

and 10% as hexaethyl tetrapolyphosphate, with the remainder corresponding to higher straight-chain homologs. There is thought to be an insignificant amount of ring compounds in this reorganization mixture.

Using two different extremely pure samples of sodium tripolyphosphate hexahydrate, amorphous "silver tripolyphosphate" was made and converted to "pentaethyl tripolyphosphate" by reaction with ethyl iodide following the method of Hood and Lange.<sup>12</sup> According to n.m.r. results on two very careful preparations from our laboratory, and a third one from another laboratory, "pentaethyl tripolyphosphate" made by this method consists of a mixture of 11.8% of the total phosphorus as ortho, 75.7% as end groups and 12.5% as middle groups. This quantitative n.m.r. analysis, which does not differentiate<sup>8</sup> between esterified or unesterified building units of the polyphosphoric or orthophosphoric acids, showed that the parameter  $R$  corresponding to this mixture is 1.99, which is close to the pyro composition. This indicates that either we had inadvertent hydrolysis during prep-

(12) A. Hood and W. Lange, *THIS JOURNAL*, **72**, 4956 (1950); also see R. Rätz and E. Thilo, *Z. anorg. u. allgem. Chem.*, **272**, 333 (1953).

aration or the "silver tripolyphosphate" contained considerable ortho- and pyrophosphate in the same manner that an X-ray diffraction study of "ferric tripolyphosphate" obtained by treating ferric sulfate with sodium tripolyphosphate showed only ferric pyrophosphate, presumably formed by the catalytic action of the immediately precipitated hydrated ferric oxide on hydrolysis of the tripolyphosphate ion.<sup>13</sup>

From the proximate analysis of 22.6% P given by Rätz and Thilo and our  $R$  value of 1.99, it appears that the "pentaethyl tripolyphosphate" is only about 90% esterified. This may explain the fact that the value of  $K_2$  calculated for this preparation from our n.m.r. data is lower than that of eq. 2 by a factor of two. Presumably the acid hydrogens make the equilibrium more like an "ionic" type and thus lower the value of  $K_2$ .<sup>6</sup> In any event, the ester we have prepared from the silver phosphate is not pentaethyl tripolyphosphate but consists of a mixture, presumably at or near reorganization equilibrium, having an over-all composition estimated to be roughly equivalent to  $9(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{H}_3\text{O}\cdot 5\text{P}_2\text{O}_5$  in the Berzelius notation.

(13) See p. 659 of ref. 6.

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

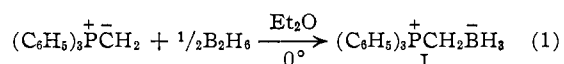
## The Reaction of Alkylidene Triphenylphosphoranes with Diborane and Trialkylamine Alkylboranes

BY M. FREDERICK HAWTHORNE

RECEIVED AUGUST 22, 1960

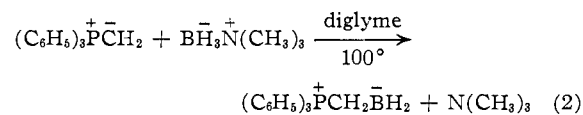
Diborane and a series of alkylidene triphenylphosphoranes combined to produce simple, charge separated complexes of the type  $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CHR}\text{B}^-\text{H}_3$ . Phenyliminotriphenylphosphorane and diborane gave an analogous product. Methylenetriphenylphosphorane readily displaced trimethylamine from a series of trimethylamine alkylboranes and trimethylaminephenyl borane. All complexes of this nature were exceedingly stable toward hydrolysis.

In a previous communication from this Laboratory,<sup>1</sup> the reaction of diborane with alkylidene triphenylphosphoranes<sup>2</sup> in diethyl ether solution was reported to produce stable adducts.<sup>3</sup>



Following the first report of these materials, Grim and Seyferth<sup>4</sup> reported the preparation of methylene triphenylphosphorane trifluoroborane which was successfully alkylated on boron to give trialkylborane analogs of I.<sup>5</sup> The reaction of methylene triphenylphosphorane with trimethyl-

amine borane also produced I in accordance with eq. 2.<sup>5</sup>



This latter reaction has been employed by us in the preparation of methylene triphenylphosphorane alkyl- and phenylboranes (*vide infra*) from trimethylamine alkyl- and phenylboranes.

**Reaction of Alkylidene Triphenylphosphoranes with Diborane.**—As previously described,<sup>1</sup> alkylidene triphenylphosphoranes rapidly react with diborane in diethyl ether at zero degrees to produce hydrolytically stable adducts (eq. 1). The structures of these adducts were established by their infrared spectra, active hydrogen analyses and C, H and B analyses. Recently a B<sup>11</sup> n.m.r. spectrum was obtained with I in methylene chloride solution. The resonance lines formed a quadruplet centered at 620 c.p.s. higher field than methyl borate. This confirms that three hydridic hydrogen atoms are attached to the boron atom in I.

Perhaps the most interesting physical feature of I and of its derivatives is their great solubility in

(1) M. F. Hawthorne, *THIS JOURNAL*, **80**, 3480 (1958).

(2) The name triphenylphosphine methylene apparently has been superseded by the alkylidene triphenylphosphorane nomenclature in describing Wittig reagents. As an example see S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).

(3) The parent compound I originally was termed triphenylphosphine methylene boron trihydride (ref. 1). A more suitable nomenclature might be constructed in which I is termed methylene triphenylphosphorane borane. This latter concept will be employed throughout this paper. The complicating factor, charge separation, is ignored for simplicity.

(4) S. O. Grim and D. Seyferth, *Chem. and Ind.*, 849 (1959).

(5) D. Seyferth, *XVII Congress of Pure and Applied Chemistry*, Munich, August 30–September 6, 1959. See also *Angew. Chem.*, **72**, 36 (1960).

TABLE I  
 PREPARATION AND CHARACTERIZATION OF X-METHYLENETRIPHENYLPHOSPHORANE BORANES

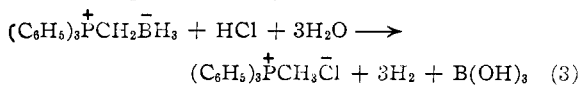
X in (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PCHX <sup>+</sup> BH <sub>3</sub> <sup>-</sup>	M.p., °C.	Yield from		Analyses %			Found		
		(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P <sup>+</sup> CH <sub>2</sub> R <sup>-</sup> , %	Moles H <sub>2</sub> /mole compd.	Calcd. C	Calcd. H	Calcd. B	C	H	B
H	191-192	81	3.01	78.65	6.95	3.72	78.40	7.16	3.50
CH <sub>3</sub>	171-172	80	2.96	78.97	7.29	3.56	78.80	7.21	3.71
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	154-156	85	2.97	79.53	7.89	3.26	79.71	7.68	3.50
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	139-140	92	3.00	80.00	8.39	3.00	80.21	8.38	3.30
C <sub>6</sub> H <sub>5</sub>	145-147	91	2.99	81.98	6.61	2.95	81.62	6.68	3.18

 TABLE II  
 PREPARATION AND CHARACTERIZATION OF METHYLENETRIPHENYLPHOSPHORANE (SUBSTITUTED)-BORANES

X in C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PCH <sub>2</sub> B <sup>-</sup> XH <sub>2</sub> <sup>+</sup>	M.p., °C.	Yield from		Carbon, %		Hydrogen, %		Position of center line relative to B(OCH <sub>3</sub> ) <sub>3</sub> , c.p.s., B <sup>11</sup> resonance
		(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P <sup>+</sup> CH <sub>2</sub> R <sup>-</sup> , %	Calcd.	Found	Calcd.	Found		
CH <sub>3</sub>	151-155	63	78.97	78.66	7.29	7.16	+546	
2-C <sub>4</sub> H <sub>9</sub>	100-104	68	79.78	79.69	8.15	8.10	+483	
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	130-134	44	79.78	79.62	8.15	8.40	+446	
C <sub>6</sub> H <sub>5</sub>	153-156	57	81.98	81.83	6.60	6.69	+500	

aromatic hydrocarbons and halogenated alkanes. This device may eventually allow useful reductions to be carried out under unusual circumstances.

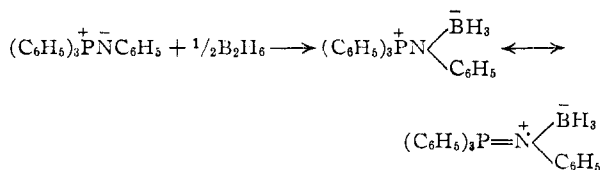
Chemically, I and its derivatives are relatively inert toward proton donors and mild oxidizing agents. Silver ion and iodine are slowly reduced by I in ethanol solution. The reaction of I and water is immeasurably slow. Indeed, acetone-water is a useful solvent for the recrystallization of these substances. With strong proton donors such as aqueous ethanolic hydrogen chloride, reaction 3 is observed quantitatively.



Thus, such treatment of I or its methylene-substituted derivatives will produce three moles of hydrogen and regenerate the original alkyltriphenylphosphonium ion. This represents a remarkably facile deboronation reaction at a saturated carbon atom. The driving force of this reaction is probably related to the stabilization afforded the deboronation transition state by  $\pi$ -overlap of an empty phosphorus *d*-orbital and the carbon orbital which holds the entering proton and the departing boron atom.

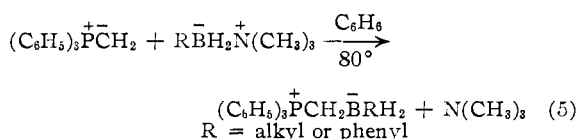
Table I presents data pertinent to the alkylidenetriphenylphosphorane boranes prepared in this study.

**Phenyliminotriphenylphosphorane Borane.**—Phenyliminotriphenylphosphorane, while not iso-electronic with benzylidene triphenylphosphorane, is closely related to this substance. Diborane was expected to form an adduct with this material as was found to be the case. Phenyliminotriphenylphosphorane in diglyme solution smoothly absorbed diborane to yield the adduct II. This adduct was comparable to I in stability and melted at 141-



142°. The infrared spectrum of II contained B-H stretching bands centered at 4.45  $\mu$ .

**Alkylidenetriphenylphosphorane Alkyl- and Phenylboranes.**—Since trimethylamine alkylboranes<sup>6</sup> and trimethylamine phenylborane<sup>7</sup> were readily available, it was possible to carry out the reactions of these substances with methylenetriphenylphosphorane.<sup>5</sup> Trimethylamine was evolved smoothly from a benzene solution of the reactants at the reflux temperature and the course of these reactions could be followed qualitatively by observing the rate of discharge of the yellow color characteristic of methylenetriphenylphosphorane.



Since the qualitative order of reactivity was R = *t*-butyl > 2-butyl > methyl, it is probable that these reactions occur *via* the combination of the free borane and substrate.<sup>8</sup> Yields were of the order of 40-60%.

The structures of the methylenetriphenylphosphorane alkyl- and phenylboranes were confirmed by their B<sup>11</sup> n.m.r. spectra. In each case a triplet was observed which was centered between 440-550 c.p.s. higher field than methyl borate (Table II). Boron-hydrogen stretching bands were observed in this series of compounds in the region 4.40-4.60  $\mu$ .

Table II presents data pertinent to the preparation and characterization of these materials.

### Experimental

**Materials.**—All alkyltriphenylphosphonium bromides were prepared by standard literature methods. Phenyliminotriphenylphosphorane was prepared as described by Staudinger.<sup>9</sup> Diborane was prepared as described by

(6) M. F. Hawthorne, *THIS JOURNAL*, **81**, 5836 (1959).

(7) M. F. Hawthorne, *ibid.*, **80**, 429 (1958).

(8) This same order of reactivity is observed in the hydroboration of olefins with these trimethylamine alkylboranes and may represent the relative steric strain in the amine boranes. A rate-determining thermal dissociation is implied but by no means has it been proved to be the case.

(9) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 86 (1921); also H. Staudinger and W. T. Braunholtz, *ibid.*, **4**, 897 (1921).

Brown and Subba Rao.<sup>10</sup> Trimethylamine alkylboranes were prepared by the lithium aluminum hydride reduction of the corresponding trialkylboroxines.<sup>6</sup> Trimethylamine phenylborane was similarly prepared.<sup>7</sup>

**General Procedure for the Preparation of Alkylidetriphenylphosphorane Boranes.**—To 0.05 mole of the appropriate alkyltriphenylphosphonium bromide suspended in 100 ml. of dry diethyl ether was added 50 ml. of 1.0 *M* phenyllithium in diethyl ether. The mixture was stirred in a nitrogen atmosphere for 1 hour. The alkylidetriphenylphosphorane solution was then transferred under nitrogen to a three-necked flask attached to a diborane generator<sup>10</sup> and a reflux condenser which in turn was attached to an absorbing bottle filled with acetone. The reaction flask contained a magnetic stirrer and was cooled by an ice-bath. The diborane generator and the connected reaction flask were swept with dry nitrogen and diborane was generated with a slow stream of nitrogen passing through the apparatus. A 100% excess of diborane (0.05 mole) was available from the reagents in the diborane generator system. As soon as the color of the alkylidetriphenylphosphorane had disappeared the generation of diborane was stopped and the system purged with nitrogen.

The contents of the reaction flask were treated with 200 ml. of water and 200 ml. of methylene chloride. The organic layer was separated, washed twice with water, dried over magnesium sulfate and the solvent removed at reduced pressure. The crystalline residue was essentially pure alkylidene-triphenylphosphorane borane as shown by infrared spectra. Crude yields are shown in Table I. Analytical samples were prepared by recrystallization from benzene-pentane or methylene-pentane mixed solvents. Melting points and analytical data are presented in Table I.

Active hydrogen analyses were obtained by treating an accurately weighed 2-mmole sample of each alkylidetriphenylphosphorane borane with 10 ml. of 1 *M* hydrogen chloride in 50:50 water-ethanol. The reactions were conducted in a vacuum line which carried a calibrated gas measuring apparatus. Moles of active hydrogen (identified by mass spectrum) obtained per mole of alkylidetriphenylphosphorane borane are given in Table I.

The solutions which remained from each active hydrogen analysis were evaporated to dryness in high vacuum. The residues were recrystallized from methanol or methanol-

(10) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1138 (1957).

diethyl ether. Infrared spectra and melting point determinations proved these materials to be the corresponding alkyltriphenylphosphonium chlorides.

**Phenyliminotriphenylphosphorane Borane (II).**—Phenyliminotriphenylphosphorane (3.5 g., 0.01 mole) was dissolved in 30 ml. of diglyme and treated with diborane as described above. The color of the reaction mixture discharged rapidly and the product precipitated. The product was removed by filtration and weighed 3.2 g. (87% of theory). An analytical sample was prepared by recrystallization from benzene-pentane; m.p. 139–140°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>28</sub>PNB: C, 78.49; H, 6.31; B, 2.95. Found: C, 78.50; H, 6.12; B, 2.73.

**General Procedure for the Preparation of Alkylidetriphenylphosphorane Alkyl- and Phenylboranes.**—To a slurry of 7.0 g. (0.02 mole) of methyltriphenylphosphonium bromide and 50 ml. of dry benzene was added 20 ml. of 1 *M* butyllithium in pentane. The reaction mixture was stirred for 1 hour at room temperature and in a nitrogen atmosphere. The trimethylamine alkyl- or phenylborane (0.02 mole) was then added and the reaction mixture heated to the reflux temperature in a slow stream of nitrogen. Trimethylamine was detected in the exit gas. Heating was continued until trimethylamine ceased to be evolved and the yellow color of the Wittig reagent had disappeared. The reaction mixture was then cooled, washed three times with water, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was then redissolved in a small amount of benzene and pentane added to the point of turbidity. Nicely defined crystals were obtained upon slowly chilling the product. Yields are recorded in Table II. In spite of many recrystallizations, the melting points of the products were not sharp, although analytical data (Table II) and other data indicated pure products. The crystal habit was excellent in all cases.

**Nuclear Magnetic Resonance Measurements.**—A Varian high resolution nuclear magnetic resonance spectrometer was employed (10<sup>8</sup> gauss field) with a 12.8 mc. B<sup>11</sup> probe. Spectra were obtained in methylene chloride solution at room temperature. Resonance line positions were determined relative to that of a methyl borate sample contained in a capillary tube and inserted in the sample tube.

**Acknowledgment.**—The author is indebted to Mrs. Carolyn Haney for the nuclear magnetic resonance experiments.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH AND DEVELOPMENT DEPARTMENT, ETHYL CORPORATION, BATON ROUGE 1, LA.]

## Preparation and Reactions of Sodium Tetraethylboron and Related Compounds<sup>1</sup>

BY JULIAN B. HONEYCUTT, JR., AND JAMES M. RIDDLE

RECEIVED AUGUST 15, 1960

Sodium hydride and triethylborane react in ethers and in aliphatic hydrocarbons to yield sodium triethylborohydride, NaB(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H. Sodium tetraethylboron, NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, may be prepared from ethylsodium and triethylborane, from ethyl chloride and triethylborane in the presence of sodium, and from ethylene and sodium triethylborohydride. Several analogs of sodium tetraethylboron have also been prepared. Sodium triethylborohydride reacts with water to liberate hydrogen and triethylborane. It undergoes disproportionation and can be decomposed by heat. Sodium tetraethylboron is stable to water but is decomposed by mineral acids. Other sodium tetraalkylboron compounds behave similarly. Lead salts react with sodium tetraethylboron to give tetraethyllead in good yields.

Investigation of the chemistry of triethylborane has led to the formation and characterization of several new complex organoboron compounds. The majority of them are derivatives of the type MB(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>R, where M is sodium and R is an alkyl group. We are here reporting the synthesis, physical properties and some of the chemical properties of these materials.

The literature contains relatively few references

(1) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

to MBR<sub>4</sub> compounds in which the R groups are all alkyl constituents, although a variety of complex organoboron derivatives containing aryl groups have been synthesized. It was first reported that heating certain organolithium or organosodium derivatives with trimethyl- or triphenylborane in ligroin was unsuccessful in preparing MBR<sub>4</sub> compounds.<sup>2</sup> A few years later, Johnson and co-workers observed an exothermic reaction between tri-*n*-butylborane and *n*-butyl- or phenyllithium in diethyl ether, but

(2) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 556 (1933).