acid in 100 cc. of ethyl alcohol was refluxed for fifteen minutes with 2.0 cc. (2.19 g., 0.02 mole) of phenylhydrazine. The mixture was cooled in an ice-bath and water was added dropwise to the solution until 100 cc. had deen added. The resulting precipitate was isolated by filtration and recrystallized from ethyl alcohol. The recrystallized phenylhydrazone melted at 264–265°.

7-Aminofluorenone-2-carboxylic Acid.—To a suspension of 10 g. (0.04 mole) of 7-nitrofluorenone-2-carboxylic acid in 600 cc. of ethyl alcohol was added 80 cc. of concentrated ammonium hydroxide. The suspension was heated to its boiling point and hydrogen sulfide gas was passed into it for one hour during which time the solid material dissolved and the solution took on a dark red color. The solution was boiled an additional half hour to remove excess hydrogen sulfide and ammonia. After cooling the solution it was filtered and the filtrate poured into 800 cc. of water. Acidification of the aqueous solution with 1:5 hydrochloric acid gave a dark red solid. The crude product was dissolved in 400 cc. of hot 2% potassium hydroxide and 0.5 g. of Darco. After filtration the hot filtrate was acidified by dropwise addition of 20 cc. of hydrochloric acid (1:5), the product separating as a precipitate. The resulting dark red powder did not melt below 360°. The yield was 7.5 g. (85%).

Anal. Calcd. for $C_{14}H_9O_3N$: C, 70.29; H, 3.77; N, 5.85. Found: C, 69.89; H, 4.00; N, 5.73.

7-Nitro-2-acetylfluorenone.—The alkali insoluble material from the oxidation described above was recrystallized twice from glacial acetic acid and once from xylene. The product formed as fine lemon-yellow needles, melting sharply at 234°.

Anal. Calcd. for $C_{15}H_9O_4N$: N, 5.24. Found: N, 5.08.

7-Nitrofluorenone-2-carbonyl Chloride.—Fifteen grams (0.056 mole) of crude 7-nitrofluorenone-2-carboxylic acid was refluxed with 400 g. of redistilled thionyl chloride for twelve hours, provision being made to trap the escaping sulfur dioxide and hydrochloric acid. The excess thionyl chloride was removed by distillation and the residue recrystallized from toluene or chlorobenzene. The yield of acid chloride was 15.0 g. (99 + % theoretical). The bright yellow crystalline compound melted at 246–248°.

Anal. Calcd. for $C_{14}H_6O_3NCl$: N, 4.87; Cl, 12.34. Found: N, 5.16; Cl, 12.42.

β-Diethylaminoethyl-7-nitrofluorenone-2-carboxylate Hydrochloride.—This preparation is typical of the method used for the preparation of the esters used in this work. To a solution of 6.5 g. (0.023 mole) of 7-nitrofluorenone-2-carbonyl chloride in 350 cc. of dry chlorobenzene in reflux was added dropwise over a period of one half hour a solution of 3.2 cc. (2.8 g., 0.025 mole) of β-diethylaminoethanol in 25 cc. of chlorobenzene. The hydrochloride of the alkylamine ester separated as a yellow crystalline solid which was collected and washed twice with 30-cc. portions of ether. The yield of the crude product was 8.5 g. (92.4 %). A portion, recrystallized from methyl alcohol, melted with decomposition at 230–232°.

The free base, prepared by dropwise addition of sufficient ammonium hydroxide to neutralize the hydrochloride, separated as bright yellow crystals which, recrystallized from a methyl alcohol–water mixture, melted at 134–136°.

Anal. Calcd. for $C_{20}H_{20}O_5N_2$: N, 7.61. Found: N, 7.67.

The nitric acid salt was prepared as a finely crystalline, water insoluble, yellow material by adding 5 cc. of dilute nitric acid (6 *N*) to a solution of 0.1 g. of the ester hydrochloride in 250 cc. of hot water. The product melted sharply at 214–215°.

Anal. Calcd. for $C_{20}H_{21}O_8N_3$: N, 9.75. Found: N, 10.03.

β-Diethylaminoethyl-7-aminofluorenone-2-carboxylate.—Six grams (0.015 mole) of β-diethylaminoethyl-7-nitrofluorenone-2-carboxylate was dissolved in 400 cc. of hot ethyl alcohol and 8 cc. of ammonium hydroxide. Hydrogen sulfide was bubbled into the hot solution over a period of one half hour, the solution changing to a dark red color. A solution of 50 cc. of 12 *N* hydrochloric acid in 400 cc. of water was added to the warm reaction mixture. The hot acid solution was filtered twice to remove free sulfur and then made alkaline with 6 *N* ammonium hydroxide and allowed to stand overnight. The bright red, finely divided precipitate which separated was recrystallized from an alcohol–water solution yielded 2.5 g. (50% theoretical) of the amine as red needles which melted at 215–216°.

Anal. Calcd. for $C_{20}H_{22}O_3N_2$: N, 8.28. Found: N, 8.02.

Summary

1. A series of alkylamino esters of 7-nitrofluorenone-2-carboxylic acid and 7-aminofluorenone-2-carboxylic acid have been prepared for evaluation as topical anesthetics or for possible antispasmodic action.

2. The preparation of pure 7-nitrofluorenone-2-carboxylic acid and the proof of its structure has resolved the question of its correct melting point.

CINCINNATI 21, OHIO RECEIVED MARCH 17, 1949

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

Lower Iodides of Boron

BY WALTER C. SCHUMB, E. LEE GAMBLE AND MARIO D. BANUS

Although numerous points of resemblance may be observed in the chemistry of boron and silicon compounds, up to the present time a striking exception in the behavior of boron has been the lack of halides other than the well-known series of trihalides, BX_3. Except for the compound B_2Cl_4, first reported by Stock,[1] who succeeded in isolating a drop of the unstable liquid, no binary halides with B–B bonds appear to have been prepared. From the known instability of Stock's B_2Cl_4, it seemed reasonable to believe that synthetic methods operating at elevated temperatures would probably fail to yield such compounds as B_2Br_4 or B_2I_4 unless some means of "freezing-out" the desired products could be resorted to, whereby their decomposition might be held in check.

Preliminary experiments in which it was planned to prepare a lower iodide of boron, such as B_2I_4, by reduction of boron triiodide under conditions favoring the prevention of decomposition of the desired product, included the use of the "hot–cold" tube devised by St. Claire Deville[2]

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[1] Stock, Brandt and Fischer, *Ber.*, **58B**, 653 (1925).

[2] St. Claire Deville, "Leçons sur la Dissociation, Leçons de Chemie," Soc. Chim. de Paris, 1864–1865.

and successfully employed by various other experimenters.[3,4] When a mixture of the vapors of boron triiodide and hydrogen was passed through such an apparatus, indications of the formation of a sub-iodide on the cold element of the tube were obtained, but in exceedingly small yields, together with a copious deposit of elementary boron on the hot glass surfaces.

Again the reduction of boron triiodide by means of metallic silver in a reaction analogous to that for the preparation of Si_2I_6[5,6] led to the result that, contrary to the earlier reports of Moissan,[7] reaction is appreciable at as low a temperature as 185°, iodine being liberated which is converted by the silver present into silver iodide, and a black, non-volatile solid being formed which was not separated in a pure form but which, from its similarity in properties to preparations by other methods, described below, we believe contained the monoiodide, $(BI)_n$.

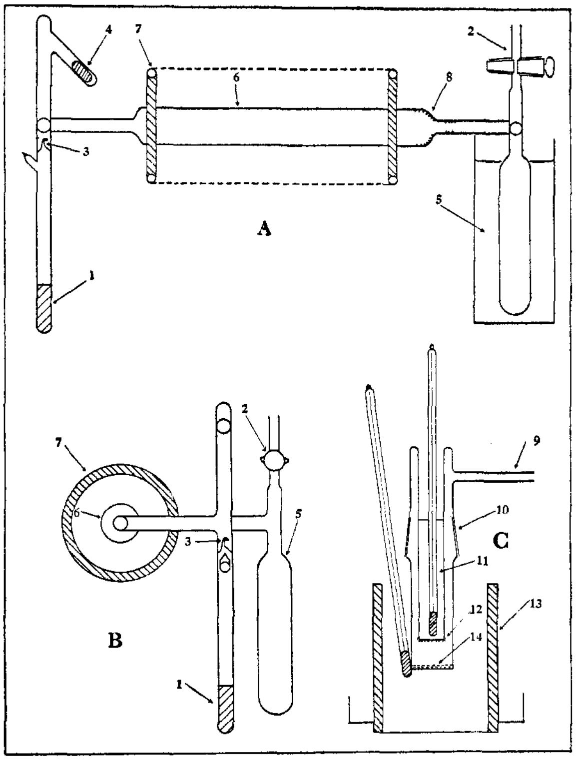

Fig. 1.—A and B: 1, Boron triiodide in sealed ampule; 2, outlet to pumping system; 3, break-off tip; 4, glass-covered steel magnetic breaker; 5, trap, cooled by liquid nitrogen; 6, 20 × 250 mm. glass tube; 7, 3″ copper solenoid, R. F. antenna; 8, crystals of yellow tetraiododiborine formed during reduction; C: 9, 9-mm. tubing to Hyvac-backed, mercury diffusion pump; 10, 29/42 ground joint; 11, ethanol cooled by Dry Ice to −20 to −30°; 12, pure tetraiododiborine as pale yellow sublimate; 13, Variac-controlled heating element; 14, crude tetraiododiborine from glow reduction.

Furthermore, it had been noted in the preparation of boron triiodide that the pure white color of the freshly prepared compound changed to a dark color when the substance was melted and that when heated above the melting point in a sealed evacuated tube boron triiodide decomposed, liberating iodine and forming a dark-colored solid, the color deepening as the temperature was increased. That an equilibrium process was not involved was shown by the fact that the depth of color did not lessen when the temperature was lowered to just above the melting point and held for a long time. The dark solid formed from 4 g. of triiodide heated at 250° for twenty-four hours in the sealed tube, when separated from unchanged triiodide by volatilization of the latter, gave reactions consistent with a lower iodide of boron and closely resembled the product described below which was obtained by the action of the electrodeless discharge on the vapors of boron triiodide.

In view of the results obtained from the exploratory experiments it was concluded that in order to prepare tetraiododiborine, a method of reduction would be required that did not raise the temperature of the products above room temperature. In the method used, a radio-frequency electrodeless discharge supplied the "cold" energy for the reduction.

Experimental

The electrodeless radio-frequency discharge apparatus used was that described by Schumb and Bickford[8] for use in the study of the dissociation of carbon dioxide at low temperatures. A 2000 v. d. c. power supply drove a 250-watt 204-A transmitting tube at frequencies from 4600 to 5200 k. c. with a tank current output of from 7–8 amp. R. F. The glass system (Fig. 1, A and B) made it possible to fill the boron triiodide ampule in the dry box with 4–8 g. of freshly sublimed boron triiodide followed by evacuation to <0.5 mm. and sealing, then to assemble the glass apparatus through the central 3″ solenoid. When the glass system was flame-dried and evacuated carefully by a Hyvac pump, the stopcock was closed, sealing the system. The break-off tip to the boron triiodide ampule was broken by the magnetic breaker allowing the iodide to sublime through the glow tube to the liquid nitrogen cooled trap. By keeping the boron triiodide supply at between 35 to 40°, a pressure of 1 to 3 mm. could be maintained in the glow tube, this vapor pressure giving an intense greenish-yellow glow when the R. F. transmitter was turned on. Under certain conditions, the glow would extend some distance beyond the ends of the glow tube in both directions. Free iodine along with the un-

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(3) See R. C. Young, *J. Chem. Education*, **20**, 8, 378 (1943).

(4) Schumb and Morehouse, THIS JOURNAL, **69**, 2696 (1947).

(5) Friedel and Ladenburg, *Bull. soc. chim.*, **12**, 92 (1869).

(6) Schwarz and Pflugmacher, *Ber.*, **75B**, 1062 (1942).

(7) Moissan, *Compt. rend.*, **112**, 717 (1891), observed no reaction up to 500°.

(8) Schumb and Bickford, THIS JOURNAL, **58**, 1038 (1936).

reacted boron triiodide condensed in the liquid nitrogen, and the boron triiodide could be recovered later for reuse.

It required from four to six hours to sublime the boron triiodide through the discharge apparatus. Shortly after the glow started, fine yellow crystals could be seen at the exit constriction of the glow tube, gradually building up to a mass of yellow, crystalline material. Near its inlet, the glow tube gradually became coated with a black deposit which spread finally along the full length of the glow tube and back toward the boron triiodide supply, becoming so dense that it obscured the glow in the tube. When all the boron triiodide had passed through, the glow tube was sealed beyond the bends at both ends and placed in the dry box where it was opened carefully and the yellow crystals and black wall deposit scraped into weighed vials. The former, when sublimed at <0.1 micron and 60 to 70° in the molecular still (C, Fig. 1) gave a pale yellow sublimate and a trace of black residue. This yellow material had to be analyzed promptly since it decomposed even at room temperature. It could be kept undecomposed for a longer period in sealed evacuated ampules if refrigerated and kept out of the light. Analysis showed this compound to be B_2I_4. From the weight of solid products obtained in the reduction, it was calculated that 40% of the boron triiodide was reduced and recovered as lower iodides. One third of the reduced portion went to B_2I_4 according to the equation: $2BI_3 \rightarrow B_2I_4 + I_2$. The rest of the reduced boron triiodide was converted to the black deposit, a boron iodide or mixture of variable composition, B_xI_y, where $x > y$, according to the equation: $xBI_3 \rightarrow B_xI_y + (3x - y)/2I_2$.

Properties of the Lower Iodides.—Tetraiododiborine (B_2I_4) is a pale yellow, crystalline substance which at room temperature showed slow decomposition which increased rapidly with rising temperature and with exposure to sunlight. This decomposition occurred according to the equation: $xB_2I_4 \rightarrow yBI_3 + (BI)_{2x-y} + (x - y)I_2$. However, at room temperature only a trace of iodine was formed so that the decomposition became essentially a disproportionation. Larger quantities of iodine were formed at higher temperatures or under the action of sunlight. The decomposition of tetraiododiborine therefore proved to be an excellent method for preparing the monoiodide of boron, $(BI)_x$, a black, non-volatile, polymerized material. Tetraiododiborine dissolved in water with rapid, vigorous hydrolysis, forming an acid solution with strong reducing properties from which silver nitrate precipitated silver iodide, followed, on adding more of the reagent, by silver metal. On hydrolysis in 10% sodium hydroxide nearly the theoretical quantity of hydrogen was evolved according to the equation: $B_2I_4 + 8OH^- \rightarrow 2HBO_3^= + H_2 + 2H_2O + 4I^-$. Tetraiododiborine showed no melting point when heated in a sealed evacuated melting point tube, but started to decompose at about 80°, being completely decomposed by 250° with I_2 and BI_3 subliming to the top of the tube, leaving behind a black residue. It was not possible to detect any solubility of the iodide in carbon disulfide, carbon tetrachloride or cyclohexane, since these solvents slowly decompose the iodide with the liberation of iodine.

The black, polymerized monoiodide of boron was far more stable than the tetraiododiborine. It could be kept apparently indefinitely at room temperature if it were in a sealed, dry vial or ampule. Like tetraiododiborine, the $(BI)_x$ was apparently insoluble in carbon disulfide and carbon tetrachloride, with the solvents decomposing the iodide and giving a concentrated solution of iodine. The monoiodide was hydrolyzed by water to give a similar clear acid solution with strong reducing properties, but in this case the silver metal precipitated at the same time as did the silver iodide, giving a red-brown curd unlike the two-layer precipitate from the hydrolysis solution of the B_2I_4. In addition it was a much harder task to oxidize all the boron back to the trivalent state in the case of the monoiodide. On heating $(BI)_x$ in a sealed, evacuated, melting point tube it gave no melting point but did decompose above 125°, giving off iodine and leaving a black residue. On rapid heating in a micro flame a second sample appeared to be decomposed into boron and iodine. $(BI)_x$ had a vapor pressure of <0.1 micron at 110°.

The boron iodide of variable composition, B_xI_y, was very similar to $(BI)_x$ and was originally thought to be the latter compound. However, with larger samples and further study, indications of difference were found, especially with regard to their hydrolysis. B_xI_y when hydrolyzed gave the expected acid solution with strong reducing properties, but in addition it always gave varying amounts of a pale yellow, highly unreactive hydrolysis product which contained boron, iodine, oxygen and probably hydrogen. When the total analysis of boron and iodine from the solution and residue was made, the atomic ratio of boron to iodine varied between 1 and 3. The material may have been a mixture of $(BI)_x$ and another iodide but since the latter was apparently just as non-volatile and insoluble as the monoiodide no separation could be made. B_xI_y was found to be very stable to heat, giving only a trace of decomposition up to 260°; but with rapid higher heating in a free flame it decomposed to the elements. It was much more stable than the other iodides described toward the solvents carbon tetrachloride, cyclohexane and benzene, being only slowly decomposed over a period of several days. It did not show any tendency to dissolve, however.

Analysis of the Lower Iodides.—The iodides were analyzed by hydrolyzing weighed samples in 50-ml., glass-stoppered Erlenmeyer flasks, diluting to volume in volumetric flasks and taking two aliquots each for the boron

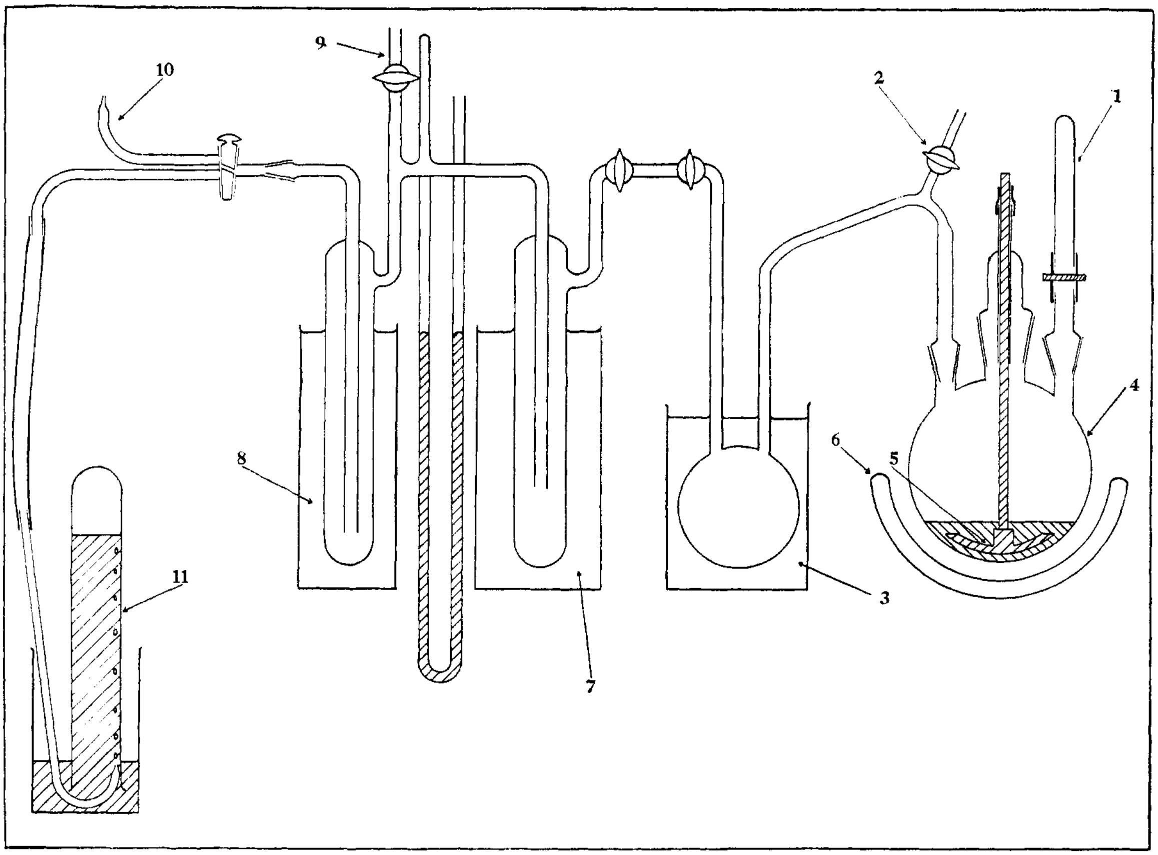

Fig. 2.—1, 20 × 170 mm. tube containing sodium or lithium borohydride; 2, inlet for dry purified nitrogen; 3, trap 1, 500-ml. flask cooled by ice; 4, 500-ml. 3-necked reaction flask containing the molten I_2; 5, nickel-shafted, Monel stirrer; 6, Variac-controlled Glas-col heating mantle; 7, trap 2, cooled by Dry Ice and ethanol; 8, trap 3, cooled by liquid nitrogen; 9, outlet to pumping system; 10, sweeping vent; 11, hydrogen measuring cylinder, 48 × 385 mm.

and iodine analyses. The aliquots were treated with 50% hydrogen peroxide and then made just basic to oxidize the boron. When the oxidation was complete, the excess hydrogen peroxide was destroyed by the use of platinum foil. For boron analysis the sample was made just acid to methyl red with sulfuric acid, then titrated to the methyl red end-point with standard base in a Koch microburet. Mannitol and phenolphthalein were added and the titration continued to the phenolphthalein end-point, giving the volume necessary for the boric acid. For iodine the sample was made acid with sulfuric acid excess, 0.2 *N* silver nitrate added, digested for one-hour hour and then filtered into weighed, fritted glass crucibles.

Analysis of B_2I_4

			Calcd.
Sample taken, g.	0.2808	0.2493	
Boron found, %	4.2	4.03	4.09
Iodine found, %	94.5	94.5	95.9
Atomic ratio of B:I	1:2.009	1:2.008	

Analysis of $(BI)_n$

			Calcd.
Sample taken, g.	0.1052	0.1075	
Boron found, %	7.7	7.8	7.9
Iodine found, %	90.9	92.7	92.1
Atomic ratio of B:I	1:1.008	1:1.013	

Preparation of Boron Triiodide.—The method developed for the preparation of boron triiodide used in the preparation of the lower iodides consisted of the reaction of sodium or lithium borohydride[9] with iodine, the reaction being carried out in a three-necked, round-bottom flask provided with an efficient mechanical stirrer and heated by means of an electric mantle. The temperature used in the case of sodium borohydride was about 200°; with lithium borohydride, 120–125°. Yields of 45–50% with the former compound and 64–66% on the basis of the boron involved with the latter were obtained. In a typical run from 5.1 g. of lithium borohydride (not recrystallized), 61 g. of BI_3 was obtained. The sodium borohydride was recrystallized before use from dried isopropylamine: the solution was centrifuged and decanted, the sodium borohydride freed from the amine by evaporation, followed by drying at 125° for thirty-six hours before it was finely powdered in an agate mortar. The reactions occurring between the borohydrides and iodine are somewhat complicated, but the principal over-all reaction deduced from the quantities of the respective products obtained may be represented as follows: $3NaBH_4 + 8I_2 \rightarrow 3NaI + 3BI_3 + 4H_2 + 4HI$; this main reaction being followed by side reactions involving reduction of boron to lower valences and to the element.

The preparation of boron triiodide was carried out in the apparatus shown in Fig. 2. Intermittent stirring was essential to high yields in the case of the preparation from sodium borohydride. On the other hand, temperature control to within the range mentioned was required for maximum yields with lithium borohydride so that a ther-

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[9] We are indebted to the Ethyl Gas Corporation, Detroit, Mich., to Metal Hydrides, Inc., of Beverly, Mass., for the sodium borohydride, and to Linde Air Products Co., Tonawanda, N. Y., for the lithium borohydride used in this work.

mocouple well and thermocouple replaced the stirrer in this case. At the end of the run, all the boron triiodide and the excess iodine were sublimed into trap no. 1, now cooled by Dry Ice and then this trap was sealed at the inlet and cut out of the system between the pair of stopcocks at the outlet of trap no. 1.

Purification of boron triiodide as obtained from the borohydrides was effected first by dissolving it and some of the excess iodine in purest carbon disulfide, reduction of the iodine by mercury and zinc dust, filtering to get a clear solution, then vacuum evaporation of the carbon disulfide to get the crude BI_3. This was then further purified by slowly subliming it over a small quantity of mercury at a pressure of about a millimeter. The resulting crystalline product was of varying shades of pink due to admixed mercuric iodide. Resublimation at low pressure in a type of molecular still (C, Fig. 1) gave colorless, glistening crystals, melting at 49.9 ± 0.5°, the melt assuming a pale pink color. The melting point previously reported for BI_3 is 43°.[6] Analysis of this purified product agreed well with the theoretical requirements of BI_3. Found: B, 2.78; I, 96.95. Calcd.: B, 2.77; I, 97.23.

Summary

1. Tetraiododiborine, B_2I_4, and a lower iodide of boron, B_xI_y, where $x > y$, have been prepared by the action of an electrodeless discharge at room temperature upon the vapors of boron triiodide at 1 to 3 mm. pressure. The decomposition is irreversible and is accompanied by a brilliant yellowish-green glow. Free iodine is formed and is trapped out by liquid nitrogen. Forty per cent. of the boron triiodide is reduced in one pass through the glow; one-third of the reduced boron triiodide is recoverable as tetraiododiborine.

2. B_2I_4 is a well-crystallized, pale yellow solid, which is slowly decomposed at room temperature, forming BI_3 and a black non-volatile residue of a polymerized monoiodide, $(BI)_x$. Decomposition is hastened by higher temperature and by the action of sunlight.

3. The lower iodides of boron are hydrolyzed by water yielding strongly reducing solutions which react with silver nitrate precipitating metallic silver and silver iodide.

4. A new and satisfactory method for the preparation of boron triiodide has been developed, in which solid sodium or lithium borohydride reacts with iodine at 200 or 120°, respectively. Yields as high as 66% on the basis of the boron involved were obtained using lithium borohydride.

5. The reduction of boron triiodide to lower iodides has been shown to occur in other ways, such as by the action of silver wool at 185° or by means of hydrogen in a "hot–cold" tube apparatus. These methods, however, are less satisfactory for preparative purposes than those employing the electrodeless discharge.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 6, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DEPAUW UNIVERSITY]

Trichloroaminoalcohols. I. 1,1,1-Trichloro-3-aminopropanol-2 and Derivatives

BY MARYANN COMPTON,[1] HARVEY HIGGINS,[2] LORNE MACBETH,[3] JANE OSBORN[4] AND HOWARD BURKETT

In 1942 Malkiel and Mason[5] described the synthesis of a compound (I), m. p. 167.4–167.7° (cor.), by the catalytic hydrogenation of 1,1,1-trichloro-3-nitropropanol-2 (II). They reported I to be 1,1,1-trichloro-3-aminopropanol-2 (III). The synthesis of III, m. p. 123°, was first reported[6] in 1935. In addition to III, Chattaway and Witherington also described and reported analyses for its hydrochloride, sulfate and oxalate salts and the mono- and di-acetyl derivatives.

Upon repeating the work of Malkiel and Mason, we obtained a product, m. p. 159–159.5° (uncor.), which was apparently the same as I. It was noted in our work that about 3.8–3.9 moles of hydrogen was consumed per mole of the nitro compound and that the product was much more soluble in water than was expected. Moreover, this product gives instantly a copious precipitate with aqueous silver nitrate. It was suspected that one of the chlorine atoms had been removed by hydrogenolysis, forming 1,1-dichloro-3-aminopropanol-2 hydrochloride (IV), which would give nearly the same nitrogen analysis as III. We have prepared the free amine and the N-benzoyl and O,N-dibenzoyl derivatives from this product, all of which give the correct analysis for the dichloro compound. As further confirmation of its structure, IV has also been synthesized as represented by the following equations.

$$\begin{tikzcd}
 & Cl_2CHCH(OC_2H_5)_2 \arrow[r] & Cl_2CHCHO \arrow[d, "CH_3NO_2"] \\
Cl_2CHCOHCH_2NH_2.HCl & & Cl_2CHCHOHCH_2NO_2 \arrow[ll]
\end{tikzcd}$$

The mixed melting point of this latter product with that from the catalytic hydrogenation of II is not depressed. From this evidence, it is thought that the compound reported by Malkiel and Mason was IV and not III.

Chattaway and Witherington prepared III by the reduction of II with tin and hydrochloric acid but they did not report the yield. A similar re-

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[4] Present address, Eli Lilly and Company, Indianapolis, Indiana.

[5] Malkiel and Mason, THIS JOURNAL, **64**, 2515 (1942).

[6] Chattaway and Witherington, *J. Chem. Soc.*, **137**, 1623 (1935).