distilled through a 20-cm. Vigreux column to give 218 g. (75.5 mole %) b.p. 31° (47 mm.) n^{25}_D 1.4110 of *N,N*-diethyltrimethylsilylamine.

The silylamines listed in Table II were prepared using similar procedures.

Addition of Trichlorosilane to Acrylonitrile Using *N,N*-Diethyltrimethylsilylamine Catalyst.—In a 300-cc. stainless steel pressure vessel was charged 53.0 g. (1 mole) of acrylonitrile, 135.5 g. (1 mole) of trichlorosilane, and 3.8 g. (2 wt. %) of *N,N*-diethyltrimethylsilylamine. The vessel was sealed and heated in a rocking furnace at 140° for 1.75 hr. The maximum pressure obtained was 200 p.s.i.g. The vessel was cooled and discharged to give 186 g. of liquid product. Distillation through a 20-cm. Vigreux column gave 139.5 g. (74 wt. % yield) b.p. 76–77° (5 mm.) of β-cyanoethyltrichlorosilane.

Anal. Calcd. for $C_3H_4SiNCl_3$: Hydrolyzable chlorine, 56.4%; Found: 56.2%.

An infrared spectrum of the product verified the compound as the beta isomer. Table I lists the addition reactions carried out in a similar manner using the various silylamine catalyst.

Reaction of *N,N*-Di-*n*-propyltrimethylsilylamine with Trichlorosilane.—In a 250-ml. flask was charged 50 ml. of xylene, 43.5 g. (0.25 mole) of *N,N*-di-*n*-propyltrimethylsilylamine, and 33.9 g. (0.25 mole) of trichlorosilane. The flask was quickly attached to a 30-cm. glass helix-packed fractionating column. The temperature of the solution rose rapidly to 63° when the materials were mixed. Gentle heat was applied to the flask after the reaction subsided and 28.4 g. of material, b.p. 56–57° identified as trimethylchlorosilane containing a trace of trichlorosilane as indicated by hydrolyzable chlorine. As described above, 3.9 g. of the remaining xylene solution was used to catalyze the addition of trichlorosilane and acrylonitrile. The reaction was run 2 hr. at 150°. On distillation, β-cyanoethyltrichlorosilane, containing a small amount of the alpha isomer was obtained in 22 mole % conversion.

Acknowledgment.—The authors wish to thank Dr. H. H. Ender, Mr. R. C. Borchert, and Mr. E. J. Pepe for aid in preparing the silylamines used in this work.

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p-Phenylenediphosphine and Related Compounds[1,2]

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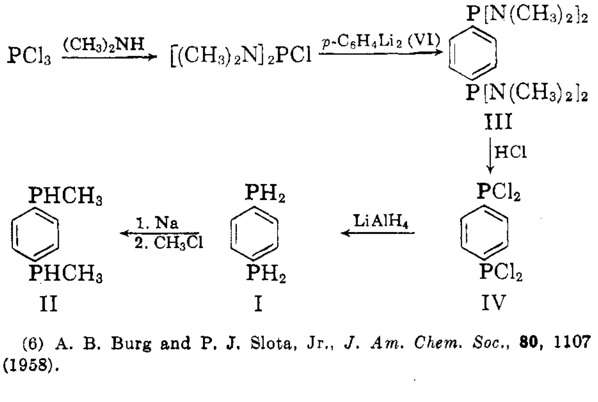
Application of the reaction of organometallic reagents with dialkylaminohalophosphines has provided a practical synthesis for aromatic diphosphorus compounds. The syntheses of the first primary and secondary aromatic diphosphines as well as the derivatives, *P,P,P′,P′*-tetrakis(dimethylamino)-*p*-phenylenediphosphine, *P,P,P′,P′*-tetrachloro-*p*-phenylenediphosphine, and *p*-phenylenebis(methylphosphinic acid), are reported. From a number of infrared spectra of a variety of dimethylaminophosphines a characteristic strong absorption at 980–950 cm.$^{-1}$ has been assigned to the P—N$(CH_3)_2$ group. The acid strengths of *p*-phenylenebis(methylphosphinic acid) (pK_{a_2} 2.67) and methylphenylphosphinic acid (pK_a 2.96) have been measured.

Primary and secondary aromatic diphosphines have not been reported previously in the chemical literature.[4] We now wish to report the preparation of *p*-phenylenediphosphine[5] (I) and *P,P′*-dimethyl-*p*-phenylenediphosphine (II) as well as the new aromatic diphosphorus compounds, *P,P,P′,P′*-tetrakis(dimethylamino-*p*-phenylenediphosphine) (III), *P,P,P′,P′* - tetrachloro - *p* - phenylenediphosphine (IV), and *p*-phenylenebis(methylphosphinic acid) (V).

The synthetic sequence outlined below was selected from a number of preliminary reactions, described later, which indicated that treatment of organolithium reagents with a bis(dialkylamino)-halophosphine[6,7] would be a practical synthetic route to trivalent diphosphorus compounds.



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[1] This research was supported in part by the United States Air Force under Contracts AF 33(616)-3506, 5433, 6913, and 7810, monitored by the Materials Laboratory, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

[2] Presented in part at the Pacific Southwest Regional Meeting of the American Chemical Society, October 25, 1958.

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[4] During the course of this investigation, the preparation of a tertiary aromatic diphosphine was reported by F. A. Hart and F. G. Mann, *J. Chem. Soc.*, **1957**, 3939 and subsequently other aromatic tertiary di- and triphosphines have been reported by F. Ramirez and D. Rhum, *J. Org. Chem.*, **24**, 894 (1959); A. F. Clifford and R. R. Olsen, Abstracts of 135th American Chemical Society Meeting, April, 1959, p. 16M; F. A. Hart, *J. Chem. Soc.*, **1960**, 3324; D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961); and R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961).

[5] All of the trivalent phosphorus compounds discussed in this paper have been named as derivatives of phosphine to emphasize their relationship to the parent compound and to each other rather than to employ the less frequently used "Index Compounds" of Chemical Abstracts. For convenience the names (and *Chem. Abstr.* indexing names) are listed for the parent compounds: H_2NPH_2, aminophosphine (phosphinous amide); H_2PCl, chlorophosphine (phosphinous chloride); $HP(NH_2)_2$, diaminophosphine (phosphonous diamide); $HPCl_2$, dichlorophosphine (phosphonous dichloride); and H_2NPClH, aminochlorophosphine (no index name listed by *Chem. Abstr.*).

[6] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

The preparation of *p*-phenylenedilithium (VI) in the high yield originally reported[8] has not been confirmed in more recent work[9] and, accordingly, we reinvestigated the preparation of this intermediate. Our results obtained using a different analytical procedure are in agreement with the later work.

A slurry of VI in petroleum ether was added to bis(dimethylamino)chlorophosphine to prepare III in 48% yield. The dimethylamino blocking groups were easily removed in 85% yield by treatment of the aminophosphine (III) with the stoichiometric quantity of anhydrous hydrogen chloride to give IV. A 23% yield of the aromatic diphosphine (I) was obtained on reduction of IV with ethereal lithium aluminum hydride in a flow system. Compound I was converted in 84% yield to its *P,P'*-dimethyl derivative (II) by alkylation of the disodium derivative in liquid ammonia.[10]

Several potential direct routes to aromatic diphosphine derivatives were tried without success. An attempt to prepare *P,P,P'P'*-tetrabromo-*p*-phenylenediphosphine from *p*-phenylenedilithium and an excess of phosphorus tribromide yielded only seemingly polymeric yellow solids which on hydrolysis formed a poorly defined acidic phosphorus-containing material. A similar attempt using the reaction product of *p*-phenylenedilithium and cadmium chloride (presumably the less reactive poly-*p*-phenylenecadmium) also produced ill-defined yellow solids. In a final unsuccessful attempt to prepare a *P,P,P',P'*-tetrahalo-*p*-phenylenediphosphine directly, no reaction was apparent upon heating phosphorus trichloride in a sealed tube with crude *p*-phenylenebis(mercury chloride) prepared from either *p*-phenylenedilithium or *p*-benzenediboronic acid[9,11] and mercuric chloride.

Initially, a number of model reactions leading to the preparation of phenylphosphine were screened to find a suitable synthetic sequence. The reaction of phenylmagnesium bromide with phosphorus trichloride, investigated over a temperature range −74° to 30°, resulted in low yields (1–8%) of phenyldihalophosphines[12] suggesting that synthesis of the difunctional analog, *P,P,P',P'*-tetrahalo-*p*-phenylenediphosphine, *via* a di-Grignard reagent would be highly impracticable. Substitution of the less reactive diphenylcadmium increased the yield of phenyldihalophosphine to 26%, a value comparable to those obtained with aliphatic analogs.[13] The poor yields of products obtained when phosphorus trihalides were treated with an organometallic reagent made it apparent that blocking groups would be required to develop a practical synthesis. The ready interconvertability of chlorophosphines and dialkylaminophosphines[6] and the lesser reactivity of the P—N bond toward organometallic reagents make dialkylamino substituents excellent blocking groups in the preparation of organochlorophosphines. A comparison of the product yields obtained on reaction of some organochlorophosphines with either Grignard or organolithium reagents suggested that the latter organometallic compounds would be the better synthetic reagents, *e.g.*, dimethylaminodi-*p*-tolylphosphine (20%) from dimethylaminodichlorophosphine and *p*-tolylmagnesium bromide; bis(dimethylamino)methylphosphine (34%) from bis(dimethylamino)chlorophosphine and methylmagnesium bromide; bis(dimethylamino)phenylphosphine (79%) from bis(dimethylamino)chlorophosphine and phenyllithium; dimethylaminomethylphenylphosphine (85%) from dimethylaminophenylchlorophosphine and methyllithium. The bis(dimethylamino)phenylphosphine was converted by treatment with hydrogen chloride to phenyldichlorophosphine which was reduced in a flow system because this means of effecting the reduction greatly increased the earlier reported yields of phenylphosphine,[14a,b] although more recently, comparable yields using a batch process have been reported.[14c] An unsuccessful attempt was made to circumvent the intermediate chlorophosphine derivative by treating the dimethylaminophosphine derivative with lithium aluminum hydride (either alone or admixed with aluminum chloride) similar to the direct reduction of ethoxy derivatives.[7]

The infrared spectrum of each of the ten dimethylaminophosphine derivatives reported in this paper shows a strong absorption in the range 980–950 cm.$^{-1}$. Bellamy[15] reports that the dimethylamino group on phosphorus exhibits a strong absorption in the 1010–990-cm.$^{-1}$ region. However, the primary reference[16] quoted by Bellamy states that the 1010–990-cm.$^{-1}$ band is "specific for the dimethylamino group in phosphonic acid esters" and the one example of a dimethylamino-substituted phosphine, dimethylaminodichlorophosphine, shows a strong absorption at 978 cm.$^{-1}$. We have confirmed in our laboratory that the absorption frequency of $P—N(CH_3)_2$ group in dimethylaminodichlorophosphine and

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[7] M. Sander, *Ber.*, **93**, 1220 (1960) reports the use of ethoxy and phenoxy blocking groups on phosphorus in similar Grignard reactions.

[8] H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940).

[9] D. R. Nielsen and W. E. McEwen, *J. Am. Chem. Soc.*, **79**, 3081 (1957).

[10] R. I. Wagner and A. B. Burg, *J. Am. Chem. Soc.*, **75**, 3869 (1953).

[11] O. C. Musgrave, *Chem. Ind.* (London), 1152 (1957).

[12] R. C. Miller, *J. Org. Chem.*, **24**, 2013 (1959) reports that *n*-octylmagnesium bromide and phosphorus trichloride yield the corresponding di-*n*-octylbromophosphine in 17% yield.

[13] R. B. Fox, *J. Am. Chem. Soc.*, **72**, 4147 (1950).

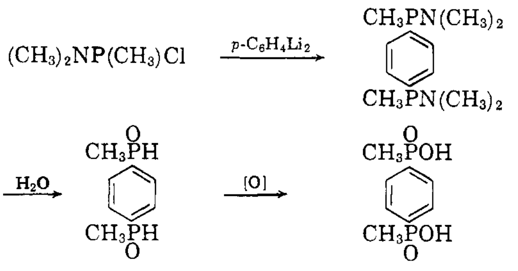
[14] (a) R. J. Hovat and H. J. Furst, *J. Am. Chem. Soc.*, **74**, 562 (1952). (b) T. H. Weil, B. Prijs, and H. Erlyenmeyer, *Helv. Chim. Acta*, **35**, 616 (1952). (c) W. Kuchen and H. Buchwald, *Ber.*, **91**, 2296 (1958).

[15] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, 1958, p. 323.

[16] R. B. Harvey and J. E. Mayhood, *Can. J. Chem.*, **33**, 1552 (1955).

six other phosphine derivatives (not reported in this paper) is in the range 980–950 cm.$^{-1}$. We have observed that in the dimethylamino-substituted phosphines the single very strong absorption band (eleven compounds) not only increases in intensity as expected but is split into two distinct bands in bis(dimethylamino) derivatives (three compounds) and into three bands in tris(dimethylamino)phosphine. This splitting was not observed with the few corresponding $\equiv$P=O compounds examined.

Syntheses of simple aromatic diphosphorus acids with both substituents on one aromatic ring are unknown in the literature.[17] The preparation of *p*-phenylenebis(methylphosphinic acid) (V) was accomplished in *ca.* 8% yield (based on *p*-dibromobenzene) by the reaction of *p*-phenylenedilithium (VI) with dimethylaminomethylchlorophosphine, followed by hydrolysis and oxidation.



V

The infrared spectrum of *p*-phenylenebis(methylphosphinic acid) shows the expected absorption bands with the exception of the P=O band which either is too weak to be observed or, more probably, is shifted to the lower limit for hydrogen-bonded phosphoryl groups.[18]

In view of the reported effects of selected substituent groups on the acid strength of benzoic acid,[19] it was of interest to compare the acid strength of *p*-phenylenebis(methylphosphinic acid) with that of methylphenylphosphinic acid. The inductive effect of a *p*-carboxy group causes an increase in acid strength (pK_a 2.95) relative to benzoic acid (pK_a 4.20) whereas that of *p*-carboxylate anion causes a decrease (pK_a 5.41). With a *p*-sulfonate anion where *d*-orbital resonance is possible the inductive effect of the anionic substituent is apparently overcome by the resonance effect since the acid strength is increased (pK_a 4.11). From consideration of the effect that the second phosphorus acid function in *p*-phenylenebis(methylphosphinic acid) would exert on the first through resonance involving phosphorus *d*-orbitals, the pK_{a1} of the difunctional acid would be expected to be smaller than the pK_a of the monofunctional acid (pK_a 2.96). The effect in pK_{a2} is less readily predictable. The experimental fact that both acid groups in *p*-phenylenebis(methylphosphinic acid) appear to be neutralized simultaneously (pK_{a2} 2.67) suggests that of the opposing *d*-orbital resonance and inductive effects the former, is of greater magnitude. Whether pK_{a1} is of nearly the same order of magnitude as pK_{a2} or is very small could not be determined from the experimental data.

Experimental

Due to the oxidative and/or hydrolytic instability of all of the compounds described (except the phosphinic acids), all work was conducted either using high vacuum techniques or under an atmosphere of dry nitrogen. The nature of the series of compounds made analyses very difficult as will be noted in the often poor results. The synthetic sequence, however, is unambiguous and it will be observed that the primary phosphine (I) shows a straight line vapor tension equation indicative of high purity and in addition shows the correct molecular weight and by-product hydrogen evolution on treatment with sodium in ammonia.[10] Analysis of the final product II is good. Infrared spectra of the series of compounds support the proposed structures.

All melting points are uncorrected. Infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Vapor phase chromatographic analyses were performed with a Perkin-Elmer Vapor Fractometer 154B using either a 2-m. Silicon Oil/Celite or Apiezon/Celite column.

***p*-Phenylenedilithium (VI).**—The gradual formation of a yellow solid was observed in a stirred solution of 0.8 mole of butyllithium (butyl chloride-free) and 90.8 g. (0.385 mole) of *p*-dibromobenzene in 1000 ml. of petroleum ether (b.p. 20–40°) during 22 hr. at reflux. Titration of a hydrolyzed aliquot of the filtered solution indicated only 0.03 mole equivalent of organolithium reagents in the filtrate. Further analysis of the filtrate by vapor fractometry showed the formation of 0.38 mole (49%) of butyl bromide and 0.068 mole of octane. A dried portion of the pyrophoric yellow precipitate, which had been twice washed with petroleum ether, was cautiously decomposed with methanol in a high vacuum system. The methanolysis was controlled by starting with methanol vapor since liquid methanol (or water vapor) caused violent carbonization. The volatile methanolysis products were analyzed by vapor fractometry and the residue was analyzed for halide. All identified products were assumed to be derived from the corresponding lithium compounds.

Further refluxing of the precipitate for an additional 23 hr. in 500 ml. of petroleum ether containing 0.16 mole of butyllithium improved the yield of *p*-phenylenedilithium as shown in Table I. From the weight of the final precipitate (92 g. containing approximately 28% petroleum ether) the yields shown parenthetically in Table I were calculated. The observed 0.003 mole of butane obtained on methanolysis is more than seven times the maximum amount obtainable from entrained liquid even if the butyllithium concentration (0.32 *M*) had not decreased and the precipitate had not been twice washed with petroleum ether. This fact suggests that butyllithium is complexed with the insoluble aryllithium

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[17] A. C. McKinnis mentions *p*-phenylenediphosphonic acid and 1,5-naphthalenediphosphonic acid in U. S. Patent 2,776,985, January 8, 1955, but no method of preparation is given; L. D. Freedman, *J. Am. Chem. Soc.*, **77**, 6223 (1955) reports 3,3′-biphenyldiphosphonic acid by catalytic reduction of 3-bromophenylphosphonic acid; H. Z. Lecher and T. H. Chao report in U. S. Patent 2,717,906, September 13, 1955, the preparation of a naphthalenediphosphonic acid of unknown structure by reaction of naphthalene and phosphorus pentoxide.

[18] L. C. Thomas and R. A. Crittenden, *Chem. Ind.* (London) 1913 (1961).

[19] H. C. Brown, D. H. McDaniel, and O. Hafliger, "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, eds., Academic Press, Inc., New York, 1955, pp. 583–593.

compounds.[20] This preparation was used in the synthesis of compound III.

Two additional parallel preparations of *p*-phenylenedilithium were made to investigate the effect of reaction time on product yield. Two 100-ml. round bottom flasks, equipped with magnetic stirrers and water-cooled reflux condensers were each charged with 2.362 g. (10.01 mmoles) of *p*-dibromobenzene and 28 ml. petroleum ether (b.p. 20–40°) solution containing 33.9 mmoles of butyllithium. The stirred solutions were refluxed for 24 and 48 hr., respectively, after which the organolithium compounds were destroyed by adding to the cooled mixture 1.1 g. (35 mmoles) of methanol in 20 ml. of petroleum ether. The resultant solid-liquid mixtures were filtered and the filter cakes washed with two 10-ml. portions of petroleum ether. Each of the combined filtrate and washings was analyzed by vapor fractometry for benzene, bromobenzene, butylbenzene, octane, and butyl bromide. The data are listed in Table I.

TABLE I

ANALYSES OF *p*-DILITHIOBENZENE PREPARATIONS

Reflux time, hr. Percent yields	22 + (addn'l 23)	24	48
$C_6H_6(p\text{-}C_6H_4Li_2)$	48 (54)	48.4	41.8
$C_6H_5Br(p\text{-}BrC_6H_4Li)$	8 (3)	7.0	5.5
$C_4H_9C_6H_5(p\text{-}C_4H_9C_6H_4Li)$	2.2 (2.6)	3.5	3.3
C_8H_{18}	9	23	34
C_4H_5Br	49	13	0.5
LiBr	42	79	94

***P,P,P′,P′*-Tetrakis(dimethylamino)-*p*-phenylenediphosphine (III).**—The 92-g. precipitate containing 18.6 g. (0.208 mole) of VI, prepared from *p*-dibromobenzene and butyllithium as described above, was slurried in 200 ml. of petroleum ether (b.p. 20–40°) and added during 15 min. to a stirred solution of 0.68 mole of bis(dimethylamino)-chlorophosphine in 1200 ml. of petroleum ether cooled to *ca.* −60° by partial immersion in a −78° cooling bath. Addition of 50 ml. of diethyl ether initiated an exothermic reaction which warmed the mixture quickly to −30° even though the reaction vessel was then completely immersed in a −78° cooling bath. After addition of another 150 ml. of ether the mixture was slowly warmed to reflux and then treated with 0.6 mole of gaseous dimethylamine to destroy residual bis(dimethylamino)chlorophosphine. The reaction mixture was then cooled to room temperature and filtered. Solvent was distilled from the filtrate to reduce the volume to about 300 ml. Upon cooling the solution in an ice water bath 13.8 g. of *P,P,P′,P′*-tetrakis(dimethylamino)-*p*-phenylenediphosphine was obtained as colorless needles. The mother liquor was distilled to remove 0.20 mole of tris(dimethylamino)phosphine[6] [b.p. 57–58°/20 mm., infrared P—N absorption triplet at 974(s), 953(vs) and 938(vs)cm.$^{-1}$] leaving a residue from which more solid product was obtained. Hot toluene extraction of the filter cake from the reaction mixture provided an additional 14.0 g. of the crystalline material. The total yield of III was 31.1 g. (48%) having a melting point 146.5–147.5° after recrystallization from petroleum ether (b.p. 65–110°). An infrared spectrum of the compound in potassium bromide showed the characteristic *para* substitution bands at 1937, 1830, and 828 cm.$^{-1}$ as well as a broad $P[N(CH_3)_2]_2$ 960–950 cm.$^{-1}$ (the poor resolution is attributed to both the solid state and too high a concentration of material).

Anal. Calcd. for $C_{14}H_{26}N_4P_2$: C, 53.49; H, 8.98; N, 17.82. Found: C, 53.16; H, 9.06; N, 17.72.

***P,P,P′,P′*-Tetrachloro-*p*-phenylenediphosphine (IV).**—A suspension of 3.014 g. (9.59 mmoles) of *P,P,P′,P′*-tetrakis(dimethylamino)-*p*-phenylenediphosphine in 50 ml. of diethyl ether at −78° was treated with 1731 cc. (77.3 mmoles) of gaseous hydrogen chloride. After allowing the reaction mixture to warm to room temperature, by-product dimethylammonium chloride containing 41.3 mmoles of Cl^- (107%) was removed and the colorless filtrate on evaporation under vacuum yielded 2 27 g. (85%) of colorless crystalline *P,P,P′,P′*-tetrachloro-*p*-phenylenediphosphine, m.p. 58–60°. After recrystallization from petroleum ether (b.p. 20–40°) the melting point was lowered to 57–59° indicating the moisture sensitivity of the compound. An infrared spectrum of a thin liquid film of the compound showed the characteristic *para* substitution bands at 1910, 1804, and 813 cm.$^{-1}$, bands at 1382 and 1013 cm.$^{-1}$ attributed to *P*-aromatic, and a strong band at 1102 cm.$^{-1}$. The remaining bands were of low intensity and difficult to assign unequivocally to IV in view of aliphatic C—H bands of equal intensity at 2900 and 2880 cm.$^{-1}$. The elemental analyses confirm the presence of some residual dimethylamino groups.

Anal. Calcd. for $C_6H_4P_2Cl_4$: C, 25.75; H, 1.43; Cl, 50.7. Found: C, 26.32; H, 2.00; Cl, 49.7.

In a second preparation a 71% yield was obtained.

Several attempts to prepared a tetrahalo-*p*-phenylenediphosphine directly were made using different organometallic reagents and phosphorus trihalides.

Method A.—The reaction slurry from 131 mmoles of butyllithium and 64.4 moles of *p*-dibromobenzene in 500 ml. of low-boiling petroleum ether was added to 15.5 mmoles of phosphorus tribromide in 100 ml. of petroleum ether at −25°. The mixture was filtered and the filtrate distilled to give unchanged phosphorus tribromide and a small amount of presumably butyldibromophosphine. Hydrolysis of the reaction solids gave a mixture of poorly defined phosphorus acids (neut. equiv. 166) insoluble in organic solvents.

Method B.—To a *p*-phenylenedilithium slurry, prepared as previously described was added an equivalent quantity of cadmium chloride. Treatment of phosphorus tribromide with this organometallic slurry led after hydrolysis to essentially the same type mixture of poorly defined phosphorus acids (neut. equiv. 675).

Method C.—Reaction of 58 mmoles mercuric chloride with *p*-phenylenedilithium prepared from 37.2 mmoles of *p*-dibromobenzene yielded a solid which was extracted with boiling water and boiling acetone primarily to remove inorganic salts. The crude *p*-phenylenebis(mercury chloride) was used described below.

Another sample of *p*-phenylenebis(mercury chloride) was prepared by slow addition of an aqueous solution of 3.91 mmoles of *p*-benzenediboronic acid to a refluxing aqueous solution (500 ml.) of 29.9 mmoles of mercuric chloride. The insoluble solid was isolated, extracted with boiling acetone, analyzed and used as described below.

Each of the samples of crude (*ca.* 70–80% pure) *p*-phenylenebis(mercury chloride) m.p. > 410°, was heated in a sealed tube with a weighed quantity (3.8843 g. and 3.8467 g.) of liquid phosphorus trichloride at 200–220° for 40 hr. From the amounts of phosphorus trichloride recovered (3.8525 g. and 3.7622 g., respectively) the reaction could not have proceeded more than 3–6%.

***p*-Phenylenediphosphine (I).**—A 220-ml. solution of 109 mmoles of lithium aluminum hydride in diethyl ether and a 150-ml. solution of 54.3 mmoles of *P,P,P′,P′*-tetrachloro-*p*-phenylenediphosphine in diethyl ether were mixed dropwise by allowing the solutions to run through a 60 mm. length of 7 mm. i.d. tubing. Excess hydride was destroyed by treating the reaction mixture with 100 ml. of an ethereal solution of 143 mmoles of ethyl acetate. After the addition of 400 ml. of degassed aqueous 0.6 *N* sodium hydroxide, the ether layer was removed by pressure siphon. The ethereal solution, together with four 100-ml. ether washes of the basic water layer, was concentrated by distillation. The residual solvent was removed under high vacuum at room temperature leaving 1.78 g. (23%) of solid colorless crude

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(20) G. Wittig, R. Ludwig, and R. Polster, *Ber.*, **88**, 294 (1955); G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 865 (1958); G. Wittig and E. Benz, *Ber.*, **91**, 873 (1958).

p-phenylenediphosphine which gave a pure product, m.p. 69.0–70.5°, after sublimation under high vacuum at room temperature into a −78° trap. An infrared spectrum of a solidified film of this material between salt plates showed only poorly resolved bands of low intensity. The characteristic *para* substitution band at 820 cm.$^{-1}$, bands at 1380 and 1020 cm.$^{-1}$ attributed to *P*-aromatic, and the P—H stretching band at 2275 cm.$^{-1}$ were observed.

Anal. Calcd. for $C_6H_8P_2$: C, 50.72; H. 5.69. Found: C, 48.97; H, 6.62.

Despite our inability to obtain good elemental analyses, the vapor tensions of liquid *p*-phenylenediphosphine shown in Table II serve to indicate the purity of the sample. These data determine the equation $\log_{10} p_{mm} = 8.168 - 2640/T$ from which the boiling point was calculated to be 226°; ΔH_v 12.08 kcal./mole, and Trouton constant 24.2 cal./deg. mole. From the vapor density of this same 0.0746 g. sample at 148.9° and 61.19 mm. the molecular weight was determined to be 145.5 (calcd. for $C_6H_8P_2$, 142.08).

TABLE II

VAPOR TENSIONS OF LIQUID *p*-PHENYLENEDIPHOSPHINE

Temp.	P_{mm} (obsd.)	P_{mm} (calcd.)
73.6	3.57	3.60
80.6	4.98	5.08
84.2	6.01	6.04
94.5	9.77	9.73
99.8	12.4	12.3
121.3	30.0	29.9
126.7	36.9	36.8
135.0	50.2	50.2

***P*,*P'*-Dimethyl-*p*-phenylenediphosphine** (II).—Into an 85-ml. glass bomb tube, containing 0.1140 g. (4.958 mmoles) of sodium in a fragile glass capsule, was condensed 0.3523 g. (2.480 mmoles) of *p*-phenylenediphosphine followed by 5.5 ml. of anhydrous ammonia. The tube was sealed under vacuum and the sodium capsule broken by mechanical shock. The resultant rapid reaction, which was moderated by cooling in a Dry Ice bath, yielded a scarlet ammonia solution of the disodium derivative, *p*-$NaPHC_6H_4PHNa$. The cooled tube was opened and 56.3 cc. of hydrogen (theory 55.6 cc., 101%) was removed. Then 114.3 cc. (5.11 mmoles) of methyl chloride was added and the tube resealed. Upon warming the alkylation reaction occurred rapidly, yielding a colorless ammonia solution and colorless solid. The portion of the reaction mixture volatile at room temperature was removed and the tube filled with nitrogen. The nonvolatile residue was dissolved in 5 ml. of degassed water and 10 ml. of diethyl ether. The lower aqueous layer was removed and the remaining ethereal solution washed with two 7-ml. portions of degassed water. The ethereal solution was reattached to the vacuum line and those components volatile at room temperature were removed. The residue was distilled at 50° under high vacuum to yield 0.3542 g. (84%) of colorless, liquid *P*,*P'*-dimethyl-*p*-phenylenediphosphine. The infrared spectrum of this material had the characteristic *para* substitution bands at 1905, 1795, and 793 cm.$^{-1}$ and a strong P—H stretching band at 2270 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{12}P_2$: C, 56.47; H, 7.11. Found: C, 56.36; H, 6.72.

***p*-Phenylenebis(methylphosphinic Acid)** (V).—A pentane slurry containing approximately 100 mmoles of *p*-phenylenedilithium (assuming a 50% yield from the reaction of 44 mmoles of butyllithium and 21.6 mmoles of *p*-dibromobenzene) was added to a rapidly stirred solution of 26.5 g. of dimethylaminomethylchlorophosphine in 100 ml. of pentane and 50 ml. of diethyl ether maintained at −60°. The reaction mixture was then allowed to warm to room temperature, stirred an additional 1.5 hr., and finally filtered under nitrogen. After removal of the solvent, vacuum distillation of the residue at 0.01–0.02 mm. yielded four indistinct fractions: (1) 3.6 g., b.p. 84–95°, (2) 6.2 g., b.p. 95–110°. (3) 3.7 g., b.p. 110–130°, (4) 2.3 g., b.p. 150–180°. The infrared spectra of fractions 2 and 3 were nearly identical and had a strong band in the 980–950-cm.$^{-1}$ region characteristic of the $P—N(CH_3)_2$ group in phosphine derivatives. A 1.1-g. quantity of fraction (2) was dissolved in 20 ml. of refluxing 6 *N* hydrochloric acid and treated with 3 ml. of 30% hydrogen peroxide. Slow evaporation on a steam bath gave a colorless sirup which crystallized on standing. A single recrystallization from a mixture of 20 ml. of ethanol and 10 ml. of benzene gave 0.39 g. of a colorless crystalline solid, m.p. 230–235°. Four additional crystallizations from ethanol followed by drying 3 hrs. at 200° under high vacuum failed to narrow the melting range, m.p. 231–236°. Infrared spectra of the acid in potassium bromide and in a Nujol mull showed a broad weak band at 2650 cm.$^{-1}$ associated with the POOH group, bands at 1408 (m) and 1378 (s) the first of which is probably *P*-aromatic, a strong $P—CH_3$ band[21] at 1305 cm.$^{-1}$, a strong band at 1138 cm.$^{-1}$ which might be associated with P=O,[18,22,23] and a strong *para* substitution band at 822 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{12}P_2O_4$: C, 41.04; H, 5.17; neut. equiv., 117.1. Found: C, 41.18; H, 5.44; neut. equiv., 118.8.

The titration of 0.1493 g. (0.638 mmoles) *p*-phenylenebis(methylphosphinic acid) in 100 ml. of water required 1.257 meq. of base and gave a curve with a single break and *p*H at one-half neutralization of 2.67, indicating it to be a strong acid. The slope at the inflection point is indicated by a *p*H change from 5.36 to 9.30 on adding 0.10 ml. of 0.1 *N* base. Further experiments indicated hydrogen peroxide to be inefficient in either acidic or basic media in the oxidation of the diphosphinous acid (presumably a secondary diphosphine dioxide) to the diphosphinic acid. Iodic acid was found to be a better oxidizing agent as shown by its more rapid removal of all traces of P—H absorption in the infrared spectrum, and a lesser amount of the partially oxidized sirupy intermediates.

Methylphenylphosphinic acid was prepared by oxidation of 5.0 g. (36.9 mmoles, vapor phase chromatographic assay 91.5%) of crude methylphenylphosphine admixed with 40 ml. of water with 80 ml. of an aqueous solution containing 5.7 g. (32.2 mmoles) of iodic acid. During the oxidation the reaction mixture was cooled in an ice bath. Iodine was removed by boiling the solution until it became colorless. Excess iodic acid was destroyed by addition of hydriodic acid until no further iodine was formed. The iodine-free solution was concentrated and crude methylphenylphosphinic acid obtained by crystallization in 75% yield. Two crystallizations from absolute ethanol provided needles, m.p. 134–136°, the infrared spectrum (KBr disk) of which showed a broad weak band at 1440 ($P—C_6H_5$), 1308 ($P—CH_3$) and 1170 cm.$^{-1}$ (P=O).

Anal. Calcd. for $C_7H_9PO_2$: C, 53.85; H, 5.81; neut. equiv. and mol. wt., 156.12. Found: C, 53.82; H, 5.71; neut. equiv., 155.0; mol. wt. (Neumayer[24] in benzene, 398; microebulliometric[25] in benzene, 354).

The aqueous titration curve of methylphenylphosphinic acid showed a sharp break with a *p*H at half neutralization of 2.96.

Bis(dimethylamino)chlorophosphine was prepared in 67% yield in 2700 ml. of diethyl ether from 280 g. (2.04 moles) of phosphorus trichloride and 392 g. (8.70 moles) of dimethylamine and had a boiling range of 93–97°/47–49 mm. In a second preparation a 79% yield was obtained. The infrared spectrum of the compound showed the expected absorption bands as well as a doublet at 978 (s) and 958 (vs) cm.$^{-1}$ attributed to $P[N(CH_3)_2]_2$.

Anal. Calcd. for $C_4H_{12}N_2PCl$: Cl, 22.94. Found: Cl, 22.9.

Bis(dimethylamino)phenylphosphine.—In a preliminary

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experiment under conditions comparable to those used to prepare III, 0.113 mole each of phenyllithium and bis(dimethylamino)chlorophosphine produced in 79% yield bis(dimethylamino)phenylphosphine, b.p. 40–43°/0.02 mm., having an infrared spectrum identical with an authentic sample (prepared by dimethylaminolysis of phenyldichlorophosphine) which showed the expected bands including the $P[N(CH_3)_2]_2$ doublet at 962 and 957 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{17}N_2P$: N, 14.28. Found: N, 14.2.

Phenyldichlorophosphine, which had an infrared spectrum identical to that of an authentic sample, was prepared in the same manner as IV in 63% yield from bis(dimethylamino)phenylphosphine and hydrogen chloride.

Several attempts to prepare phenyldichlorophosphine by direct reaction of equimolar quantities of phenylmagnesium bromide and phosphorous trichloride at 30° (20-fold excess of phosphorus trichloride), 22° , 17°, 2°, and −74° produced only poor yields of halophosphines. The preparation done at −74° is typical. To 500 ml. of an ethereal solution of 21.3 g. (0.155 mole) of phosphorus trichloride cooled to −74° was added 50.0 ml. (0.150 mole) of 3 *M* phenylmagnesium bromide. The mixture was warmed to ambient temperature and an insoluble orange solid was removed by filtration. Distillation of the filtrate yielded primarily arylbromophosphines indicating halogen exchange had occurred. The three distillation fractions were as follows: (a) 3.45 g., b.p. 65–70°/0.4 mm., found to contain 0.88 g. of biphenyl on hydrolysis; (b) 1.15 g., b.p. 70–115°/0.4 mm.; (c) 0.82 g., b.p. 115–116°/0.4 mm. Each fraction was hydrolyzed and analyzed for halide.

Anal. Calcd. for $C_6H_5PX_2$: Br, 59.7; Cl, 39.6. Calcd. for $C_{12}H_{10}PX$: Br, 30.1; Cl, 16.1. Found: (a) Br, 48.7; Cl, 5.1 (values corrected for biphenyl); (b) Br, 44.3; Cl, 1.8; (c) Br, 29.4; Cl, 2.2. From these data the following yields from fractions (a) and (c) were calculated: 5.2% $C_6H_5PBr_2$, 1.2% $C_6H_5PCl_2$, 4.0% $(C_6H_5)_2PBr$, and 0.7% $(C_6H_5)_2PCl$.

From the distillation residue and the orange solids 3.79 g. (0.0136 mole, 27% yield) of triphenylphosphine oxide was obtained by hydrolysis and solvent extraction.

The final attempt to synthesize phenyldichlorophosphine directly used diphenylcadmium prepared by the method used by Fox[13] for dialkylcadmiums. Phenylmagnesium chloride[26] (55% yield) was used in place of the bromide in preparing the organocadmium reagent to preclude a product containing mixed halogens. The diphenylcadmium, prepared from 9.08 g. (49.8 mmoles) of cadmium chloride, was added to 18.2 g. (133 mmoles) of phosphorus trichloride in 100 ml. ether at −25°. The mixture was then refluxed for 2 hr., cooled, and filtered. The filtrate was distilled to give 4.9 g. (28 mmoles, 28%) of phenyldichlorophosphine, b.p. 42–46°/> 1 mm., identified by infrared analysis.

Phenylphosphine was obtained in 47% yield by reduction of phenyldichlorophosphine with lithium aluminum hydride (as in the preparation of I).

Dimethylaminophenylchlorophosphine was prepared by reaction of 131.0 g. (0.732 mole) of phenyldichlorophosphine with 70.0 g. (1.55 moles) of dimethylamine in 630 ml. of diethyl ether. The product was isolated in 73% yield by distillation, b.p. 78°/2 mm. An infrared spectrum of the liquid showed the characteristic monosubstituted aromatic pattern in the 2000–1700-cm.$^{-1}$ region, bands at 748 and 694 cm.$^{-1}$ and a strong absorption band attributed to $P—N(CH_3)_2$ at 978 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{11}PNCl$: Cl, 18.90. Found: Cl, 18.9.

Dimethylaminomethylphenylphosphine was prepared by reaction of 90.0 g. (0.456 mole) of dimethylaminophenylchlorophosphine in 650 ml. of diethyl ether at *ca.* −70° with 525 ml. 0.868 M ethereal methyllithium. Solvent ether was replaced by benzene to facilitate removal of lithium salts before the product was fractionated to give an 85% yield of liquid, b.p. 66–70°/1 mm. The infrared spectrum was virtually identical to that of dimethylaminophenylchlorophosphine except that a new band appears at 1260 cm.$^{-1}$ ($P—CH_3$). The $P—N(CH_3)_2$ band occurs at 968 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{14}PN$: N, 8.38. Found: N, 8.58.

Attempt to Reduce Dimethylaminomethylphenylphosphine.—An attempt to reduce 20.7 g. (0.124 mole) of dimethylaminomethylphenylphosphine by adding it to 5.2 g. (0.137 mole) of ethereal lithium aluminum hydride was indicated, by infrared analysis of the water-washed and dried ethereal solution, to have failed to yield any P—H containing material. No methylphenylphosphine was obtained on fractional distillation of the ether soluble material until the temperature reached 74°/1 mm. ($CH_3C_6H_5PH$, b.p. 24–27°/1 mm.) suggesting that hydrolysis of the P—N bond and disproportionation of the resulting secondary phosphine oxide could account for the observed 14% yield.

Dimethylaminodi-*p*-tolylphosphine was prepared under experimental conditions comparable to those used to synthesize III except that diethyl ether was the only solvent. The reaction of 0.42 mole of dimethylaminodichlorophosphine with 0.84 mole of *p*-tolylmagnesium bromide produced in 20% yield dimethylaminodi-*p*-tolylphosphine after separation from an appreciable quantity of bitolyl, m.p. 121.5–122.0°. Separation of the bitolyl, which was of comparable volatility, was effected by repeated high vacuum distillation at *ca.* 95° and mechanical removal of the solid portion of the distillate. That the process was not efficient is indicated by the elemental analysis. An infrared spectrum of the liquid showed the characteristic *para* substitution bands at 1910, 1805 and 805 cm.$^{-1}$, bands at 1458 and 1053 cm.$^{-1}$ attributed to *P*-aromatic and a $P—N(CH_3)_2$ band at 967 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{20}NP$: C, 74.68; H, 7.83; N, 5.44. Found: C, 75.27; H, 8.52; N, 5.34.

Bis(dimethylamino)methylphosphine was obtained in 34% yield from 570.6 g. (3.69 moles) of bis(dimethylamino)chlorophosphine and 3.7 moles of methylmagnesium bromide in *ca.* 7000 ml. of diethyl ether at −70°. The boiling range of the product was 64–67°/49–50 mm. An infrared spectrum of the compound showed the expected absorption bands and a $P[N(CH_3)_2]_2$ doublet at 972 (s) and 953 (vs) cm.$^{-1}$.

Methyldichlorophosphine, prepared in 2000 ml. of diethyl ether from 169.7 g. (1.27 moles) of bis(dimethylamino)methylphosphine and 184 g. (5.05 moles) of hydrogen chloride, was obtained in 43% yield and had a boiling range of 81–82°.[27] An infrared spectrum[21] of the vapor showed the $P—CH_3$ absorption band near the expected frequency, 1288 cm.$^{-1}$.

Dimethylaminomethylchlorophosphine was prepared in 53% yield in 500 ml. of diethyl ether from 39.2 g. (0.335 mole) of methyldichlorophosphine and 30.2 g. (0.670 mole) of dimethylamine. Boiling range of the product was 142.0–142.5° at atmospheric pressure. An infrared spectrum of the compound showed the expected absorption bands and a $P—N(CH_3)_2$ band at 978 cm.$^{-1}$.

Anal. Calcd. for C_3H_9PNCl: Cl, 28.2. Found: Cl, 28.1.

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