Sublimation of the crude red solid at 1-mm pressure and *less than* 50° gave purified thionphthalic anhydride, mp 91–96°, rearranging and reacting on melting.

Anal. Calcd for $C_8H_4O_2S$: C, 58.50; H, 2.45; S, 19.55. Found: 58.38; H, 2.51; S, 18.82.

The sublimed red thionphthalic anhydride (III) was shown by its infrared spectrum to be free of phthalic anhydride and thiophthalic anhydride.[9] An absorption at 8.68 μ (1155 cm^{-1}) may be assigned as a thiocarbonyl stretching frequency.[10]

The ultraviolet spectrum of III in cyclohexane had absorptions with the extinction coefficients stated as follows: 2350 A, 6666; 2873 A, 6620; 2945 A, 6764; 3147 A, 4611; and 3279 A, 3888. On the same Cary ultraviolet spectrophotometer, Model 20, phthalic anhydride showed absorbancies at 2479 A (1179), 2857 A (461), and 2948 A (567); thiophthalic anhydride showed absorbancies at 2464 A (2153), 2906 A (1834), and 2960 A (1742). The nmr spectrum of III observed in carbon disulfide solution at 60 Mc/sec on a Varian A-60 spectrometer had a complex absorption pattern in the region characteristic for phenyl hydrogens with the most intense absorption at 8.0 ppm downfield from tetramethylsilane. The complex splitting pattern was definitely not A_2B_2 and appeared to be ABCD. In contrast, under the same conditions, phthalic anhydride and thiophthalic anhydride gave nmr spectra with an A_2B_2 pattern for the phenyl protons.

Attempts to purify III by crystallization or by column chromatography led to rearrangement of III to thiophthalic anhydride. Oxidation of III by aqueous basic potassium permanganate gave a quantitative yield of phthalic acid which was identified by mixture melting point with an authentic sample, mp 192–193°, and by superimposable infrared spectra.

Thiophthalic Anhydride (IV).—This white compound was prepared for analytical comparisons from phthaloyl chloride and hydrogen sulfide by the method described by Chakravarti and had mp 113–114° in agreement with the literature.[11]

Registry No.—III, 13699-68-8; hydrogen disulfide, 13465-07-1; phthaloyl chloride, 88-95-9.

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[9] The spectra of these compounds are available in the Master's Thesis submitted to San Diego State College by Mr. Dodd-Wing Fong in partial fulfillment of the Master's Degree. This paper is taken in part from that thesis.

[10] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 177–181.

[11] G. C. Chakravarti, *J. Indian Chem. Soc.*, **5**, 405 (1928).

Reaction of Triphenylphosphine Dihalides with Grignard and Organolithium Reagents

DONALD B. DENNEY AND FRANK J. GROSS[1]

Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903

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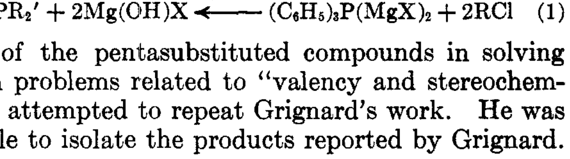
In 1931, Grignard and Savard[2] reported the synthesis of pentasubstituted phosphorus compounds by the reactions given in eq 1. Blount,[3] noting the importance of the pentasubstituted compounds in solving certain problems related to "valency and stereochemistry," attempted to repeat Grignard's work. He was not able to isolate the products reported by Grignard.



$$\begin{array}{ccc} (C_6H_5)_3P{=}O + PCl_5 & \longrightarrow & (C_6H_5)_3PCl_2 + POCl_3 \\ & & \Big\downarrow{\scriptstyle 2RMgX} \\ (C_6H_5)_3PR_2' + 2Mg(OH)X & \xleftarrow{2R'OH} & (C_6H_5)_3P(MgX)_2 + 2RCl \end{array} \quad (1)$$

He attributed his lack of success to the destruction of the triphenylphosphine dihalide when Grignard's procedure was followed; that is, when the dihalide was washed with water and aqueous sodium bicarbonate, it was converted to the phosphine oxide.

When Blount repeated this work with an authentic sample of triphenylphosphine dichloride, he was still unable to isolate pentasubstituted phosphorus compounds. He suspected that alkyltriphenylphosphonium halides were formed; however, he was not able to confirm this. He concluded that "the substance was either very complicated or very impure."

In a subsequent publication,[4] he reported that the product was indeed an alkyltriphenylphosphonium salt and that the anomalous evidence obtained from the first reaction was due to "the peculiar depression in the melting point of ethyltriphenylphosphonium iodide upon exposure to air."

The reaction of an organometallic compound with a trialkyl or triarylphosphine dihalide to give tetrasubstituted phosphonium salts could be a particularly attractive route to these materials. Generally these salts are simply prepared by allowing the appropriate trisubstituted phosphine to react with an alkyl halide; however, this method is not satisfactory for most aryl halides or alkyl halides which do not undergo S_N2 or S_N1 reactions. Examples of these are some tertiary halides, highly hindered halides, and certain bicyclic halides. It seemed of interest, therefore, to investigate in some detail the reactions of triphenylphosphine dihalides with Grignard and organolithium reagents.

Reaction of triphenylphosphine dibromide with butyllithium at −10° (eq 2) for 4 hr afforded as major products triphenylphosphine (88%), triphenylphosphine oxide (12%), and butyl bromide. Similar results were obtained when butylmagnesium bromide was allowed to react with the dibromide. Triphenylphosphine dichloride was allowed to react with butyllithium. The major products were triphenylphosphine and butyl chloride. Reactions of the dichloride with phenyllithium afforded triphenylphosphine and chlorobenzene as major products.

$$(C_6H_5)_3\overset{+}{P}X\ X^- + RM \longrightarrow (C_6H_5)_3P + RX + MX \quad (2)$$

$$X = Cl, Br;\ M = Li, Mg$$

These results show quite clearly that under the conditions used little or no phosphonium salt is being formed and the major mode of reaction involves displacement on halogen. Blount[4] did not describe his reaction conditions in detail; however, in general it appears that he added a slurry of triphenylphosphine dichloride in benzene to a large excess (5 moles) of the Grignard, which was probably in ether. No cooling was used and the reaction was exothermic. After the addition, the mixture was heated under reflux for 2 hr.

Repetition of Blount's experiment using methylmagnesium iodide resulted in an excellent yield of triphenylmethylphosphonium iodide (eq 3). When triphenylphosphine dichloride was allowed to react with phenylmagnesium bromide under the same condi-

$$(C_6H_5)_3\overset{+}{P}Cl + Cl^- + CH_3MgI \longrightarrow (C_6H_5)_3\overset{+}{P}CH_3 + I^- \quad (3)$$

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[1] F. J. G. wishes to acknowledge his gratitude to the American Cyanamid Co. for a Junior Educational Award and to the Hatco Chemical Division of W. R. Grace Co. for a fellowship.

[2] V. Grignard and J. Savard, *Compt. Rend.*, **192**, 592 (1931).

[3] B. K. Blount, *J. Chem. Soc.*, II, 1891 (1931).

[4] B. K. Blount, *ibid.*, I, 337 (1932).

tions, the products were triphenylphosphine (90%) and tetraphenylphosphonium bromide (6.7%). The results of these experiments indicate that attack on phosphorus can occur with the production of phosphonium salts. It is not clear how much of the triphenylmethylphosphonium salt arose by this route. This salt could have also been formed by reaction of triphenylphosphine with generated methyl chloride or by reaction with residual methyl iodide left over from the Grignard preparation. These possibilities do not need to be considered with the phenylmagnesium bromide reaction and thus attack on phosphorus has been demonstrated. It is not unreasonable that there should be more attack on phosphorus by methylmagnesium iodide than phenylmagnesium bromide. Steric effects could certainly be playing a role in influencing the rates of displacement on phosphorus.

The results of all of these experiments indicate that attack can occur on halogen or phosphorus of triphenylphosphine dihalides. In general it appears that it may be possible to direct the substitution so that attack occurs in the main on phosphorus; however, this may require considerable experimentation.

Experimental Section[5]

Formation and Reaction of Triphenylphosphine Dibromide with Butyllithium.—A solution of 13.2 g (0.05 mole) of triphenylphosphine in 100 ml of anhydrous ether at −10° was treated dropwise with 8.0 g (0.05 mole) of bromine.[6] Butyllithium (0.05 mole; 32 ml of a 1.6 *M* solution in hexane) was then added dropwise to the cold, stirred slurry. The slurry slowly disappeared as a second, finely divided precipitate began to appear. Stirring at −10° was continued for an additional 4 hr. The reaction mixture was hydrolyzed by the addition of 50 ml of a 10% aqueous ammonium bromide solution. During the hydrolysis a gummy solid formed. The ether layer was separated and evaporated to give 11.5 g (88%) of crude triphenylphosphine, mp 63–74°. The gummy solid was treated with saturated aqueous sodium bicarbonate solution. Carbon dioxide was evolved and a solid was formed. The material weighed 2.35 g and melted at 150–155°. The infrared spectra of these materials were entirely in accord with the structural assignments of triphenylphosphine and triphenylphosphine oxide.

The ethereal distillate which had been condensed at −78° was distilled through an 8-in. column packed with glass helices. The pot residue, bp >50°, was analyzed by glpc. Two components were found. The first had the same retention time as ether and the second had the same retention time as *n*-butyl bromide. Addition of *n*-butyl bromide increased the size of the second peak.

Reaction of Triphenylphosphine Dibromide with *n*-Butylmagnesium Bromide.—The same molar quantities of reactants were used and the isolation procedures were identical. The yield of crude triphenylphosphine was 10.7 g (81%). Recrystallization from ethanol gave material of mp 76–77.5° (lit.[7] mp 80–81°). There was also obtained 3.4 g of triphenylphosphine oxide, mp 155–157° (lit.[7] mp 155–157°), after one crystallization from petroleum ether (bp 30–60°).

Formation and Reaction of Triphenylphosphine Dichloride with Butyllithium.—Triphenylphosphine (26.2 g, 0.10 mole) was dissolved in hexane and treated at −10° with gaseous chlorine. A white precipitate formed. The solvent was evaporated *in vacuo* on a steam bath. The residue was slurried in dry hexane and treated with 65.0 ml of a 1.6 *M* solution of butyllithium in hexane at 5°. As the reaction mixture warmed to room temperature, the white solid disappeared and it was replaced by a finely divided yellow precipitate. The reaction mixture was heated under reflux for 2 hr. Hydrolysis with 100 ml of 10% aqueous ammonium chloride followed by separation of the hexane solution and evaporation of the hexane afforded 19.0 g (75%) of crude triphenylphosphine, mp 58–80°. One crystallization from ethanol raised the melting point to 79–80°. The insoluble material gave 6.2 g (23%) of crude triphenylphosphine, mp 72–78°. The infrared spectrum was identical with that of an authentic sample. Glpc analysis of the hexane distillate showed a peak with the same retention time as *n*-butyl chloride. In another experiment, the dichloride was prepared and an ethereal slurry was allowed to react with *n*-butyllithium at −10°. Hydrolysis gave primarily triphenylphosphine oxide, indicating that little or no reaction had occurred.

Reaction of Triphenylphosphine Dichloride with Phenyllithium.—Phenyllithium (30.0 ml of a 1.86 *M* solution) in benzene–ether was added to the dichloride prepared from 13.1 g (0.05 mole) of triphenylphosphine in 250 ml of hexane. After the addition, the mixture was heated under reflux for 4 hr. Hydrolysis gave essentially a quantitative yield of triphenylphosphine, mp 77.5–80°, after one crystallization.

The hexane distillate was fractionated through an 8-in. helices packed column until the head temperature reached 70°. Glpc analysis of the pot residue showed a material with the same retention time as chlorobenzene was present. This material was collected. Its infrared spectrum was identical with that of chlorobenzene.

Reaction of Triphenylphosphine Dichloride with Methylmagnesium Iodide.—Triphenylphosphine dichloride was prepared by allowing 13.1 g (0.05 mole) of triphenylphosphine in 100 ml of benzene to react with excess chlorine gas. The benzene was evaporated *in vacuo* to remove excess chlorine and the residue was suspended in 100 ml of benzene. The slurry was added with stirring to 249 ml of a 0.85 *N* solution of methylmagnesium iodide in diethyl ether. Heat was evolved and a reddish orange oil separated. The reaction mixture was heated under reflux with stirring for 2 hr. The cooled reaction mixture was treated with 100 ml of 2.5 *N* hydrochloric acid. A solid formed at the interface. The solid was isolated by filtration; after drying for several hours in the air it weighed 18.6 g, mp 88–120°. Evaporation of the dried organic phase yielded 3.5 g of solid. Treatment of a small portion of the insoluble material with aqueous sodium bicarbonate solution gave some evolution of carbon dioxide. The recovered material had mp 182–188°. The rest of the material was recrystallized from water with a Darco treatment, mp 185–187°; an authentic sample had mp 185.5–188°. The mixture melting point of these substances was 185–187°. The infrared spectra of the two materials were identical. The theoretical yield of triphenylmethylphosphonium iodide is 20.2 g. The crude yield of insoluble material was 18.6 g and the benzene-ether-soluble material (3.5 g) probably included some of this material.

Reaction of Triphenylphosphine Dichloride with Phenylmagnesium Bromide.—A slurry of 0.05 mole of triphenylphosphine dichloride was added with stirring to 280 ml of a 0.9 *N* solution of phenylmagnesium bromide in ether. Heat was evolved and a small amount of white solid formed. The reaction mixture was heated under reflux for 2 hr and then hydrolyzed with 100 ml of 2.5 *N* hydrochloric acid. The mixture was filtered to give a small amount of solid. The organic layer was separated and dried. Evaporation afforded a semicrystalline material which had the odor of chlorobenzene. This material, (15.2 g) was dried *in vacuo* at 45° for several hours. The dried material, (11.9 g) had mp 65–78°. One crystallization from ethanol raised this to 77–79°. A mixture melting point determination with an authentic sample gave mp 77–79°. The solid obtained by filtration (1.4 g) was recrystallized from water, mp 296–298°. The infrared spectrum was identical with that of an authentic sample of tetraphenylphosphonium bromide and there was no depression of the melting point on admixture. The crude yield of triphenylphosphine was 90.5% and 6.7% of tetraphenylphosphonium bromide was obtained.

Registry No.—Triphenylphosphine dibromide, 1034-39-5; butyllithium, 109-72-8; *n*-butylmagnesium bromide, 693-03-8; triphenylphosphine dichloride, 2526-64-9; phenyllithium, 591-51-5; methylmagnesium iodide, 917-64-6; phenylmagnesium bromide, 100-58-3.

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[5] Melting points were determined with a Mel-Temp block and they are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 21 spectrometer. Glpc data were obtained with an F & M Model 700.

[6] In a separate experiment the product from this reaction was hydrolyzed to give triphenylphosphine oxide in essentially quantitative yield.

[7] D. B. Denney and L. C. Smith, *J. Org. Chem.*, **27**, 3404 (1962).