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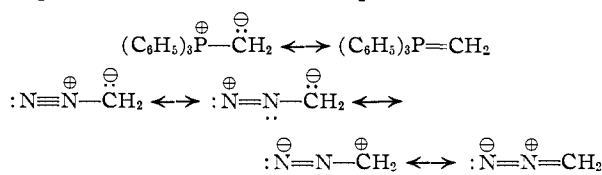
Studies in Phosphinemethylene Chemistry. I. Nucleophilic Displacement of Halide Ion in Metal Halides by Triphenylphosphinemethylene. A New Synthesis of Organometallic-substituted Phosphonium Salts¹

BY DIETMAR SEYFERTH AND SAMUEL O. GRIM

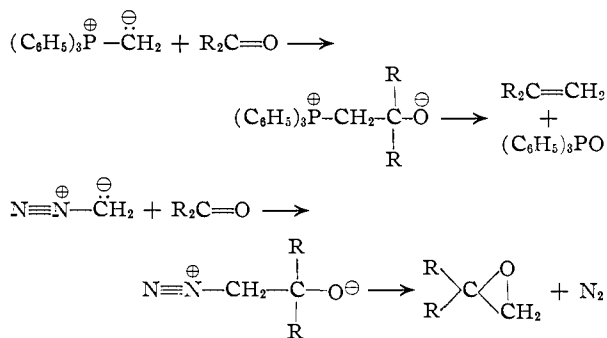
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Triphenylphosphinemethylene reacts with mercuric bromide, trimethylbromosilane, triphenylbromogermane, trimethyltin bromide, dimethyltin dibromide and dimethyltin dichloride in ether solution to form phosphonium salts in which the respective metal atom is linked to phosphorus by a methylene group. Water-insoluble derivatives of these metal-substituted phosphonium ions have been prepared.

The electronic structure of triphenylphosphinemethylene is formally analogous to that of diazomethane, in that a resonance hybrid in which the methylene carbon atom bears a negative charge is required to describe both compounds.



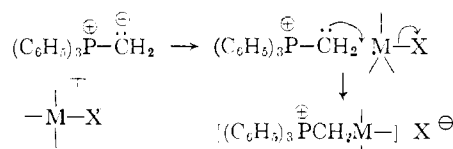
Triphenylphosphinemethylene reacts with ketones (Wittig reaction²) in a manner quite analogous to the reaction of diazomethane with ketones,³ although the course of the reaction after the formation of the initial adducts is different.



The reaction of diazomethane with metallic and organometallic halides, a method for the synthesis of halomethyl derivatives of metals, has received considerable study,⁴ and the formal resemblance between triphenylphosphinemethylene and diazomethane led to the proposal to investigate the reaction of triphenylphosphinemethylene with metallic and organometallic halides.

This study showed that triphenylphosphinemethylene reacts with metallic and organometallic halides of Groups II and IV (and Group V⁵) to form quaternary phosphonium salts with the metal atom as a substituent in the side chain. This reaction

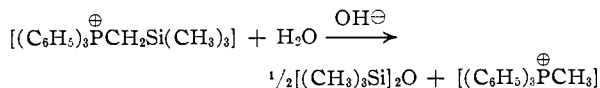
can be pictured as a normal nucleophilic displacement reaction of the type which these halides are known to undergo readily with reagents such as hydroxide and alkoxide ion



Thus the similarity to the reaction of these metallic halides with diazomethane is established, the one important difference being that in the diazomethane reaction nitrogen is lost, owing to the high heat of formation of the nitrogen molecule and loss of resonance stabilization energy of the free diazomethane molecule. This general behavior was found in the reaction of triphenylphosphinemethylene with trimethylbromosilane, triphenylbromogermane, trimethyltin bromide, dimethyltin dibromide and mercuric bromide.

The reaction of triphenylphosphinemethylene in ether with trimethylbromosilane gave ether-insoluble trimethylsilylmethyltriphenylphosphonium bromide. The proof for the structure of this phosphonium salt was furnished by its independent

synthesis *via* the reaction between triphenylphosphine and bromomethyltrimethylsilane; by its infrared spectrum which showed the bands expected for this structure; by the characterization of insoluble derivatives, such as the reineckate, picrate and tribromomercurate; and by its cleavage in alkaline solution to methyltriphenylphosphonium cation and hexamethyldisiloxane.



The purification of trimethylsilylmethyltriphenylphosphonium bromide, as well as of the other products obtained in this general reaction, was extremely difficult. Any trace of moisture in the reaction system or reagents, before, during or after the reaction (when excess of or unreacted triphenylphosphinemethylene was still present) resulted in the formation of methyltriphenylphosphonium cation. Although the decomposition of phosphonium hydroxides is well established, the rate is slow

(1) This work was summarized in part in a preliminary communication, S. O. Grim and D. Seyferth, *Chem. and Ind. (London)*, 849 (1959).

(2) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954); see also U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

(3) (a) C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954); (b) B. Eistert, in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 513-570.

(4) D. Seyferth, *Chem. Revs.*, **55**, 1155 (1955).

(5) D. Seyferth and K. A. Brandle, Part IV of this series, in preparation.

and the compounds do exist in solution for a reasonable length of time; the cation, when formed in ether solution, might precipitate in the presence of bromide ion. For example, methyltriphenylphosphonium chloride can be prepared from the hydroxide by the addition of hydrochloric acid, and in this study it was shown that hydrolysis of triphenylphosphinemethylene, followed by addition of sodium tetraphenylborate, resulted in precipitation of methyltriphenylphosphonium tetraphenylborate. Obviously the presence of the methyltriphenylphosphonium cation complicates the purification of other phosphonium salts. Indeed, methyltriphenylphosphonium bromide was obtained many times during attempts to recrystallize the products of this general reaction.

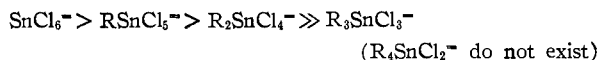
As has been mentioned, the silicon-containing phosphonium compound was decomposed by base to give methyltriphenylphosphonium cation, presumably by nucleophilic attack by the hydroxide ion on the silicon atom. The ready cleavage of the silicon-carbon bond in this cation is not surprising, since electron-attracting groups on a carbon atom adjacent to silicon facilitate nucleophilic attack on the silicon atom.⁶ To insure absence of such cleavage, dilute aqueous acetic acid and dilute hydrobromic acid were used as recrystallizing media for trimethylsilylmethyltriphenylphosphonium bromide.

The reaction of triphenylphosphinemethylene with triphenylbromogermane produced triphenylgermylmethyltriphenylphosphonium bromide. The white solid is not very soluble in water but is extremely soluble in methanol; recrystallization was effected by adding water slowly to a methanol solution of the crude product. The cation was characterized as the tetraphenylborate.

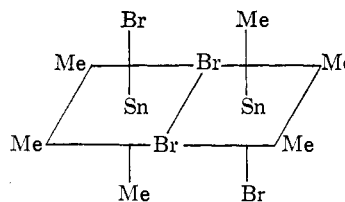
With methyltin bromides, this reaction was somewhat more complicated, since products were obtained in which complex anions, formed by coordination of bromide ion to the organotin bromide reactant, were present. The exact constitution of the solid which precipitated when triphenylphosphinemethylene and dimethyltin dibromide solutions were mixed is not known, but on recrystallization from dilute hydrobromic acid, crystals of stoichiometry $\{[(C_6H_5)_3PCH_2]_2Sn(CH_3)_2\}[(CH_3)_2SnBr_4]$ were obtained. Salts containing complex organotin anions of this type are known through the work of Pfeiffer⁷ and, more recently, of Reutov.⁸ They usually form only in the presence of large organic cations, e.g., $[C_5H_5N]_2[(C_2H_5)_2SnCl_4]$ and $[ArN]_2[(C_2H_5)_2SnCl_4]$, and so our product is not unusual. In the reaction of dimethyltin dichloride with triphenylphosphinemethylene a similar complex anion undoubtedly was present in the product, which however, was not isolated in analytical purity. The cation formed when either dimethyltin dihalide was used was characterized as the reineckate, $\{[(C_6H_5)_3PCH_2]_2Sn(CH_3)_2\} [Cr(NH_3)_2(SCN)_4]_2$, and as the tetraphenylborate. The mercuric bromide complex also was prepared from

the product obtained with dimethyltin dichloride, and its constitution, $\{[(C_6H_5)_3PCH_2]_2Sn(CH_3)_2\} [HgBr_2Cl]_2$, showed that in this case halogen exchange had not taken place.

The recrystallized (from dilute hydrobromic acid) product from the triphenylphosphinemethylene-trimethyltin bromide reaction had the unexpected composition $[(C_6H_5)_3PCH_2Sn(CH_3)_3] - [(CH_3)_3SnBr_2]$. In all known complex organotin anions, tin had the coordination number six. Only one compound, $[(C_6H_5)_3C][SnCl_5]$, has been reported where this is not so.⁹ However, it is known that the stability of hexacoordinated tin anions falls as the number of electronegative halogen substituents decreases



The $R_3SnCl_3^-$ species are barely stable, and only dipyrindinium triphenyltrichlorostannate is known as a pure compound.⁷ Since methyl is less electronegative than phenyl, the trimethyltrichlorostannate ion should be less stable than the triphenyl analog. These considerations lead us to suggest that the seemingly pentacoordinated anion in our product, $[(CH_3)_3SnBr_2]^\ominus$, is a halogen-bridged dimer in which tin has its preferred coordination num-



ber of six. Investigation of this interesting structural side issue was beyond the scope of this study, but it would be worthwhile to examine this matter in more detail. That our product containing this anion may be the first member of a more general class of organotin complexes was shown by the preparation of $[(C_2H_5)_4N][[(CH_3)_3SnBr_2]$. This complex salt crystallized when an aqueous solution containing tetraethylammonium bromide and trimethyltin bromide was evaporated using a rotary evaporator. The trimethylstannylmethyltriphenylphosphonium cation was characterized as the mercuric bromide adduct, $[(C_6H_5)_3PCH_2Sn(CH_3)_3][HgBr_3]$, and as the reineckate.

The study of the reaction between triphenylphosphinemethylene and mercuric bromide was complicated not only by the great tendency for mercuric bromide to complex halide ion but also by the great insolubility of phosphonium bromomercurates. The initial reaction product, probably a mixture of bis-(triphenylphosphoniomethyl)-mercury tri- and tetrabromomercurates, was somewhat soluble in hot methanol, and treatment of its methanol solution with hot, concentrated methanolic mercuric bromide, followed by cooling, gave a precipitate of pure $\{[(C_6H_5)_3PCH_2]_2Hg\} [HgBr_3]_2$. The cation was also isolated in the form of its tetraphenylborate.

(6) P. D. George, M. Prober and J. R. Elliott, *Chem. Revs.*, **56**, 1065 (1956).

(7) P. Pfeiffer, *Ann.*, **376**, 310 (1910).

(8) O. A. Reutov, O. A. Ptitsyna and N. D. Patrina, *Zhur. Obshchet Khim.*, **28**, 588 (1958).

(9) J. L. Cotter and A. G. Evans, *J. Chem. Soc.*, 2988 (1959).

Experimental¹⁰

Reaction of Triphenylphosphinemethylene with Trimethylbromosilane.—Freshly distilled trimethylbromosilane (6.2 g., 0.04 mole) was dissolved in 100 ml. of diethyl ether, which had been distilled from lithium aluminum hydride immediately before it was used, in a 500-ml., 3-necked flask fitted with inlet transfer tube, mechanical stirrer and outlet tube leading to an overpressure valve. The triphenylphosphinemethylene solution² (0.04 mole) was transferred under nitrogen to the reaction flask. A white precipitate formed immediately, and the yellow color of the phosphinemethylene reagent was discharged. After about one third of the phosphinemethylene solution had been added, the reaction mixture became permanently yellow. The mixture was stirred at room temperature for 15 minutes after addition of the phosphinemethylene had been completed. The mixture was filtered in a nitrogen atmosphere, washed with ether and dried in vacuum at 50°. The crude product weighed 12.2 g. and gave a strong positive lithium flame test. Analysis showed it to contain more bromine than calculated for the expected phosphonium salt. Attempts to purify the product by recrystallization from ethanol-ether, dichloromethane-ether, tetrahydrofuran and 2-propanol-ether either gave oils or resulted in decomposition, giving methyltriphenylphosphonium bromide, which was identified by its infrared spectrum and its m.p. of 230°.

A pure sample of $[(C_6H_5)_3PCH_2Si(CH_3)_3]Br$ was prepared as follows: one gram of crude product was placed in 18 ml. of water and 0.5 ml. of glacial acetic acid. The solid did not dissolve completely on stirring. The mixture was filtered and filtrate evaporated using a rotary evaporator at room temperature and reduced pressure. Crystallization took place, and 0.4 g. of product was collected. The white crystals, decomp. 175°, were dried over potassium hydroxide in vacuum for ten hr. at 50°.

Anal. Calcd. for $C_{22}H_{26}BrPSi$: C, 61.53; H, 6.10; Br, 18.61. Found: C, 61.13; H, 5.97; Br, 18.64.

The infrared spectrum (KBr pellet) of trimethylsilylmethyltriphenylphosphonium bromide has the bands characteristic of the trimethylsilyl group at 752, 850 and 1246 cm^{-1} (lit.,¹¹ at 754–756, 841 and 1250 cm^{-1}). It is soluble in water, acetone, methanol, ethanol and methylene chloride; insoluble in benzene, ether and aliphatic hydrocarbons. It is worth noting that the infrared spectrum (KBr pellet) of methyltriphenylphosphonium bromide has a strong doublet at 925 and 913 cm^{-1} . This is not present in this silicon-substituted phosphonium salt, nor in any of the other phosphonium salts prepared in this study, and thus proved very useful for determining whether the desired compound contained any methyltriphenylphosphonium bromide impurity. The derivatives of the methyltriphenylphosphonium ion, such as the tetraphenylborate, did not have the doublet, but their infrared spectra showed a strong band at *ca.* 900 cm^{-1} instead.

Preparation of Derivatives of the Trimethylsilylmethyltriphenylphosphonium Cation.—When an aqueous solution of reinecke salt was added slowly to $[(C_6H_5)_3PCH_2Si(CH_3)_3]Br$ dissolved in 0.08 *N* hydrobromic acid, the insoluble reineckate precipitated. It was filtered, washed with water and dried. The pure compound melted at 142–144°, and its infrared spectrum showed the characteristic bands of the trimethylsilyl group.

Anal. Calcd. for $C_{26}H_{32}N_6S_4PSiCr$: C, 46.75; H, 4.83. Found: C, 47.16; H, 4.70.

Addition of ethanolic mercuric bromide solution to the phosphonium salt in ethanol resulted in a turbid solution. Enough ethanol was added to give a clear solution. Crystals were deposited after the solution had been allowed to stand for five days. These were collected and dried to give pure $[(C_6H_5)_3PCH_2Si(CH_3)_3][HgBr_3]$, m.p. 134–135°.

(10) Analyses were performed by Dr. S. M. Nagy (M. I. T.) and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were determined using a calibrated Fisher-Johns or Mel-Temp melting point apparatus. All reactions were carried out in an atmosphere of prepurified nitrogen, and all possible precautions were taken to exclude air and moisture from the reaction system before, during and after the reaction. Starting materials either were purchased and, if necessary, subjected to further purification or were prepared by standard methods described in the literature.

(11) N. Wright and M. J. Hunter, *THIS JOURNAL*, **69**, 803 (1947).

Anal. Calcd. for $C_{22}H_{26}Br_3PSiHg$: C, 33.45; H, 3.32; Hg, 25.40. Found: C, 33.26; H, 3.37; Hg, 25.94.

The picrate, dec. 110–122°, was prepared by H. M. Colten in this Laboratory.

Anal. Calcd. for $C_{28}H_{28}O_7N_3PSi$: C, 58.22; H, 4.89; N, 7.28. Found: C, 58.45; H, 4.88; N, 7.36.

Decomposition of the Trimethylsilylmethyltriphenylphosphonium Cation by Base.—Trimethylsilylmethyltriphenylphosphonium bromide, 0.3 g., was placed in a small flask with 25 ml. of 0.11 *N* NaOH solution and 5 ml. of carbon tetrachloride. The mixture was shaken for ten min. and then acidified with 0.5 *N* sulfuric acid. The layers were separated. The aqueous layer gave a precipitate with reinecke salt, which was identified (m.p. 143–145° and infrared spectrum) as methyltriphenylphosphonium reineckate. The carbon tetrachloride layer was dried over sodium sulfate, and its infrared spectrum was identical with that of an authentic sample of hexamethyldisiloxane in this solvent.

Reaction of Triphenylphosphine with Bromomethyltrimethylsilane in Benzene.—Into a 100-ml., 3-necked flask equipped with a mechanical stirrer and water condenser with a nitrogen inlet tube was charged 5.6 g. (0.021 mole) of triphenylphosphine, 5 g. (0.03 mole) of freshly distilled (b.p. 116–118°) bromomethyltrimethylsilane and 10 ml. of dry benzene. The flask was wrapped in aluminum foil and heated at reflux for 2 hr. After the first hour, a moderate amount of solid had formed; after the second hour, the solution was pale yellow. The mixture was filtered, and the solids, after drying, weighed 2.4 g. (27% yield). The infrared spectrum indicated the crude product to be principally trimethylsilylmethyltriphenylphosphonium bromide contaminated with some methyltriphenylphosphonium bromide. A sample of the product was recrystallized from 0.08 *N* HBr using a rotary evaporator. The infrared spectrum and the behavior on melting of the purified material were identical with that of the pure product from the triphenylphosphine-methylene-trimethylbromosilane reaction.

Reaction of Triphenylphosphinemethylene with Triphenylbromogermane.—Triphenylbromogermane (5.8 g., 0.015 mole) was dissolved in 150 ml. of warm anhydrous ether and placed in a reaction flask equipped with a nitrogen inlet tube, stirrer and an addition tube fitted with a sintered glass filtering disc. The triphenylphosphinemethylene solution (*ca.* 0.02 mole) was filtered under nitrogen into the stirred triphenylbromogermane solution. A large amount of white solid precipitated immediately. After the mixture had been stirred for five min., the solids were filtered, washed with ether and dried to give 8.5 g. of product which was not very soluble in water but very soluble in methanol. To 1.4 g. of the crude product was added 15 ml. of 0.04 *M* aqueous hydrobromic acid, and then methanol was added until the solid was nearly dissolved. The mixture was filtered and water added slowly to the filtrate. Crystals of $[(C_6H_5)_3PCH_2Ge(C_6H_5)_3]Br$, m.p. 121–122°, formed, which after drying weighed 1.1 g.

Anal. Calcd. for $C_{37}H_{32}BrPGe$: C, 67.32; H, 4.89. Found: C, 67.14; H, 5.13.

The tetraphenylborate was prepared from the purified bromide and sodium tetraphenylborate in 70:30 methanol-water. It was recrystallized by dissolving it in 1:1 methanol-ether in the cold and evaporating at reduced pressure using a rotary evaporator. The resulting white solid, m.p. 84–85°, was sensitive to light and turned yellow after thirty min. in sunlight.

Anal. Calcd. for $C_{81}H_{52}PBGe$: C, 81.45; H, 5.83. Found: C, 81.29; H, 5.78.

Reaction of Triphenylphosphinemethylene with Trimethyltin Bromide.—Freshly distilled (76° (43 mm.)) trimethyltin bromide (8.3 g., 0.034 mole) was sealed in a thin glass ampoule and placed in the reaction flask containing freshly distilled ether. When the stirrer was started, the ampoule broke, releasing the tin compound. Triphenylphosphinemethylene (*ca.* 0.034 mole) in ether was added. The mixture was stirred for five min. and filtered under nitrogen. The solid was washed with ether and dried in a vacuum desiccator to give 11.3 g. of crude product. A sample (1.2 g.) of this material was placed in 50 ml. of 0.02 *M* HBr. The resulting solution was filtered, and the filtrate was evaporated slowly using a rotary evaporator operated at 20 mm. and a bath temperature of 50°. Crystals of $[(C_6H_5)_3PCH_2Si-$

$(\text{CH}_3)_3$ $[(\text{CH}_3)_3\text{SnBr}_2]$ formed before the solution was concentrated to half of the original volume. The crystals were dried over concentrated sulfuric acid for two weeks. They decomposed over a wide temperature range, starting at 152° .

Anal. Calcd. for $\text{C}_{26}\text{H}_{36}\text{Br}_2\text{PSn}_2$: C, 39.31; H, 4.62. Found: C, 39.79; H, 4.69.

A sample of pure product was dissolved in water and added to an aqueous solution of reinecke salt. The resulting insoluble reineckate, m.p. $123\text{--}125^\circ$, was washed with water and dried.

Anal. Calcd. for $\text{C}_{26}\text{H}_{32}\text{N}_6\text{S}_4\text{PSnCr}$: C, 41.20; H, 4.26. Found: C, 41.42; H, 4.38.

A second sample was dissolved in dilute HBr and added to an aqueous solution of mercuric bromide. The mixture became turbid, and a sticky precipitate formed. The latter solidified on standing and was pulverized with a stirring rod, filtered, washed with water and dried to give pure $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Sn}(\text{CH}_3)_3][\text{HgBr}_2]$, m.p. $165\text{--}168^\circ$.

Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{Br}_2\text{PSnHg}$: C, 30.02; H, 2.98; Hg, 22.78. Found: C, 30.28; H, 2.84; Hg, 22.70.

The Reaction of Trimethyltin Bromide with Tetraethylammonium Bromide.—Tetraethylammonium bromide (1.05 g., 0.005 mole) was dissolved in 3 ml. of water, and 6.10 g. (0.025 mole) of trimethyltin bromide was added. Two layers formed, which on addition of 2 ml. of water formed a homogeneous solution. The solution was concentrated at reduced pressure (23 mm.) using a rotary evaporator at room temperature. Eventually crystals formed; these were filtered, washed with a methanol-ether mixture and then with ether alone. The crystals, $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{CH}_3)_3\text{SnBr}_2]$, were dried for one hr. at 73° ; when heated in a sealed tube, they decomposed between $150\text{--}165^\circ$.

Anal. Calcd. for $\text{C}_{11}\text{H}_{29}\text{NBr}_2\text{Sn}$: C, 29.11; H, 6.44; N, 3.08. Found: C, 29.47, 29.41; H, 6.32, 6.57; N, 2.86.

Reaction of Triphenylphosphinemethylene with Dimethyltin Dichloride.—Dimethyltin dichloride (0.04 mole) was dissolved in 350 ml. of ether and placed in a 1-liter reaction flask. Triphenylphosphinemethylene solution (ca. 0.04 mole) was added *via* a transfer tube under nitrogen pressure. Its yellow color was discharged immediately, and white solid precipitated. The crude product weighed 18 g., and attempts to purify it failed.

A small amount (0.5 g.) of the crude product was dissolved in 100 ml. of water, and a freshly prepared aqueous solution of sodium tetraphenylborate was added. The white precipitate, $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Sn}(\text{CH}_3)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3][\text{B}(\text{C}_6\text{H}_5)_4]_2$, m.p. $78\text{--}81^\circ$, was collected, washed with water and dried in vacuum over phosphorus pentoxide at room temperature.

Anal. Calcd. for $\text{C}_{38}\text{H}_{50}\text{P}_2\text{B}_2\text{Sn}$: C, 78.88; H, 6.02. Found: C, 78.95; H, 6.04.

The water-insoluble di-reineckate, m.p. $115\text{--}119^\circ$, was prepared in a similar manner.

Anal. Calcd. for $\text{C}_{48}\text{H}_{62}\text{N}_{12}\text{S}_6\text{P}_2\text{SnCr}_2$: C, 43.08; H, 3.92. Found: C, 43.33; H, 4.06.

An ethanolic solution of mercuric bromide was added to 0.2 g. of the crude product dissolved in ethanol. A white precipitate formed, which dissolved when the solution was heated. On cooling, crystals of the bis-dibromochloromercurate formed. These were filtered, washed with ethanol and dried at 60° in vacuum for 3 hr.; m.p. $139\text{--}140^\circ$.

Anal. Calcd. for $\text{C}_{40}\text{H}_{40}\text{Cl}_2\text{Br}_4\text{P}_2\text{SnHg}_2$: C, 32.17; H, 2.70; Hg, 26.87. Found: C, 32.77; H, 2.94; Hg, 27.83.

Reaction of Triphenylphosphinemethylene with Dimethyltin Dibromide.—The reaction of triphenylphosphinemethylene with dimethyltin dibromide in 1:1 molar ratio was carried out on a 0.032 mole scale. The product weighed 10.9 g. A sample was recrystallized from dilute hydrobromic acid by evaporation using a rotary evaporator until crystals of $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{Sn}(\text{CH}_3)_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3][(\text{CH}_3)_2\text{SnBr}_4]$ formed. This compound was stored over phosphorus pentoxide for three weeks before it was analyzed; it decomposed over a wide range, beginning at 135° .

Anal. Calcd. for $\text{C}_{42}\text{H}_{46}\text{Br}_4\text{P}_2\text{Sn}_2$: C, 43.12; H, 3.96. Found: C, 43.35; H, 3.97.

Reaction of Triphenylphosphinemethylene with Mercuric Bromide.—A solution of 7 g. (0.02 mole) of mercuric bromide in 400 ml. of ether was added rapidly with stirring to 0.04 mole of triphenylphosphinemethylene in ether. A large amount of white solid precipitated immediately. The mixture was stirred for 15 min. and then was filtered under nitrogen. The residue was washed with ether. The dried product, 15.3 g., was not appreciably soluble in water, acetone or ethanol but was somewhat soluble in hot methanol.

Only part of a 0.4 g. sample of the product dissolved in 30 ml. of boiling methanol. The undissolved solid was filtered off, and the filtrate was added to a hot, concentrated solution of mercuric bromide in methanol. On cooling, a white powder, $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{HgCH}_2\text{P}(\text{C}_6\text{H}_5)_3][\text{HgBr}_2]_2$, m.p. $123\text{--}126^\circ$, came out of solution.

Anal. Calcd. for $\text{C}_{38}\text{H}_{34}\text{Br}_4\text{P}_2\text{Hg}_2$: C, 27.93; H, 2.10; Hg, 36.83. Found: C, 28.04; H, 2.22; Hg, 37.02.

One gram of the crude product dissolved only partially in 100 ml. of a 70:30 methanol-water solution. The mixture was filtered, and to the filtrate was added a concentrated solution of sodium tetraphenylborate in the same solvent mixture. The precipitate which formed was centrifuged and washed with methanol and water until the wash water no longer gave a positive bromide ion test. The white bis-tetraphenylborate melted at $101\text{--}104^\circ$.

Anal. Calcd. for $\text{C}_{86}\text{H}_{74}\text{P}_2\text{B}_2\text{Hg}$: C, 74.22; H, 5.36; Hg, 14.41. Found: C, 74.68; H, 5.52; Hg, 14.20.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE MASSACHUSETTS]

Studies in Phosphinemethylene Chemistry. II. Adducts of Triphenylphosphinemethylene with Boron Compounds¹

BY DIETMAR SEYFERTH AND SAMUEL O. GRIM

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Stable solid adducts are formed between triphenylphosphinemethylene and boron trifluoride, boron trichloride, triphenylborane and borane; between triphenylphosphineethylidene and boron trifluoride and triphenylborane; and between triphenylphosphinechloromethylene and triphenylborane. Triphenylphosphinemethylenetrifluoroborane may be reduced to the B-trihydro compound with lithium aluminum hydride and arylated to B-triaryl compounds with aryl Grignard reagents. Triphenylphosphinemethylene does not appear to form stable adducts with trialkylboranes.

In a previous study² it was shown that triphenylphosphinemethylene reacts with metallic and

(1) This work was summarized in part in a paper presented at the XVII Congress of Pure and Applied Chemistry, München, August 30–September 6, 1959; cf. *Angew. Chem.*, **72**, 36 (1960).

organometallic halides of Periodic Groups II and IV to form organometallic-substituted phosphonium salts by a displacement mechanism which,

(2) S. O. Grim and D. Seyferth, *Chem. and Ind. (London)*, 849 (1959); Part I of this series, *J. Am. Chem. Soc.*, **83**, 1610 (1961).