The solution was refluxed for 1 hr and another 0.44 g (0.009 mole) of methanethiol in 3 ml of methanol was added. Reflux was contained for another 7 hr. The mixture was filtered and the filtrate was evaporated. The residue was partitioned between 25 ml of chloroform and 25 ml of water. The chloroform layer was washed with 25 ml of water, dried with magnesium sulfate, and evaporated to leave a yellow solid. The solid was recrystallized from pentane–ether to give 0.5 g, mp 52.2–53.7°, with XXII mmp 52.1–53.3°. The infrared spectrum was identical with that of XXII.

Registry No.—IIIa, 10191-60-3; VI, 10191-61-4; VIII, 10191-62-5; IX, 10191-63-6; Xa, 10239-65-3; Xb, 10191-64-7; Xc, 10191-65-8; Xd, 10191-66-9; Xe, 10191-67-0; Xf, 10191-68-1; Xg, 10191-69-2; Xh, 10191-70-5; Xi, 10191-71-6; XI, 10191-72-7; XII, 10191-73-8; XV, 10191-74-9; XVII, 10191-75-0; XVIII, 10191-76-1; XIXa, 10191-77-2; XIXb, 10191-78-3; XIXc, 10191-79-4; XIXd, 10191-80-7; XIXe, 10191-81-8; XIXf, 10191-82-9; XIXg, 10191-83-0; XIXh, 10191-84-1; XX, 10191-85-2; XXIa, 10191-86-3; XXIb, 10191-87-4; XXIc, 10191-88-5; XXId, 10191-89-6; XXII, 10191-90-9; XXIII, 10191-91-0; cyanodithioimidocarbonic acid, 108-04-3; cyclic methylene cyanodithioimidocarbonate, 10191-92-1; 2-imino-1,3-dithiolane hydrochloride, 1072-49-7.

Arylenebis(tertiary phosphines) and -(phosphinic acids)

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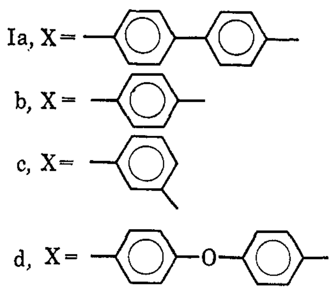
Received October 10, 1966

n-Butyllithium has been effectively utilized to prepare arylenemono- or -dilithiums from which monosubstituted tertiary phosphines and phosphinic acids as well as bis(tertiary phosphines) and bis(phosphinic acids) have been obtained. Monobromo-substituted tertiary phosphines were similarly converted to bis(tertiary phosphines). The use of tetrahydrofuran as the reaction solvent at low temperatures (below −65°) generally provided the best reaction conditions.

In previous papers from this laboratory we have described the preparation of several arylenebisphosphorus compounds leading to *p*-phenylenebis(methylphosphinic acid)[1] and of several bis(tertiary phosphines).[2] While other recent papers have described several related *p*-phenylenebis(methyl- and phenylphosphinous esters and amides),[3] *p*-phenylenebis(phosphonous acid) and related compounds,[4] and several bis(tertiary phosphines),[5] this area of arylenebisphosphorus compounds has received relatively little attention. Since these bis compounds are of interest in several thermally stable polymer systems and as chelate ligands, we wish now to report the improved syntheses of arylenebis(tertiary phosphines) and the syntheses of arylenebis(phosphinic acids) and tris(tertiary phosphines).

Bis(tertiary phosphines).—Some of the problems encountered in the previous syntheses of arylenebis(tertiary phosphines) have been briefly described.[2,5] Thus, while reasonable yields of *p*-phenylenebis(diphenylphosphine) (Ib) have been obtained from the use of either the di Grignard reagent[2] or lithium diphenylphosphinide,[5c] extensions of these techniques to the syntheses of other bis(tertiary phosphines) have been of only limited success.[2] Thus, while 4,4′-biphenylenebis(diphenylphosphine) (Ia) has now been obtained from the di Grignard reagent using a tetrahydrofuran–benzene solvent mixture, the product was grossly contaminated, purification was tedious, and the yields were low. Our continued investigation of the syntheses of these compounds has shown that the use of a hexane solution of *n*-butyllithium in tetrahydrofuran (THF) to form the necessary arylenedilithium intermediates, generally at low temperatures, frequently results in higher yields of more pure products in considerably shortened reaction times. However, as will be seen from the following discussion, the choice of reaction conditions can greatly effect the yield and even the product obtained (eq 1).

$$\text{Br–X–Br} + n\text{-C}_4\text{H}_9\text{Li} \xrightarrow{\text{THF}} [\text{Li–X–Li}] \xrightarrow{2(\text{C}_6\text{H}_5)_2\text{PCl}} (\text{C}_6\text{H}_5)_2\text{P–X–P}(\text{C}_6\text{H}_5)_2 \quad (1)$$



Thus, high yields (94–98%) of 4,4′-biphenylenebis(diphenylphosphine) (Ia) were obtained when a hexane solution of *n*-butyllithium was added to 4,4′-dibromobiphenyl in tetrahydrofuran at −66°, or vice versa, and the mixture was warmed over 0.5 hr to 0° and then recooled to −66° before the addition of 2 equiv of diphenylchlorophosphine was begun. However, elimination of the warm-up step decreased the yield to 64% of less pure Ia. The use of 20 and 30% excesses of *n*-butyllithium resulted in roughly 80 and 70% yields of Ia, respectively.

However, when *p*-dibromobenzene was treated similarly with first *n*-butyllithium and then diphenylchlorophosphine, only a 57% yield of (4-bromophenyl)diphenylphosphine (IIIa) was obtained. Subsequently, the best yield of *p*-phenylenebis(diphenylphosphine) (58%) was obtained by refluxing 4 equiv of *n*-butyllith-

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(1) E. M. Eveleth, Jr., L. D. Freeman, and R. I. Wagner, *J. Org. Chem.*, **27**, 2192 (1962).

(2) R. A. Baldwin and R. M. Washburn, *ibid.*, **30**, 3860 (1965).

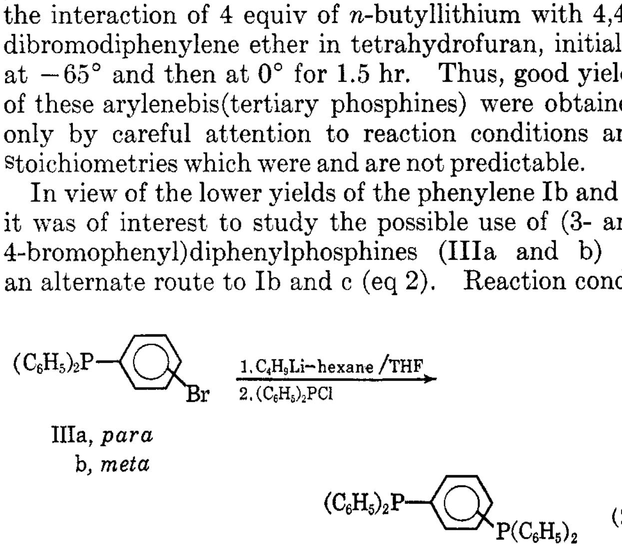
(3) E. Steininger, *Ber.*, **96**, 3184 (1963).

(4) P. G. Chantrell, C. A. Pearce, C. R. Toyer, and R. Twaits, *J. Appl. Chem.*, 563 (1964).

(5) (a) F. A. Mann, *J. Chem. Soc.*, 3324 (1960); (b) D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961); (c) A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *ibid.*, **28**, 2091 (1963); (d) H. Zorn, H. Schindlbauer, and H. Hagen, *Ber.*, **98**, 2431 (1965).

ium with *p*-dibromobenzene for 2.75 hr in an ether-hexane mixture. The preparation of *m*-phenylenebis(diphenylphosphine) (Ic) has been inconclusive since Ic has only been isolated as an extremely viscous oil. (However, see below for an alternate synthesis of Ic). The best yields of 4,4′-diphenylene ether bis(diphenylphosphine) (Id) (70–80%) were routinely obtained by the interaction of 4 equiv of *n*-butyllithium with 4,4′-dibromodiphenylene ether in tetrahydrofuran, initially at −65° and then at 0° for 1.5 hr. Thus, good yields of these arylenebis(tertiary phosphines) were obtained only by careful attention to reaction conditions and stoichiometries which were and are not predictable.

In view of the lower yields of the phenylene Ib and c, it was of interest to study the possible use of (3- and 4-bromophenyl)diphenylphosphines (IIIa and b) in an alternate route to Ib and c (eq 2). Reaction conditions again influenced the yields of Ib by this route; the best yields were obtained by first adding IIIa in tetrahydrofuran to the *n*-butyllithium solution at −65° or less and then immediately adding 1 equiv of diphenylchlorophosphine. Since the crude yields of Ib were nearly quantitative, the over-all yield *via* the two-step procedure from *p*-dibromobenzene was approximately 70–80%. Attempts to carry out this two-step synthesis without the intermediate isolation of IIIa have thus far resulted in only 50–55% yields of Ib. The yield of the *meta* isomer Ic has not been accurately determined since Ic is a viscous, low melting substance which has not yet been induced to crystallize.[6] As a result, Ic was characterized by formation of the yellow, crystalline bis(phosphonium iodide) derivative.

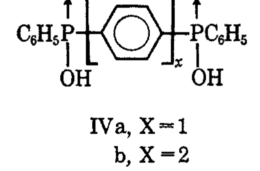


IIIa, *para*
b, *meta*

(2)

Ib, *para*
c, *meta*

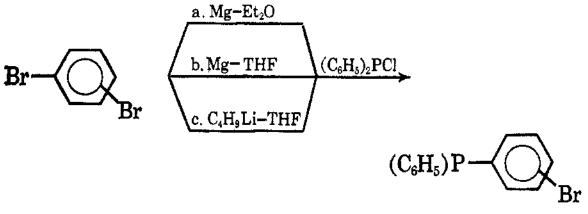
Arylenebis(phosphinic acids).—In a companion study, the further utilization of the above arylenedilithium intermediates for the syntheses of bis(phosphinic acids) was investigated. Reaction of the *p*-phenylene and 4,4′-biphenylenedilithium intermediates with N,N-dimethylphenylphosphonamidic chloride and subsequent acid hydrolysis of the intermediate amides has resulted in low yields of the respective bis(phosphinic acids) IVa and b (eq 3). As was observed above in the preparation of *p*-phenylenebis(diphenylphosphine) (Ib), considerable quantities of the monolithium derivative were also formed which resulted in the subsequent isolation of (4-bromophenyl)phenylphosphonic acid. While low yields of IVa were not then unexpected, the low yield of IVb was unexpected in view of the above high conversions of 4,4′-dibromobiphenyl to the corresponding dilithium derivative. The recent observation that both the chlorine and dimethylamino groups of N,N-dimethylmethylphosphonamidic chloride were labile in reactions with both phenols and anilines[7] suggested a like reactivity of N,N-dimethylphenylphosphonamidic chloride with the arylenedilithium compounds (eq 3). As a result, the formation of tertiary phosphine oxides through reaction of both the chlorine and amino groups would decrease the yields of the acids IVa and b. In contrast, N,N-diethylmethylphosphonamidic chloride was reported[7] to yield monosubstituted products. However, use of the analogous N,N-diethylphenylphosphonamidic chloride in the reaction of eq 3, failed to result in an increase in the yield of IVb.



(3)

IVa, X = 1
b, X = 2

(Bromophenyl)diphenylphosphines.—Since the (bromophenyl)diphenylphosphines IIIa and b were of interest for the syntheses of a variety of new organophosphorus compounds, several routes to these intermediates were investigated in an effort to optimize their syntheses. Of the three routes illustrated in eq 4, the *n*-butyllithium in tetrahydrofuran method (4c) appears to give consistently the best yields (frequently 100% of pure IIIa).



(4)

IIIa, *para*
b, *meta*

Small amounts of grossly contaminated IIIa could be obtained *via* method 4b only by the "reverse addition" of aliquots of magnesium to 1,4-dibromobenzene in tetrahydrofuran at ambient temperature. Even then carbonation of the reaction mixture gave a mixture *p*-bromobenzoic acid and terephthalic acid showing that some conversion to the di Grignard was taking place. If the "normal" Grignard procedure was followed in tetrahydrofuran, the product most readily isolated was 1,4-bis(diphenylphosphino)benzene (Ib). Method 4a was facile but did not give as high yields of pure products as did the *n*-butyllithium method 4c.[8a] However, both methods 4a and c are more facile and give better yields than earlier[8b] preparations of IIIa.

Yields of the liquid *meta* isomer IIIb by either method 4a or c were consistently lower than those obtained for the *para* isomer. In an effort to gain some

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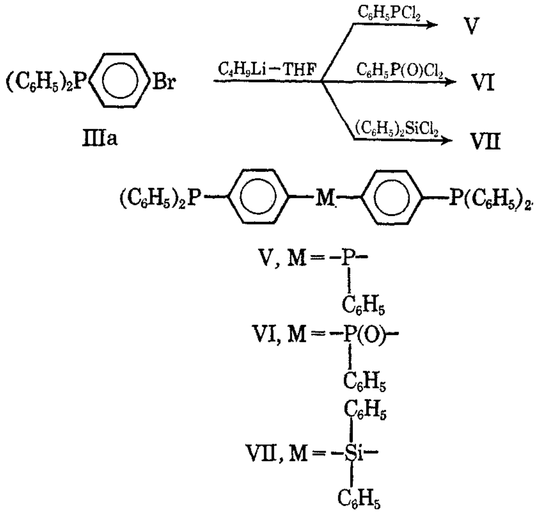
(6) H. Zorn, *et al.* (ref 5d), have recently reported the synthesis of 1,3-bis(diphenylphosphino)benzene (Ic) from potassium diphenylphosphide and sodium 1,3-benzenedisulfonate. These workers imply also this noncrystalline nature of Ic.

(7) N. N. Mel'nikov, A. F. Grapov, and N. V. Lebedeva, *Zh. Obshch. Khim.*, **36**, 457 (1966) (Consultants Bureau Translation).

(8) (a) After these studies had been completed, the same ether method 4a was reported by G. P. Schiemenz, *Ber.*, **99**, 504 (1966); (b) for example, see H. Goetz, F. Nerdel, and K. Wiechel, *Ann.*, **665**, 1 (1963).

insight into the conversion of *m*-dibromobenzene into the monolithium intermediate *via* reaction 4c, the intermediate was also treated with N,N-dimethylphenylphosphonamidic chloride. After hydrolysis of the phosphinamide, a 76% yield of (3-bromophenyl)phenylphosphinic acid was obtained. Thus, the conversion is high and it should be possible to further increase the yield of (3-bromophenyl)diphenylphosphine (IIIb).

Compounds which can be readily prepared from IIIa, in addition to the previously described *p*-phenylenebis(diphenylphosphine) (Ib), are the tris(tertiary phosphine) V, the monooxide VI, and the silicon-linked bis(tertiary phosphine) VII (eq 5). While the yields of V and VII were good, the monooxide VI was obtained only in a semipure state. However, both V and VI were oxidized to the same high melting tris(tertiary phosphine oxide). The monobromo III also served as the starting material for the synthesis of a series of mixed tertiary phosphine–phosphinic acids.[9] Thus, IIIa and *n*-butyllithium provide a quick and convenient route to many new organophosphorus compounds.



(5)

An interesting property of the tertiary phosphines V and VII is their ability to fluoresce under ultraviolet radiation. Phosphine V exhibited a blue-white fluorescence while VII was somewhat weaker. Neither compound fluoresced as strongly as did anthracene. This property was destroyed when V and VII were oxidized or sulfurized. Thus, it would appear that the nonbonding electron pairs on the phosphorus atoms are involved in this fluorescence. However, none of the tertiary phosphines Ia–d or IIIa and b fluoresced under the same ultraviolet radiation.

Infrared Spectra.—Since the bis(tertiary phosphines) described above were to be treated subsequently with phosphorus (+5) azides to form polyphosphoranes,[10] it was necessary to have these phosphines as pure as possible, particularly with respect to phosphine oxide contamination. Furthermore, since most of the tertiary phosphines of this study generally contained some infrared absorption at about 8.5 μ, the position of the P–O absorption in these compounds, there was always some question as to the purity of the phosphines. However, since it had been observed[11] that phosphine oxides contain, in addition to the strong P–O absorption, a second strong absorption at about 8.95 μ, it appeared that both absorptions must be present to indicate the presence of phosphine oxide contamination. The spectra of the phosphine sulfides and phosphonium salts of this study also contained the strong absorption at about 8.95 μ but not the P–O absorption at 8.5 μ. This absorption at about 8.95 μ has been identified as a substituent sensitive C–H planar bending vibration.[12] Together, these two absorptions represent a most useful and diagnostic method for identifying the presence of oxide contamination in tertiary arylphosphines. Thus, partially oxidized tertiary phosphines were found to contain increasing absorptions at about 8.5 and 8.95 μ as the oxidation was continued.

It was then of interest to determine the minimum amount of phosphine oxide contamination which could be determined in the sample as a potassium bromide pellet, as evidenced by the two absorptions at 8.5 and 8.95 μ. Thus spectra of "pure" 4,4′-biphenylenebis(diphenylphosphine) (Ia) and 4,4′-diphenylene ether bis(diphenylphosphine) (Id) were determined in potassium bromide pellets at a concentration of 1 mg/300 mg. The phosphine Ia contained weak absorptions at 8.49 μ and at 8.67 μ as well as a somewhat stronger absorption at 9.15 μ. The bis oxide of Ia contained extremely strong absorptions at 8.45 and 8.96 μ with a shoulder at 8.65–8.7 μ. The absorption originally present in the phosphine at 9.17 μ was still present in the oxide at 9.15 μ at a slightly reduced intensity. The spectra of Id and its dioxide were very similar except for the strong aromatic ether absorptions at 8.55 μ. Then spectra of mixtures of tertiary phosphine with added phosphine oxide were obtained at the same concentration. As little as 2.5% added phosphine oxide was readily distinguished while 1.5% was questionable. Increasing the mixture concentration to 3 mg/300 mg of potassium bromide clearly confirmed the presence of 1.5% oxide and even as little as 0.8% was identifiable. As the concentration of the oxide increased in either case, the absorptions at about 8.5 and 8.95 μ also increased. It, therefore, is concluded that the presence of small amounts of phosphine oxides can be readily identified in aromatic tertiary phosphines by the observations of these two absorptions.

Experimental Section

All organolithium reactions were carried out under dry nitrogen and in anhydrous solvents. Infrared spectra of liquid samples were determined as thin films on a Beckman IR-5 spectrophotometer. The spectra of solids were determined as potassium bromide pellets on a Perkin-Elmer Model 21 spectrophotometer. Molecular weights were determined using a Neumayer thermistor molecular weight apparatus.[13] Melting points were taken in a Thomas–Hoover capillary melting point apparatus. Boiling and melting points were not corrected.

p-**Phenylenebis(diphenylphosphine) (Ib). A.** *Via* *n*-**Butyllithium.**—The following appears to be the best synthesis of Ib utilizing *p*-dibromobenzene and *n*-butyllithium. A solution containing 0.20 mole of *n*-butyllithium in 125 ml of hexane, 11.8 g (0.05 mole) of *p*-dibromobenzene, and 125 ml of ether was held

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[9] R. A. Baldwin, M. T. Cheng, and G. D. Homer, *J. Org. Chem.*, in press.

[10] R. A. Baldwin, *ibid.*, **30**, 3886 (1965).

[11] M. Halmann and S. Pinchas, *J. Chem. Soc.*, 3264 (1958); G. Witschard and C. E. Griffin, *Spectrochim. Acta*, **19**, 1905 (1963).

[12] R. D. Kross and V. A. Fassel, *J. Am. Chem. Soc.*, **77**, 5858 (1955); L. A. Harrah, M. I. Ryan, and C. Tamborski, *Spectrochim. Acta*, **18**, 21 (1962).

[13] J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

at the reflux temperature for 2.75 hr. After cooling, 22.1 g (0.1 mole) of neat diphenylchlorophosphine was added to the reaction mixture which was held at less than 4° during the addition. Removal of the solvents and digestion with methanol and with water gave 12.9 g (0.029 mole, 58% yield) of Ib melting at 162–168° and 2.5 g (11% yield) less pure Ib.

B. *Via* **Two-Step** ***in Situ*** **Reaction.**—The following experiment describes an attempt to effect the two-step conversion of *p*-dibromobenzene to *p*-phenylenebis(diphenylphosphine) (Ib) without the intermediate isolation of (4-bromophenyl)diphenylphosphine (IIIa).

In the first step, (4-bromophenyl)diphenylphosphine (IIIa) was formed *in situ* as described below in this Experimental Section. The cold and tetrahydrofuran–hexane solution of IIIa was then dropped into a second equivalent of *n*-butyllithium in hexane and 30 ml of tetrahydrofuran at −66°. Subsequent addition of the second equivalent of diphenylchlorophosphine, however, resulted in a clear reaction mixture which was concentrated to give a yellow, semisolid residue. Digestion with methanol and with ether resulted in the isolation of 39.5 g (0.088 mole, 59% yield) of Ib melting over the range 163–172°, lit.[2] mp 166–168°.

C. *Via* **Di Grignard Reagent.**—In an attempt to improve upon the previously described[2] synthesis of Ib *via* the di Grignard reagent, use of a tetrahydrofuran–benzene solvent system[14] was investigated. Work-up of the reaction mixture gave only 23 g of crude Ib from which 11 g (25% yield) of Ia, mp 164–166°, was obtained after recrystallization from toluene and methanol. Previous yields using only tetrahydrofuran were in the range of 50–60%.

4,4′-Biphenylenebis(diphenylphosphine) (Ia). A. *Via* **Di Grignard Reagent.**—The di Grignard reagent was formed from 31.2 g (0.1 mole) of 4,4′-dibromodiphenyl and 4.8 g (0.2 g-atom) of magnesium turnings in 125 ml of tetrahydrofuran and 50 ml of benzene after a reflux period of 13 hr. After the initially exothermic additon of 44.1 g (0.2 mole) of diphenylchlorophosphine in 30 ml of tetrahydrofuran, the reaction mixture was further refluxed for 1.5 hr. Subsequent hydrolysis by means of 55 ml of saturated ammonium chloride solution, separation of the yellow organic phase, and concentration of the organic phase yielded a bright, yellow tacky residue. Digestion with methanol yielded 22.9 g of crude 4,4′-bis(diphenylphosphino)biphenyl, having a wide melting range. Exhaustive purification of these impure fractions of Ia by recrystallization from ethylene glycol dimethyl ether and/or tetrahydrofuran–methanol was necessary in order to obtain melting at 191–193°, lit.[2] mp 192.5–194°.

From the methanol extracts of Ia there was recovered a yellow oil which precipitated some white solids. Infrared examination of the yellow oil indicated it to be the same cleavage product of the tetrahydrofuran which had been previously identified by Garner and Tedeschi[15] to be diphenyl-4-hydroxybutylphosphine oxide.

B. *Via* ***n*-Butyllithium.**—A 74.5-g (0.24 mole) quantity of 4,4-dibromobiphenyl and 200 ml of tetrahydrofuran was cooled to −66° before 0.48 mole of *n*-butyllithium in 300 ml of hexane was added slowly through an addition funnel. After warming to 0° and recooling to −66°, 105.4 g (0.48 mole) of neat diphenylchlorophosphine was added. The reaction mixture was warmed to room temperature and filtered to remove the majority of the product. After washing with water and digestion with methanol, 117 g (0.224 mole, 94% yield) of Ia melting at 190–191° was recovered.

This product was further characterized by the formation of its bis(benzylphosphonium chloride) salt, mp >330°.

Anal. Calcd for $C_{50}H_{42}Cl_2P_2$: C, 77.42; H, 5.46. Found: C, 77.36; H, 5.32.

4,4′-Diphenylene Ether Bis(diphenylphosphine) (Id).—A 0.05-mole quantity of 4,4′-dibromodiphenyl ether dissolved in 100 ml of tetrahydrofuran was added to 0.2 mole of *n*-butyllithium in hexane held at about −66° by means of a Dry Ice–acetone bath. The mixture was then warmed to 0° and then stirred at this temperature for 1.5 hr. After recooling to −66°, 0.1 mole of neat diphenylchlorophosphine was slowly introduced after which the reaction mixture was warmed to room temperature, 10 ml of methanol was added, and the solvents were removed at reduced pressure.

These crude products could be purified by digestion with methanol and/or by solution in ether, filtration to remove insolubles, concentration, and finally methanol digestion. Analytical samples, melting at 115–116°, were obtained by recrystallization from ethyl acetate.

Anal. Calcd for $C_{36}H_{28}OP_2$: C, 80.29; H, 5.23; P, 11.5; mol wt, 538. Found: C, 79.51; H, 5.33; P, 11.3; mol wt, 538.

For further characterization, 5 g of Id was dissolved in acetone and titrated with potassium permanganate in acetone. Recrystallization from ethanol–water gave 2.8 g (about 53%) of white crystalline bis oxide melting at 191–193°.

Anal. Calcd for $C_{36}H_{28}O_3P_2$: C, 75.81; H, 4.90; P, 10.85. Found: C, 74.45; H, 5.08; P, 10.8.

Additionally, Id was characterized as the bis(benzylphosphonium chloride) salt, mp 321–323°.

Anal. Calcd for $C_{50}H_{42}Cl_2OP_2$: C, 75.85; H, 5.35. Found: C, 75.62; H, 5.32.

(4-Bromophenyl)diphenylphosphine (IIIa). A. *Via* ***n*-Butyllithium.**—The following procedure appears to be the best route to IIIa. To 0.30 mole of *n*-butyllithium in hexane which had been prechilled to −66° was slowly added (−60° or less) 70.7 g (0.30 mole) of *p*-dibromobenzene dissolved in 200 ml of tetrahydrofuran. As soon as the *p*-dibromobenzene had been added, 66.1 g (0.3 mole) of diphenylchlorophosphine was slowly introduced from a second addition funnel. The reaction mixture was allowed to warm to room temperature, filtered under nitrogen, and the filtrate was concentrated at reduced pressure to yield a semisolid residue. Trituration with methanol yielded a white, crystalline solid (quantitative crude yield). After two additional washings with methanol, 83 g (0.243 mole, 81% yield) of (4-bromophenyl)diphenylphosphine melted at 75–77°. An analytical sample from methanol melted at 78.5–79.5°, lit.[8] mp 79–80°.

Anal. Calcd for $C_{18}H_{14}BrP$: C, 63.38; H, 4.13; Br, 23.42; P, 9.08; mol wt, 341.2. Found: C, 63.52; H, 4.34; Br, 23.8; P, 9.2; mol wt, 343.

In a second duplicate experiment, only the addition sequence was changed with the *n*-butyllithium in hexane being added to the *p*-dibromobenzene in tetrahydrofuran at −66°. Following the usual work-up, only 46 g (0.135 mole, 45% yield) of (4-bromophenyl)diphenylphosphine was isolated.

B. *Via* **Grignard Reagent in Ether.**—To the mono Grignard, prepared from 118 g (0.5 mole) of *p*-dibromobenzene and 12 g (0.5 g-atom) of magnesium turnings in 400 ml of diethyl ether and held at 0°, was added 110.3 g (0.5 mole) of diphenylchlorophosphine. After stirring overnight at ambient temperature and hydrolysis with saturated ammonium chloride solution, the ether phase was decanted from the white solids. These solids were well washed with ether and with tetrahydrofuran, and the organic phases were combined and concentrated to yield a yellow viscous oil. The oil, heated at 100° and 0.1 mm until no further *p*-dibromobenzene sublimed, slowly crystallized at ambient temperature over 2 weeks. The solid was broken up and digested with methanol to yield 125.4 g (0.368 mole, 73.6% yield) of pale yellow (4-bromophenyl)diphenylphosphine, melting at 65–69°.

C. *Via* **Grignard Reagent in Tetrahydrofuran.**—Small portions of 11.4 g (0.47 g-atom) of magnesium turnings were dropped over several hours into a solution of 130 g (0.55 mole) of *p*-dibromobenzene in 600 ml of tetrahydrofuran at ambient temperature. After the magnesium had dissolved, 101.9 g (0.462 mole) of diphenylchlorophosphine was added at −10° to the Grignard solution. Hydrolysis with saturated ammonium chloride solution, separation, and concentration of the organic phase, resulted in the isolation of an oil. The oil, dissolved in ether and filtered, with the ether removed, was held at 100° (0.1 mm) to remove unreacted *p*-dibromobenzene. On standing overnight, the oil partially solidified to a yellow, crystalline mass (79% yield). This material was purified by recrystallization from ethanol and/or by chromatography on activated alumina. The reverse addition of *p*-dibromobenzene to the magnesium yielded largely *p*-phenylenebis(diphenylphosphine) (Ib) with some recovery of (4-bromophenyl)diphenylphosphine (IIIa).

The phosphine IIIa was characterized by oxidation to (4-bromophenyl)diphenylphosphine oxide by means of either hydrogen peroxide or potassium permanganate in acetone. The oxide was found to melt at 151.5–153.5° (lit. mp 154–156°[8a] and 133–134°[8b]). Infrared examination of the crystals revealed strong absorptions at 8.45 and 9.0 μ due to the P–O combination

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[14] M. Bennett, N. B. Sunshine, and G. F. Woods, *J. Org. Chem.*, **28**, 2514 (1963).

[15] A. Y. Garner and A. A. Tedeschi, *J. Am. Chem. Soc.*, **84**, 4734 (1962).

as well as a strong absorption at 12.29 μ assigned to the *para*-substituted benzene.

Anal. Calcd for $C_{18}H_{14}BrOP$: Br, 22.39; P, 8.67. Found: Br, 21.9; P, 8.8.

(3-Bromophenyl)diphenylphosphine (IIIb).—To 100 g (0.424 mole) of *m*-dibromobenzene dissolved in 750 ml of tetrahydrofuran was slowly added, over a 6-hr period, increments of 10.3 g (0.424 g-atom) of magnesium turnings. The temperature of the reaction mixture which increased exothermically to 42° during the initial additions was then held at 34° by means of a water bath. Neat diphenylchlorophosphine, 93.5 g (0.424 mole), was added to give a clear, yellow solution. After 1 hr at the reflux temperature, the mixture was cooled and 60 ml of saturated ammonium chloride was added. The tetrahydrofuran solution was decanted from the tacky, white residue and concentrated to yield 102.5 g of a tan, viscous residue. Distillation at reduced pressure gave 8 g (0.0356 mole, 8.4%) of recovered *m*-dibromobenzene (n^{24}D 1.6034) and 41.1 g of (3-bromophenyl)-diphenylphosphine (IIIb), boiling point of 157–162° at about 0.01 mm (n^{22}D 1.6740–1.6754). The yield was 31.2% based on consumed *m*-dibromobenzene.

Anal. Calcd for $C_{18}H_{14}BrP$: Br, 23.4; P, 9.08. Found: Br, 23.7; P, 9.27.

Similar yields (33–53%) of distillated (3-bromophenyl)diphenylphosphine have also been obtained *via* the use of *n*-butyllithium.

3-(Bromophenyl)diphenylphosphine (IIIb) was further characterized by oxidation to the oxide by means of potassium permanganate in acetone. After recrystallization from toluene and methylcyclohexane, the (3-bromophenyl)diphenylphosphine oxide melted at 113–115°.

Anal. Calcd for $C_{18}H_{14}BrOP$: Br, 22.39; P, 8.67; mol wt, 357.2. Found: Br, 22.5; P, 9.02; mol wt, 355.

In an effort to ascertain the quantities of mono and di Grignard reagents formed in this reverse addition technique, both Grignard reagents obtained from both *p*-dibromobenzene and *m*-dibromobenzene were carbonated. Melting points and somewhat low bromine contents of the resulting acids indicated the presence of terephthalic and isophthalic acids. An ether extraction of the acid mixtures suggested about 80% 3- and 4-bromobenzoic acids.

Reactions of (3- and 4-Bromophenyl)diphenylphosphine.—The following general procedure was utilized to prepare a variety of derivatives of the (3- and 4-bromophenyl)diphenylphosphines (IIIa and b, respectively). To a hexane solution of *n*-butyllithium at about −65 to −70° was slowly added a tetrahydrofuran solution of an equivalent amount of the bromophenyl IIIa and b. Without delay, metalloid chloride, neat if liquid and in tetrahydrofuran if solid, was introduced to the cold reaction mixture. After warming to ambient temperature, the mixture was briefly refluxed (~15 min) before the solvents were removed at reduced pressure. The resulting residue was generally digested with methanol or methanol–water to induce granularization of the products. The results of these experiments are summarized below.

A. ***p*-Phenylenebis(diphenylphosphine) (Ib).**—The addition of 6.5 g (0.29 mole) of diphenylchlorophosphine to an equivalent amount of the above lithium derivative of IIIa resulted in the isolation of 10.4 g (0.233 mole, 80.3% yield) of Ib melting at 161–162°.

B. ***m*-Phenylenebis(diphenylphosphine) (Ic).**—Similarly, the addition of diphenylchlorophosphine to the lithium derivative of IIIb and subsequent work-up yielded a tacky, yellow-brown residue which contained the expected infrared absorptions. This residue was dissolved in hot isopropyl alcohol and water and left to cool at 0°. The solvents were decanted from the clear glass which had separated during the cooling. This glass liquefied on warming to room temperature and had an infrared spectra which appeared to be very much the same as the starting material (3-bromophenyl)diphenylphosphine.

From the alcohol–water phase, a clear, yellow oil was then recovered. Attempts to solidify and/or purify this oil were not rewarding. Thus, the oil was dissolved in chloroform and 2 ml of methyl iodide was added. After 2 hr at reflux, an additional 2 ml of methyl iodide was added. Subsequent addition of ether precipitated a yellow solid and an oil. The solvents were decanted to yield a tacky solid which was completely soluble in water. Recrystallization from ethanol yielded beautiful yellow crystals melting at 282–284°.

Anal. Calcd for $C_{32}H_{30}I_2P_2$: C, 52.63; H, 4.14; I, 34.75; P, 8.48. Found: C, 52.46; H, 4.44; I, 34.7; P, 8.73.

C. **Bis(4-diphenylphosphinophenyl)phenylphosphine (V).**—After the addition of 179 g (0.139 mole) of neat phenyldichlorophosphine, to the lithium derivative of IIIa, the mixture was warmed to 20° and then held at reflux for 2 hr. The crude product was dissolved in concentrated hydrochloric acid and precipitated by pouring into ice. The resulting white solid was digested in ethanol containing a small amount of ethyl acetate to give 50.3 g (0.0798 mole, 57.4% yield) of V melting at 154–158°. The infrared spectrum of this material contained the expected absorptions and no absorption due to P–O. Purification of an analytical sample by column chromatography on alumina followed by recrystallization from ethyl acetate–ethanol gave crystals melting at 161–163°.

Anal. Calcd for $C_{42}H_{33}P_3$: C, 79.99; H, 5.27; P, 14.73; mol wt, 630.7. Found: C, 79.51; H, 5.20; P, 14.1; mol wt, 599.

The tris oxide of V was prepared by slurrying the tris(tertiary phosphine) in glacial acetic acid and then adding 10% hydrogen peroxide in glacial acetic acid. The reaction exothermed slightly and the solids dissolved. The tris oxide was precipitated by further dilution with water and subsequently was recrystallized from isopropyl alcohol and water. The resulting powder melted above 320° and contained strong absorptions at 8.4 and 8.95 μ typical of aromatic tertiary phosphine oxides while the *para* absorption at 12.15 μ was weak. The tris oxide was too insoluble in chloroform to carry out a molecular weight determination.

Anal. Calcd for $C_{42}H_{33}O_3P_3$: C, 74.33; H, 4.90; P, 13.69. Found: C, 74.78; H, 4.85; P, 13.8.

The tris(tertiary phosphine) V was further characterized by conversion to the tris(tertiary phosphine sulfide). The phosphine (3.15 g) was slurried with 100 ml of toluene and 0.48 g of sulfur and heated to reflux with almost complete solution occurring. After about 20 min a heavy, white precipitate had formed. The white solids were removed by filtration and vacuum dried to yield 3.4 g (94.4%) of tris sulfide. An analytical sample was recrystallized from chloroform and ethanol and melted at 295–298°.

Anal. Calcd for $C_{42}H_{33}P_3S_3$: C, 69.40; H, 4.58; P, 12.78; S, 13.23; mol wt, 726.8. Found: C, 68.69; H, 4.35; P, 12.7; S, 13.0; mol wt, 724.

D. **Bis(4-diphenylphosphinophenyl)diphenylsilane (VII).**—The reaction of diphenyldichlorosilane (11.1 g, 0.044 mole) with the lithium derivative of IIIa resulted in a thick, brown reaction mixture which was not readily filterable. Water was added and the mixture was digested on a steam bath until the solids became granular. Following filtration and further digestion with methanol, 29.5 g (0.042 mole, 95% yield) of VII melting at 246–248° was recovered. Recrystallization from toluene gave an analytical sample melting at 250–252°.

Anal. Calcd for $C_{48}H_{38}P_2Si$: C, 81.79; H, 5.39; P, 8.79. Found: C, 82.34; H, 5.27; P, 8.88.

A 2-g quantity of the bisphosphine VII was treated with sulfur in refluxing toluene to give a 92% yield of the disulfide which melted at 305–308°.

Anal. Calcd for $C_{48}H_{38}P_2S_2Si$: C, 74.97; H, 4.98; P, 8.06; S, 8.34. Found: C, 75.25; H, 5.20; P, 8.20; S, 8.38.

E. **Bis(4-diphenylphosphinophenyl)phenylphosphine Oxide (VI).**—Reaction of the lithium derivative of IIIa with phenylphosphonic dichloride (7.0 g, 0.036 mole), resulted in the isolation of 30 g of a yellow, friable solid. Attempts to recrystallize this material were unsuccessful even though the infrared spectrum contained only the expected absorptions, *i.e.*, absorptions at 8.45, 8.95, and 12.2 μ. The identity of this material as the desired monooxide was confirmed by its oxidation, with potassium permanganate in acetone, to the same tris oxide as was obtained from the oxidation of bis(4-diphenylphosphino)phenylphosphine (V) (see above).

Column Chromatography Separation of Tertiary Phosphine Mixtures.—Since the purification of tertiary phosphines via column chromatography on alumina had been useful, it was of interest to develop information about the quantitative aspects of this technique. Thus, a 100-ml buret was filled to the 100-ml level with 80–200 mesh activated alumina which had been oven-dried at 130° for 2 hr. The column was carefully filled with *n*-hexane before the mixtures in benzene were placed on the column top. Initial elution was with benzene–hexane (1:1). After the tertiary phosphine had been collected (*via* change in index of refraction), the column was stripped with tetrahydrofuran or benzene. The results of two separations are shown in Table I.

TABLE I

SEPARATION OF TERTIARY PHOSPHINE MIXTURES ON ALUMINA

Mixture, g	1st recovery, g	2nd recovery, g
2.37 $(C_6H_5)_3P^a$	2.0^a	...
2.0 $(C_6H_5)_3PO^b$	...	2.0^b
2.0 $(C_6H_5)_3P^a$	2.0^a	...
2.0 $(C_6H_5)_3PS^c$	...	2.0^c

[a] Mp 80–82.5°. [b] Mp 154–156°. [c] Mp 160–161°.

(3-Bromophenyl)phenylphosphinic Acid.—To 0.1 mole of *n*-butyllithium in hexane at −68° was slowly added 23.6 g (0.01 mole) of *m*-dibromobenzene dissolved in 80 ml of tetrahydrofuran. The reaction was carried out in a Morton flask fitted with an external cooling jacket through which extended a bottom take-off with a stopcock which was in turn attached to a second reaction flask, also cooled to −68°. The system was pressure equalized and under a dry nitrogen atmosphere at all times. After 10 min of stirring, the white slurry was dropped into a slight excess of N,N-dimethylphenylphosphonamidic chloride dissolved in tetrahydrofuran. After warming to ambient temperature and a 15-min reflux period, the solvents were removed at reduced pressure. The residual material was heated with 50 ml of concentrated hydrochloric acid on a steam bath. The resulting white solid was recrystallized from isopropyl alcohol and water to yield 22.6 g (0.0761 mole, 76% yield) of (3-bromophenyl)phenylphosphinic acid melting at 163–164° (lit.[16] mp 161–162°) and having a neutralization equivalent of 298 (theory 297.1).

***p*-Phenylenebis(phenylphosphinic Acid) (IVa).**—Under an atmosphere of nitrogen and in the same two-flask reaction apparatus described above in the synthesis of (3-bromophenyl)phenylphosphinic acid, 4.8 g (0.02 mole) of *p*-dibromobenzene in 25 ml of tetrahydrofuran, and 0.08 mole (100% excess) of *n*-butyllithium were reacted at −70°. After 1 hr at −70°, the mixture was allowed to warm to room temperature before being dropped into a solution of 8.1 g (0.04 mole) of N,N-dimethylphenylphosphonamidic chloride and 50 ml of tetrahydrofuran. After the reaction mixture was then warmed to ambient temperature and the solvents were removed at reduced pressure, the residue was digested on a steam bath with concentrated hydrochloric acid for 18 hr. The solids were dissolved in sodium hydroxide solution, treated with Norit A, reacidified, and then digested with methanol. The resulting white, methanol-insoluble powder (4 g), melting above 315°, was identified as the desired *p*-phenylenebis(phenylphosphinic acid) (IVa).

Anal. Calcd for $C_{18}H_{16}O_4P_2$: C, 60.34; H, 4.50; P, 17.3; neut equiv, 179. Found: C, 60.19; H, 4.82; P, 17.3; neut equiv, 183.

Additionally, some experiments also yielded (4-bromophenyl)-phenylphosphinic acid as a methanol-soluble product melting at 174–176° (lit.[17] mp, 174.5°) in yields to 15%.

Anal. Calcd for $C_{12}H_{10}BrO_2P$: C, 48.51; H, 3.39; Br, 26.90; neut equiv, 297. Found: C, 48.75; H, 3.45; Br, 26.6; neut equiv, 289.

4,4′-Biphenylenebis(phenylphosphinic acid) (IVb).—Following the same general procedure as described above for the other phosphinic acids, 25 g (0.08 mole) of 4,4′-dibromobiphenyl dissolved in 200 ml of tetrahydrofuran was treated with 2 equiv of *n*-butyllithium in hexane at or below −65°. Subsequent reaction with 2 equiv of either N,N-dimethyl- or N,N-diethylphenylphosphonamidic chloride in 75–100 ml of tetrahydrofuran at the same low temperature, followed by removal of the solvents and acid hydrolysis, gave yields of 4,4′-biphenylenebis(phenylphosphinic acid) (IVb) of 30–40%. This acid was more soluble in organic solvents than the *p*-phenylene homolog IVa and could be recrystallized from isopropyl alcohol–water mixture to give beautiful, featherlike crystals, mp 213–215°C.

Anal. Calcd for $C_{24}H_{20}O_4P_2$: C, 66.36; H, 4.64; P, 14.4; neut equiv, 217. Found: C, 66.84; H, 4.94; P, 14.1; neut equiv, 217.

Registry No.—Ia, 4129-44-6; bis(benzylphosphonium chloride) salt of Ia, 10211-97-9; Ib, 1179-06-2; Ic, 1179-05-1; Id, 10211-98-0; bis oxide of Id, 10211-99-1; bis(benzylphosphonium chloride) salt of Id, 10212-00-7; IIIa, 734-59-8; oxide of IIIa, 5525-40-6; IIIb, 10212-03-0; oxide of IIIb, 10212-04-1; IVa, 10212-05-2; IVb, 10212-06-3; V, 10212-07-4; tris oxide of V, 10212-08-5; tris(tertiary phosphine) sulfide of V, 10212-09-6; VI, 10212-10-9; VII, 10212-11-0; disulfide of VII, 10235-66-2; triphenylphosphine, 603-35-0; $(C_6H_5)_3PO$, 791-28-6; $(C_6H_5)_3PS$, 3878-45-3.

Acknowledgments.—This investigation was supported by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contracts AF 33(657)-11129 and 33(615)-3570. We wish to thank Messrs. Karl Sterner and William Birch for the elemental analyses and Messrs. G. David Homer and Robert J. Mitchell for their laboratory assistance.

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[16] J. M. Denham and R. K. Ingham, *J. Org. Chem.*, **23**, 1298 (1958).

[17] W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 276 (1944).

Aromatic Nitrile Oxides[1]

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Received November 22, 1966

The synthesis of 12 new isoxazolines and oxadiazoles has been achieved in a study of the reactions of 1- or 2-methyl-5-vinyltetrazole and 1- or 2-methyl-5-cyanotetrazole with nitrobenzonitrile oxides. Infrared and nmr spectral data of the compounds are consistent with proposed structures.

Aromatic nitrile oxides are labile compounds formed by the action of dilute alkali on hydroxamoyl chlorides which dimerize readily to furoxans.[2] The rate of the dimerization depends upon the nature of the substituent on the aromatic ring. The greater the electron-donor character of the substituent group the faster the dimerization occurs. Recently Grundmann and Dean[3,4] showed that aromatic nitrile oxides can be stabilized with sterically hindered groups. This encouraged us to study the isomers of nitrobenzonitrile oxide with 1- or 2-methyl-5-vinyltetrazole (MVT) and 1- or 2-methyl-5-cyanotetrazole (MCT) to ascertain the influence of the electrical nature of the nitro group and the effect of its position on the addition reaction.

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[1] This work was supported by the Foundational Research Program of the Naval Ordnance Systems Command.

[2] R. Huisgen, *Angew. Chem.*, **75**, 751 (1963).

[3] C. Grundmann and J. M. Dean, *ibid.*, **76**, 682 (1964).

[4] C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).