tected from air and moisture throughout its isolation, weighed 3.60 g., 96% calculated as $C_6H_5As(COONa)_2$.

Treatment of the product with water in the presence of air resulted in an exothermic reaction. A strong arsinelike odor was noticeable and a dark brown water-insoluble solid (1.47 g.) was produced. Crystallization of this solid from chlorobenzene (25 mg./ml.) at 0° gave 0.42 g. (21%) of arsenobenzene, m.p. 201–204°.

Potentiometric titration of the water-soluble carbonate confirmed the sodium analysis of 2.0 atoms of sodium for each atom of arsenic.

1 Arsenobenzene-tetrasodium adduct: 1 arsenobenzene: 4 methyl chloride. The arsenobenzene-tetrasodium adduct was prepared from 2.92 g. (0.009 mole) of arsenobenzene and was added to 2.92 g. (0.009 mole) of arsenobenzene. An exothermic reaction ensued and the yellow-green color gradually deepened as the suspended arsenobenzene changed from white to dark brown while it dissolved. The supernatant liquid phase changed to a red color during 45 min. The system was stirred at 25° for a total of 23 hr., after which there was only a little solid in the dark red solution.

Treatment with methyl chloride and subsequent processing was the same as that used for the experiment with the di-adduct: yield of dimethyldiphenylbiarsine, 4.74 g. (74%), m.p. 73–77°, crystallized from petroleum ether, m.p. 81.5–82.0°. Arsenobenzene was recovered in a 2% yield.

An experiment of this type where methyl sulfate was used in place of methyl chloride gave similar results.

1 Arsenobenzene-tetrasodium adduct:3 arsenobenzene:2 methyl sulfate. The arsenobenzene-tetrasodium adduct was prepared from 0.53 g. (0.0019 mole) of arsenobenzene and was added to 1.91 g. (0.0057 mole) of arsenobenzene. The sequence of color changes was identical to that observed in the previous experiment and all but a trace of the arsenobenzene went into solution.

Treatment of the mixture with 0.57 g. (0.0045 mole) of methyl sulfate and subsequent processing by the method outlined above gave recoveries of 0.92 g. (81%) of arsenobenzene and 0.75 g. (60%) of dimethyldiphenylbiarsine, calculated on the basis of the equations which we have suggested for this reaction.

Benzoic acid titration of arsenobenzene-disodium adduct. Disodium arsenobenzene, prepared from 2.44 g. (0.008 mole) of arsenobenzene in 40 ml. of 2,5-dioxahexane was titrated with a dioxahexane solution of benzoic acid (0.306 g./ml.). During this process the mixture became so viscous, due to the precipitation of sodium benzoate, that adequate stirring was difficult. Complete decolorization occurred after 5.0 ml. of the acid solution had been added. The diadduct content, calculated on the basis of the titration was 78.4%. A value of 72.7% was obtained by sodium analysis of the residues.

On the basis of the sodium analyses and the reaction scheme proposed by Wittig *et al.*, 1.55 g. of arsenobenzene should have been found. A recovery of 1.61 g. actually was obtained.

Dimethyldiphenylbiarsine. Phenylmethylarsinic acid (0.374 g., 0.0019 mole), m.p. 179–179.5°, with 0.66 g. (0.01 mole) of aqueous 50% hypophosphorous acid and 5 ml. of absolute ethanol was refluxed for 6 hr. under nitrogen. The system rapidly became murky and a rust-colored precipitate appeared. Upon cooling the ethanol was vacuum-evaporated from the suspension of white crystals. The remainder was extracted at 25° with 5 ml. of petroleum ether. This extract was filtered and cooled to 0° to yield 0.18 g. (63%), m.p. 81.5–82°. A mixture melting point with other samples was not lowered. Microanalysis for arsenic gave low results: As, 43.4, 43.7, 43.4; calcd. for $C_{14}H_{16}As_2$: As, 44.8.[10]

Oxidation of dimethyldiphenylbiarsine. A mixture of 20 ml. of petroleum ether and 10 ml. of water was added to 1.58 g. (0.0047 mole) of dimethyldiphenylbiarsine, m.p. 74–77°, and the whole was shaken at 25° in contact with air for 11 hr. Then the two phases were separately evaporated to dryness. The aqueous layer yielded 0.892 g. (0.0045 mole) of impure methylphenylarsinic acid, m.p. 158–166°; solution in 2 ml. of water and precipitation by addition of 10 ml. of acetone raised this melting point to 179–179.5°, recovery 42%. The oil (0.55 g.) from the petroleum ether phase spontaneously crystallized slowly to give 0.35 g., m.p. 167–171°, and 0.21 g., m.p. 163–169°. Total recovery of methylphenylarsinic acid, m.p. 158–174°, was 1.14 g. (60%).

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(10) O. Wintersteiner and H. Hannel, *Mikrochemie*, **4**, 155 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Phosphorobenzene-Alkali Metal Adducts

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Phosphorobenzene has been shown to exist in mono-, di-, and polymeric forms. Each of these forms is converted by treatment with metallic sodium in 2,5-dioxahexane to the phosphorobenzene-disodium adduct. This adduct is converted by methyl chloride into the oxygen-sensitive dimethyldiphenylbiphosphine and by benzoyl chloride into dibenzoyldiphenylbiphosphine.

The addition of alkali metals to phosphorus-phosphorus double bonds has not been reported. Indeed the literature relating to phosphorobenzene (V) itself is sparse and confused. Michaelis and Kohler[1] first reported phosphorobenzene as the final product of a reaction series commencing with phenylphosphonous acid, I. When the acid was heated it disproportionated into phenylphosphonous acid (III) and phenylphosphine (II). The latter compound when heated with phenyldichlorophosphine, IV, yielded a pale yellow crystalline mass of melting point 149–150°, the carbon hydrogen analysis of which corresponded to that expected for $C_6H_5PPC_6H_5$. This product (V) was decomposed by hydrogen chloride into II and IV and by chlorine[2] into IV alone.

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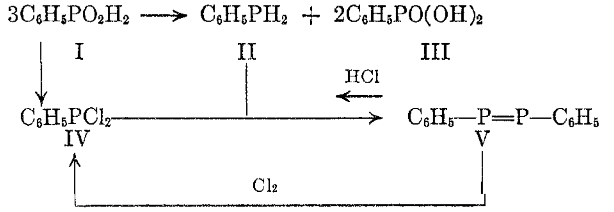
(1) A. Michaelis and H. Kohler, *Ber.*, **10**, 807 (1877).

(2) W. Schlenk and F. Bergmann, *Ann.*, **463**, 1 (1928).



We have repeated these reactions and have found them to be reliable, but have purified the material until it melts at 154.5–156° in a sealed tube.

However, Erlenmeyer *et al.*[3] claim to have improved the preparation of phosphorobenzene by gently warming crude phenylphosphine (II) (prepared by the reduction of phenyldichlorophosphine with lithium aluminum hydride) with phenyldichlorophosphine. A white crystalline solid, melting at 193° in a sealed tube, was obtained. The analyses for carbon, hydrogen and phosphorus corresponded to $C_{12}H_{10}P_2$. Also the molecular weight as determined by the camphor method was reported as 198, thus corresponding roughly to the monomeric formula. These workers concluded that the product of Michaelis and Kohler was grossly impure.

We have repeated the work of Erlenmeyer *et al.* without difficulty by following their directions exactly; however, when the size of the experiment was increased sixfold a different product was obtained which melted at 252–256°, finally becoming clear at 278°. When either this high-melting product, or the one melting at 193°, was quickly heated to the melting point the resolidified material melted at 148°. This discovery has indicated a reexamination of the molecular weight, which we have carried out by an isopiestic method in carbon disulfide.[4] According to this analysis (when biphenyl is used as a standard) the molecular weight of the compound melting at 154–156° is 206 (calculated, 216) and that of the substance melting at 193° is 402 (calculated, 432) while the high melting material seems to be polymeric. It is evident that the dimer, m.p. 193°, was wrongly designated as a monomer by Erlenmeyer *et al.* because it depolymerized at the high temperature (about 170°) employed in the Rast camphor method.

The ultraviolet absorption spectrum of what we now call dimeric phosphorobenzene has been reported.[3] We have examined both the monomer and dimer in chloroform solution and find similar general absorption for both forms increasing from 360 mμ (log E 2.8) to a peak at 245 mμ (log E_{max} for monomer, 4.12; for dimer, 4.25). The infrared spectra of Nujol mulls show grossly two large peaks at 13.45 and 14.32 microns for the dimer while double peaks at about the same wavelengths (13.41 and 13.54; 14.29 and 14.40) are characteristic of the monomer.

We have been able to increase the yield of phosphorobenzene from a 55% maximum by the reported methods to 82% of monomer on the basis of phenyldichlorophosphine. The improvement is accomplished simply by adding dropwise a lithium aluminum hydride solution in ethyl ether to phenyldichlorophosphine. The phenylphosphine reacts, *in situ* as it is formed, with excess phenyldichlorophosphine. The product, as well as its dimer, may be purified by crystallization from carbon disulfide and from ethanol. These operations should be carried out under nitrogen since phosphorobenzenes are slowly oxidized in the solid state but are much more quickly oxidized in solution.

All three forms of phosphorobenzene react with sodium in 2,5-dioxahexane, although the dimer and polymer are sluggish either because of limited solubility, or because they must depolymerize. At the beginning of the reaction all three form a deep red homogeneous solution which gradually becomes orange because of a yellow precipitate in the red solution. No further color change is observed during the addition, which requires 3 or 4 days. Analysis for combined sodium in all three systems shows them to be identical, corresponding with the additions of 2 atoms of sodium to 1 molecule of phosphorobenzene. We have not seen any indication of the existence of a mono-adduct or "tetra-adduct."[5]

The solution of phosphorobenzene-disodium adduct is decolorized rapidly by methyl chloride. The crystalline crude product, m.p. 55–65°, is obtained in 83% yield calculated as dimethyldiphenylbiphosphine. The compound melts at 75–77° after crystallization from petroleum ether, but air must be excluded rigorously. The compound oxidizes so readily that in the finely divided state it inflames in air. The oxidation product is phenylmethylphosphonous acid, and the yield of this compound from oxidation of a petroleum ether solution of dimethyldiphenylbiphosphine is taken as the analytical basis for identity.

The solution of phosphorobenzene-disodium adduct reacts with benzoyl chloride with evolution of heat. The crude product, melting at 105–115°, is obtained in 94% yield calculated as *P,P'*-dibenzoyl-*P,P'*-diphenylbiphosphine. After three crystallizations from methanol the bright yellow crystalline solid melts at 117–117.5°. It is oxidized by air though at a slower rate than is the analogous dimethyl compound. However manipulative difficulties have prevented us from obtaining good analytical values. The identity of the product is supported by its reaction with chlorine, which gives 86% of the benzoic acid and 91% of the

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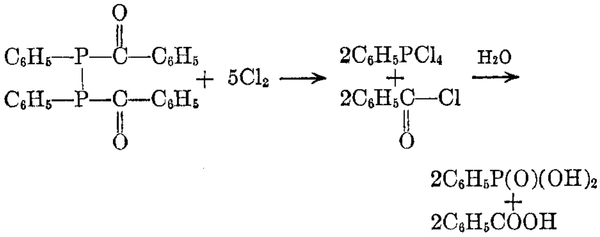
(3) Th. Weil, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, **35**, 616 (1952).

(4) F. Schneider, *Qualitative Organic Microanalysis*, John Wiley & Sons, New York, 1946, p. 118.

(5) J. W. B. Reesor and G. F Wright, *J. Org. Chem.* **22**, 382 (1957).

phenylphosphonic acid expected from the reaction.



$$\begin{array}{l} C_6H_5{-}P{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \\ \quad | \\ C_6H_5{-}P{-}\underset{O}{\underset{\|}{C}}{-}C_6H_5 \end{array} + 5Cl_2 \longrightarrow \begin{array}{c} 2C_6H_5PCl_4 \\ + \\ 2C_6H_5\underset{O}{\underset{\|}{C}}{-}Cl \end{array} \xrightarrow{H_2O} \begin{array}{c} 2C_6H_5P(O)(OH)_2 \\ + \\ 2C_6H_5COOH \end{array}$$

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EXPERIMENTAL

All melting points have been corrected against reliable standards. All manipulations were carried out under pure nitrogen. In every instance when petroleum ether was employed it was the grade boiling at 60–70°, freed from alkenes, moisture, and peroxides.

Monomeric phosphorobenzene. Excess lithium aluminum hydride (1.2 g., 0.032 mole) in 10 ml. of diethyl ether (clear, filtered solution) was added dropwise to 11.0 g. (0.061 mole) of phenyldichlorophosphine[6] in 30 ml. of dry ether. The temperature of the reaction was controlled to 0–5°. At first a second phase separated which solidified as more hydride was added. The system was stirred for 12 hr. at 25° subsequent to addition.

The ether solution of aluminum chloride and excess hydride was decanted under nitrogen through a plug of glass wool. The product, which remained in the flask, was washed with ether, stirred with 20 ml. of 10% aqueous sodium hydroxide for an hour, and then washed with water (20 ml.), ethanol (20 ml.), and ether (20 ml.). Drying was effected by maintenance at 25° (2 mm.) for 2 hr. A yield of 5.46 g. (82%) of monomeric phosphorobenzene was obtained (m.p. 148.5–151.5°).

Purification of phosphorobenzene. (a). Monomer. The crude monomer described above was treated with carbon disulfide (10 ml. per g.) and allowed to stand for 2 hr. at room temperature. Most of the sample dissolved at once. The system was filtered and 20 ml. of absolute ethanol was added to the filtrate. After slow crystallization (25°), 28% of the weight of the crude monomer was obtained in a purified state, m.p. 154.5–156°.

(*b*) *Dimer.* The crude dimer (m.p. 182–185°) was suspended in carbon disulfide (11 ml. per g.). After 2 hr. of shaking at room temperature, the suspension was filtered and 87% of the starting material was recovered (m.p. 182–185°). Addition of absolute alcohol (3 ml. per ml. of carbon disulfide) to the filtrate brought about the crystallization of a purified dimeric phosphorobenzene, m.p. 188–192°, in a sealed tube. The recovery was 7% of the weight of the crude dimer.

(*c*) *Polymer.* No solvent could be found for the polymer.

Interconversion of phosphorobenzenes. Samples of monomeric and dimeric phosphorobenzenes (0.25 g.) were heated under nitrogen at 195° (oil bath) for 20 min. The light yellow melts were allowed to cool during 20 min.; they formed yellow glasses which solidified when mulled with hot ethanol. The solids were washed with ethanol and ether and were dried *in vacuo*. Both samples melted at 153–155° (sealed tubes).

A sample of polymeric phosphorobenzene (0.948 g.) was heated under nitrogen in a tube immersed in a salt bath which was allowed to rise from 200 to 280° during 10 min. The yellow melt was cooled quickly and the yellow glass was mulled with hot ethanol. The resulting solid was washed with ethanol and ether, then dried *in vacuo*. Recovery was 0.45 g. (47%), sealed tube melting point 149–153°, slightly cloudy.

Phosphorobenzene-disodium adduct. Using the technique described previously[7] with thoroughly externally flamed apparatus and pure dry nitrogen, 2.16 g. (0.01 mole) of monophosphorobenzene, or the equivalent in dimer or polymer, was shaken with an excess of sodium metal in a single block. The reaction medium consisted of 40 ml. of 2,5-dioxahexane purified by distillation from sodium benzophenone ketyl. After the reaction was judged to be complete (3–4 days) the adduct suspension was transferred to a 100-ml. multinecked nitrogen-filled (and protected) flask equipped with stirrer.

Dimethyldiphenylbiphosphine. The suspension of adduct described above was stirred at 0–5° while methyl chloride was introduced into the flask during 20 min. When the color of the system had changed from orange to white the reaction medium was evaporated under 10 mm. pressure at room temperature. The residue was twice extracted with 30-ml. portions of ether leaving a residue containing 95% of sodium ion expected from the di-adduct if its yield had been quantitative. The ether extracts were evaporated leaving 2.04 g. (83%) of crude product, m.p. 58–70°. This was twice crystallized from petroleum ether at 0° under nitrogen, the crystals washed with methanol at 0° and the product dried under vacuum, m.p. 75–77°.

Air oxidation of dimethyldiphenylbiphosphine. A solution of 1.70 g. (0.0069 mole) of dimethyldiphenylbiphosphine, m.p. 69–74°, in 100 ml. of petroleum ether was exposed to air for 48 hr. in order to obtain complete oxidation. Evaporation of the solvent left 2.25 g. of impure methylphenylphosphonous acid, m.p. 121–129° (103% of theory). Two crystallizations from water raised the melting point to 133–134°.[8] The compound also was characterized as its cinchonidine salt, m.p. 153–154°.[8]

Dibenzoyldiphenylbiphosphine. A suspension of di-adduct, prepared as described above from 1.08 g. (0.005 mole) of monophosphorobenzene in 40 ml. of dioxahexane, was treated with 1.40 g. (0.01 mole) of benzoyl chloride in 5 ml. of dioxahexane. The evolution of heat was regulated by an ice-water bath which maintained the system at 0–5°. When the color had changed from orange through brown to yellow, the reaction medium was evaporated under 10 mm. pressure at room temperature and the solid residue was extracted with two 30-ml. portions of ether. Evaporation of these extracts left 2.02 g. (95%) of crude dibenzoyldiphenylbiphosphine, m.p. 105–115°. Three crystallizations from hot methanol raised the melting point to 117–117.5°. The color of this substance is bright yellow.

Chlorination of dibenzoyldiphenylbiphosphine. A solution of 0.177 g. (0.000415 mole) of dibenzoyldiphenylbiphosphine in 10 ml. of carbon tetrachloride was treated with gaseous chlorine at 20–25° for 10 min. Then 5 ml. of water was added and the system was evaporated to dryness in an air stream. The residue was extracted five times with 5-ml. portions of petroleum ether. Crystallization of the residue left after evaporation of the petroleum ether from a minimum of water gave 0.087 g. (87%) of benzoic acid, m.p. 119.5–121°; mixture melting point was not lowered. The petroleum ether insoluble portion weighed 0.119 g. (91%), m.p. 154–156°, and was identified as phenylphosphonic acid by mixture melting point.

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[6] B. Buchner and L. B. Lockhart, Jr., *J. Am. Chem. Soc.*, **73**, 755 (1951).

[7] J. W. B. Reesor, J. G. Smith, and G. F Wright, *J. Org. Chem.*, **19**, 940 (1954).

[8] W. J. Pope and C. S. Gibson, *J. Chem. Soc.*, **101**, 740 (1912).