X-Ray Diffraction.—The X-ray diffraction patterns of lycoctonine, anthranoyllycoctonine and ajacine were determined using a General Electric XRD-1 unit (Figs. 1–3). The X-ray tube had a copper target. A nickel filter was used to provide Kα radiation. The samples were prepared by mixing the finely powdered crystalline material with du Pont liquid cement to give an adhesive mixture. This mixture was rubbed between two microscope slides until a thin pencil of sample, about 0.5 mm. in diameter, was formed. The exposures were four hours in duration using 40,000 volts and 20 milliamperes.

Ultraviolet Absorption.—These data were obtained by using a model DU Beckman spectrophotometer. The solvent was in all cases purified 95% ethanol.[14] The results are plotted as specific extinction coefficient *vs.* wave length in mμ (Figs. 4–6). It will be noted that lycoctonine exhibits strong adsorption in the region 220 to 260 mμ. This phenomenon has previously been observed by Craig, *et al.*,[15] in the cases of other aconite alkamines.

Acknowledgment.—The author wishes to express his appreciation to Mr. C. S. Gilbert, Dr. E. R. Schierz and Dr. C. D. Heaton for their active interest and aid during the course of this investigation.

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[14] G. R. Harrison, R. C. Lord, J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 418.

[15] L. C. Craig, L. Michaelis, S. Granick and W. A. Jacobs, *J. Biol. Chem.*, **154**, 293 (1944).

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Studies Relating to Boron. IV. *n*-Butylboron Chlorides[1]

BY ROBERT B. BOOTH[2] AND CHARLES A. KRAUS

The preparation of dibutylboron chloride and butylboron dichloride are described. The chlorides undergo ammonolysis in liquid ammonia and ethylamine. A method is described for analyzing for boron in the presence of interfering elements such as germanium. Dibutylboron chloride reacts with sodium triphenylgermanide in ether solution.

I. Introduction

During the course of investigations relating to the chemistry of certain compounds of boron we have had occasion to prepare alkylboron chlorides as starting compounds for certain reactions.[3] Since alkyl derivatives of the type $(C_4H_9)_2BCl$ and $C_4H_9BCl_2$ were unknown at the time, it was necessary to devise methods for their preparation. We have prepared the monochloride by treating tri-*n*-butylborane with anhydrous hydrogen chloride. In addition, we found it convenient to prepare the dichloride by treating hydrogen chloride with dibutylboron chloride (or tributylboron) in the presence of aluminum chloride.[4]

The monochloride was found to ammonolyze in liquid ammonia and ethylamine, the corresponding amino compounds being formed. Ammonolysis of butylboron dichloride results in the formation of *n*-butylboron imine, doubtless as a polymer.

Lastly, the reaction of dibutylboron chloride with sodium triphenylgermanide was studied in a preliminary fashion. Evidence was obtained which indicates the formation of a bond between germanium and boron, but the nature of the product was not established.

II. Materials, Apparatus and Procedure

1. **Materials. Boron Trichloride.**—Boron trichloride, prepared by Dr. J. E. Smith[3] was on hand in the laboratory.

Tri-*n*-butylborine.—This compound was prepared by treating boron trichloride with *n*-butylmagnesium bromide according to the procedure described by Smith.[3] By using an efficient column, a 70% yield of product was obtained which distilled between 208–210°. This material was analyzed for boron by Smith's method[3] with the following results: wt. subst., 0.3272, 0.2607 g.; 15.50, 12.45 cc. 0.1175 *N* NaOH; found: B, 6.02, 6.07; calcd. for Bu_3B: B, 5.94.

Solvents.—Ether was purified and dried with sodium benzophenone as recommended by Smith.[3] Liquid ammonia and ethylamine were treated with alkali metal as described in earlier papers from this Laboratory.

2. **Apparatus and Procedure.**—Reactions in liquid ammonia and ethylamine were carried out in an apparatus similar to those described in earlier papers.[5] Gases evolved during reaction were dried over phosphorus pentoxide and purified. Gas densities were determined by weighing bulbs of known volume containing the gas at measured temperature and pressure. Volatile products of reaction were purified by fractional, vacuum distillation and were collected in fragile, weighed, glass traps as described by Kraus and Toonder.[5a]

The alkyl boron halides were prepared in an all-glass apparatus, provided with an electrically heated reaction tube, a generator for producing hydrogen chloride and a trap cooled with liquid ammonia for trapping volatile products which might be carried over with the exit gases.

Tributylborine was introduced through a side-arm on the reaction tube, with purified nitrogen passing through the system to prevent the entrance of air. The side tube was sealed off and the system was exhausted to remove the nitrogen. Dry hydrogen chloride was introduced at controlled rates into the reaction vessel through a sealed-in tube which extended beneath the surface of the borine.

Exit gases were passed through a cold trap to remove volatile products and then over caustic to remove hydrogen chloride. Product gases were identified by analysis and molecular weight determinations. Liquid products were distilled into a trap *in vacuo*, fractionated and collected in weighed, fragile bulbs.

3. **Boron Analysis.**—Boron in the alkylborines or partially chlorinated borines may be determined readily by Smith's method.[3] However, in the presence of compounds containing interfering elements, such as germanium, the boron must first be separated out quantitatively. In such cases, a convenient method is to convert the boron to its methyl ester whose azeotrope with methanol boils at 56°. In the procedure developed by Chapin[6] the boron is first

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[1] This paper is based on a portion of a thesis presented by Robert B. Booth in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1934.

[2] University Fellow in Brown University, 1931–1932; Herbert W. Rice Fellow, 1932–1933.

[3] J. E. Smith and C. A. Kraus, THIS JOURNAL, **73**, 2751 (1951).

[4] In a more recent investigation, J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., *ibid.*, **60**, 115 (1938), have described the preparation of dibutylboron bromide using much the same method. In addition they found that bromine is capable of converting the borine to the dibromide. Also, E. Wiberg and J. Ruschmann, *Ber.*, **70**, 1583 (1937), prepared dimethylboron chloride.

[5] See, for example: (a) C. A. Kraus and F. E. Toonder, THIS JOURNAL, **55**, 3552 (1933); (b) C. A. Kraus and C. L. Brown, *ibid.*, **52**, 4031 (1930).

[6] W. H. Chapin, *ibid.*, **30**, 1691 (1908).

oxidized to boric acid, anhydrous methanol is added and the ester is distilled off and hydrolyzed in dilute caustic solution. Ordinarily, to separate the boron completely, at least 200 cc. of distillate must be collected.

We have been able to shorten the time required for analysis materially by modifying the distillation process somewhat. The apparatus was constructed entirely of glass and an effective fractionating column of the Eastman type[7] was employed to obtain more efficient fractionation of the boron methyl ester. Complete removal of boron was effected in 30–40 cc. of distillate, and, as pointed out by Schaak,[8] methanol need not be removed before titration.

The method was checked by analyzing known amounts of boric acid alone and in mixtures with hexaphenyldigermane as described below. Blanks were run on all reagents. Boric acid was twice recrystallized from water; hexaphenyldigermane was available in the laboratory.

Using 70 mg. of boric acid, 50 cc. of methyl alcohol and one drop to 10 cc. of sulfuric acid in different determinations, four successive fractions of 10 cc. were taken off and titrated with 0.05795 *N* sodium hydroxide; the titrated values checked the original sample to ± 0.16%.

By use of 100 cc. of methanol, 10 cc. of sulfuric acid, 60 mg. of boric acid and 200 mg. of hexaphenyldigermane, four 12-cc. fractions of distillate were collected and titrated. Before adding the methanol, the digermane was heated in the sulfuric acid until well charred. In two determinations, 16.54 and 17.86 cc. of 0.05795 *N* NaOH were used in titration, the calculated amounts were, respectively, 16.45 and 17.80 cc. Approximately 80% of the ester came over in the first sample (12 cc.) of distillate and 17% in the second.

From the close agreement between the amount of sodium hydroxide used and that calculated, it is apparent that the method may be applied satisfactorily for the determination of boron in the presence of germanium.[9]

III. Experimental

1. Di-*n*-butylboron Chloride.—Practically quantitative yields of dibutylboron chloride may be obtained by passing anhydrous hydrogen chloride through tri-*n*-butylborine heated to 110°. Reaction proceeds substantially according to the equation

$$Bu_3B + HCl = Bu_2BCl + C_4H_{10} \qquad (1)$$

Further cleavage of alkyl groups does not occur under these conditions, but, at higher temperatures, the dichloride and boron trichloride are also formed. In addition, butylene and hydrogen are formed, and the proportion of butylene decreases with increasing temperature.

Twelve grams of tri-*n*-butylborine was treated with anhydrous hydrogen chloride at 110° according to the procedure outlined above. In all, 220 cc. of hydrogen chloride was passed through the borine over a period of 22 hours. The molecular weight of the exit gas was 55, indicating that it was essentially butane (mol. wt. 58). The product was collected in fragile bulbs as described above; distillation commenced at 0.95 mm. and proceeded more rapidly at 0.6 mm. A very small residue of higher boiling material was not collected.

Analyses.—Analyses were made for boron and chlorine. Weighed bulbs of the substance were broken under a solution consisting of 50 cc. of water, 2 cc. of 6 *N* NaOH and 5 cc. of 30% hydrogen peroxide. Boron was determined as described above and chlorine was determined as AgCl. **Boron**: wt. subst., 0.3484, 0.2529 g., 37.50, 27.0 cc. 0.05773 *N* NaOH; found: B, 6.72, 6.69; calcd. for Bu_2BCl: B, 6.75. **Chlorine**: wt. subst., 0.3484, 0.2529, 0.3617 g.; wt. AgCl, 0.3096, 0.2236, 0.3205 g.; found: Cl, 21.98, 21.87, 21.91; calcd. for Bu_2BCl: Cl, 22.10.

Properties.—Di-*n*-butylboron chloride is a clear, colorless liquid boiling at 173°; at room temperature it boils at approximately 1 mm. It is readily hydrolyzed and ammonolyzed. It may be chlorinated by anhydrous hydrogen chloride in the presence of aluminum chloride to yield *n*-butylboron dichloride.

2. Di-*n*-butylboron Amine.—When a solution of dibutylboron chloride in liquid ammonia is treated with sodium, hydrogen is evolved and di-*n*-butylboron amine may be isolated from the reaction products. Apparently, the chloride ammonolyzes according to the equation

$$(C_4H_9)_2BCl + 2NH_3 = (C_4H_9)_2BNH_2 + NH_4Cl \qquad (2)$$

In this respect, boron differs from gallium, since dimethylgallium chloride does not ammonolyze in liquid ammonia.[5a]

When a fragile bulb containing dibutylboron chloride was broken in a reaction tube containing gaseous ammonia, reaction took place immediately with the evolution of heat and the formation of a white solid. Ammonia was condensed in the tube and a slight excess over the equivalent amount of sodium was added in small pieces. Gas was evolved, and, on the addition of the last piece of sodium, the solution acquired the blue color of free metal. The gas evolved was identified as hydrogen. Following are data from two experiments: (1) mmoles Bu_2BCl, 3.181; m.at. Na, 3.241; m.at. H_2 evolved, 3.210; at. H/at.B, 1.009. (2) 1.848; 1.901; 1.777; 0.962. In expt. (1), the molecular weight of the evolved gas was 3.58; evidently, it was hydrogen contaminated with air and a correction was made for air in calculating the milliatoms of hydrogen evolved. In reaction (2), the determined molecular weight was 2.42, which was within the error of weighing.

The residue, after evaporation of the ammonia, was a pasty material from which a liquid product, identified as di-*n*-butylboron amine, was obtained by distilling at 100° under a pressure of 0.01 mm. The compound solidifies at a temperature slightly below the boiling point of ammonia, −33.4°.

Analyses.—Analyses were made for boron and nitrogen. Sealed, fragile bulbs of the amine were broken under approximately 50 cc. of standard hydrochloric acid. The boron compound appeared to react at once, and the oily layer which formed on the surface of the acid solution went into solution immediately on the addition of 2 cc. of 30% hydrogen peroxide. Nitrogen was determined by titrating the excess hydrochloric acid with standard base to the methyl red end-point. Boron was then determined in the usual fashion. **Nitrogen**: wt. subst., 0.1578, 0.3266 g.; 30.94, 76.61 cc. 0.05621 *N* HCl; 10.92, 35.07 cc. 0.05773 *N* NaOH; found: N, 9.85, 9.78; calcd. for Bu_2BNH_2: N, 9.94. **Boron**: wt. subst., 0.1578, 0.3266 g.; 19.25, 39.91 cc. 0.05781 *N* NaOH; found: B, 7.60, 7.63; calcd. for Bu_2BNH_2: B, 7.67.

3. Di-*n*-butylboron Ethylamine.—The reaction of di-*n*-butylboron chloride with ethylamine is analogous to that with ammonia. On the addition of lithium to a solution of the chloride in ethylamine, hydrogen is evolved and di-*n*-butylboron ethylamine may be isolated from the reaction products. Apparently, reaction with the amine occurs according to the equation

$$(C_4H_9)_2BCl + 2C_2H_5NH_2 = (C_4H_9)_2BC_2H_5NH + C_2H_5NH_3Cl \qquad (3)$$

The amine was distilled from the reaction vessel into weighed fragile bulbs. It distilled readily at 100° under a pressure of approximately 0.02 mm. Data on two reactions follow: (1) mmoles Bu_2BCl, 3.081; m.at. Li, 3.141; m.at. hydrogen evolved, 3.029 (mol. wt. 2.05); at.H/at.B, 0.982. (2) 2.987, 3.040, 2.938 (mol. wt. 2.03); 0.984.

Analyses.—Analyses for boron and nitrogen were made by the procedure described above. **Nitrogen**: wt. subst., 0.1929, 0.2942 g.; 40.73, 37.22 cc. 0.07071 *N* HCl; 30.32, 15.89 cc. 0.05749 *N* NaOH; found: N, 8.26, 8.18; calcd. for $Bu_2BC_2H_5NH$: N, 8.22. **Boron**: wt. subst., 0.1929, 0.2942 g.; 19.71, 29.29 cc. 0.05781 *N* NaOH; found: B, 6.38, 6.22; calcd. for $Bu_2BC_2H_5NH$: B, 6.40.

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[7] H. T. Clarke and E. J. Rahrs, *J. Ind. Eng. Chem.*, **15**, 349 (1923).

[8] M. F. Schaak, *J. Soc. Chem. Ind.*, **23**, 699 (1904).

[9] For the analysis of boron in the presence of fluorine, see D. L. Fowler and C. A. Kraus, THIS JOURNAL, **62**, 1143 (1940).

4. Reaction with $NaGePh_3$.—Although definite products were not isolated when di-*n*-butylboron chloride and sodium triphenylgermanide reacted in equivalent amounts in ether solution, indications were that a Ge–B bond was formed. Approximately 90% of the chlorine was recovered as sodium chloride. On evaporating the ether, a viscous, non-volatile, yellow liquid was obtained which contained both boron and germanium (an analysis gave 1.5 at. B/at. Ge) and which partially solidified at liquid ammonia temperatures. Attempts to work up crystalline products failed and a variety of substances were obtained, probably through air oxidation. Although the product did not react with sodium in liquid ammonia, treatment with bromine yielded triphenylgermanium bromide, together with an unidentified liquid containing approximately two atoms of bromine per atom of boron.

5. *n*-Butylboron Dichloride.—When tri-*n*-butylborane was treated with hydrogen chloride at temperatures between 180 and 210°, both butylboron dichloride and boron trichloride were formed. However, the products were contaminated with substantial quantities of the monochloride and purification proved difficult. On treating the monochloride with hydrogen chloride in the presence of aluminum chloride at 110°, approximately equal quantities of boron trichloride and butylboron dichloride were obtained. Since the boiling points of the two compounds differ widely, they may be separated readily by distillation. The less volatile product was fractionated and collected in fragile bulbs. The material distilled rapidly between 2.0 and 2.5 cm. pressure at room temperature.

Analyses.—The compound was analyzed for boron and chlorine using the procedure outlined in the case of the monochloride. Boron: wt. subst., 0.3136, 0.3233 g.; 39.28, 40.18 cc. 0.05773 *N* NaOH; found: B, 7.84, 7.76; calcd. for $BuBCl_2$: B, 7.80. **Chlorine:** wt. subst., 0.3126, 0.3233 g.; wt. AgCl, 0.6457, 0.6651 g.; found: Cl, 50.93, 50.88; calcd. for $BuBCl_2$; Cl, 51.08.

Properties.—*n*-Butylboron dichloride is a colorless liquid boiling at 107.9°. It fumes in air, but appears stable toward oxygen. It undergoes ammonolysis in liquid ammonia.

6. *n*-Butylboron Imine.—On treating a solution of butylboron dichloride in liquid ammonia with two equivalents of sodium, hydrogen was evolved and the imine was isolated as a slightly volatile liquid. Either the imine or the diamine might be expected as product, but under the conditions of the experiment, only the imine was obtained.

The ammonolysis was carried out as described above. After removing solvent, the tube was heated to 100–110° and exhausted with a pump. Material commenced to distill at 0.005 mm.; this was collected in fragile bulbs for analysis. The compound probably exists as some form of polymer.

Analyses.—Analyses were made for nitrogen and boron. Attempts to hydrolyze the product with a dilute solution of sodium hydroxide and peroxide were unsuccessful. Accordingly, the material was dissolved in concentrated sulfuric acid, and decomposed by heating until slight charring occurred. To ensure complete oxidation, a few cc. of 30% hydrogen peroxide were added (these operations were carried out in an evacuated tube). After cooling, the solution was made basic and the ammonia was distilled into a known volume of standard acid. The excess acid was titrated with standard base to determine the ammonia. Boron in the solution was determined after the nitrogen analysis. **Nitrogen:** wt. subst., 0.1194, 0.1673 g.; 75.95, 50.60 cc. 0.05621 *N* HCl; 49.22, 14.30 cc. 0.05773 *N* NaOH; found: N, 16.80, 16.91; calcd. for BuBNH: N, 16.90. **Boron:** wt. subst. 0.1194, 0.1673 g.; 24.72, 34.27 cc. 0.05781 *N* NaOH; found: B, 12.93, 12.80; calcd. for BuBNH: B, 13.05

Properties.—At room temperature, butylboron imine is a clear colorless liquid; the solid melts slightly above the boiling point of liquid ammonia (−33.4°). It may be distilled at 100° at 0.005 mm.

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