OCO-*i*-C_3H_7, 29.1. Found: Sn, 39.9; OCO-*i*-C_3H_7, 29.0, 29.2, 29.2.

Reactions of Organotin Oxymonocarboxylates.—Reflux of 0.26 g. of *n*-butyltin oxyacetate and 0.7 g. of glacial acetic acid (3 min.) and distillation at 1 mm. pressure furnished 0.33 g. (88% yield) of *n*-butyltin triacetate, with normal b.p. 278° dec. Similarly, *n*-butyltin oxy-*n*-butyrate and *n*-butyric acid gave a 60% yield of *n*-butyltin tri-*n*-butyrate, b.p. 315°, $d^{20}{}_4$ 1.281, and bearing 60.2% *n*-butyrate. However, 1.5 g. of phenyltin oxyisobutyrate and 10 g. of isobutyric acid upon slow evaporation on a hot plate yielded approximately 1.2 g. of crude tin tetraisobutyrate, m.p. *ca.* 106–107°, b.p. 160–170° (1 mm.); this involved elimination of the phenyl group. *Anal.* Found: Sn, 25.4; isobutyrate, 74.5.

Reactions of *n*-Butanestannonic Acid Anhydride.—Anhydride (5 g.) and 7 g. of glacial acetic acid upon 1 hr. of reflux, then careful distillation of aqueous carboxylic acid, next addition of 3 g. of acetic acid, followed by distillation of acetic acid and finally of *n*-butyltin triacetate furnished 7.4 g. (89% yield) of the latter, b.p. 125–129° (1 mm.). A similar reaction with propionic acid gave an 84% yield of *n*-butyltin tripropionate, b.p. 286° and n^{20} 1.467.

Conductance.—In absolute ethanol 0.0655 *M* *n*-butyltin triisobutyrate had a molar conductance of only 7.6×10^{-2} cm.^{2} ohm^{-1} mole^{-1}.

Infrared Absorptions.—A Perkin-Elmer Model 421 spectrophotometer served for measurements on organotin oxycarboxylates in KBr pellets (1%) and on organotin tricarboxylates (1%) in carbon tetrachloride. Carbonyl absorption as in organic esters at approximately 1700 cm.$^{-1}$ was completely absent from four organotin oxycarboxylates: *n*-butyltin oxyacetate, with strong antisymmetric carboxylate absorption at 1570, 1548, and 1533 cm.$^{-1}$ and strong symmetric carboxylate at 1421 cm.$^{-1}$; *n*-butyltin oxypropionate, with corresponding absorptions at 1532, 1424, and 1408 cm.$^{-1}$; *n*-butyltin oxy-*n*-valerate at 1560, 1548, 1530, 1420, and 1400 cm.$^{-1}$; phenyltin oxyisobutyrate at 1548, 1530, 1426, and 1416 cm.$^{-1}$. *n*-Butyltin triacetate had weak ester carbonyl absorption at 1705 cm.$^{-1}$, possibly due to slight hydrolysis, and strong absorptions at 1560, 1549, 1542, 1534, 1420, and 1410 cm.$^{-1}$; *n*-butyltin triisobutyrate also had weak ester carbonyl at 1699 cm.$^{-1}$ and strong absorptions at 1532 and 1426 cm.$^{-1}$. *n*-Butyltin tri-*n*-valerate had medium ester carbonyl at 1701 cm.$^{-1}$, strong absorptions at 1579, 1543, and 1533 cm.$^{-1}$, and medium absorption at 1412 cm.$^{-1}$. Phenyltin tripropionate had weak ester carbonyl at 1706 cm.$^{-1}$, strong absorptions at 1544 and 1532 cm.$^{-1}$, and medium absorptions at 1422 and 1410 cm.$^{-1}$. Phenyltin triisobutyrate had weak absorption at 1699 cm.$^{-1}$, strong at 1532 cm.$^{-1}$, and medium at 1426 cm.$^{-1}$. Antisymmetric carboxylate absorption was always stronger than that of symmetric carboxylate; CH_2 deformation gave strong absorption in the region 1441–1466 cm.$^{-1}$ with all eight compounds studied.

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Large Scale Synthesis of $H_2B(NH_3)_2{}^+BH_4{}^-$ and H_3NBH_3

BY S. G. SHORE AND K. W. BÖDDEKER

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Two compounds of empirical composition BNH_6 are known: the diammoniate of diborane, $H_2B(NH_3)_2{}^+BH_4{}^-$, and ammonia–borane, H_3NBH_3, the products of unsymmetrical and symmetrical cleavage, respectively, of diborane.[1] Previous synthetic procedures for $H_2B(NH_3)_2{}^+BH_4{}^-$ required slow, low temperature (below −100°) addition of diborane to ammonia in order to avoid vigorous reaction which could lead to side products.[1,2] Yields were restricted to several hundred milligrams (2–4 mmoles).

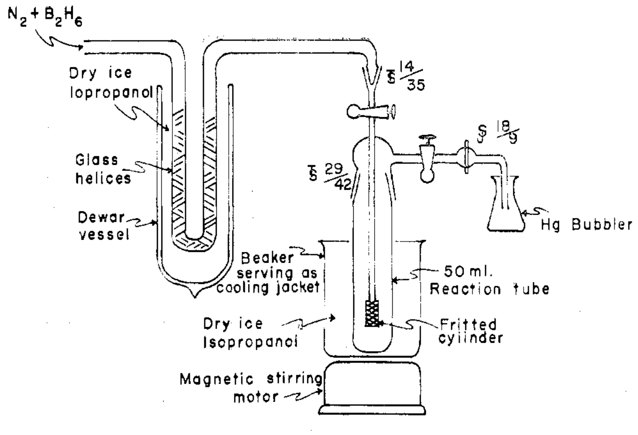

Fig. 1.—Reaction system.

We have found that by passing a stream of diborane, diluted in N_2, into liquid ammonia at −78°, an essentially quantitative yield of $H_2B(NH_3)_2{}^+BH_4{}^-$ is produced. The procedure described below is not only convenient, but is easily adaptable to relatively large scale runs. As much as 30 g. of diammoniate (0.5 mole) has been prepared at one time. However, the usual synthesis involves the preparation of 2 to 4 g. of product.

In a typical preparation of the diammoniate, diborane was generated according to the method of Shapiro and co-workers[3] by slowly dropping 15 ml. of $BF_3{\cdot}(C_2H_5)_2O$ into a suspension of 3 g. of $LiAlH_4$ in 150 ml. of ether. A continuous stream of N_2 flowing through the system carried the B_2H_6 from the generator to the reaction tube (Fig. 1), where it was dispersed through a frit beneath the surface of 20 ml. of liquid NH_3, at −78°. The solution was stirred continuously by means of a magnetic stirrer. One-half hour after the last drop of $BF_3{\cdot}(C_2H_5)_2O$ had been added to the $LiAlH_4$ solution, the side arm of the reaction tube was connected to a vacuum system; the solution was frozen in liquid nitrogen and NH_3 was sublimed away at −78°.

Diammoniate of diborane obtained from this procedure is a white, microcrystalline, free flowing solid. Its X-ray powder diffraction pattern is identical with that of diammoniate prepared in the conventional way. (Table I). No more than a trace amount of H_3NBH_3 can be extracted with ether from the solid product. Fresh samples of $LiAlH_4$, rated at 95+% (Metal

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[1] D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958); S. G. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958); R. W. Parry and S. G. Shore, *ibid.*, **80**, 15 (1958); R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958).

[2] H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 290 (1938); G. W. Schaeffer, M. D. Adams, and F. J. Koenig, *ibid.*, **78**, 725 (1956).

[3] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *ibid.*, **74**, 901 (1952).

Hydrides, Inc., Beverly, Mass.), have given maximum yields of 97% diammoniate.

Approximately equimolar amounts of diammoniate of diborane and ammonia-borane have been synthesized in the apparatus in Fig. 1. Diborane was dispersed in tetrahydrofuran at −78° to form THF·BH$_3$. About 10 ml. of liquid NH$_3$ was distilled onto the THF solution and the system was stirred for approximately 1 hr. at −78°. Ammonia and THF were distilled away and H$_3$NBH$_3$ was extracted with ether from the remaining solid mixture of ammonia-borane and diammoniate of diborane.

TABLE I
POWDER DIFFRACTION DATA[a]
FOR THE DIAMMONIATE OF DIBORANE

Relative intensity	d, Å.	Relative intensity	d, Å.
w	7.60	m	2.68
vw	6.69	m	2.59
w	5.99	w	2.51
w	5.37	w	2.40
w	5.13	m	2.31
vs	4.63	w	2.14
vs	4.25	m	2.089
w	4.05	vw	1.986
w	3.88	w	1.788
vw	3.62	w	1.753
vs	3.50	w	1.732
vw	3.10	w	1.696
m	2.93	m	1.667
m	2.83		

[a] Cu Kα radiation.

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CONTRIBUTION FROM THE AIR FORCE CAMBRIDGE RESEARCH
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A New Compound, Boron Triiodide–Phosphorus Triiodide

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Lewis acid–base complexes of BBr$_3$ with PCl$_3$ and PBr$_3$ have been reported by Holmes.[1] Garrett and Urry[2] report a complex between B$_2$Cl$_4$ and PCl$_3$. This subject has also been reviewed recently by Stone.[3] In work relating to the preparation of boron phosphide, the authors have recently synthesized a new compound, boron triiodide–phosphorus triiodide, I$_3$B:PI$_3$. The only earlier reported results on iodides of boron and phosphorus are those of Moissan,[4] who reported the reaction $2BI_3 + 3P \rightarrow 2BPI_2 + PI_2$. Heating the BPI$_2$ in hydrogen produces BPI and finally BP.

Experimental

Synthesis.—Phosphorus triiodide is prepared from the elements in carbon disulfide solution, a modification of the method of Germann and Traxler.[5] Boron triiodide is also prepared directly from the elements using the method of McCarty and Carpenter.[6] For the synthesis of I$_3$P:PI$_3$, BI$_3$ (about 0.1 mole) in 100 ml. of CS$_2$ is added to 200 ml. of CS$_2$ containing PI$_3$ (about 0.1 mole). The purple color of the latter solution indicates the presence of excess iodine. A yellow precipitate forms immediately, which is collected by filtering and washed with CS$_2$ until the filtrate is colorless. All operations are performed under a helium atmosphere. The material is then vacuum dried and stored in an inert atmosphere.

The boron content was determined by the quinalizarin method,[7] the phosphorus by the magnesium pyrophosphate method,[8] and the iodine by precipitation as AgI.[9] *Anal.* Calcd. for I$_3$B:PI$_3$: B, 1.34; P, 3.86; I, 94.8. Found: B, 1.33; P, 3.85; I, 97.4. This would correspond more closely to BPI$_{6.2}$; the excess iodine probably is the result of iodine occlusion in the precipitate.

Results

Properties.—The compound formed does not melt below 225° but some decomposition is observed even below this temperature. The vapor pressure at 20°

TABLE I
X-RAY STRUCTURE OF IODIDE COMPOUNDS[a]

BPI$_6$		BI$_3$		PI$_3$	
I/I_0	d, Å.	I/I_0	d. Å	I/I_0	d, Å.
m	3.57	m	3.71	vw	4.70
w	3.39	w	3.49	m	3.67
m	3.30	s	3.18	w	3.52
m	3.23	vw	2.79	vw	3.28
w	3.19	m	2.55	s	3.19
s	3.09	w	2.30	vw	2.83
w	2.84	s	2.035	m	2.55
w	2.74	w	1.955	vw	2.32
vw	2.55	w	1.87	m	2.05
vw	2.47	m	1.785	m	2.02
vw	2.42	m	1.71	vw	1.96
w	2.16	w	1.685	vw	1.84
m	2.10	w	1.65	m	1.79
w	1.99	w	1.59	m	1.725
w	1.90	vw	1.54	w	1.66
w	1.87	vw	1.452	w	1.64
m	1.795	w	1.435	vw	1.60
m	1.775	m	1.375	vw	1.545
vw	1.74			w	1.44
vw	1.72			vw	1.38
vw	1.705			vw	1.37
vw	1.695				
+15 very weak lines down to 1.1 Å.					

[a] I/I_0 = relative intensity; I_0 is the intensity of the strongest line. s, strong; m, medium; w, weak; vw, very weak.

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(2) A. G. Garrett and G. Urry, *Inorg. Chem.*, **2**, 400 (1963).

(3) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

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(5) F. E. E. Germann and R. N. Traxler, *J. Am. Chem. Soc.*, **49**, 307 (1927).

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(7) D. Boltz, Ed., "Colorimetric Determination of Non-metals," Interscience Publishers, New York, N. Y., 1958, p. 343.

(8) J. H. Hildebrand, *et al.*, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 702.

(9) Reference 8, p. 734.