gave 179 mg. of colorless needles, m.p. 144–146°. Recrystallization from acetone–hexane gave colorless prisms, m.p. 142–143°, $[\alpha]^{28}D$ +53° (c 0.72); λ_{max} 5.68, 5.78, 6.24 and 11.04 μ; λ_{max} 267 mμ (ϵ 800); n.m.r. spectrum: 3.17(m, 1, CH-1), 3.31(m, 1, CH-3), 5.32(m, 1, CH-17), 7.78(s, 3), 7.83(s, 3), 8.00(s, 3), and 9.22(s, 3, CH₃-18) τ.

Anal. Calcd. for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.8; H, 8.25.

2,17β-Dihydroxy-4-methyl-1,3,5(10)-estratriene (19c).—A solution of 59 mg. of diacetate **19b** and 2 ml. of 40% sodium hydroxide in 10 ml. of methanol and 1 ml. of water was heated under reflux in an atmosphere of nitrogen for 1 hr. The solution was concentrated on a rotary evaporator, acidified with concentrated hydrochloric acid, and extracted with three 50-ml. portions of ethyl acetate. The organic extracts were combined, washed with 50 ml. of saturated sodium bicarbonate solution and 50 ml. of saturated sodium chloride solution, then dried over anhydrous sodium sulfate. Removal of solvent at reduced pressure gave 47 mg. of needles. Recrystallization from acetonitrile gave colorless needles, m.p. 256–258°, reported[21] m.p. 257–259°; λ_{max}^{KBr} 3.05, 6.30, 11.78 μ; λ_{max} 281–286 mμ (ϵ 2100). The infrared and ultraviolet spectra were identical with those of an authentic sample.[21]

1-Methylestradiol Diacetate (22b).—Treatment of a portion of the 1-methylestradiol 17-acetate described above with a 2:1 mixture of pyridine–acetic anhydride overnight at room temperature gave, after recrystallization from methanol, colorless blades,

m.p. 178–180°, $[\alpha]^{26}D$ +112° (c 0.78), λ_{max} 5.72 and 5.82 μ, and λ_{max} 269 (ϵ 580); reported[20]: 178–180°, $[\alpha]^{20}D$ 111°, λ_{max} 268 (ϵ 340).

For the preparation of an authentic sample, 200 mg. of androsta-1,4-dien-3-one-17β-ol acetate (**1a**) was treated with 5 ml. of 50% sulfuric acid at 100° for 30 min. according to the general procedure of Dreiding, Pummer and Tomasewski.[38] The reaction mixture was then neutralized with saturated sodium bicarbonate solution and extracted with four 50-ml. portions of ethyl acetate. The combined extracts were dried over saturated sodium chloride solution and anhydrous sodium sulfate and evaporated to dryness under reduced pressure to give 223 mg. of an amber oil. Acetylation by the pyridine–acetic anhydride procedure gave 242 mg. of a semicrystalline amber solid, which was chromatographed on 9 g. of silica gel. Elution with 400 ml. of 1:99 ether–benzene gave 93 mg. of a colorless oil, which crystallized when seeded with a specimen of the above diacetate. Recrystallization from ether–hexane and then methanol gave colorless blades, m.p. 178–180°. The melting point was unchanged on admixture with the material described above.

Acknowledgments.—The authors express their sincere appreciation to Drs. T. J. Flautt and D. H. Gustafson of these laboratories for numerous helpful discussions.

(38) A. S. Dreiding, W. J. Pummer and A. J. Tomasewski, *J. Am. Chem. Soc.*, **75**, 3159 (1953).

Some Aspects of the Chemistry of Cyclopolyphosphines

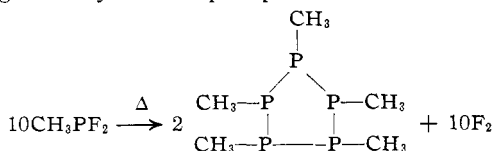By Wm. A. Henderson, Jr., Martin Epstein and Francis S. Seichter

Several new cyclotetraphosphines, (RP)₄, have been synthesized by the reduction of primary dihalophosphines with magnesium, the dehydration of primary phosphine oxides, and by methods already reported in the literature. The dehydration reaction constitutes the first example of the formation of a P–P bond by loss of water. The vapor phase ultraviolet spectra of alkylcyclotetraphosphines have been found to be characteristic of the ring and different from that of cyclopentaphosphines, (RP)₅. Evidence is presented for the existence of two tetraphenylcyclotetraphosphines, $(C_6H_5P)_4$, and for the nonexistence of $(C_6H_5P)_2$.

As has been suggested by Mahler and Burg,[1] cyclotetraphosphines (tetraphosphetanes) might well be expected to exhibit electron delocalization and, perhaps, aromatic character through the contribution of resonance structures such as Ia and Ib. Presumably, these
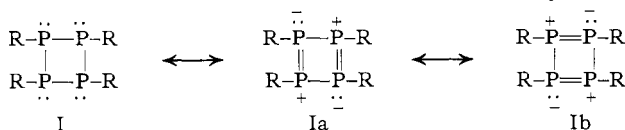
structures would involve pπ–dπ bonding and would result in significant departures from normal phosphine behavior. This should be apparent both in the physical and chemical properties of cyclopolyphosphines. Because of the obviously interesting properties of these compounds, we have initiated a study of this area, the results of which are reported here.

Alkylcyclopolyphosphines.—A few alkylcyclopolyphosphines have been reported in the literature. Pentamethylcyclopentaphosphine has been synthesized by heating methyldifluorophosphine.[2] Issleib and co-

workers have prepared tetraethylcyclotetraphosphine[3a]

(1) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **79**, 251 (1957); **80**, 6161 (1958).

(2) V. N. Kulakova, Y. U. M. Zinovev, and L. Z. Soborovskii, *Zh. Obsch. Chem.*, **29**, 3957 (1959).

(3) (a) K. Issleib and B. Mitscherling, *Z. Naturforsch.*, **15b**, 267 (1960); (b) K. Issleib and W. Seidell, *Z. anorg. allgem. Chem.*, **30B**, 155 (1960).

and tetracyclohexylcyclotetraphosphine[3b] by reaction of the alkylphosphine and alkyldichlorophosphine in refluxing toluene.

$$2RPH_2 + 2RPCl_2 \xrightarrow{\Delta} (RP)_4 + 4HCl$$
$$R = C_2H_5, \text{cyclo-}C_6H_{11}$$
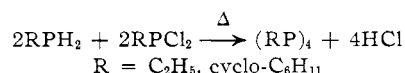
Burg has made the trifluoromethyl tetramer and pentamer by reduction of trifluoromethyldiiodophosphine with mercury.[1] The former compound has also been prepared in low yield by the reaction of trifluoromethyl radicals with elemental phosphorus.[4]

Tetra-*n*-butylcyclotetraphosphine has been prepared by Rauhut and Semsel of this Laboratory[5] by the reaction of *n*-butylmagnesium bromide, *n*-butyl bromide, and phosphorus.

Synthetic Methods.—A summary of our synthetic routes to alkylcyclopolyphosphines is given in Fig. 1 and in Table I. It will be noted that the preparations involving the dehydration of a phosphine oxide and the reduction of a primary dichlorophosphine with magnesium are new as are several of the compounds prepared. A detailed discussion of the above synthetic methods follows.

The reaction of a primary phosphine with the corresponding dihalophosphine is the simplest method of preparing cyclopolyphosphines.

$$2RPCl_2 + 2RPH_2 \longrightarrow (RP)_4 + 4HCl$$
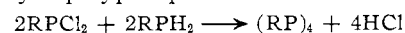
The dihalophosphines may best be obtained by chlorination of the primary phosphine with phosgene[6] or alter-

(4) W. H. Watson, *Texas J. Sci.*, **11**, 471 (1959).

(5) M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **28**, 473 (1963).

(6) W. A. Henderson, Jr., S. A. Buckler, N. E. Day, and M. Grayson, *ibid.*, **26**, 4770 (1961).

TABLE I

SYNTHESIS OF CYCLOPOLYPHOSPHINES

Compound	Method[a]	Yield, %	B.p. °C.	B.p. mm.	M.p., °C.	Mol. weight Calcd.	Mol. weight Found	N.m.r. shift[b]
$(CH_3P)_5$	2	19	110–112	1		230	222	−21
	4	63						
$(C_2H_5P)_4$	2	70	124–129	0.05		240	232	−17
	4	81						
$(n\text{-}C_3H_7P)_4$	1	92	140–145	.03				−13
$(i\text{-}C_3H_7P)_4$	2	80	110–114	.04	23–24			+66
$(CNCH_2CH_2P)_4$	1	43			87–89	191	187	− 2
$(n\text{-}C_4H_9P)_4$	1	82	170	.02				−14
$(i\text{-}C_4H_9P)_4$	1	78	140	.1[c]		352	365	−13
	2	60						
	4	60						
$[(C_2H_5)_2CHP]_4$	3	15			91–92	408	387	+70
$(cyclo\text{-}C_6H_{11}P)_4$	1	77			222–224	456	438	+70
	3	22						
$(n\text{-}C_8H_{17}P)_4$	1	92	230	.1[c]		577	551	−13
	2	44						
$(C_6H_5P)_4$ A	1	93			153–155	432	402	+ 9
	5	58			148–150			
	2	84			148–152			
$(C_6H_5P)_4$ B	1	77			195–199	432	441	[d]
$(C_6H_5P)_n$ C	1	100			270–283		Poly.	
$(C_6H_5P)_n$ D	1	96			260–285		Poly.	

[a] Methods are: 1, reaction of the primary phosphine and primary dichlorophosphine; 2, reduction of the primary dichlorophosphine with magnesium; 3, dehydration of the primary phosphine oxide; 4, reduction of the primary dichlorophosphine with lithium; and 5, reduction of the primary dichlorophosphine with lithium aluminum hydride.   [b] Run in CS_2; shifts in p.p.m. relative to 85% H_3PO_4.   [c] Molecular distillation.   [d] Too insoluble to measure.

natively with chlorine[7] or by the reaction of an alkyl-cadmium compound with PCl_3.[8] This condensation reaction is facilitated by the use of refluxing solvents such as benzene or hexane. With bulky substituent groups on phosphorus, the use of even higher boiling solvents such as toluene or xylene is required to realize reasonable reaction times. Yields, as listed in Table I, are over 75%.
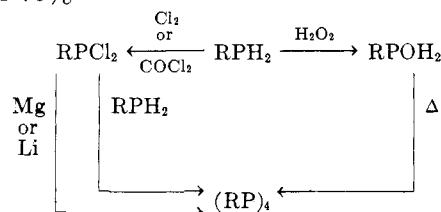
$$RPCl_2 \xleftarrow[COCl_2]{\overset{\overset{Cl_2}{or}}{}} RPH_2 \xrightarrow{H_2O_2} RPOH_2$$

Fig. 1.—Synthetic routes to cyclotetraphosphines.

The formation of polyphosphines by the reduction of phenyldichlorophosphine with lithium[9] has been extended to the alkyl series. Although the reaction is slow in ether through coating of the metal, it is moderately fast in tetrahydrofuran and is to be recommended in those cases where use of the primary phosphine is awkward, as with the very low boiling methylphosphine.

Formation of cyclopolyphosphines by reduction of aryl and alkyl dichlorophosphines with magnesium in tetrahydrofuran proceeds much more rapidly than reduction with lithium. The reaction with phenyldichlorophosphine is so vigorous as to require external cooling, whereas the alkyl compounds require refluxing for several hours.[10]

The conversion of a primary phosphine oxide to a cyclotetraphosphine is the first example of the formation of a P–P bond by dehydration. The reaction is thus a new and fundamentally different route to the

(7) C. Walling, U. S. Patent 2,437,796.

(8) R. B. Fox, J. Am. Chem. Soc., 72, 4147 (1950).

(9) P. R. Bloomfield and K. Parvin, Chem. Ind. (London), 541 (1959).

(10) It was thought that in this and the preceding reactions, the intermediate RP might be formed. Attempts to trap this phosphorus analog of a carbene using cyclohexene, butadiene, and tolane as solvents were unsuccessful, as were attempts to generate RP thermally from (RP)4.

cyclotetraphosphine moiety. The reaction takes place on heating the crude oxide, prepared by the method of Buckler and Epstein,[11] while removing the volatile products with an oil-pump. Yields are poor, presumably through a side reaction involving disproportionation to the primary phosphine and phosphinous acid.

Ultraviolet Spectra.—In Fig. 2 are given the ultraviolet spectra of several of the compounds prepared in
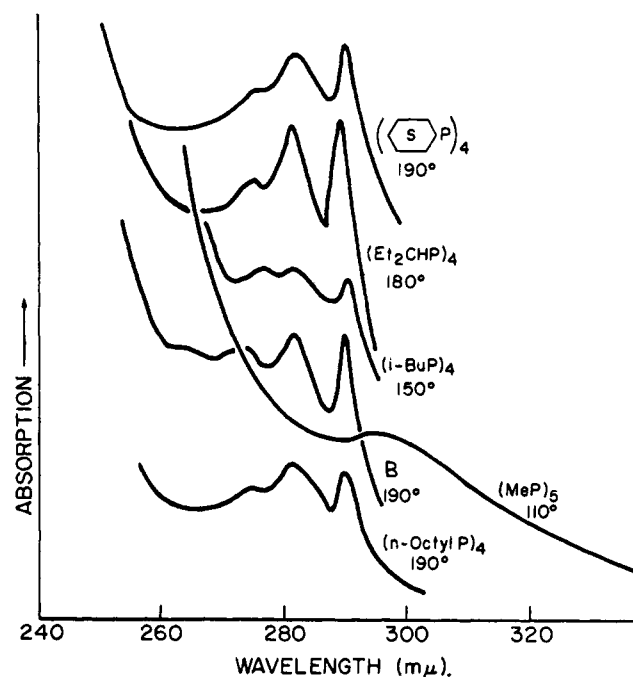

Figure 2.

our investigation. Spectra were taken in the vapor phase in evacuated, heated cells to avoid the difficulties with oxidation experienced in solution work. This technique also afforded sharper spectra (in solution, cyclotetraphosphines exhibit only one broad peak with

(11) S. A. Buckler and M. Epstein, J. Am. Chem. Soc., 82, 2076 (1960).

λ_{max} ~300 mμ), but made the determination of extinction coefficients prohibitively difficult.

Inspection of Fig. 2 shows that alkylcyclotetraphosphines have a characteristic ultraviolet spectrum comprised of three peaks at 275, 282, and 290 mμ. On the other hand, the methyl pentamer shows only a single peak in this region.
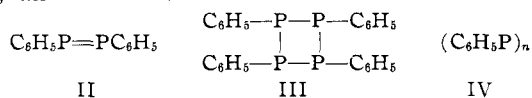
The only vapor phase ultraviolet spectra in the literature are those of Mahler and Burg[1] for the trifluoromethyl tetramer and pentamer. Their spectra also show three maxima for the tetramer and only one for the pentamer, although the peaks are shifted from the above positions through the difference in electronegativity of the trifluoromethyl group.

The intense ultraviolet spectra observed in the cyclotetra- and cyclopentaphosphines, coupled with the fact that phosphines, R_3P, do not absorb strongly in the normal ultraviolet, indicate a high degree of electron delocalization in these compounds, as was anticipated. The existence of electron delocalization is further substantiated by the fact that the cyclopolyphosphines are nonbasic. The alkyl tetramers have a pK_a of < 1, while tertiary phosphines have pK_a's of 2–10.[12]

Arylcyclopolyphosphines.—The first polyphosphine of the formula (ArP)$_n$ was prepared by Michaelis and Köhler[13] in 1877. Their preparation of "phosphorobenzene," A, with the composition $(C_6H_5P)_n$ and melting point 149–150°, thus antedated the preparation of alkylcyclopolyphosphines by almost a century. Since that time, two other compounds of the formula $(C_6H_5P)_n$ have been found; compound B, m.p. 190°[14], and an insoluble and presumed polymeric form, C, m.p. 252–280°.[15]

Various methods have been used to prepare these compounds. Compound A has been formed by the reaction of phenyldichlorophosphine and phenylphosphine[13,15,16,17] and by reduction of phenyldichlorophosphine with lithium aluminum hydride,[15,16] lithium,[9] lithium hydride,[18] and sodium and ethanol.[16] Compound B has been prepared by the reaction of phenyldichlorophosphine and phenylphosphine[14,15] as has compound C.[15] Despite apparently similar reaction conditions, various workers obtain either A or B from the last reaction; only Reesor and Wright[15] have succeeded in preparing both.

The question of the molecular weights of A and B is also one of controversy. Using several isopiestic, ebullioscopic, and cryoscopic methods, various workers have proposed the identities A = B = II[14]; A = II, B = III[15]; and A = III.[16,17]

$$C_6H_5P{=}PC_6H_5 \qquad \begin{matrix} C_6H_5{-}P{-}P{-}C_6H_5 \\ | \quad | \\ C_6H_5{-}P{-}P{-}C_6H_5 \end{matrix} \qquad (C_6H_5P)_n$$

$$\text{II} \qquad\qquad \text{III} \qquad\qquad \text{IV}$$

In our hands, the direction of the reaction of phenyldichlorophosphine and phenylphosphine has been no less perplexing. The reaction goes smoothly in ether or other solvents at room temperature, but it has not been possible to define the conditions under which A, B, and C are formed. (In one case, a second insoluble form, D, m.p. 260–285°, was obtained; this differed in infrared spectrum from compound C.) The effect of reactant quantities and concentrations, the rate and order of addition of reactants, the purity of reactants, the use of slight excesses of reagents, seeding, and aging of the

reaction mixture were all investigated. Only the first variable seemed of importance; large quantities of reactants favor the formation of C, as was observed by Reesor and Wright.[15] Nor do apparently identical conditions always yield the same results; repetition of conditions yielding A often afforded C and occasionally B.

Several physical properties of the compounds A and B were determined. The molecular weights were measured by various methods in several solvents (see Table I). The values obtained were 402 ± 40 for A and 441 ± 13 for B; hence, both compounds must have the composition $(C_6H_5P)_4$, molecular weight 432.

That neither compound A nor B is the dimer II is further shown by the fragments obtained on mass spectrographic analysis; A and B afforded similar spectra with peaks corresponding to the fragments $(C_6H_5)_4$, $(C_6H_5P)_3$, and $(C_6H_5P)_2$, as well as further decomposition products.

With some difficulty, the ultraviolet spectrum of B was determined as before and it was the same as that of the alkylcyclotetraphosphines. Numerous attempts to determine the spectrum of A failed, as a result of thermal decomposition of the compound.

The infrared spectra of A and B are virtually identical in CS_2 solution, both showing single peaks at 692 and 741 cm.$^{-1}$. In a Nujol mull, the spectrum of B is not changed, but A shows two doublets at 685 and 690 cm.$^{-1}$ and at 735 and 740 cm.$^{-1}$.

The Raman spectra of crystalline A and B are almost identical, showing asymmetric and symmetric ring stretches near 500 and 450 cm.$^{-1}$, respectively,[19] and are similar to those for alkylcyclotetraphosphines.[20]

The proton n.m.r. spectra of A and B are distinctly different in CS_2 solution (see Experimental section). It was not possible to determine the phosphorus n.m.r. shift of B through the lack of solubility of the compound. The single phosphorus n.m.r. peak of compound A shows all the phosphorus atoms to be identical.

The molecular weights, analyses, and mass spectrographic data given above establish that A and B have the composition $(C_6H_5P)_4$. The molecular weights and Raman spectra of A and B, the ultraviolet spectrum of B, and the phosphorus n.m.r. spectrum of A show that both are cyclotetraphosphines.

The question then arises as to whether A and B are crystalline modifications of the same compound or whether they differ in solution as well. Of the physical evidence presented above, only the proton n.m.r. spectra of the two compounds point to a definite difference between A and B in the liquid phase. While there are very slight differences in the solution infrared spectra, these may well be within experimental error. However, further evidence for an energy barrier between A and B and hence their nonidentity in solution is found in seeding experiments. A solution of B seeded with A always precipitates B and vice versa. That the barrier is not insurmountably high is shown by the fact that B (and even C) sublimes at 153° to give A.

From the above evidence, the authors reach the interesting conclusion that A and B are tetraphenylcyclotetraphosphines, differing in solution as well as in the solid state, and hence must be stereoconformers.[21] They may differ in that one has a planar P_4 ring with

(12) W. A. Henderson, Jr., and C. A. Streuli, J. Am. Chem. Soc., **82**, 5791 (1960).

(13) H. Köhler and A. Michaelis, Ber., **10**, 807 (1877).

(14) T. H. Weil, B. Prijs, and H. Erlenmeyer, Helv. Chim. Acta, **35**, 616 (1952).

(15) J. W. B. Reesor and G. F. Wright, J. Org. Chem., **22**, 386 (1957).

(16) W. Kuchen and H. Buchwald, Ber., **91**, 2296 (1958).

(17) F. Pass and H. Schindlbaur, Monatsh., **90**, 148 (1959).

(18) L. Horner, H. Hoffmann, and P. Beck, Ber., **91**, 1583 (1958).

(19) R. L. Amster, W. A. Henderson, Jr., and N. B. Colthup, to be published.

(20) R. L. Amster, N. B. Colthup and W. A. Henderson, Jr., to be published.

(21) One of the referees of the manuscript, Anton B. Burg, has suggested the interesting possibility that compounds A and B do not differ in the P_4 ring, but differ in that the phenyl substituents adopt different rotational conformations.

substituents out of the plane of the ring, and the other a puckered ring, such as is found for $(CF_3P)_4$[22] and (cyclo-$C_6H_{11}P)_4$.[23] Thus, the two most probable structures are V and VI, but others cannot be excluded.
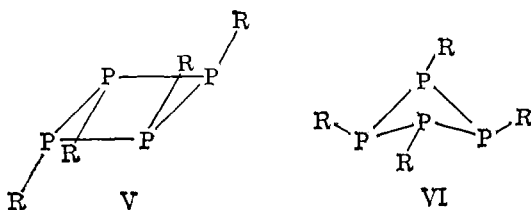
Presumably, the energy barrier between A and B, whatever their respective conformations, is that involved in inverting the configuration of one or more of the P atoms. A similar and substantial energy barrier exists for the inversion of simple trigonal phosphorus compounds, as is shown by the surprising thermal stability of optically active tertiary phosphines.[24]

Experimental

All manipulations were carried out under nitrogen. Melting points and boiling points are uncorrected.

Pentamethylcyclopentaphosphine. (a) From Methyldichlorophosphine and Lithium.—At $-40°$ in a 250-ml. erlenmeyer flask was placed 50 ml. of tetrahydrofuran distilled from lithium aluminum hydride, 2.85 g. (0.42 mole) of lithium ribbon, and 20 g. of glass chips. To this was added with vigorous magnetic stirring 23.0 g. (0.20 mole) of methyldichlorophosphine, whereupon reaction commenced as shown by brightening of the metal. The reaction mixture was gradually warmed to room temperature and stirred for 48 hr. Solvent and product were then distilled from the salt to a temperature of 200° (1 mm.). Redistillation gave 6.1 g. (63%) of pentamethylcyclopentaphosphine, b.p. 110–112° (1 mm.) (reported[2] 123° (2 mm.).

(b) From Methyldichlorophosphine and Magnesium.—A solution of 20 g. (0.17 mole) of methyldichlorophosphine in 50 ml. of tetrahydrofuran was slowly added to 4.0 g. (0.17 mole) of magnesium metal turnings suspended in 30 ml. of tetrahydrofuran. The addition was extremely exothermic and was carried out at $-30°$. The reaction mixture was then stirred at room temperature for 24 hr. The solvent was stripped, leaving a heavy, white gel from which the product was distilled directly at a pot temperature of 250° and at a pressure of 0.05 mm. Redistillation gave 1.5 g. (19% yield) of product, b.p. 110–114° (1 mm.)

Tetraethylcyclotetraphosphine. (a) From Ethyldichlorophosphine and Lithium.—In a 500-ml. erlenmeyer flask was put 27.5 g. (0.233 mole) of ethyldichlorophosphine, 3.22 g. (0.467 mole) of lithium ribbon, some glass chips, and 250 ml. of dry tetrahydrofuran. The mixture was stirred and refluxed 6 days and then distilled to give 12.7 g. of crude material. This was redistilled to yield 11.0 g. (81%) of tetraethylcyclotetraphosphine, b.p. 124–129° (0.05 mm.) (reported[3a] 168–170°).

(b) From Ethyldichlorophosphine and Magnesium.—A solution of 43 g. (0.33 mole) of ethyldichlorophosphine in 75 ml. of dry, freshly distilled tetrahydrofuran was slowly added to 8 g. (0.33 mole) of magnesium metal turnings and some glass chips in 125 ml. of tetrahydrofuran. The reaction mixture was stirred rapidly and the temperature was maintained at 45–50° with external cooling during the first half of the addition. Due to coating of the metal, no exotherm was observed during the latter portion of the addition. After the addition was completed, the reaction mixture was stirred at 55° for 12 hr. Very little Mg metal remained. The solvent was stripped and 100 ml. of N₂-purged water was added to the white mass which was then repeatedly extracted with N₂-purged benzene. The combined benzene extracts were dried over $MgSO_4$, filtered, and stripped. Distillation of the residual oil gave 14 g. (70% yield) of product.

Tetra-n-propylcyclotetraphosphine.—A 500-ml. flask was charged with 15 g. (0.20 mole) of n-propylphosphine, 29 g. (0.20 mole) of n-propyldichlorophosphine, and 300 ml. of dry, N₂-purged benzene. The mixture was heated at 50° until the evolution of HCl ceased. The benzene was stripped and the residual oil distilled. Distillation gave 27 g. (92% yield) of product, b.p. 140–145° (0.03 mm.).

Anal. Calcd. for C_3H_7P: C, 48.66; H, 9.53; P, 41.83. Found: C, 49.07; H, 9.52; P, 40.66.

Tetraisopropylcyclotetraphosphine.—A solution of 14.5 g. (0.10 mole) of isopropyldichlorophosphine, in 50 ml. of tetrahydrofuran, was slowly added to 2.4 g. (0.10 mole) of magnesium

metal turnings in 50 ml. of tetrahydrofuran. The remainder of the procedure was carried out in identical fashion to that of the tetraethyl homolog (method b). Distillation gave 6.0 g. (80% yield) of product, b.p. 110–114° (0.04 mm.), m.p. 23–24°.

Anal. Calcd. for C_3H_7P: P, 41.83. Found: P, 41.64.

Tetracyanoethylcyclotetraphosphine.—To 1.78 g. (0.02 mole) of cyanoethylphosphine and 3.76 g. (0.04 mole) of pyridine in 40 ml. of chloroform was added with stirring at 0° 3.16 g. (0.02 mole) of dichlorocyanoethylphosphine. After 2 hr., the solution was extracted two times with 20 ml. of water and then dried. Removal of the chloroform yielded an oil which crystallized after 2 days. Recrystallization from acetone–water afforded 1.5 g. (43%) of large, equant crystals, m.p. 87–89°.

Anal. Calcd. for C_3H_4PN: C, 42.36; H, 4.74; P, 36.42. Found: C, 41.70; H, 4.81; P, 35.48.

Tetra-n-butylcyclotetraphosphine.—In a 100-ml. flask were placed 4 g. (0.025 mole) of n-butyldichlorophosphine and 2.3 g. (0.025 mole) of n-butylphosphine in 60 ml. of dry benzene. This mixture was gently refluxed until hydrogen chloride evolution ceased. Distillation gave 82% of product, b.p. 120° (0.02 mm.).

Anal. Calcd. for C_4H_9P: C, 54.53; H, 10.30; P, 35.17. Found: C, 54.18; H, 10.30; P, 35.62.

Tetraisobutylcyclotetraphosphine. (a) From Isobutyldichlorophosphine and Isobutylphosphine.—In a 50-ml. flask were put 6.0 g. (0.04 mole) of isobutyldichlorophosphine, 3.4 g. (0.04 mole) of isobutylphosphine, and 10 ml. of xylene. The solution was refluxed 30 min., after which evolution of gas had ceased. Distillation afforded 78% of tetraisobutylcyclotetraphosphine, b.p. 135–138° (0.24 mm.).

Anal. Calcd. for C_4H_9P: C, 54.54; H, 10.30; P, 35.17. Found: C, 54.31; H, 10.43; P, 34.06.

(b) From Isobutyldichlorophosphine and Lithium.—In a 250-ml. erlenmeyer flask were placed 8.0 g. (0.05 mole) of isobutyldichlorophosphine, 0.7 g. (0.10 mole) of lithium ribbon, 25 g. of glass chips, and 50 ml. of dry THF. After the initial vigorous reaction subsided, the solution was refluxed with stirring for 2 days. Work-up by the same method as for the methyl compound afforded 2.6 g. (60%) of product, b.p. 132–138° (0.25 mm.).

(c) From Isobutyldichlorophosphine and Magnesium.—This reaction was carried out in identical fashion to the preparation of the tetraethyl homolog (method b). Distillation afforded a 60% yield of product.

Tetra-3-pentylcyclotetraphosphine.—The primary phosphine oxide prepared from 35 g. (0.4 mole) of 3-pentanone, phosphine, and 125 ml. of 12 N hydrochloric acid by the method of Buckler and Epstein[11] was put in a 500-ml. flask. This was evacuated to a pressure of 1 mm. and held there while the flask was slowly heated to 60° on an oil-bath. Pumping and heating were continued for 6 hr., after which the flask was allowed to cool. The crystalline residue was recrystallized twice at Dry Ice temperature from the minimum volume of petroleum ether and then vacuum dried to give a 15% yield of tetra-3-pentylcyclotetraphosphine as white needles, m.p. 91.0–91.4°.

Anal. Calcd. for $C_5H_{11}P$: C, 58.80; H, 10.86; P, 30.34. Found: C, 58.79; H, 10.52; P, 30.01.

Tetracyclohexylcyclotetraphosphine. (a) From Cyclohexyldichlorophosphine and Cyclohexylphosphine.—Into a 500-ml. flask were put 13.3 g. (0.115 mole) of cyclohexylphosphine, 21.3 g. (0.115 mole) of cyclohexyldichlorophosphine, and 200 ml. of toluene. The solution was refluxed 4 hr. until evolution of hydrogen chloride had ceased and then allowed to cool. Most of the solvent was stripped to yield crystals which were collected and dried. The yield was 19.2 g. (77%) of material, m.p. 218–220° (reported[3b] 219–220°).

(b) From Cyclohexylphosphine Oxide.—Cyclohexylphosphine (10.9 g., 0.095 mole) was oxidized with hydrogen peroxide to the phosphine oxide by the method of Buckler and Epstein.[11] The oxide was treated in the same way as the 3-pentyl compound and recrystallized from 65 ml. of benzene to give 2.4 g. (22%) of white crystals, m.p. 222–224°.

Tetra-n-octylcyclotetraphosphine. (a) From n-Octyldichlorophosphine and n-Octylphosphine.—In a 100-ml. flask were put 6.4 g. (0.03 mole) of n-octyldichlorophosphine, 4.4 g. (0.03 mole) of n-octylphosphine and 20 ml. of toluene. The solution was refluxed 3 hr. and solvent was then stripped. The residual liquid was molecularly distilled at 230° (0.25 mm.) to give 7.7 g. (92%) of tetra-n-octylcyclotetraphosphine.

Anal. Calcd. for $C_8H_{17}P$: C, 66.61; H, 11.80; P, 21.48. Found: C, 67.17; H, 12.04; P, 21.45.

(b) From n-Octyldichlorophosphine and Magnesium.—To 0.48 g. (0.02 mole) of magnesium in 20 ml. of dry tetrahydrofuran was added with stirring 4.28 g. (0.02 mole) of n-octyldichlorophosphine. After the initial reaction had moderated, the reaction mixture was refluxed for 1 day. The solution was hydrolyzed with water and the dried organic layer molecularly distilled at 230° (0.25 mm.) to give 1.35 g. (46%) of product.

(22) G. J. Palenik and J. Donohue, *Acta Cryst.*, **15**, 564 (1962).

(23) Preliminary X-ray work by L. A. Siegel of this Laboratory.

(24) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Letters*, **5**, 161 (1961).

Tetraphenylcyclotetraphosphine, A. (a) **From Phenyldi-chlorophosphine and Phenylphosphine.**—Phenylphosphine (9.3 g., 0.085 mole) in 20 ml. of ether was added all at once at room temperature with stirring to 15 g. (0.085 mole) of phenyldichloro-phosphine in 20 ml. of ether. Precipitation of product began immediately, followed by vigorous evolution of hydrogen chloride. The mixture was refluxed 2 hr. and then allowed to cool. The solid cyclotetraphosphine was filtered, washed with ether, and dried at 80° (1 mm.) to give 16.5 g. (93%) of white crystals, m.p. 153–155° (reported[15] 154.5–156°).

(b) **From Phenyldichlorophosphine and Magnesium in Ether.**—Phenyldichlorophosphine (8.9 g., 0.05 mole) was added with stirring to 1.2 g. (0.05 mole) of magnesium turnings in 75 ml. of ether. Precipitation and some coating of the metal began after 30 min. After 1 hr., the reaction mixture was refluxed for 2 days. The solid material formed was filtered and washed with water and acetone to afford 4.0 g. of crude A, m.p. 142–148°. Recrystallization from acetonitrile gave off-white crystals, m.p. 149–152°.

(c) **From Phenyldichlorophosphine and Magnesium in Tetra-hydrofuran.**—The same quantities of reagents as in (b) were allowed to react in 50 ml. of tetrahydrofuran as solvent. The reaction was so exothermic as to require the use of a condenser, slow addition of the phenyldichlorophosphine, and occasional external cooling with a water-bath. After most of the phosphine was added, salt began to precipitate. Addition was complete after 30 min., and after several hours only traces of metal remained. The salts were dissolved by addition of a small amount of acetone, and the magnesium was filtered off. Addition of 30 ml. of water formed a two-phase system composed of an organic layer and a salt–water layer. Addition of a second portion of water to the organic layer precipitated 4.0 g. (84%) of tetra-phenylcyclotetraphosphine, m.p. 148–152°.

Tetraphenylcyclotetraphosphine, B.—To 5.0 g. (0.033 mole) of phenyldichlorophosphine in 15 ml. of benzene was added all at once 3.1 g. (0.033 mole) of phenylphosphine. The solution was warmed until gas evolution ceased. The precipitate which formed on cooling was collected and dried to yield tetramer, m.p. 173–192°, in 77% yield. Two recrystallizations from ace-tonitrile gave material, m.p. 195–199° (reported[15] 188–192°).

Phenylphosphine Polymer, C.—Phenylphosphine (3.1 g., 0.033 mole) in 10 ml. of benzene was added at room temperature with stirring over 10 min. to 5.0 g. (0.033 mole) of phenyldichloro-phosphine in 15 ml. of benzene. After 12 hr. at room temperature, the reaction mixture was filtered, and the solid product was washed with petroleum ether to yield 100% of finely crystalline polymer, m.p. 265–285° (reported[15] 252–278°).

Phenylphosphine Polymer, D.—Phenylphosphine (6.1 g., 0.065 mole) in 25 ml. of cyclohexane was stirred at room temperature while 10.0 g. (0.065 mole) of phenyldichlorophosphine in 15 ml. of cyclohexane was added during the course of 1 hr. After gas evolution had ceased, the reaction mixture was filtered and the solid material washed with hexane. The product was dried to afford 11.5 g. (96%) of material, m.p. 260–285°.

Anal. Calcd. for C_6H_5P: C, 66.67; H, 4.66; P, 28.66. Found: C, 66.39; H, 4.55; P, 28.88.

Molecular Weight Determinations.—Molecular weight measurements were carried out largely by the isopiestic method of Clark[25] in the apparatus described by him. The solvents used for the alkyl compounds were methylene chloride, carbon disulfide, and chloroform. The molecular weight of compound A was determined isopiestically in ether, carbon disulfide, methylene chloride, and chloroform; cryoscopically in benzene; and ebullioscopically in chloroform (average of ten determinations). That of compound B was determined isopiestically in chloroform and carbon disulfide and ebullioscopically in benzene (average of six determinations).

Mass Spectrometric Analyses.—Mass spectra were run on a CEC 21–103 C instrument with a heated inlet operating at 200°. The results for the aryl compounds A and B are given in Table II.

Ultraviolet Spectra.—Spectra were run in heated 2-cm. Pyrex cells with quartz glass windows. A sample of 5–10 mg. was in-

(25) E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

TABLE II

Mass	Ion	Rel. peak height A	B	Mass	Ion	Rel. peak height A	B
432	$(C_6H_5P)_4$	0.4	0.2	216	$(C_6H_5P)_2$	2.6	1.8
324	$(C_6H_5P)_3$	28.8	26.3	186	$(C_6H_5)_2PH$	2.0	1.9
262	$(C_6H_5)_3P$	51.2	41.8	110	$C_6H_5PH_2$	15.0	28.0

troduced and the cell evacuated to a pressure of 0.2–1.0 mm. and sealed. The ultraviolet spectrum was then recorded at 10 or 20° temperature intervals until a suitable spectrum was obtained. Under these conditions, no value of ε could be obtained, the intensity of the peaks being a reflection of the volatility of the compound and the temperature obtaining. The spectra of several of the alkyl compounds and of compound B are given in Fig. 2. Compound A decomposed thermally too rapidly for its spectrum to be determined.

Infrared Spectra.—Infrared spectra of alkyl cyclopolyphos-phines were run on the pure liquids and on Nujol mulls of the crystalline compounds. Besides peaks characteristic of the alkyl substituent, those compounds with a —CH₂P— showed a strong peak at 1600–1610 cm.⁻¹.

The infrared spectra of the aryl compounds A, B, C, and D in Nujol mulls and CS_2 solution are given in Table III.

TABLE III
INFRARED SPECTRA OF ARYL POLYPHOSPHINES

A, Nujol	A, CS₂	B, Nujol	B, CS₂	C, Nujol	D, Nujol
1580[a]m[b]		1580w		1580w	1580m
1432[c]s		1430s		1430s	1430s
	1332w	1325w	1332w		1320w
1300w	1305w	1300w	1307w	1300w	1300w
1182w	1190w	1180w	1187w	1180w	1188w
1158w	1160w	1158w	1162w	1158w	1158w
1085[c]w	1085w	1092m	1094w	1085m	1085w
	1071w	1075m	1072w		
1067[c]m		1067m		1067m	1067m
1030[c]m	1030m	1030m	1030m	1030m	1030m
1000[c]m	1003m	1000m	1003m	1000w	1000m
975w		967w		965w	970w
908w		915w		913w	908w
742[c]s	742s	740s	743s	739s	742s
735s					735s
695[c]s	693s	691s	692s	691s	693s
687[d]s					685[d]s

[a] Wave lengths in cm.⁻¹. [b] w denotes weak, m denotes medium, s denotes strong. [c] Peak characteristic of a phenyl substituent on phosphorus. [d] Shoulder.

Nuclear Magnetic Resonance Spectra. (a) **Phosphorus.**—Solids were run in CS_2 solution; liquids were run neat. Only one phosphorus resonance was observed for each compound, as given in Table I.

(b) **Hydrogen.**—Spectra for the phenyl cyclotetraphosphines were obtained using CS_2 solutions. Peaks, reported in parts per million relative to $(CH_3)_4Si$, were reproducible to within ±0.02. Compound A showed four sharp peaks at 2.95, 2.81, 2.87 and 2.75 in order of decreasing intensity and a broad band at 2.28. Compound B showed four sharp peaks at 2.94, 2.98, 3.04, and 3.08 in order of decreasing intensity and a broad band at 2.65.