crystallized from ligroin (bp 60–65°) giving the pure product, 3.5 g, 85%, mp 53–54°.

Anal. Calcd for $C_9H_{11}BrO$: C, 50.2; H, 5.1; Br, 37.2. Found: C, 50.6; H, 5.4; Br, 37.6.

4-Chloromethyl-2,6-dimethylbromobenzene (36).—The 4-hydroxymethyl derivative (26 g, 0.12 mol) in dry benzene (100 ml) was treated with thionyl chloride (25 g). After 30 min the benzene was evaporated and the residue recrystallized from ligroin (bp 35–40°) at low temperature to yield the pure product, 20 g, 75%, mp 43–44°.

Anal. Calcd for $C_9H_{10}BrCl$: C, 46.2; H, 4.3; Br, 34.2. Found: C, 46.5; H, 4.5; Br, 33.8.

4-Deuteriomethyl-2,6-dimethylbromobenzene (37).—The chloromethyl derivative (19 g, 0.08 mol) in dry ether (200 ml) was treated with lithium aluminum deuteride (5 g, 0.12 mol). The mixture was heated under reflux for 6 hr and then treated with water and dilute hydrochloric acid. The ether layer was separated, dried, and evaporated to yield the crude deuterated product. It distilled at 225–227° (lit.[18] 225°, undeuterated), 13 g, 81%. The nmr ($CDCl_3$) spectrum showed absorption bands at δ 6.85 (s, 2 H), 2.37 (s, 3 H), and 2.2 (1:1:1 t, 2 H).

3-Bromo-2,4,6,4′-tetramethylbiphenyl.—A solution of *p*-toluidine (53 g, 0.5 mol) in water (100 ml) and concentrated hydrochloric acid (100 ml) was diazotized at 0–5°. The resulting solution was added to 2-bromomesitylene (250 ml). To this mixture was added, with vigorous stirring, ice-cold 50% sodium hydroxide solution until the mixture was basic. The organic layer was separated, washed with water, dried, and evaporated to yield a colored residue. This residue was treated with ligroin (1000 ml, bp 60–65°) and the solution poured through a 3 × 3 in. column of alumina (Woelm neutral activity grade I). Evaporation of the eluent afforded a pale yellow oil (10 g) which was distilled under vacuum to give a fraction, bp 114–118° (0.3 mm), 8.0 g, 6%.

Anal. Calcd for $C_{16}H_{17}Br$: C, 66.4; H, 5.9; Br, 27.7. Found: C, 66.8; H, 6.3; Br, 27.7.

***n*-Butoxymesityl-4-tolylborane.**—4-Tolylboronic acid was heated with *n*-butyl alcohol providing the di-*n*-butoxy-4-tolylborane. This diester (124 g, 0.5 mol) in dry ether was vigorously stirred and treated at −70° with the Grignard reagent prepared from 2-bromomesitylene (100 g, 0.5 mol) in dry ether. The resulting suspension was allowed to warm to room temperature overnight and then washed with 10% aqueous hydrochloric acid. The ether layer was separated, washed with water, dried, and evaporated to yield a colorless residue. It was treated with *n*-butyl alcohol (30 ml) and then fractionated to give the desired compound, 66 g, 45%, bp 182–185° (1.4 mm).

Anal. Calcd for $C_{20}H_{27}BO$: C, 81.6; H, 9.2; B, 3.7. Found: C, 81.3; H, 9.6; B, 3.6.

(2,4,4′,6-Tetramethyl-3-biphenylyl)mesityl-4-tolylborane (40).—The mesityltolyl ester (2.9 g, 0.01 mol) in dry ether (30 ml) was treated with a solution of the lithium reagent prepared from the 3-bromo-2,4,4′,6-tetramethylbiphenyl (2.9 g, 0.01 mol) and *n*-butyllithium (5 ml, 2 *M* solution) in dry ether (20 ml). The solution was then heated under reflux for 1 hr and poured into dilute hydrochloric acid. The ether layer was washed with water, dried, and evaporated to give a pale yellow oil. This oil was triturated with methanol (two 5-ml portions) and the methanol discarded. The oil was scratched under ether (5 ml) to yield a crystalline residue, mp 178–182°. This residue was washed with warm ether to yield the pure borane, 1.1 g, 26%, mp 185–186°.

Anal. Calcd for $C_{32}H_{35}B$: C, 89.3; H, 8.2; B, 2.5. Found: C, 89.1; H, 8.4; B, 2.8.

Registry No.—**1**, 20623-88-5; **1**-d_2, 26985-33-1; **2**-*d*, 26965-68-4; **3**-d_2, 26965-69-5; **27**, 26985-34-2; **35**, 27006-02-6; **36**, 26965-70-8; **38**-*d*, 26965-71-9; **40**, 26992-54-1; 3-bromo-2,4,4′,6-tetramethylbiphenyl, 26941-22-0; *n*-butoxymesityl-4-tolylborane, 26941-23-1.

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[18] P. S. Varma and T. S. Subrahmanian, *J. Indian Chem. Soc.*, **13**, 192 (1936).

Displacement of Tertiary Phosphines from Methylolphosphonium Salts by Tributylphosphine

ARLEN W. FRANK* AND GEORGE L. DRAKE, JR.

Southern Regional Research Laboratory,[1] New Orleans, Louisiana 70119

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Tributylphosphine displaces tris(hydroxymethyl)phosphine (II), triphenylphosphine, and, to a limited extent, butylbis(hydroxymethyl)phosphine (Vb) from the corresponding methylolphosphonium salts. No formaldehyde is liberated. Tetrakis(hydroxymethyl)phosphonium chloride (I) reacts with mercuric chloride in ethanol giving the mercuric chloride adduct of II, $(HOCH_2)_3P \cdot HgCl_2$, in 88% yield.

In connection with some other work in these laboratories on the flameproofing of cotton, we had a need for a method of preparing formaldehyde-free methylolphosphines and, in particular, tris(hydroxymethyl)phosphine (II). Methylolphosphines such as Va or Vb [$RP(CH_2OH)_2$, R = Me or Bu] can be rendered formaldehyde-free by repeated distillation, but II decomposes when distilled under vacuum.[2]

Methylolphosphines are usually prepared from the corresponding methylolphosphonium salts by treatment with a base (B) such as sodium hydroxide[3] or triethylamine.[4] Formaldehyde (1 equiv) is liberated in the process by either reagent.

$$\underset{\text{I}}{(HOCH_2)_4PCl} + B \longrightarrow \underset{\text{II}}{(HOCH_2)_3P} + CH_2O + B \cdot HCl$$

Gordon's method,[5] in which the base was sodium sulfite, was an effort to overcome this problem by tying up the formaldehyde as the bisulfite addition compound. This procedure, however, requires a careful attention to pH, as the sodium hydroxide liberated in the formation of the bisulfite addition compound is capable of destroying the product.[6a]

In this paper, we report our investigation of the use of a tertiary phosphine as the base, on the premise that tertiary phosphines, unlike tertiary amines,[7] are

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] K. A. Petrov and V. A. Parshina, *Usp. Khim.*, **37**, 1218 (1968); *Russ. Chem. Rev.*, **37**, 532 (1968).

[3] M. Grayson, *J. Amer. Chem. Soc.*, **85**, 79 (1963); U. S. Patent 3,243,450 to American Cyanamid Co. (March 29, 1966).

[4] K. A. Petrov, V. A. Parshina, and M. B. Luzanova, *Zh. Obshch. Khim.*, **32**, 553 (1962).

[5] I. Gordon and G. M. Wagner, U. S. Patent 3,257,460 to Hooker Chemical Corp. (June 21, 1966).

[6] J. F. Walker, "Formaldehyde," 3rd ed, Reinhold, New York, N. Y., 1964: (a) p 486; (b) p 494; (c) p 493; (d) p 507.

[7] Crystalline *N*-methylol compounds having the composition $R_3NCH_2OH^+Cl^-$ can be prepared from tertiary amines, but decompose in water; see T. D. Stewart and H. P. Kung, *J. Amer. Chem. Soc.*, **55**, 4813 (1933).

capable of reacting with formaldehyde in the presence of acid forming stable *P*-methylol phosphonium salts.[8,9]

Results and Discussion

Tributylphosphine reacted with tetrakis(hydroxymethyl)phosphonium chloride (I) in ethanol within 30 min at reflux, giving tris(hydroxymethyl)phosphine (II) and tributylhydroxymethylphosphonium chloride (IIIa). The product, a colorless oil, was soluble in

$$\underset{\text{I}}{(HOCH_2)_4PCl} + Bu_3P \longrightarrow \underset{\text{II}}{(HOCH_2)_3P} + \underset{\text{IIIa}}{[Bu_3PCH_2OH]Cl}$$

ether (I is not) and gave only a faint test with carbon disulfide,[10] showing that the displacement was substantially complete, but unfortunately the solubility characteristics of II and IIIa were so similar that we were unable to separate them by partition between solvents, either by extraction or by chromatography on a cellulose powder column.

The presence of II in the oil was established by nmr which clearly showed the II methylene doublet at δ 4.28 (J = 7.5 Hz) superimposed on the spectrum of IIIa (minus the OH peak, owing to exchange with II), and by precipitation of the mercuric chloride adduct,[5,11] mp 133–134° dec, in 58% yield when the oil was treated with mercuric chloride in ethanol. The phosphonium salt (IIIa), which has not been described previously, was precipitated in 90% yield as the tetraphenylboron derivative (IIId), mp 135–136°, when the oil was treated with $NaBPh_4$ in water. IIIa does not react with mercuric chloride in ethanol, nor II with $NaBPh_4$ in water. Analysis of the oil for free formaldehyde by the dimedone method[6b] showed that only 0.03% was present.

No reaction was observed when I was treated under the same conditions with triphenylphosphine, a much weaker base.

The reaction of tributylphosphine with butyltris(hydroxymethyl)phosphonium bromide (IV) gave a mixture of butylbis(hydroxymethyl)phosphine (Vb) and unreacted tributylphosphine.

$$\underset{\text{IV}}{BuP(CH_2OH)_3Br} + Bu_3P \longrightarrow \underset{\text{Vb}}{BuP(CH_2OH)_2} + \underset{\text{IIIb}}{Bu_3P(CH_2OH)Br}$$

The composition of the mixture was estimated from its refractive index and nmr spectrum to be 1.2:1, on a molar basis. The mixture also contained some free formaldehyde (1.46%), but this was traced to the starting material (IV).

The reaction of tributylphosphine with triphenylhydroxymethylphosphonium chloride (VI) gave, under the same conditions, a 95% yield of triphenylphosphine, mp 79–80°.

$$\underset{\text{VI}}{Ph_3P(CH_2OH)Cl} + Bu_3P \longrightarrow Ph_3P + \underset{\text{IIIa}}{Bu_3P(CH_2OH)Cl}$$

It appears, therefore, that methylolphosphines such as II and Vb are *capable of being displaced from the corresponding methylolphosphonium salts by strongly basic tertiary phosphines*, such as tributylphosphine (pK_a = 8.43),[12] *but not by weakly basic tertiary phosphines*, such as triphenylphosphine (pK_a = 2.30,[13] 2.73[12]).

The base strength of II, based on titration data with I, has been calculated to be 5.5 pK_a units.[3,14] Use of the σ^* value[15] of +0.555 for the methylol group in the Henderson–Streuli equation[16] gives a theoretical pK_a of 3.40. Fodor[17] argues that the titration data should include a term for formaldehyde release, and estimates the basicity of II itself to be very much lower ($pK_a < 3$) than the basicity of its formaldehyde adduct $(HOCH_2)_3P^+CH_2O^-$ (pK_a = 7.06). The present work places II in the range between 2.30 and 8.43.[18,19]

The base strength of Vb is not known, but by analogy with methylbis(hydroxymethyl)phosphine (Va), which has a pK_a of 7.18,[11b] it must be much closer to tributylphosphine than to II. The relative order of basicity is, then, $Ph_3P < II < Va,b < Bu_3P$.

In other experiments incidental to this work it was discovered that the methylolphosphonium salts could be purified by steam distillation, to remove the excess formaldehyde, and that I reacts with mercuric chloride, even at room temperature, giving the mercuric chloride adduct of II, mp 133–134° dec.

Experimental Section[20]

Starting Materials.—Tributylphosphine (FMC Corp.)[21] and triphenylphosphine (Eastman Kodak Co.) were used as obtained. Tetrakis(hydroxymethyl)phosphonium chloride (I) (Hooker Chemical Corp.) was recrystallized, mp 149–149.5° (*i*-PrOH). Butyltris(hydroxymethyl)phosphonium bromide (IV), $n^{20}D$ 1.5403, and triphenylhydroxymethylphosphonium chloride (VI), mp 190–192° (*i*-PrOH), were prepared by known methods.[3,9] Butyl = *n*-butyl throughout this paper.

All operations with tertiary phosphines were carried out under nitrogen.

Reactions of Tributylphosphine. A. With Tetrakis(hydroxymethyl)phosphonium Chloride (I).—Tributylphosphine (4.0 g, 0.02 mol) was added rapidly from a gas-tight syringe to a solution of 3.8 g (0.02 mol) of I in 25 ml of anhydrous ethanol and heated to reflux for 30 min. No solids separated on cooling, nor when ether was added (I is insoluble in ether). The solvents were distilled off, and the residual oil was taken up in 25 ml of water, transferred to a separatory funnel (under nitrogen), and extracted twice with ether. The extract gave only a faint red color with carbon disulfide.[10] The aqueous layer was concentrated under reduced pressure, distilled with benzene to remove the last of the water as the azeotrope,[22] and stripped again under reduced pres-

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[8] H. Hoffmann, L. Horner, and G. Hassel, *Chem. Ber.*, **91**, 58 (1958).

[9] H. Hellmann, J. Bader, H. Birkner, and O. Schumacher, *Justus Liebigs Ann. Chem.*, **659**, 49 (1962).

[10] Tributylphosphine and Va both give strongly positive tests (red color) with carbon disulfide; II does not. This test is characteristic of tertiary phosphines; see G. M. Kosolapoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950, pp 25–26.

[11] (a) M. Reuter and L. Orthner, German Patent 1,035,135 to Farbwerke Hoechst A.-G. (July 31, 1958); (b) E. I. Grinshtein, A. B. Bruker, and L. Z. Soborovskii, *Zh. Obshch. Khim.*, **30**, 302 (1966).

[12] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

[13] H. Goetz and A. Sidhu, *Justus Liebigs Ann. Chem.*, **682**, 71 (1965).

[14] P. A. Chopard, unpublished work, cited by E. A. C. Lucken, *J. Chem. Soc. A*, 1357 (1966).

[15] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 619.

[16] W. A. Henderson, Jr., and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960).

[17] L. M. Fodor, Ph.D. Dissertation, Cornell University, 1963, p 14.

[18] Since there is no gain or loss of formaldehyde in the exchange, it should not matter whether one compares the base strengths of II and tributylphosphine or of the corresponding phosphonium hydroxides.

[19] An example of the displacement of an even weaker base from a phosphonium salt by II was given by E. S. Kozlov, A. I. Sedlov, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **38**, 1881 (1968).

[20] *All melting points are corrected.* Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were run on a Perkin-Elmer Model 137B spectrophotometer with NaCl optics. Nmr spectra were taken on a Varian A-60 spectrometer using TMS as internal standard.

[21] Naming of firms or their products in this paper does not imply their endorsement by the Department of Agriculture.

[22] R. K. Valetdinov, E. V. Kuznetsov, R. R. Belova, R. K. Mukhaeva, T. I. Malikina, and M. Kh. Khasanov, *Zh. Obshch. Khim.*, **37**, 2269 (1967.

sure, giving 7.8 g (100%) of colorless oil, n^{20}_D 1.5165. The oil was soluble in water, ethanol, and acetone, partially soluble in methylene chloride, and insoluble in other organic solvents.

A portion of the oil (0.660 g, 1.68 mmol) was taken up in 3 ml of anhydrous ethanol and treated with a solution of 1.0 g of mercuric chloride in 10 ml of ethanol. The white, crystalline solid which separated was collected next day on a filter, washed with ethanol, and dried, giving 0.381 g (58%) of $(HOCH_2)_3P \cdot HgCl_2$, mp 133–134° dec (lit.[5,11] mp 135°), ir and melting point identical with those of the complex prepared from II.

Another portion of the oil (0.743 g, 1.89 mmol) was taken up in 5 ml of water and treated with s solution of 0.75 g of sodium tetraphenylboron in 10 ml of water. The tetraphenylboron derivative (IIId) separated within minutes as a mass of fine needles, 0.932 g (90%), mp 135–136°.

Anal. Calcd for $C_{37}H_{50}BOP$: C, 80.42; H, 9.10; P, 5.61. Found: C, 80.06; H, 9.15; P, 4.90.

In separate experiments, it was established that II does not react with sodium tetraphenylboron, nor IIIa with mercuric chloride.

The original experiment was then repeated in order to ascertain the composition of the reaction mixture by nmr. After 30 min reflux, the solvent was stripped carefully under vacuum, leaving 8.1 g of a colorless oil containing only 0.03% CH_2O by dimedone analysis. Its nmr spectrum showed the II methylene doublet at δ 4.28 ppm (J = 7.5 Hz) superimposed on the usual IIIa spectrum, minus its OH peak (see below), together with a little solvent ethanol. The CH_2 (II):Bu (IIIa) ratio was 4.5:27 (theoretical 4.0:27).

B. With Butyltris(hydroxymethyl)phosphonium Bromide (IV).—A similar reaction between tributylphosphine (4.0 g, 0.02 mol) and IV (5.2 g, 0.02 mol) in 25 ml of anhydrous ethanol gave, on work-up, an ether-soluble fraction, 2.8 g, n^{20}_D 1.4808, and an ether-insoluble fraction, 6.4 g, n^{20}_D 1.5198. The ether extract, which gave a strong red color with CS_2,[10] contained bands in the ir spectrum (neat) at 3330 s (OH) and 1020 vs (C–O) cm^{-1} which were not present in the tributylphosphine, but its refractive index was much too low for Vb (lit.[22] n^{20}_D 1.5010), suggesting that the product might contain some unreacted tributylphosphine.[23] The nmr spectrum ($CDCl_3$) confirmed this [δ 4.38 (s, 2 H, $CH_2O\mathbf{H}$, vanishes when D_2O is added), 4.03–4.33 (m, 4 H, $\mathbf{CH_2}OH$) and the 2:4:3 butyl peaks at 1.61, 1.39, and 0.97 ppm (m, 31.4 H, $C_4\mathbf{H}_9$; IIc has only 9 H)]. From the $HOCH_2$:Bu ratio it was calculated that the ether extract contained 47.2% Vb and 52.8% tributylphosphine. The composition calculated from the refractive index data[23] was almost identical.

Distillation of the extract gave a fraction, bp 91–92° (5.0 mm), n^{20}_D 1.4735, enriched in tributylphosphine, but still containing some Vb (ir, nmr).

Analysis of the ether extract for free formaldehyde by the dimedone method showed that it contained 1.46% CH_2O. This was traced to the IV from which it was prepared (CH_2O, 1.40%).

C. With Triphenylhydroxymethylphosphonium Chloride (VI).—A mixture of tributylphosphine (4.0 g, 0.02 mol) and VI (6.6 g 0.02 mol) in 25 ml of anhydrous ethanol gave a negative CS_2 test[10] after 30-min reflux. Triphenylphosphine (2.6 g, mp 79–80°) crystallized on cooling; another 2.35 g, mp 79–80° (95% total), separated upon dilution with water. Extraction of the aqueous solution with ether gave 0.25 g of low-melting solid which yielded 0.05 g (0.9%) of triphenylphosphine oxide, mp 152–154° (correct ir), upon precipitation from benzene with low-boiling petroleum ether. The aqueous solution, stripped to dryness on a rotary evaporator, left 5.2 g (98%) of a colorless oil, n^{20}_D 1.5075, which crystallized after drying in a drying pistol at 80° (1 mm): mp 47–49°; ir (CH_2Cl_2) almost identical with that of pure IIIa.

Formaldehyde Analysis.—Since the objective of this work was to prepare formaldehyde-free phosphorus compounds, a reliable method of analyzing for small quantities of formaldehyde was needed. Tests showed that the methylolphosphines (II, Va, and Vb) interfered with both the sulfite method[6a] and the hydroxylamine method.[6c,25]

A small sample of Va (112.0 mg) was covered with 25 ml of saturated aqueous dimedone reagent[6b] and stirred on a mechanical stirrer for 20 hr, in a stoppered flask under nitrogen, and then filtered; the crystalline methylene bismethone was washed with water and air-dried, yielding 14.0 mg (1.3%), mp 188–188.5° (lit.[6b] mp 189°), correct ir. Further stirring of the undiluted filtrate produced only a trace of solid.

This method was applied to several other tertiary phosphines and phosphonium salts with encouraging results (Table I).

TABLE I

EFFECT OF STEAM DISTILLATION ON FREE FORMALDEHYDE CONTENT OF METHYLOLPHOSPHINES AND -PHOSPHONIUM SALTS

	Per cent CH_2O	
Compd	Before	After
I	0.60[a]	0.26[a]
II[b]		0.02
IIIa	0.78	0.06
IIIb[c]	0.58	0.42
IV	1.40	1.68
Va	0.19	1.45
Vb[d]	1.46	
VI		1.18[e]

[a] Methylene bismethone, mp 187.5-188.5° (lit.[6b] mp 189°). [b] Freshly prepared from I by treatment with 1 N NaOH to pH 7.40, and kept under nitrogen until used. [c] Mixture with IV. [d] Mixture with tributylphosphine. [e] Together with 13.0% triphenylphosphine.

The sample size was such that not more than 10 mg of formaldehyde (equivalent to 100 mg of the methylene bismethone) was present, owing to the limited solubility of the reagent in water.[6b]

Compound VI gave erroneous results, owing to a tendency to precipitate triphenylphosphine. This could be corrected by dissolving the methylene bismethone in 1 N NaOH, filtering, and reprecipitating the methylene bismethone with dilute HCl; concentrated HCl dissolves both substances.

Steam Distillation.—The phosphonium salt IV used in the preparation of Vb was found to contain 1.40% free formaldehyde, which subsequently contaminated the products (see above). Table I summarizes the results of efforts to purify IV and other phosphonium salts, and also some tertiary phosphines, by steam distillation. A simple assembly was used in which the evolved formaldehyde was trapped under water and subsequently was analyzed by the dimedone method. The time was 1 hr in every case.

The phosphonium salts IIIa, IIIb, IV, and even, surprisingly, VI, appeared to be unaffected by this treatment, although some triphenylphosphine was precipitated from VI during the subsequent dimedone analysis. I, which is reported to be stable to boiling water,[26] was recovered virtually unchanged. The melting point was low (140–142°) and the product had an offensive, phosphine-like odor, but the ir and nmr were correct and the recovery was quantitative (99.7%).

The two tertiary phosphines subjected to steam distillation, II and Va, were both partially converted to the phosphine oxides, despite the care taken to avoid oxidation during the steam distillation or after.

An inspection of the data in Table I revealed that formaldehyde could be removed from some compounds by this method, while others showed little or no improvement.

Tributylhydroxymethylphosphonium Chloride (IIIa).—Hellmann's method[9] gave a product which was high in carbon and chlorine. The following is an adaptation of Vullo's method.[27]

Tributylphosphine (4.0 g, 0.02 mol) was added in one portion to a solution of 37% formalin (2.0 g, 0.025 mol), 10 ml of ethanol, and 10 ml of water containing 3 drops of phenolphthalein indicator. The solution turned pink immediately.[27] An attempt to titrate the solution under nitrogen with 1 N HCl was unsuccessful as the reaction was slow, even when heated to 50° and treated with another 2.0 g of formalin. The remainder of the HCl (total 20.0 ml, 0.02 mol) was then run in, and the solution,

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(23) The best literature data, based on MR_D fits, are, for Vb,[22] bp 120–122° (5 mm), n^{20}_D 1.5010, d^{20}_4 1.0252 (MR_D, calcd 43.16; found 43.15), and, for tributylphosphine,[24] bp 83–84° (1 mm), n^{20}_D 1.4630, d^{20}_4 0.8201 (MR_D, calcd 67.99; found 67.95). Based on these values a mixture having n^{20}_D 1.4808 contains 46.8% Vb and 53.2% tributylphosphine.

(24) Z. N. Mironova, E. N. Tsvetkov, A. V. Nikolaev, and M. I. Kabachnik, *Zh. Obshch. Khim.*, **37**, 2747 (1967).

(25) W. M. D. Bryant and D. M. Smith, *J. Amer. Chem. Soc.*, **57**, 57 (1935).

(26) A. Hoffman, *ibid.*, **43**, 1684 (1921).

(27) W. J. Vullo, *J. Org. Chem.*, **33**, 3665 (1968).

now colorless, was heated to reflux for 15 min, allowed to cool (I_2 test negative), and extracted with benzene to remove any organic impurities. The aqueous layer, stripped of solvent under reduced pressure, left a colorless oil, 5.1 g, $n^{20}D$ 1.5040, with a faint formaldehyde odor (CH_2O, 0.78%).

The product was taken up in 25 ml of water, steam distilled for 1 hr, and again stripped under vacuum to constant weight at 60-70°: 5.1 g of colorless oil, $n^{20}D$ 1.5032, neutral to pH paper and odorless (CH_2O, 0.06%). It crystallized in the freezer, mp 40-47°.

Anal. Calcd for $C_{13}H_{32}ClO_2P$ (hydrate): C, 54.43; H, 11.25; Cl, 12.36; P, 10.80. Found: C, 54.86; H, 11.18; Cl, 13.27; P, 10.93.

The analyses showed the substance to be a hydrate which was then heated for several hours in a drying pistol at 80° (0.8 mm). On cooling, it solidified to a hard mass of crystals: mp 49-50°; ir (CH_2Cl_2) 3300 m, sh, 3100 vs (OH), 1370 m, 1090 s, 1055 vs (C-O), 1000 m, 965 m, 910 cm^{-1} s; nmr ($CDCl_3$ δ 6.35 (s, 1.3 H, $CH_2O\mathbf{H}$, vanishes when D_2O added), 4.62 (s, 2 H, $C\mathbf{H}_2OH$; like compound IV,[28] not split in $CDCl_3$), and the 2:4:3 butyl triad[29] at 2.38, 1.56, and 0.99 ppm (m, 27 H, $C_4\mathbf{H}_9$).

Reaction of IIIa with sodium iodide in acetone gave the iodide (IIIc), $n^{20}D$ 1.5386, mp 14-17° (lit.[22] yellowish oil), ir almost identical with that of IIIa. With sodium tetraphenylboron in water, IIIa gave the tetraphenylboron derivative (IIId): mp 134.5-135° after recrystallization from either isopropyl alcohol or benzene; soluble in ethanol, acetone, and chloroform and insoluble in water; ir (Nujol) 3500 m (OH, not H-bonded), 1590 w (arom), 1185 w, 1145 w, 1050 w, 1035 w (C-O), 848 w, 743 vs, 735 s, 709 cm^{-1} vs (arom); nmr ($CDCl_3$) δ 7.03-7.53 (m, 20 H, $C_6\mathbf{H}_5$), 2.74 (q, 3 H, $C\mathbf{H}_2O\mathbf{H}$), 0.89, 1.13 ppm (m, 27 H, $C_4\mathbf{H}_9$). Addition of D_2O changes the quartet at 2.74 to a sharp doublet, δ 2.80 ppm (d, 2 H, $C\mathbf{H}_2OH$, J = 2.0 Hz).

Reaction of Tetrakis(hydroxymethyl)phosphonium Chloride (I) with Mercuric Chloride.—In experiments carried out in connection with the identification of the products of the reaction of I with tributylphosphine, it was established that mercuric chloride did not react with paraformaldehyde, tris(hydroxymethyl)-phosphine oxide, or IIIa, but a slow reaction did take place with I, giving 15% of the II adduct, $(HOCH_2)_3P\cdot HgCl_2$, mp 133-134° dec, after 3 days at room temperature, and another 42% after 17 days. The same reaction took place in 30 min at 78°, as follows.

A solution of 0.579 g (2.13 mmol) of mercuric chloride in 10 ml of anhydrous ethanol was added all at once to a warm solution of 0.258 g (1.36 mmol) of I in 20 ml of ethanol and heated to reflux in an assembly protected from moisture but not from air. Solids started to separate in less than 1 min. The mixture was heated at reflux for 30 min, allowed to cool with constant stirring, and filtered. The product, a white, crystalline solid, was washed thoroughly with ethanol and dried, giving 0.472 g (88%) of $(HOCH_2)_3P\cdot HgCl_2$, mp 133-134° dec, identical with the product prepared from pure II: ir (Nujol) 3350 s (OH), 1410 w, 1265 w, 1170 w, 1035 s (C-O), 909 w, 885 w, 808 w, 749 cm^{-1} w.

Portions of the filtrate were analyzed for free formaldehyde by the sulfite method[6a] (after carefully neutralizing with NaOH) and by the dimedone method;[6b] both were negative. A phloroglucinol test for combined formaldehyde in formals,[6d] however, was positive. The amount of resin obtained corresponded to 67.5 mg of CH_2O (theoretical 40.8 mg, 1.36 mmol).

Attempts to further characterize the $II\cdot HgCl_2$ adduct were not successful. The adduct was insoluble in all the common organic solvents and gave an immediate black precipitate with ammonia, pyridine, or dimethyl sulfoxide. It hydrolyzes in water, forming a gray, opalescent solution which is strongly acidic. When heated to boiling, a flocculent yellow precipitate forms and then redissolves, depositing mercury.

The mercuric bromide adduct, $(HOCH_2)_3P\cdot HgBr_2$, was prepared by refluxing 0.360 g (1.0 mmol) of mercuric bromide with 0.194 g (1.0 mmol) of I in 30 ml of anhydrous ethanol for 6 hr, yielding a pale yellow, crystalline solid, 0.177 g (37%): mp 121-122° dec; ir (Nujol) 3330 s (OH), 1270-1280 w, 1150-1170 w, and 1025 cm^{-1} s (C-O). Similarly, with red mercuric iodide, I gave the bright yellow $(HOCH_2)_3P\cdot HgI_2$ complex (9%): decomposes >160°; ir (Nujol) 3340 s (OH), 1270-1300 w, 1160 w, 1030 s (C-O), 890 cm^{-1} w.

Registry No.—Tributylphosphine, 998-40-3; I, 2245-60-5; II-mercuric bromide adduct, 27150-36-5; II-mercuric iodide adduct, 27150-41-0; IIIa, 20507-22-6; IIId, 27178-07-0; IV, 4762-82-7; VI, 5293-83-4.

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[28] D. W. Allen, I. T. Millar, and J. C. Tebby, *Tetrahedron Lett.*, 745 (1968).

[29] Butyl proton resonances in $[Bu_3PR]^+X^-$ appear at δ 2.42-2.53 (2 H, PCH_2), 1.45-1.60 (4 H, CH_2CH_2), and 0.90-0.98 (3 H, CH_3) ppm: C. E. Griffin and M. Gordon, *J. Organometal. Chem.*, **3**, 414 (1965).