

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  $C_{24}H_{28}PNB$ : 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 ( $10^8$  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,  $NaB(C_2H_5)_3H$ . Sodium tetraethylboron,  $NaB(C_2H_5)_4$ , 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  $MB(C_2H_5)_3R$ , 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  $MBR_4$  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  $MBR_4$  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).

could isolate no product.<sup>3</sup> Schlesinger and Brown then found that approximately an equimolar quantity of trimethylborane was absorbed by ethyllithium.<sup>4</sup> The product was a white, crystalline solid with the empirical composition  $\text{LiC}_2\text{H}_5\cdot\text{B}(\text{CH}_3)_3$ . The solid dissolved in water to give a solution which slowly evolved a gas. Hurd prepared lithium tetramethylboron from trimethylborane and methyllithium.<sup>5</sup> The product dissolved in a large volume of water to give a reducing solution. If only a small quantity of water was added to a relatively large amount of the lithium tetramethylboron, ignition generally occurred. The reaction between phenylethynylsodium and boron tribromide or trichloride was reported by Krüerke to give sodium tetrakis-(phenylethynyl)-boron,  $\text{NaB}(\text{C}\equiv\text{CC}_6\text{H}_5)_4$ , but no analysis was reported.<sup>6</sup> More recently, Parsons, *et al.*, treated propenyl-lithium with trimethylborane.<sup>7</sup> The proportions of the reagents consumed were close to those required for the formation of  $\text{LiB}(\text{CH}_3)_2(\text{CH}\equiv\text{CHCH}_3)$ . Hydrolysis of the product gave a mixture of propenylmethylboranes along with trimethylborane, methane and propene. Finally, Ashby and Foster reported the preparation of sodium tetraethynylboron,  $\text{NaB}(\text{C}\equiv\text{CH})_4$ , from sodium acetylide and trimethyl borate.<sup>8</sup>

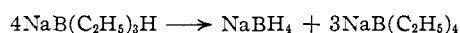
Wittig and co-workers described derivatives of the type  $\text{MB}(\text{C}_6\text{H}_5)_3\text{H}$  from the reaction of triphenylborane with the hydrides of lithium and sodium.<sup>9</sup> Brown, *et al.*, later reported that essentially equimolar quantities of sodium hydride and triethylborane reacted as would be expected in the formation of  $\text{NaB}(\text{C}_2\text{H}_5)_3\text{H}$ .<sup>10</sup>

We have also treated sodium hydride with triethylborane. The product has been shown to be sodium triethylborohydride,  $\text{NaB}(\text{C}_2\text{H}_5)_3\text{H}$ . We conducted the reaction in solvents rather than in a vacuum system as was done by Brown.<sup>10</sup> With an aliphatic hydrocarbon as the medium, there was no reaction between sodium hydride and triethylborane at ambient temperatures. When the mixture was warmed to about 55–60°, however, the hydride dissolved in the triethylborane solution. On occasions a sudden and very exothermic reaction occurred which could be controlled with difficulty. An easily manageable condensation took place when triethylborane was added to a refluxing suspension of sodium hydride in hexane. Removal of the solvent left sodium triethylborohydride. In an ethereal medium, the condensation of sodium hydride and triethylborane proceeded very

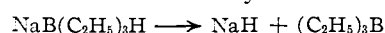
smoothly at room temperature. Both diethyl ether and diglyme<sup>11</sup> permitted ready reaction.

Sodium triethylborohydride is a colorless, viscous oil with a translucent appearance. It is readily miscible with ethers and is also soluble in saturated aliphatic hydrocarbons. The compound is extremely unstable to moist air, visibly evolving a gas on exposure to the atmosphere. It ignites spontaneously in air, presumably because triethylborane is released. Sodium triethylborohydride reacts vigorously with alcohols or water. Hydrogen and triethylborane are liberated. No ethane could be detected in the hydrolysis gas. This indicates that the boron-ethyl bond is not cleaved. The reaction with water, or alcohol, is complete and acidification of the hydrolysis mixture liberates no additional gas. The reaction of olefins with sodium triethylborohydride is discussed below.

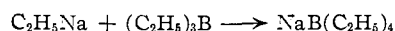
Both disproportionation and decomposition can be effected by heating sodium triethylborohydride. Refluxing a diglyme solution of the hydride for 2 hours gave sodium borohydride and sodium tetraethylboron.



Unreacted sodium triethylborohydride also remained. The identity of the products was deduced from hydrolysis data. Careful treatment of the reaction product with water rapidly liberated hydrogen. This behavior is that shown by unreacted sodium triethylborohydride. Acidification of the hydrolysis mixture with dilute hydrochloric acid generated an approximately equimolar mixture of hydrogen and ethane. Such behavior with a non-oxidizing acid is characteristic of both sodium borohydride and sodium tetraethylboron, neither of which evolve much gas on treatment with water. When heated alone, sodium triethylborohydride decomposes. At 135° and 1–2 mm. pressure, the triethylborohydride breaks down into its component parts. Triethylborane is removed, leaving a residue of sodium hydride.



The direct preparation of sodium tetraethylboron



from ethylsodium and triethylborane was carried out in petroleum ether. Extraction of the reaction solids with diethyl ether dissolved some sodium, thereby indicating that sodium tetraethylboron had been formed. Since ethylsodium is insoluble in diethyl ether, the triethylborane brought the organosodium derivative into solution, *i.e.*, complexed it to form sodium tetraethylboron. Sodium *n*-butyl-triethylboron,  $\text{NaB}(\text{n-C}_4\text{H}_9)(\text{C}_2\text{H}_5)_3$ , was later formed from *n*-butylsodium and triethylborane as further evidence that the direct preparation of  $\text{NaBR}_4$  or  $\text{NaBR}_3\text{R}'$  compounds is feasible. Lithium tetraethylboron was similarly formed when ethyllithium was treated with triethylborane.

Because of the difficulties associated with the formation and isolation of ethylsodium, alternate routes to sodium tetraethylboron were investigated. Several were found and are considered preferable to the direct preparation. In the first of these other

(11) Diethylene glycol dimethyl ether.

(3) J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., *THIS JOURNAL*, **60**, 115 (1938).

(4) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(5) D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

(6) U. Krüerke, *Z. Naturforsch.*, **11b**, 364 (1956).

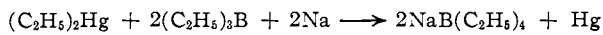
(7) T. D. Parsons, M. B. Silverman and D. M. Ritter, *THIS JOURNAL*, **79**, 5091 (1957).

(8) E. C. Ashby and W. E. Foster, Abstracts of Papers, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958, p. 36L.

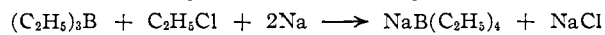
(9) G. Wittig, G. Keicher, A. Rückert and P. Raff, *Ann.*, **563**, 110 (1949).

(10) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, *THIS JOURNAL*, **75**, 192 (1953). This work was done under contracts with U. S. Govt. agencies during the years 1940–1946. Publication was withheld because of wartime restrictions.

routes, the addition of metallic sodium to a solution of diethylmercury and triethylborane in diethyl ether slowly gave sodium tetraethylboron.



Sodium tetraethylboron was also synthesized by the addition of sodium to a solution of triethylborane and ethyl chloride in diethyl ether.



This procedure gave a cleaner, faster preparation. By a similar reaction, sodium *n*-butyltriethylboron and sodium phenyltriethylboron were formed from 1-chlorobutane and chlorobenzene, respectively.

The most satisfactory synthesis of sodium tetraethylboron was through the addition of ethylene to sodium triethylborohydride at elevated temperature and pressure.



The presence of triethylborane was essential for the reaction, for isolated sodium triethylborohydride and ethylene in diglyme did not yield the desired product. When the ethylene addition reaction was conducted in aliphatic hydrocarbons, sodium tetraethylboron was obtained as a precipitate. Optimum conditions for rapid reaction seemed to be 1000 p.s.i. of ethylene and 150–175°. At 175–180° and pressures of 200 p.s.i. and 500 p.s.i., the reaction was first-order with respect to both ethylene and sodium triethylborohydride. When diglyme was the reaction solvent, a dietherate,  $NaB(C_2H_5)_4 \cdot 2C_6H_{14}O_3$ , was obtained. Attempts to displace the diglyme with diethyl ether were unsuccessful, as was heating *in vacuo* to about 140°. Reaction in 1,2-dimethoxyethane gave a monoetherate. Tetrahydrofuran gave a mixture of the mono- and ditetrahydrofuranates of sodium tetraethylboron. The complexed solvent could be displaced by diethyl ether. Subsequent heating at reduced pressure gave the ether-free tetraethyl derivative.

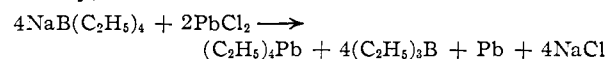
Sodium *n*-octyltriethylboron was similarly prepared in refluxing diglyme from sodium triethylborohydride and octene-1. This reaction also required the presence of triethylborane. Experiments in which sodium triethylborohydride and octene-1 were heated alone or in diglyme gave only unreacted starting materials.

Sodium tetraethylboron is a white hygroscopic powder. It is stable to the atmosphere although it does absorb moisture rapidly. The material is soluble in water and in ethers, but insoluble in hydrocarbons. By contrast, the diethyl etherate of sodium tetraethylboron,  $NaB(C_2H_5)_4 \cdot C_4H_{10}O$ , is somewhat soluble in aromatic hydrocarbons. This etherate crystallizes as needles from diethyl ether at –78°. Heating at 120° and 1 mm. decomposes the etherate to give non-solvated sodium tetraethylboron.

There is no reaction when sodium tetraethylboron is dissolved in water. The addition of hydrochloric acid, however, causes a rapid evolution of ethane. The residue is a mixture of triethylborane and sodium chloride. The various etherates of sodium tetraethylboron also liberate ethane and triethylborane. The liberation of both methane and propene by hydrolysis of the product from trimethyl-

borane and propenyllithium<sup>7</sup> indicates that the hydrolysis is not selective, *i.e.*, no one trialkylborane is formed exclusively. We found that such was also the case in the acid hydrolysis of unsymmetrical sodium tetraalkylboron compounds. Sodium *n*-butyltriethylboron evolved both ethane and *n*-butane. Mass spectrometer analyses of the gases from two experiments showed ethane:butane ratios of 4:1 and 7:3, respectively. Ethane was liberated upon treatment of sodium *n*-octyltriethylboron with dilute hydrochloric acid. *n*-Octane was detected in the hydrolysis mixture. Similarly, sodium phenyltriethylboron gave ethane and benzene. The unsymmetrical  $NaB(C_2H_5)_3R$  derivatives which were just described all dissolve in water without reaction.

Sodium tetraethylboron reacts with divalent lead compounds to give high yields of tetraethyllead. The reaction was generally carried out so as to use only one ethyl group from the  $B(C_2H_5)_4^-$  moiety, as in the reaction with lead chloride



Since triethylborane will also alkylate lead salts,<sup>12</sup> a different stoichiometry would yield additional tetraethyllead from each mole of sodium tetraethylboron.

The alkylation reaction was carried out in water, tetrahydrofuran or diglyme. Solubility of reagents and ease of product isolation make water the solvent of choice. Lead acetate, lead chloride, yellow lead monoxide and lead sulfate were used in the study. Table I shows representative reaction conditions and tetraethyllead yields. The various lead salts tested were all capable of giving high yields of tetraethyllead.

TABLE I  
TETRAETHYLLEAD PREPARATION<sup>a</sup>

Lead compd.	Method <sup>b</sup>	Temp., °C.	Time, hr.	Product yield, % ( $(C_2H_5)_4Pb$ / $(C_2H_5)_3B$ )	
$Pb(OCOCH_3)_2$	A <sup>c</sup>	26	0.75	80.5	..
$Pb(OCOCH_3)_2$	A <sup>d</sup>	85	1	81.2	..
$PbCl_2$	A	80	1	97.8	92.5
$PbCl_2$	A-1	26	1	82.6	50.0
$PbCl_2$	B	70	0.75	68.5	77.0
$PbCl_2$	C	100	0.75	90.0	88.0
$PbCl_2$	A <sup>e</sup>	{ 26 98	{ 2.75 1.75	13.5	..
$PbO$	A	26	2.5	37.0	..
$PbO$	A	72	0.5	85.0 <sup>f</sup>	..
$PbO$	A <sup>g</sup>	85	0.25	44.0	12.0
$PbO$	A-1	70	0.75	82.0	48.0
$PbO$	B	70	0.75	97.0	50.0
$PbO$	C <sup>h</sup>	99	1/3	33.5	47.5
$PbSO_4$	A	80	1	44.0	..

<sup>a</sup> In water and with  $NaB(C_2H_5)_4$  as the added reagent unless otherwise noted. <sup>b</sup> See Experimental. <sup>c</sup> In tetrahydrofuran. <sup>d</sup> Used didiglyme etherate,  $NaB(C_2H_5)_4 \cdot 2C_6H_{14}O_3$ . <sup>e</sup> In diglyme. <sup>f</sup>  $(C_2H_5)_4Pb$  isolated by distillation. <sup>g</sup>  $PbO$  was the added reagent. <sup>h</sup>  $PbO$  in 2 *N* NaOH was the added reagent.

Positions of infrared absorption bands of three complex organoboron compounds, and of sodium borohydride, are given in Table II. The ethyl

(12) J. B. Honeycutt, Jr., and J. M. Riddle, *THIS JOURNAL*, **82**, 3051 (1960).

borane absorption bands that are presented show consistency only in the series given. Comparison with other ethyl-metal compounds is useless due to the low weight of the boron.

TABLE II  
INFRARED BAND POSITIONS OF NaBR<sub>4</sub> COMPOUNDS<sup>a</sup>

NaB(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> <sup>b</sup>	NaB(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> - (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> <sup>b, c</sup>	NaBH <sub>4</sub> <sup>b</sup>	NaB(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> H <sup>d</sup>
3.5(s)	3.5(s)	4.25(sh) 4.40(s) 4.52(w)	3.5(s)  5.4(vs, broad)
6.85(s)	6.87(s)		6.87(s)
7.36(w)	7.35(w)		7.30(w)
7.90(m)	7.96(m)		7.90(m)
8.16(w)	8.18(w)	8.90(s)	
9.34(s)	9.55(s)		9.30(s)
10.30(w)			10.90(s)
11.36(s)	11.50(s, broad)		
11.66(s)			11.70(m) 12.60(m)

<sup>a</sup> Samples prepared in inert atmosphere. Intensities indicated as very strong, strong, medium, weak and shoulder; wave lengths in  $\mu$ . <sup>b</sup> Run as KBr disk. <sup>c</sup> B-phenyl absorptions, as in NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, not listed. <sup>d</sup> Run as a smear.

The boron-hydrogen band observed in sodium triethylborohydride shows the bonding to be different from the simple borohydride. The position of the band at 5.4 $\mu$  suggests a dimeric or associated anion, for the band is in the region generally attributed to boron-hydrogen bridging bonds.

### Experimental

Air- and moisture-sensitive reagents were handled in an inert atmosphere box and all reactions were carried out under dry nitrogen. The hydrocarbon solvents were dried over calcium hydride. Diethyl ether was distilled from lithium aluminum hydride prior to use. Tetrahydrofuran was treated with solid potassium hydroxide, then distilled from lithium aluminum hydride. Diglyme was distilled from calcium hydride at atmospheric pressure, then redistilled from lithium aluminum hydride at reduced pressure (b.p. 75° at 35 mm.). Triethylborane was purified by distillation at reduced pressure (b.p. 56-57° at 220 mm.). The lead salts were commercial products and were used without further purification.

**Preparation of Sodium Triethylborohydride in Hexane.**—To a gently refluxing mixture of 1.2 g. (0.05 mole) of sodium hydride<sup>13</sup> and 25 ml. of *n*-hexane was slowly added, with stirring, 10 ml. (0.07 mole) of triethylborane. The heating and rate of addition were adjusted to maintain gentle reflux. The hydride slowly dissolved to give a translucent solution which was refluxed for 30 minutes longer. The solvent and excess triethylborane were distilled off, the final traces being removed at 100° and 1 mm. The residual sodium triethylborohydride was a viscous, colorless oil.

*Anal.* Calcd. for C<sub>6</sub>H<sub>16</sub>BNa: Na, 18.85; Na/hydride hydrogen, 1.00. Found: Na, 19.0; Na/hydride hydrogen, 1.09.

**In Ethers.**—A mixture of 4.8 g. (0.2 mole) of sodium hydride and 50 ml. of diethyl ether was stirred while 50 ml. (0.35 mole) of triethylborane in 50 ml. of diethyl ether was added at a rate which sustained gentle refluxing. The hydride slowly dissolved to give a translucent solution. The solvent and excess triethylborane were removed *in vacuo* to give viscous sodium triethylborohydride.

*Anal.* Calcd. for C<sub>6</sub>H<sub>16</sub>BNa: Na, 18.85; Na/hydride hydrogen, 1.00. Found: Na, 18.0; Na/hydride hydrogen, 0.99.

A smooth reaction also occurred in diglyme to yield an oily residue upon removal of the solvent. Analysis and infrared examination revealed the presence of a small amount of diglyme.

**Sodium Tetraethylboron. From Sodium Triethylborohydride and Ethylene in Ethers.**—Sodium triethylborohydride (from 0.1 mole of sodium hydride and 0.14 mole of triethylborane) in 50 ml. of diglyme was agitated and heated at 99-123° in a 250-ml. Magne-Dash reactor under 4050-5100 p.s.i. of ethylene. (The excess triethylborane had not been removed from the sodium triethylborohydride solution.) After 4.75 hours the mixture was cooled to room temperature and vented. The bomb was opened in a dry-box and the contents were washed out with hexane. Two liquid layers resulted. The lower phase was separated and washed repeatedly with additional portions of hexane until it became solid. No evidence for any unreacted sodium triethylborohydride could be found in the hexane washings. The white solid product was dried at 100° and 0.2 mm. for an hour. Its properties and analysis showed that it was the di-diglyme etherate of sodium tetraethylboron, NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>·2C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>.

*Anal.* Calcd. for C<sub>20</sub>H<sub>48</sub>BNaO<sub>6</sub>: B, 2.58; Na, 5.50. Found: B, 2.51; Na, 4.96.

To 4.8 g. (0.2 mole) of sodium hydride and 200 ml. of diglyme in a 1-liter Parr reactor was added slowly 40.0 ml. (0.28 mole) of triethylborane under a slight nitrogen pressure. The reactor was closed and pressurized to 500 p.s.i. with ethylene and then heated to 150°. The pressure was raised to 1000 p.s.i. with additional ethylene. The mixture was stirred for 4.25 hours at 145-152° and then allowed to cool. The product was worked up as described above to give an 87% yield of NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>·2C<sub>6</sub>H<sub>14</sub>O<sub>3</sub> identical to that above. At 100° and 1000 p.s.i. an 81% yield was obtained. Identification was established by reactions of the type described below.

**In Hydrocarbons.**—A 1-liter Parr reactor was charged with 4.8 g. (0.2 mole) of sodium hydride, 250 ml. of *n*-hexane and 40 ml. (0.28 mole) of triethylborane. The mixture was stirred and heated to 151°, then charged with ethylene to 1000 p.s.i. pressure. After 8 hours the reactor was vented and cooled. The solid sodium tetraethylboron (90%) was filtered off and dried *in vacuo*.

*Anal.* Calcd. for C<sub>8</sub>H<sub>20</sub>BNa: B, 7.21; Na, 15.32. Found: B, 7.09; Na, 15.0.

**From Diethylmercury, Sodium and Triethylborane.**—To a stirred solution of 50 ml. (0.35 mole) of triethylborane and 46.5 g. (0.18 mole) of diethylmercury in 400 ml. of diethyl ether was added 8.3 g. (0.36 g. atom) of sodium. The sodium was added in three portions over a 2-hour period at 5-10°. The mixture was allowed to warm to room temperature and stirred for 22 hours. A dark solid was filtered off and the filtrate was chilled in a Dry Ice-acetone-bath at -78° to give 53 g. (70%) of colorless needles. The product was recrystallized from diethyl ether at -78°, then dried at 2.5 mm. and room temperature to give the diethyl etherate of sodium tetraethylboron.

*Anal.* Calcd. for C<sub>12</sub>H<sub>30</sub>BNaO: B, 4.82; Na, 10.27. Found: B, 4.66, 4.92; Na, 9.59, 9.48.

Drying the etherated product at 120° and 1 mm. gave ether-free sodium tetraethylboron.

*Anal.* Calcd. for C<sub>8</sub>H<sub>20</sub>BNa: B, 7.21; Na, 15.32. Found: B, 7.13; Na, 15.20.

**From Ethyl Chloride, Sodium and Triethylborane.**—Into 98.0 g. (1.0 mole) of triethylborane and 400 ml. of diethyl ether at 4° was passed 64.5 g. (1.0 mole) of ethyl chloride. With stirring, 46.0 g. (2.0 g. atoms) of sodium sand was added in four portions over approximately a 2-hour period. The temperature was maintained at 4-10° during the addition. The purple mixture was allowed to warm to room temperature and was then filtered to remove the sodium chloride. The filtrate was chilled at -78° to crystallize sodium tetraethylboron etherate which on heating at 110° and 1 mm. gave 112 g. (74%) of ether-free sodium tetraethylboron identified by reactions of the type described below.

**Sodium *n*-Butyltriethylboron.**—*n*-Butylsodium (from 0.1 mole of 1-chlorobutane and 0.2 g. atom of sodium) suspended

(13) G. W. Mattson and T. P. Whaley, *Inorg. Syntheses*, **5**, 10 (1957).

in 2,2,5-trimethylhexane was treated with 17.0 ml. (0.12 mole) of triethylborane at 19–33°. The mixture was stirred at room temperature for 1.5 hours, then warmed to 65° for 0.5 hour. The solids were filtered from the cooled mixture and washed with several small portions of diethyl ether. The solvents were distilled from the combined filtrates at 100–110° and 0.2 mm. to give clear, viscous, liquid sodium *n*-butyltriethylboron which did not solidify on cooling to room temperature.

*Anal.* Calcd. for  $C_{10}H_{14}BNa$ : B, 6.09; Na, 12.91. Found: B, 6.10; Na, 14.30.

Sodium *n*-butyltriethylboron was also prepared from 1-chlorobutane, sodium and triethylborane in diethyl ether. The procedure was the same as for the ethyl chloride route to sodium tetraethylboron. The yield of  $NaB(n-C_4H_9)(C_2H_5)_3$  was 75%.

*Anal.* Calcd. for  $C_{10}H_{14}NBa$ : B, 6.09; Na, 12.91. Found: B, 6.10; Na, 12.90.

Sodium *n*-Octyltriethylboron.—Sodium triethylborohydride (from 0.15 mole of sodium hydride and 0.18 mole of triethylborane) in diglyme was treated at room temperature with 24.2 g. (0.22 mole) of octene-1. The solution was refluxed for 2 hours, then cooled. Unconsumed octene (10.4 g., 43.0%) was distilled out. The excess triethylborane and diglyme were removed at reduced pressure to give a viscous oil which was a diglyme etherate of sodium *n*-octyltriethylboron,  $NaB(n-C_8H_{17})(C_2H_5)_3 \cdot C_6H_{14}O_2$ . The identity of this compound was confirmed by its chemical behavior.

*Anal.* Calcd. for  $C_{20}H_{40}BNa_3$ : Na, 6.24. Found: Na, 5.83.

Sodium Phenyltriethylboron.—Sodium sand (4.6 g., 0.2 g. atom) and 200 ml. of diethyl ether were stirred vigorously. Slowly, 11.2 g. (0.1 mole) of chlorobenzene and 15.0 ml. (0.1 mole) of triethylborane in 50 ml. of ether were added. The mixture was stirred for 1.5 hours and the solids were filtered off. The filtrate was evaporated at reduced pressure (finally at 100° and 1 mm. for 3.5 hours) to give solid, pale yellow sodium phenyltriethylboron. The identity was confirmed by its chemical behavior.

*Anal.* Calcd. for  $C_{12}H_{20}BNa$ : Na, 11.61. Found: Na, 12.10.

Disproportionation of Sodium Triethylborohydride.—A solution of 0.1 mole of sodium triethylborohydride was prepared in 50 ml. of diglyme and 20 ml. of diethyl ether. Distillation to a pot temperature of 50° at 10 mm. removed the ether and the excess triethylborane. The vacuum was broken with nitrogen. The solution was heated to a gentle reflux (169–171°) and there maintained for 2 hours. After the solution had cooled, water was added cautiously. Mass spectrometer analysis of the evolved gas showed that it was nearly pure hydrogen. The hydrolysis mixture was acidified with dilute hydrochloric acid to liberate hydrogen and ethane in approximately equal amounts. An unknown

quantity of the ethane remained dissolved in the hydrolysis solution.

**Tetraethyllead. Method A.**—At room temperature, 4.8 g. (0.12 mole) of sodium tetraethylboron in 100 ml. of water was added to 19.5 g. (0.06 mole) of lead acetate in 150 ml. of water with stirring. The addition was complete in 30 minutes. The mixture became dark as metallic lead separated. Gradually the lead agglomerated and two liquid phases could be observed. After an additional 30 minutes, 150 ml. of hexane was added, followed by 100 ml. of 10% aqueous potassium hydroxide. The organic phase was separated and extracted with two 50-ml. portions of hydroxide solution. The residual hexane solution was diluted to 250 ml. Analysis<sup>14</sup> showed the tetraethyllead yield was 96.5%.

**Method A-1.**—The reaction procedure was the same except that potassium hydroxide was not used to separate the triethylborane. Instead the hexane phase was separated and the borane was distilled from it at reduced pressure (b.p. 56–57° at 220 mm.). Analysis of the residue showed an 85% yield of tetraethyllead.

**Method B.**—The reaction flask was equipped with a 6-inch Vigreux column and downward-directed condenser for distillation at reduced pressure. To a suspension of 13.4 g. (0.06 mole) of lead oxide and 100 ml. of water was added, with stirring, 18.75 g. (0.125 mole) of sodium tetraethylboron in 100 ml. of water. The pressure in the system had been reduced to 220 mm. and the oxide suspension had been heated to 80° prior to the addition. The addition rate was controlled so as to be approximately equal to the distillation rate. After a total reaction time of 45 minutes the mixture was allowed to cool and was returned to atmospheric pressure with nitrogen. The organic phase of the distillate was separated and diluted with 2,2,5-trimethylhexane. Triethylborane (51%) was distilled out at reduced pressure. The residual material was combined with a 2,2,5-trimethylhexane extract of the reaction flask contents. Analysis showed a 72% yield of tetraethyllead.

**Method C.**—The procedure was the same as that in method B except that the reaction was carried out at atmospheric pressure. The temperature was about 100°.

**Acknowledgments.**—The authors wish to thank Professor H. C. Brown of Purdue University and Dr. E. C. Ashby of this Laboratory for their suggestions. They also express their appreciation to Dr. R. P. Curry for infrared data, J. B. Chidester for mass spectrometric gas analysis, and the following members of the Analytical Group: R. A. Ashby, Ann K. Breaux, V. H. Dayan, W. J. Easley, J. W. Figgins, S. R. Henderson, J. L. Russell and G. Z. Smith.

(14) M. E. Griffing, A. Rozek, L. J. Snyder and S. R. Henderson, *Anal. Chem.*, **29**, 190 (1952).

[CONTRIBUTION FROM THE DIAMOND ALKALI CO. RESEARCH DEPARTMENT, PAINESVILLE, OHIO]

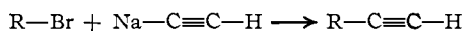
## A Novel Synthesis of Polyacetylenes<sup>1</sup>

BY JOHN H. WOTIZ, ROBERT F. ADAMS AND CHARLES G. PARSONS

RECEIVED JULY 28, 1960

Novel non-conjugated, linear and cyclic polyacetylenes were prepared in a simple manner by the reaction of  $\alpha,\omega$ -dihalides with mixtures of mono- and disodium acetylides. Some physical and thermal properties are described.

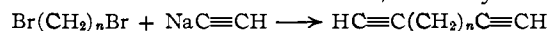
The alkylation of monosodium acetylide,  $Na-C\equiv C-H$ , with alkyl bromides in liquid ammonia is well known.<sup>2</sup> The reaction also proceeds in organic



(1) Presented in part at the 136th Meeting of the American Chemical Society, Sept. 1959, Atlantic City, N. J., Abstracts p. 91-P.

(2) T. L. Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 1-78, and references therein.

solvents of high dielectric constant such as dimethylformamide.<sup>3,4</sup> In this manner  $\alpha,\omega$ -dibromides were also converted to  $\alpha,\omega$ -diacetylenes<sup>2,3</sup>



A "one-step" synthesis of dialkylacetylenes was described by Bried and Hennion<sup>5</sup> who treated  $NaC$

(3) M. Kracht and H. Pasdach, German Patent 944,311 (1956).

(4) T. F. Rutledge, U. S. Patent 2,846,491 (1958).

(5) E. A. Bried and G. F. Hennion, *THIS JOURNAL*, **59**, 1310 (1937).