified as HCF_3 by its molecular weight (70), its vapor tensions (14 mm. at −129° and 41 at −121° and its infrared spectrum. The yield, 0.275 mmole, accounted for 49.8% of the CF_3 groups in the tetramer sample.

Under similar conditions a 0.242 mmole sample of $(CF_3P)_5$ produced 0.602 mmole of HCF_3, representing 49.8% of the CF_3 groups. Fluoride ion was detected in the basic solutions remaining after the hydrolysis of the tetramer and the pentamer.

Stability of the Tetramer toward Acids.—Neither hydrogen chloride nor boron trifluoride showed any reaction with $(CF_3P)_4$ at temperatures below 300°, where thermal decomposition began. In benzene solution there was no evidence of formation of an HCl adduct. Diborane failed to attack $(CF_3P)_4$ during 3 months at room temperature and 6 hr. at 70°. There was no reaction of the tetramer with concd. H_2SO_4 at 100°; a slight solubility was noted, with recrystallization upon cooling.

The Reaction of the Tetramer with Pure Water.—A sample of $(CF_3P)_4$ representing 14.8 mmoles of CF_3P units showed no reaction with 40 mmoles of water during 12 hr. at 120°, in a 500-ml. Pyrex bulb. After 96 hr. at 140° only 67% of the tetramer had reacted, for an amount representing 4.88 mmoles of CF_3P units was recovered. The volatile products were 0.10 mmole of H_2, 2.1 mmoles of CF_3PH_2, 3.6 mmoles of HCF_3 and 0.94 mmole of the new biphosphine $(CF_3PH)_2$ (identification: see next section). The remaining aqueous solution was subjected to potentiometric titration, showing the presence of 3.6 mmoles of phosphorous acid ($pK_1 = 1.8$; $pK_2 = 6.3$; accepted values, 1.8 and 6.15). The HCF_3 was identified by its mol. wt. and volatility; and CF_3PH_2 by its mol. wt. (102) and by its H^1 and F^{19} nuclear magnetic resonance spectra[21]; the line multiplicities and relative intensities were in accord with theoretical expectations.[22] The vapor tension of CF_3PH_2 at −78.5° was measured as 45 mm.

Proof and Properties of 1,2-Bis-(trifluoromethyl)-biphosphine.—The formula $(CF_3PH)_2$ was demonstrated by the mol. wt. (199; calcd., 202) and the stoichiometry of thermal decomposition. A 0.348 mmole sample, heated in a sealed tube at 200° for 18 hr., gave some $(CF_3P)_4$, recognized as crystals at room temperature. A further 6 hr. at 225° destroyed all but 0.04 mmole of the $(CF_3PH)_2$ to form 0.258 mmole of CF_3PH_2, 0.055 mmole of $(CF_3)_2PH$ and 0.031 mmole of HCF_3—all identified by their vapor tensions and infrared spectra. The slightly volatile fraction was almost pure CF_3P tetramer (m.p. 62–64.5°) with a little pentamer; yield 0.178 mmole of CF_3P, quantitatively converted to CF_3PI_2. The yellow-green inevaporable oil remaining in the reaction tube was treated with chlorine; the non-volatile product was 0.06 mmole of PCl_5 and the volatile product was reduced by mercury to form 0.037 mmole of CF_3PCl_2. These results together demonstrate the literal molecular formula $(CF_3)_{1.99}P_{1.91}H_{1.95}$, satisfactorily close to $(CF_3PH)_2$.

The room temperature hydrolysis of 0.104 mmole of $(CF_3PH)_2$ with 10% sodium hydroxide solution gave 0.104 mmole of HCF_3.

The vapor tensions of $(CF_3PH)_2$, shown in Table V, determine the equation $\log p_{\text{mm.}} = 6.4475 - 0.006115T + 1.75 \log T - 2024/T$, according to which the normal b.p. would be 69.5° and the Trouton constant 20.9 cal./deg. mole.

TABLE V

VAPOR TENSIONS OF $(CF_3PH)_2$

t (°C.)	−40.0	−29.0	−20.0	−14.4	0.00	10.8	19.0
p_{mm} (obsd.)	3.08	6.92	12.88	18.44	43.2	75.3	110.7
p_{mm} (calcd.)	3.05	6.97	12.88	18.44	42.8	75.3	111.7

The infrared spectrum of $(CF_3PH)_2$ vapor was recorded by means of a Perkin–Elmer Model 13 spectrophotometer. The peaks and their relative intensities are shown in Table VI.

TABLE VI

INFRARED SPECTRUM OF $(CF_3PH)_2$ VAPOR

Frequency (cm.$^{-1}$)	2330	1250	1150	1135	1027	868	845	730
Intensity	Med.	Weak	V. str.	V. str.	Weak	Med.	Str.	Med.

The absorption at 2330 cm.$^{-1}$ is attributed to the P-H stretching vibration; at 1135 and 1150, to C–F stretching. It is a general observation,[12] justified by theory, that such C–F absorption is split into at least $n + 1$ bands, where n is the number of CF_3 groups on each phosphorus atom. In this case the splitting into no more than two components confirms the CF_3PPCF_3 situation of the CF_3 groups.

The Reaction of the Pentamer with Water.—A sample of the pentamer $(CF_3P)_5$ was only slightly attacked by water during 3 months at 110–140° but did produce traces of HCF_3 and fractions corresponding to the biphosphine $(CF_3PH)_2$ and triphosphine $H_2(CF_3P)_3$. The reaction was far more satisfactory when diglyme (β,β′-dimethoxy-diethyl ether) was used as a solvent. A pentamer sample estimated as 4 mmoles (2 g.), with 0.5 ml. of water in 1.5 ml. of diglyme at 50°, reacted during three 5-min. intervals (between which pressure-relief was necessary) to give 2.2 mmoles of CF_3PH_2,

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(21) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

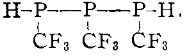
(22) D. A. Dows, private communication.

1.47 mmoles of $(CF_3PH)_2$ and 129.5 mg. of a liquid having 3.7 mm. vapor tension at 0°. The gas volume of this sample implied a mol. wt. value of 298; calcd. for the formula $H_2(CF_3P)_3$, 302. The yield, from a far-from-complete reaction, was 10%.

Proof and Properties of 1,2,3-Tris-(trifluoromethyl)-triphosphine.—A sample of the supposed triphosphine weighed as 85.7 mg. (0.284 mmole) was left in contact with an active nickel surface (formed by the decomposition of nickel carbonyl in the vacuum system) at 25°. The decomposition, signalled by a pressure increase, was essentially complete in 24 hr. After six days the products were separated by fractional condensation to give 0.28 mmole of CF_3PH_2 (identified by its infrared spectrum) and a tetramer–pentamer mixture equivalent to 0.560 mmole of CF_3P units, as shown by conversion to CF_3PCl_2. Thus the total CF_3P groups amounted to 0.840 mmole (calcd., 0.852) and the hydrogen 0.56 mg. atom (calcd., 0.568). Thus the formula of the triphosphine was not in doubt. Although unstable on the active nickel surface, this triphosphine showed no tendency toward decomposition in two months of storage in a clean Pyrex-glass tube. Its formation even at 140° also argues for its stability in the practical sense.

The room temperature hydrolysis of 0.246 mmole of $H_2(CF_3P)_3$ with 10% sodium hydroxide gave 0.236 mmole of HCF_3.

The infrared spectrum of the triphosphine is represented in Table VII. The separation of the peaks due to the C–F vibrations (1145 and 1160 cm.$^{-1}$) is typical for one CF_3 group on each phosphorus atom, and supports the open chain structure



$$\underset{CF_3}{\underset{|}{H\text{-}P}}\text{——}\underset{CF_3}{\underset{|}{P}}\text{——}\underset{CF_3}{\underset{|}{P\text{-}H}}.$$

TABLE VII

INFRARED SPECTRUM OF THE TRIPHOSPHINE

Frequency (cm.$^{-1}$)	2330	2260	1160	1145	870	850	745
Intensity	Med.	Weak	V. str.	V. str.	(Infl.)	Str.	Med.

In the ultraviolet the triphosphine shows an absorption peak at 2075 Å. (molar extinction coefficient ε 7,600) and a shoulder at 2240 Å. (ε 5,500). The shift toward the visible region, relative to the biphosphine $(CF_3PH)_2$ (maximum at 2040 Å.) is qualitatively in agreement with expectations, since more resonance structures can be written for the triphosphine. Since all of the resonance structures (except the classical Lewis picture) involve charge-separations, these make their major contribution to the excited state, lowering it relative to the ground state.

LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

A New Metal Carbonyl Synthesis[1]

BY REX D. CLOSSON, LLOYD R. BUZBEE[2] AND GEORGE G. ECKE[2]

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The reaction of benzophenone sodium with chromic chloride in tetrahydrofuran yielded an intermediate, which upon carbonylation at 200 atmospheres and 100° for 1 hr., gave chromium carbonyl in 59% yield. The use of manganese chloride in an analogous carbonylation after hydrolysis gave a 32% yield of manganese carbonyl. This new process appears to offer advantages in yield and ease of operation.

The preparation of the carbonyls of iron, cobalt and nickel has been effected in a variety of ways, including direct reaction of the metal with carbon monoxide. On the other hand, synthesis of chromium and manganese carbonyls has required more elegant methods. One such method involves treating a mixture of a Grignard reagent and a salt of the metal with carbon monoxide. This procedure has given yields of up to 67% of chromium carbonyl[3] and also gave the first indication that a carbonyl of manganese could be prepared.[4]

More recently chromium carbonyl was prepared in substantial yields by Brimm, Lynch and Sesny.[5] They carbonylated a mixture of chromic chloride, magnesium and iodine in ethyl ether to obtain a 57% yield. Natta, Ercoli, Calderazzo and Rabizzoni[6] carbonylated a mixture of chromic acetylacetonate, magnesium and iodine in pyridine to obtain an 82% yield. Fischer and Hafner[7] report an 83% yield from the carbonylation of a reaction mixture prepared from chromic chloride, aluminum powder, aluminum chloride and benzene.

The first preparation of manganese carbonyl that yielded enough material for adequate characterization was the reaction of manganese iodide, copper and magnesium in ethyl ether with carbon monoxide.[8] The yield was about 1%. Somewhat improved yields have been reported by a modified Grignard procedure.[9]

This paper describes the results of an investigation in these laboratories in which it was found that the action of carbon monoxide on chromium benzophenone ketyl in tetrahydrofuran yielded chromium carbonyl in 59% yield. Application of the reaction to manganese gave manganese carbonyl in 32% yield.

The preparation and the chemistry of the benzophenone ketyls of the alkali and alkaline earth elements has been studied by Bachmann[10] and many of the anomalous results of previous literature have been elucidated. In contrast, the preparation and chemistry of ketyls of the metals of other groups has received little attention. This may have been due, in part, to the fact that preparing the ketyls directly from the ketone and the metal is in many cases difficult or even thermodynamically impossible. In the present investigation, the ketyls were

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[1] Presented in part before the Division of Inorganic Chemistry at the 134th meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

[2] Koppers Company, Pittsburgh, Pennsylvania.

[3] B. B. Owen, J. English, H. G. Cassidy and C. V. Dundon, THIS JOURNAL, **69**, 1723 (1947).

[4] D. T. Hurd, G. W. Sentell, Jr., and F. J. Norton, *ibid.*, **71**, 1899 (1949).

[5] E. O. Brimm, M. A. Lynch and W. J. Sesny, U. S. Patent 2,803,525 (August 20, 1957).

[6] G. Natta, R. Ercoli, F. Calderazzo and A. Rabizzoni, THIS JOURNAL, **79**, 3611 (1957).

[7] E. O. Fischer and W. Hafner, *Z. Naturforschg.*, **10B**, 665 (1955); German Patent 1,007,305 (May 2, 1957).

[8] E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, THIS JOURNAL, **76**, 3831 (1954); M. A. Lynch, Jr., U. S. Patent 2,825,631 (March 4, 1958).

[9] V. Hnizda, U. S. Patent 2,822,247 (February 4, 1958).

[10] W. E. Bachmann, THIS JOURNAL, **55**, 1179 (1933).