798. *The Chemistry of Boron. Part II.* A Method for the Preparation of Iodoborines.*

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Tri-*n*-propylborine reacts with iodine above 140°. The main products are di-*n*-propyliodoborine of b. p. approx. 174° (slight disproportionation), plus *n*-propyl iodide, but there are small quantities of other products. A mechanism is postulated for the reaction, and the effect of disproportionation is discussed. Hydrolysis in the absence of air leads to di-*n*-propylborinic acid.

HALOGEN derivatives of the boron aryls but not of the boron alkyls were known when Krause and von Grosse produced their comprehensive treatise on organometallic compounds (" Die Chemie der Metallorganischen Verbindungen," Borntraeger, Berlin, 1937). Shortly afterwards, Wiberg and Ruschmann (*Ber.*, 1937, **70**, 1583) prepared methyldichloroborine, $BMeCl_2$, and dimethylchloroborine, BMe_2Cl, by the interaction of the appropriate boron halide and zinc alkyl, and commented that they are " very unstable " and disproportionate on fractional distillation *in vacuo*.

Three further methods for preparing alkylhalogenoborines have been developed in unpublished work by Wiberg and his collaborators (cf. Goubeau, F.I.A.T. Review of German Science 1939—1946, Inorganic Chemistry, Part I, 1948, p. 215).

The comparatively easy disproportionation has not prevented isolation and determination of the more important physical properties of some of the methyl- and ethyl-halogenoborines. Earlier reports of their instability thus appear to be somewhat exaggerated. In addition, Burg (*J. Amer. Chem. Soc.*, 1940, **62**, 2228) has prepared methyldifluoroborine, $BMeF_2$, and dimethylfluoroborine, BMe_2F, commenting that both compounds appear to be permanently stable at room temperature; it has proved possible to determine their structures by electron-diffraction experiments (Bauer and Hastings, *ibid.*, 1942, **64**, 2686).

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* Part I, *J.*, 1951, 1608.

n-Butylbromoborines have been prepared by the action of bromine on tri-*n*-butylborine (Johnson, Snyder, and Van Campen, *ibid.*, 1938, **60**, 115), but bromination of the alkyl groups also occurs to some extent. The corresponding chloro-compounds have recently been prepared by Booth and Kraus (*ibid.*, 1952, **74**, 1415) from tri-*n*-butylborine and hydrogen chloride.

It is in part by the use of the foregoing and related methods that analogous compounds of aluminium (see, *e.g.*, Bähr, F.I.A.T. Review, *op. cit.*, p. 155; von Grosse and Mavity, *J. Org. Chem.*, 1940, **5**, 106), silicon (Burkhard, Rochow, Booth, and Hartt, *Chem. Reviews*, 1947, **41**, 98), germanium (Johnson, *ibid.*, 1951, **48**, 259; Anderson, *J. Amer. Chem. Soc.*, 1951, **73**, 5440; 1952, **74**, 2370), and tin (Bähr, *op. cit.*) have also been prepared.

In the present work the action of iodine on tri-*n*-propylborine has been investigated. In spite of statements that the alkylborines do not react with iodine (Johnson *et al.*, *loc. cit.*; Frankland, *Proc. Roy. Soc.*, 1862, **12**, 123; *Annalen*, 1862, **124**, 129), a slow reaction was found to occur above 140° leading to the replacement of alkyl radicals by iodine, and the production of di-*n*-propyliodoborine in fair yield. A similar reaction occurs with tetra-alkylsilanes (Eaborn, *J.*, 1949, 2755). Tri-*n*-propylborine was chosen as the simplest alkyl of boron to possess a sufficiently high boiling point for reaction to be effected in the liquid phase; furthermore, halogen-substituted derivatives of borine containing the *n*-propyl radical were as yet unknown.

In this reaction there was no evidence for the halogenation of the alkyl chains and no detectable quantity of hydrogen iodide was evolved, in contrast with the liberation of hydrogen bromide when bromine reacts with tri-*n*-butylborine (Johnson *et al.*, *loc. cit.*). However, a trace of ethyl iodide (in addition to larger quantities of *n*-propyl iodide) was found among the products, as well as a combustible water-insoluble gas (apparently mainly propane) (Johnson *et al.* report the production of *n*-butane during the reaction between tri-*n*-butylborine and bromine). In addition, small amounts of carbon and boron were precipitated.

It was found most convenient to heat pure tri-*n*-propylborine with iodine at the boiling point of the former (156°) in a system facilitating the continuous removal of the *n*-propyl iodide (b. p. 102°), thus preventing the temperature of the reactants from falling below that at which reaction occurs. The whole is carried out in an atmosphere of nitrogen to prevent oxidation of the tri-*n*-propylborine. After about 3 hr. the reaction is complete, and the di-*n*-propyliodoborine may be purified by fractional distillation. Because of the side reactions, the maximum yield is obtained with rather less than the theoretical quantity of iodine. Further replacement of alkyl radicals probably occurs with larger amounts of iodine, since a higher proportion of less volatile material is formed which has a higher vapour density and gives a more volatile product on chlorination (see following paper). The substitution of a second *n*-propyl group by iodine is however very slow, and *n*-propyldi-iodoborine was not isolated in the present work. Eaborn (*loc. cit.*) has noted a similar progressive increase in resistance to the replacement of successive alkyl groups of tetra-alkylsilanes by iodine.

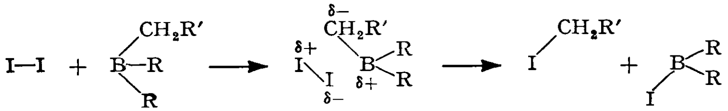
The method should be serviceable for the preparation of other iodoborines. To date, only one other alkyl iodoborine has been described, namely, dimethyliodoborine (Goubeau, *loc. cit.*).

Di-*n*-propyliodoborine is a colourless liquid with a characteristic pungent odour and can apparently be kept indefinitely in the absence of air. The melting point is −87° (pentane thermometer) and the boiling point about 174° (corr.) but, since at elevated temperatures there is evidence of a slight disproportionation, a sharp value was not observed. The vapour pressure has been measured over a wide pressure range below atmospheric pressure.

Agreement between the thermometer readings for the vapour and liquid indicated that disproportionation is negligible at temperatures below the boiling point. The latent heat of vaporisation is 10·03 kcal./mole and the Trouton constant is 22·4. The liquid density at 20° is 1·521 ± 0·002. Vapour-density measurements have established the monomeric formula.

Di-*n*-propyliodoborine fumes in air, and is rapidly oxidised by it with the copious liberation of iodine. It is also rapidly hydrolysed by water liberating hydriodic acid, which can be determined volumetrically: $BPr^n{}_2I + H_2O \longrightarrow BPr^n{}_2{\cdot}OH + HI$. The di-*n*-propylborinic acid produced can be titrated in a large volume of water (partial oxidation should not in theory affect the results) after addition of glycerol, and this provided a convenient means of analysis, although it was found better to oxidise the boron to boric acid and determine this. Hydrolysis of di-*n*-propyliodoborine in the presence of atmospheric oxygen eventually leads to *n*-propylboronic acid, $BPr^n(OH)_2$, a rather volatile yellowish-white solid (cf. Krause and Nitsche, *Ber.*, 1921, **54**, 2784). No attempts were made to purify the liquid di-*n*-propylborinic acid, which presumably behaves like its *n*-butyl analogue (Johnson *et al.*, *loc. cit.*) and readily splits off water to form the anhydride.

It remains to suggest a reaction mechanism whereby the formation of the iodoborine can be satisfactorily accounted for. When the trialkylborine is approached by an iodine molecule, the tendency for the attacking molecule to donate an electron pair to the boron atom would result in an increase in electron density on the iodine atom nearest to the boron atom. If now the approach is broadside the corresponding decrease in electron density round the second iodine atom will further an accumulation of negative charge on the carbon atom nearest to the second iodine atom, thus favouring a " switch " of electron pairing:



The production of a small quantity of propane is however evidence that free alkyl radicals are occasionally produced, so that the foregoing mechanism may not provide the complete picture. The introduction of the electronegative iodine atom would tend to discourage further dealkylation by a mechanism of this type. Hence the slow formation of a di-iodoborine possibly arises through disproportionation of the monoiodoborine first formed. Whether, however, such a disproportionation is truly homolytic or involves heterolytic steps such as

$$R_2BI + IBR_2 \rightleftharpoons R_2BI_2^- + BR_2^+ \rightleftharpoons RBI_2 + BR_3$$

has still to be established. The difficulty experienced in attempting to purify di-*n*-propyliodoborine by fractional distillation is evidence that the disproportionation plays a definite rôle in further dealkylation, even if not an exclusive one. The rate of disproportionation is however sufficiently slow, even at the boiling point, to enable a reasonably pure specimen of the compound to be obtained by fractionation at atmospheric pressure.

EXPERIMENTAL

*Preparation of Tri-*n*-propylborine.*—The method was slightly modified from that described by Krause and Nitsche (*loc. cit.*). Instead of passing gaseous boron trifluoride into the Grignard reagent prepared from *n*-propyl chloride, the equivalent amount of boron trifluoride–ether complex was run in slowly with stirring under nitrogen. This modification, which has been formerly applied in preparing other alkylborines (Brown, *J. Amer. Chem. Soc.*, 1945, **67**, 374), gave as good a yield (50—60%) while considerably simplifying the procedure. Attempts to improve the yield by carrying out the subsequent distillation under reduced pressure failed. When the rather slow distillation of the tri-*n*-propylborine from the solid matter remaining after the reaction was avoided altogether by destroying the excess of Grignard reagent with water and extracting the required product with ether, the amount of higher-boiling material (boiling range 162—190°) was larger and the yield of tri-*n*-propylborine lower (35—45%). The fraction boiling at 150—162° was collected and refractionated. The pure compound boils at 156°.

*Reaction between Tri-*n*-propylborine and Iodine.*—In a typical experiment, pure tri-*n*-propylborine (50 g.) was heated with iodine (77 g., 85%) in a Kon flask (nitrogen atmosphere) at 155—165° (oil-bath). *n*-Propyl iodide produced, together with any other lower-boiling products, distilled off as formed through the fractionating arm of the flask. Heating was continued until the colour of the iodine disappeared. The liquid product was then distilled over from the solid residue and refractionated through a Vigreux column in an atmosphere of nitrogen. The main fraction came over at 162—184°, the yield of crude material being 55 g. (69%). Two refractionations, the last through a column filled with Fenske single-turn glass helices, gave *di*-n-*propyliodoborine*, b. p. 172—176° (corr.). Further refractionations did not yield a sharper boiling point, but provided evidence of a slight but progressive disproportionation on heating.

The distillate collected during the reaction was boron-free and was shown to consist of a mixture of *n*-propyl and ethyl iodides by means of the picrates of the β-naphthyl ethers. In the experiment quoted, this distillate on refractionation yielded 4 g. of material boiling at 68—87° and 25 g. boiling at 87—104°.

A few g. of gas were evolved during the reaction and condensed in a liquid-oxygen trap (−183°) to a colourless liquid. The gas was capable of burning with a luminous flame. It was insoluble in water and shown to be free from hydrogen iodide. The vapour pressure lay close to that for propane (*e.g.*, 378 mm. at −60°; propane 358 mm.; propylene 408 mm.).

The optimum conditions required 85% of the theoretical quantity of iodine. Larger proportions required prolonged heating and resulted in a diminished yield with more material boiling above 184°.

Analysis.—Ampoules containing about 0·5 g. each of di-*n*-propyliodoborine were sealed off *in vacuo*. A mark was scored round the centre of each ampoule before weighing. The ampoule was then cracked at the line (hot glass) and opened under water. Hydrolysis was rapid but not uncontrollably violent. The fragments of the ampoule were weighed, to give by difference the weight of substance taken. The hydrogen iodide was estimated by (i) titration with sodium hydroxide, (ii) Volhard's method, and (iii) gravimetrically as silver iodide. Boron was estimated by oxidation with nitric acid to boric acid, followed by distillation as trimethyl borate after the addition of excess of methyl alcohol; the trimethyl borate was hydrolysed, any mineral acid present just neutralised to methyl-red, and the boric acid then titrated to phenolphthalein with sodium hydroxide in the presence of excess of glycerol. Similar but less reliable results were obtained by direct titration of the di-*n*-propylborinic acid formed in the presence of excess of glycerol after the neutralisation of the hydrogen iodide; the end-point (phenolphthalein) was however less satisfactory. Presumably the complex of glycerol and the dialkylborinic acid is a weaker acid than that with boric acid. The following results were obtained: Found: I (by NaOH), 57·53, 56·92, 56·87; (Volhard), 56·94, 56·61, 57·36; (as AgI), 57·89, 57·93; B (as H_3BO_3), 4·81, 4·84, 4·78; (as $BPr^n_2\cdot OH$), 4·27, 4·54, 4·63% ($C_6H_{14}IB$ requires I, 56·68; B, 4·83%).

Physical Properties of Di-n-*propyliodoborine.*—*Vapour pressure.* The corrected temperatures of distillation in an atmosphere of nitrogen at a series of progressively decreasing pressures were observed, one series with the bulb of the thermometer immersed in the vapour and the other with it in the liquid, care being taken to avoid superheating. The two series agreed closely and exhibited no systematic deviation that might have been attributed to disproportionation. The points are well represented by the vapour-pressure equation: $\log p_{\text{mm.}} = -2191/T + 7{\cdot}7791$. This provides the extrapolated b. p. 174°.

Melting point. Small samples were distilled *in vacuo* into capillary tubes and the melting temperatures observed while these were immersed in a cooling bath in an unsilvered Dewar flask. The temperature of melting was noted in each case by means of a pentane thermometer. The values observed were: −89° to −87°, −88° to −87°, −88° to −86°. From these, the m. p. may be taken as −87°. The absolute accuracy of the pentane thermometer readings is probably not better than ±2°.

Liquid density. Two methods were used. In the first (method A) a small specific-gravity bottle of known volume was filled and weighed. For method B a number of bulbs of about 3-ml. capacity were blown on the ends of short pieces of capillary tubing sealed on to ordinary quill tubing. These were attached to a high-vacuum apparatus and the bulbs completely filled with the compound by distillation *in vacuo*. The bulbs were sealed off and weighed. After the position of the meniscus in the capillary at 20° had been marked, the neck of each bulb above the capillary was severed, and the two pieces of glass weighed empty and with the bulb filled up with water to the mark. In calculating the liquid density, buoyancy corrections were applied to the weighings. The values obtained at 20° were: (method A) 1·5193, 1·5235; (method B) 1·5169, 1·5235, 1·5206, 1·5235. The mean value is 1·521 ± 0·002 at 20°.

Vapour density. The compound has too low a volatility and reacts too readily with vacuum grease for the vapour density to be determined by the usual vacuum-technique. Since it also reacts with air, Dumas's method was adopted, the bulbs being previously filled with nitrogen.

Experiments with samples of di-*n*-propyliodoborine of various boiling ranges between 169° and 180° showed a general tendency for vapour density to increase with boiling range :

Boiling range	169—170°	169—170°	170—172°	170—172°	172—173·5°	172—173·5°
Obs. mol. wt.	229·6	232·8	240·4	231·2	231·6	250·8
Deviation (%) from that required for BPr_2I ...	+2·5	+4·0	+7·5	+3·3	+3·4	+12·0

Boiling range	173·5—174°	173·5—174°	173·5—174°	174—176°	176—180°
Obs. mol. wt.	252·2	234·8	255·2	240·4	271·4
Deviation (%) from that required for BPr_2I ...	+12·6	+4·9	+14·0	+7·4	+21·2

Although the results from this method will be a few units % high, they nevertheless suggest that a little of the di-iodo-compound may be present in the highest-boiling fraction. The results for the fractions boiling between 172° and 176° indicate that the vapour is monomeric.

*Chemical Properties of Di-*n*-propyliodoborine.*—In contact with the air, the borine fumes and is rapidly oxidised (liberation of iodine). Although heat is evolved, the compound does not inflame spontaneously at room temperature. In contact with water, di-*n*-propyliodoborine is rapidly hydrolysed. In the absence of air and with a limited quantity of water, di-*n*-propylborinic acid, $BPr^{n}_{2}\cdot OH$, is readily isolated as a colourless oil which is less dense than water and only slightly soluble in it. On exposure to air, further rapid conversion into a yellowish-white solid, *n*-propylboronic acid, $BPr^{n}(OH)_2$, occurs. The latter compound has a characteristic smell and is very soluble in hot water but much less so in cold. After recrystallisation it melted at 107° [Krause and Nitsche, *loc. cit.*, report m. p. 107° (uncorr.)].

The authors are indebted to the Imperial Smelting Corporation for supplying boron trifluoride in cylinders, and one of them (D. D.) gratefully acknowledges a maintenance grant from the Department of Scientific and Industrial Research.

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[*Received, June 29th,* 1953.]