

would expect only about one sodium ion to be bound per protein molecule under these conditions and this is close to Carr's experimental error. We have made some preliminary measurements of the sodium ion mobility under our conditions using  $\text{Na}^{22}$ . In a 0.01  $M$ -1% protein system an average reduction of the mobility of all sodium ions of about 5% is found, corresponding to a maximum of three sodium ions being associated per molecule of protein. This is reduced to about half if one attempts to take into account the relaxation effect.

From the available data, one estimates that about one veronal ion is adsorbed by the albumin molecule in 0.01  $M$  solution and that this number increases to about eight in 0.1  $M$  solutions. A

similar increase in sodium ion association seems reasonable for a ten-fold increase in concentration. Thus the net charge might well stay nearly constant.

One might expect that a better experimental test for the adsorption hypothesis would be possible at the higher sodium ion concentrations, particularly since the relaxation retardation decreases for our system as the ionic strength is raised beyond 0.05 (compare Fig. 3). Unfortunately, the swamping effect of the excess sodium ions increases, making experimental studies again difficult. It thus remains to be proven whether alkali ion association does play a significant part in the control of the electrophoretic charge of the albumin molecule.

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

### Studies in Phosphinethylene Chemistry. IV. The Reaction of Triphenylphosphinethylene and Triphenylphosphinevinylmethylene with Phenylbromophosphines<sup>1</sup>

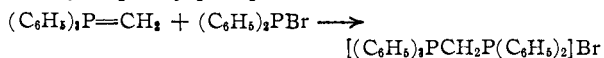
BY DIETMAR SEYFERTH AND KARL A. BRÄNDLE

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The reaction of triphenylphosphinethylene with diphenylbromophosphine produces diphenylphosphinomethyltriphenylphosphonium bromide; similar compounds are produced in the reaction of triphenylphosphinethylene with phenyldibromophosphine and dimethylbromostibine and of triphenylphosphinevinylmethylene with diphenylbromophosphine. The bromination of  $[(\text{C}_6\text{H}_5)_3\text{PCH}(\text{CH}=\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}$  is of interest, since the initial step apparently is the formation of the insoluble tribromide salt of this cation; the latter then is the active brominating agent which gives the product,  $[(\text{C}_6\text{H}_5)_3\text{PCH}(\text{CH}=\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}_2$ .

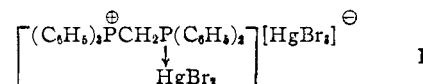
It has been established previously that triphenylphosphinethylene reacts with halides of metals of Periodic Groups II and IV to produce organometallic-substituted phosphonium salts.<sup>2</sup> It was expected therefore that the reaction of triphenylphosphinealkylidenes with phosphorus halides would proceed in a similar manner.

This research showed such to be the case. Addition of diphenylbromophosphine to a solution of triphenylphosphinethylene in ether resulted in the immediate precipitation of diphenylphosphinomethyltriphenylphosphonium bromide.



Attempts to isolate this product as well as all the other phosphonium bromides prepared in this study in the pure crystalline state were unsuccessful; in all cases oils which could not be crystallized resulted when recrystallization was attempted. However, the phosphonium cations formed could be characterized by conversion of the crude bromides to a suitable insoluble derivative, such as the tetraphenylborate or the tri- or tetrabromomercurate. In the case of diphenylphosphinomethyltriphenylphosphonium bromide, an analytically pure tetraphenylborate could be

prepared. However, the crude bromide reacted with two moles of mercuric bromide, since two functions capable of complexing mercuric bromide were present, bromide ion and a trivalent phosphorus atom, and the adduct of structure I was formed.



Phenyldibromophosphine reacted with triphenylphosphinethylene to form a diphosphonium salt,  $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3]\text{Br}_2$ , characterized as the bis-tetraphenylborate. Triphenylphosphinevinylmethylene underwent an analogous reaction with diphenylbromophosphine.

These phosphonium salts containing trivalent organophosphorus substituents could be quaternized with methyl bromide to give polyphosphonium salts such as  $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3]\text{Br}_3$  and  $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3]\text{Br}_2$ .

Of particular interest was the bromination of  $[(\text{C}_6\text{H}_5)_3\text{PCH}(\text{CH}=\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2]\text{Br}$ , since this compound contained at first sight two functions capable of reacting with bromine: the olefinic double bond and the trivalent phosphorus atom. The product of the bromination, which was carried out in methanol, was characterized as the complex with mercuric bromide. The analytical results fit either of two structures:  $[(\text{C}_6\text{H}_5)_3\text{PCH}(\text{CH}=\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2\text{Br}_2][\text{HgBr}_3]$  or  $[(\text{C}_6\text{H}_5)_3\text{PCH}(\text{CH}=\text{CH}_2)\text{P}(\text{C}_6\text{H}_5)_2\text{Br}][\text{HgBr}_4]$ . In view of

(1) This work was summarized in part at the XVII International Congress of Pure and Applied Chemistry, München, August 30-September 6, 1959; cf. *Angew. Chem.*, **72**, 36 (1960). For Part III, see D. Seyferth, S. O. Grim and T. O. Read, *J. Am. Chem. Soc.*, **83**, 1617 (1961).

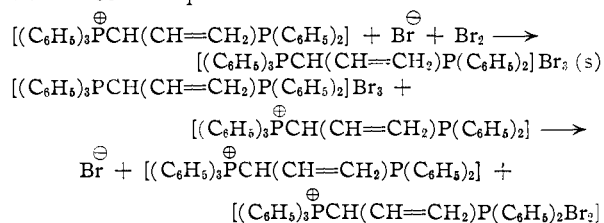
(2) S. O. Grim and D. Seyferth, *Chem. and Ind. (London)*, 849 (1959); *J. Am. Chem. Soc.*, **83**, 1610 (1961).

TABLE I  
 PRODUCTS OF THE TRIPHENYLPHOSPHINEALKYLIDENE-PHENYLBROMOPHOSPHINE REACTIONS AND THEIR DERIVATIVES

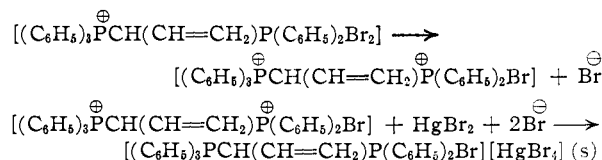
Compound	M.p., °C.	Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found
$[(C_6H_5)_3PCH_2(C_6H_5)_2][B(C_6H_5)_4]$	185.5-186	84.61	84.87	6.07	6.20
$[(C_6H_5)_3PCH_2P(C_6H_5)_2][HgBr_3]^a$	195-196	29.49	29.13	2.16	2.32
↓ HgBr <sub>2</sub>					
$[(C_6H_5)_3PCH_2P(C_6H_5)_2CH_3][B(C_6H_5)_4]_2$	194	86.17	85.84	6.33	6.58
$[(C_6H_5)_3PCH_2(C_6H_5)_2CH_3][HgBr_3]_2$	201	28.32	28.32	2.23	2.39
$[(C_6H_5)_3PCH_2P(C_6H_5)CH_2P(C_6H_5)_3][B(C_6H_5)_4]_2$	128-130	85.05	84.16	6.13	6.39
$[(C_6H_5)_3PCH_2P(C_6H_5)(CH_3)CH_2P(C_6H_5)_3][B(C_6H_5)_4]_3$	177-179	86.03	85.90	6.30	6.13
$[(C_6H_5)_3PCH(CH=CH_2)P(C_6H_5)_2][B(C_6H_5)_4]$	132-133	84.86	83.91	6.12	6.13
$[(C_6H_5)_3PCH(CH=CH_2)P(C_6H_5)_2CH_3][HgBr_4]$	134-135	39.93	39.69	3.15	3.24
$[(C_6H_5)_3PCH(CH=CH_2)P(C_6H_5)_2CH_3][B(C_6H_5)_4]_2$	137-138	86.32	85.62	6.36	6.38
$[(C_6H_5)_3PCH(CH=CH_2)P(C_6H_5)_2Br][HgBr_4]$	137-138	36.44	36.59	2.69	2.80

<sup>a</sup> Hg: Calcd., 31.66. Found, 31.85.

the studies of Issleib and Seidel<sup>3</sup> which showed that triorganodibromophosphoranes behaved like phosphonium salts,  $[R_3PBr]Br$ , in solution, we favor the second structure. The infrared spectrum of the product showed the double bond to be still present. However, the course of the bromination reaction appeared to be more complicated than expected, and the following observations were made. Addition of a small amount of bromine in methanol solution to a solution of the vinyl-containing phosphonium salt immediately produced a yellow flocculent precipitate. The solid dissolved again while the solution was stirred. Addition of another small portion of bromine solution precipitated more solid which dissolved on stirring. This procedure could be repeated until one equivalent of bromine had been added. Addition of a small excess of bromine produced more precipitate which did not dissolve on stirring. However, addition of more phosphonium salt to this solution caused this precipitate to dissolve. A probable explanation of these observations is that neither the olefinic double bond nor the trivalent phosphorus atom suffers initial attack by the bromine. Instead bromide ion complexes bromine to give tribromide ion, which is known to form insoluble compounds with large inorganic and organic cations. The insoluble  $[(C_6H_5)_3PCH(CH=CH_2)P(C_6H_5)_2]Br_3$  then is the active brominating agent, and its bromination of the trivalent phosphorus atom of either its own cation or of another cation in solution shifts the solubility equilibrium until all of the tribromide has dissolved. Finally, when bromination of the trivalent phosphorus present is complete, addition of bromine in excess precipitates a tribromide which does not dissolve again, since bromine transfer to phosphorus can no longer take place. The equations below summarize this reaction sequence.



(3) K. Issleib and W. Seidel, *Z. anorg. u. allgem. Chem.*, **288**, 201 (1956).



Dimethylbromostibine reacted readily with triphenylphosphinethylene to give dimethylstibinomethyltriphenylphosphonium bromide, quaternization of which with methyl bromide or methyl iodide resulted in novel mixed phosphonium-stibonium salts,  $[(C_6H_5)_3PCH_2Sb(CH_3)_3]X_2$ .

#### Experimental<sup>4</sup>

(1) **Reaction of Triphenylphosphinethylene and Triphenylphosphinevinylmethylene with Phenylbromophosphines.**—The reaction of triphenylphosphinethylene with diphenylbromophosphine is described to illustrate the procedure used.

To a filtered solution of ca. 0.04 mole of triphenylphosphinethylene in ether, prepared by the reaction of methyltriphenylphosphonium bromide with phenyllithium,<sup>5</sup> was added with vigorous stirring a solution of 10.6 g. (0.04 mole) of diphenylbromophosphine<sup>6</sup> in benzene. The deep yellow phosphinethylene solution became lighter in color as the addition progressed, and a white flocculent solid precipitated. The latter was filtered after the addition had been completed, washed well with benzene and ether and dried. The dry solid (19 g.) was a white, moisture-sensitive powder, soluble in polar solvents such as methanol, ethanol and dimethylformamide (DMF). Attempted recrystallization or reprecipitation was unsuccessful; either oils which would not crystallize were obtained, or decomposition resulted. This general procedure also was used in the reaction of triphenylphosphinethylene with phenyldibromophosphine and of triphenylphosphinevinylmethylene<sup>6</sup> with diphenylbromophosphine.

Methanol solutions of these products should not be heated; in some cases cleavage to produce methyltriphenylphosphonium ion appeared to occur under these conditions.

(2) **Preparation of Derivatives. Tetraphenylborates.**—A solution of crude diphenylphosphinethyltriphenylphosphonium bromide in methanol was added dropwise with stirring to a methanol solution containing an excess of sodium tetraphenylborate at 0°. A white microcrystalline solid precipitated. The tetraphenylborate salt thus obtained was dissolved in a small amount of DMF and reprecipitated by

(4) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were determined using a calibrated Fisher-Johns 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.

(5) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

(6) Prepared by phenylation of phenyldichlorophosphine (Victor Chemical Works) with diphenylmercury and conversion of the resulting chloride to the bromide by treatment with anhydrous HBr.

adding the DMF solution to a dilute solution of sodium tetraphenylborate in methanol.

**Bromomercurates.**—A similar procedure—the addition of a solution of the crude phosphonium bromide in methanol to a methanolic solution of mercuric bromide—was used to prepare the bromomercurate derivatives. Purification of the latter was effected by adding their DMF solutions to a solution of mercuric bromide in methanol. Apparently the concentration of the mercuric bromide solutions used in the precipitation and purification steps is critical in determining whether a tribromomercurate or a tetrabromomercurate is formed. As can be seen in Table I, both types of these complex salts resulted in this work. This point was not investigated further.

**Quaternization.**—A methanolic solution of crude diphenylphosphinomethyltriphenylphosphonium bromide and a large excess of methyl bromide were sealed in a pressure bottle and left to stand for eight days at room temperature. The resulting methanolic solution was treated with methanolic sodium tetraphenylborate and mercuric bromide, respectively, to prepare the derivatives listed in Table I. The other crude bromides also were quaternized in this manner.

**(3) Dimethylstibinomethyltriphenylphosphonium Bromide and Its Derivatives.**—A slurry of 1.4 g. (0.006 mole) of dimethylbromostibine<sup>7</sup> in ether was added to a slight excess of triphenylphosphinemethylene in ether. The resulting

(7) We are grateful to Dr. Ludwig Maier of Monsanto Research S.A., Zürich, for a sample of this compound.

heterogeneous reaction mixture was stirred under nitrogen for 40 hr. The solid was filtered, washed well with ether and dried to give a white powder. In air this product turned red and decomposed.

One g. of this product was dissolved in 30 ml. of methanol. The resulting yellow solution was heated at reflux for 2 hr. to give an orange solution. Addition of methanolic sodium tetraphenylborate to this solution precipitated methyltriphenylphosphonium tetraphenylborate in 81% yield, identified by m.p. and mixed m.p.

Three g. of crude dimethylstibinomethyltriphenylphosphonium bromide and 15 ml. of methyl bromide were stirred under nitrogen for 20 hr. in a flask equipped with a low temperature condenser. The resulting white powder was washed well with ether and dried (2.9 g.); m.p. 93°.

*Anal.* Calcd. for  $C_{22}H_{26}Br_2PSb$ : C, 43.83; H, 4.35. Found: C, 44.10; H, 4.35.

A similar derivative,  $[(C_6H_5)_2PCH_2Sb(CH_3)_3]BrI$ , was prepared by the reaction of the crude bromide (2.0 g.) with methyl iodide (18 ml.). The resulting light yellow powder (1.7 g.) sintered before it melted at 107–110°.

*Anal.* Calcd. for  $C_{22}H_{26}BrIPSb$ : C, 40.65; H, 4.03. Found: C, 40.68; H, 4.00.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, ETHYL CORPORATION, BATON ROUGE, LA.]

## Reductive Carbonylation Synthesis of Metal Carbonyls. IV. Synthesis of Group VI-B Metal Carbonyls Using Sodium as the Reducing Agent<sup>1</sup>

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A novel and simple sodium route has been developed for preparing the Group VI-B metal carbonyls in high yields. The method consists essentially of reductively carbonylating the metal chloride with sodium and carbon monoxide in diglyme at -10 to 25°, and then hydrolytic carbonylation at 0°. The metal carbonyl appears to be produced initially as a sodium salt  $Na_2M(CO)_6$  which subsequently is converted to the metal carbonyl by reaction with mineral acid and carbon monoxide.

Although various metallic reducing agents such as zinc<sup>3</sup> and aluminum<sup>4</sup> have found considerable use for the preparation of molybdenum carbonyl and tungsten carbonyl, metallic reducing agents *per se* have been of little or no value for the preparation of chromium carbonyl.<sup>5</sup> However, respectable yields can be achieved if there are also present appreciable amounts of certain additives, such as iodine when magnesium is employed<sup>6</sup> or aluminum chloride when aluminum is employed.<sup>7</sup> Recently, it was reported<sup>8</sup> that sodium can be used for the preparation of chromium carbonyl in 37% yield from chromic chloride in pyridine. This report prompts us to publish at this time some of

our work on the sodium route to metal carbonyls, particularly the Group VI-B metal carbonyls.<sup>9</sup> Our observations on the course of the reaction in diglyme<sup>10</sup> and conditions for obtaining 80% yields are herein reported.

### Results

**Reaction Variable Study.**—It was initially found that little or no carbon monoxide was absorbed upon heating a mixture of chromic chloride and sodium dispersion in various solvents in contact with carbon monoxide. The yield of chromium carbonyl in the best case (75° in diglyme) was only 10–15%. At higher temperatures the yield decreased to 3% or less. In every case it was found that the reaction mixture contained appreciable quantities of black colloidal chromium. At this point the effect of temperature on the yield of chromium carbonyl was investigated carefully. It was found that the yield unexpectedly increased with a decrease in temperature and amounted to about 30% at 0° and a 6:1 mole ratio of sodium to chromic chloride in diglyme. The amount of colloidal chromium also decreased at the lower temperatures.

(1) For paper III, see R. P. M. Werner and H. Podall, *Chem. and Ind.*, in press (1961); paper II, H. Podall, J. H. Dunn and H. Shapiro, *J. Am. Chem. Soc.*, **82**, 1325 (1960).

(2) To whom all correspondence should be addressed: Melpar, Inc., Physical Sciences Laboratory, Falls Church, Virginia.

(3) K. A. Kocheskov, A. N. Nesmeyanov, *et al.*, *Compt. rend. acad. sci. U.R.S.S.*, **26**, 54 (1940).

(4) D. T. Hurd (to General Electric), U. S. 2,554,194, May 22, 1951.

(5) K. N. Anisimov and A. N. Nesmeyanov, *Compt. rend. acad. sci. U.R.S.S.*, **26**, 58 (1940).

(6) G. Natta, R. Ercoli, F. Calderazzo and A. Rabizzoni, *J. Am. Chem. Soc.*, **79**, 3611 (1957).

(7) E. O. Fischer and W. Hafner (to Badische Anil. and Soda Fabrik.), German Patent 1,007,305, May 2, 1957.

(8) A. N. Nesmeyanov, E. P. Mikheev, K. N. Anisimov and N. P. Filimonova, *Russian J. Inorg. Chem.*, **4**, 889 (1959).

(9) H. E. Podall, U. S. Patents 2,952,521–2–3 (Sept. 1960).

(10) Dimethyl ether of diethylene glycol.