799. The Chemistry of Boron. Part III.* Halogen-exchange Reactions of Halogenoborines.

By D. Dollimore and L. H. Long.

The iodine of di-*n*-propyliodoborine is smoothly replaced by bromine or chlorine when the borine is heated with the corresponding antimony trihalide. The products are di-*n*-propyl-bromoborine and -chloroborine. Attempts to prepare the corresponding monofluoroborine by the use of antimony trifluoride, plumbous fluoride, and argentous fluoride failed: where reaction occurred, unexpected modes of decomposition were observed.

The preparation of alkylhalogenoborines by reactions involving halogen-exchange with purely inorganic halides has apparently not been undertaken hitherto, although such methods succeeded with, *e.g.*, halogenated silanes (Emeléus and Wilkins, *J.*, 1944, 454), germanes (Anderson, *J. Amer. Chem. Soc.*, 1951, **73**, 5439), and arsines (Long, Emeléus, and Briscoe, *J.*, 1946, 1123). In the case of the trialkylmonohalogenosilanes, Eaborn (*J.*, 1950, 3077) proposed a " conversion series," according to which any member of the series may be converted into any other member on its right but not on its left. Thus iodides may be converted into bromides or chlorides (but not chlorides into bromides or iodides) by treatment with the appropriate silver salt. Strictly speaking, such a " conversion series " established with respect to the salts of one metal would not necessarily be expected to be the same with respect to the salts of another, as there will be a difference in the energetic factors involved (cf. Long, *Quart. Reviews*, 1953, **7**, 134). Thus it is not surprising to find that aluminium halides largely reverse the foregoing " conversion series " and cause the fluorine of trialkylfluorosilanes to be replaced by other halogens (Eaborn, *J.*, 1953, 494).

In the present work, attempts were first made to effect halogen-substitution in di-*n*-

---

* Part II, preceding paper.

propyliodoborine (see Part II *) by the use of antimony trihalides in excess. The reaction succeeded in the case of antimony tribromide and trichloride, being complete within about 2 hours at 100° and giving di-*n*-propyl-bromoborine and -chloroborine respectively in good yield.

$$3BPr^n_2I + SbX_3 \longrightarrow 3BPr^n_2X + SbI_3 \ (X = Cl \text{ or } Br)$$

With antimony trifluoride, surprisingly, reaction occurred much less readily and followed a different course without going to completion. Di-*n*-propylfluoroborine was not obtained, and the only volatile reaction product which could be identified (along with unchanged di-*n*-propyliodoborine) was tri-*n*-propylborine. No fluorine could be detected among the volatile products, so that it appears that if di-*n*-propylfluoroborine is initially formed it immediately disproportionates to form tri-*n*-propylborine and boron trifluoride, the latter being held back either in the form of a non-volatile co-ordination compound with the antimony or as a fluoroborate of antimony. The amount of volatile material recovered at the end of the reaction supports this suggestion. Thus in spite of the successful use of antimony trifluoride to prepare fluorosilanes by simple halogen-exchange (Emeléus and Wilkins, *loc. cit.*; Booth and Carnell, *J. Amer. Chem. Soc.*, 1946, **68**, 2650; Booth and Halbedel, *ibid.*, p. 2652), it is not suitable for the preparation of fluoroborines.

The actions of lead fluoride (a milder fluorinating agent) and silver fluoride (a more vigorous fluorinating agent) were also studied. Although the former did not react, with silver fluoride an exothermic reaction went to completion at room temperature. However, in spite of the fact that the experiment was designed to minimise decomposition, no di-*n*-propylfluoroborine could be detected in the products. The reaction proved to be surprisingly complex, as boron trifluoride, hydrogen iodide, *n*-propyl fluoride, ethyl iodide, *n*-propyl iodide, and tri-*n*-propylborine were all identified among the volatile products. It follows that fission of boron–carbon and even carbon–carbon bonds is involved. Even though boron trifluoride has long been known to catalyse the cracking of hydrocarbons at comparatively low temperatures, the degradation of such a large proportion of the original di-*n*-propyliodoborine in this way is difficult to account for. Here, in contrast to the reaction with antimony trifluoride, fluorine (the larger part in the form of boron trifluoride) is found among the volatile products of reaction, while the residue—which had only been gently heated during the low-pressure distillation of the volatile products—failed to give a positive test for boron. It thus appears that silver fluoroborate, which is now known to be stable and decomposes rapidly only at 200° (Sharpe, *J.*, 1952, 4538), is not formed.

Di-*n*-propyl-bromoborine and -chloroborine are colourless liquids of melting points $-94°$ (pentane thermometer) and $<-125°$, and boiling points 145° and 127° respectively. The boiling points, particularly that of the chloro-compound, were sharper than for the iodo-compound (Part II), so that the tendency to disproportionation during distillation is presumably less. The vapour pressures have been measured over a wide range below atmospheric pressure. The latent heats of vaporisation derived from the Clausius–Clapeyron relation are 9·70 and 9·41 kcal./mole respectively, corresponding to 23·2 and 23·5 for the values of the Trouton constant. These values are slightly higher than for the corresponding methyl and ethyl compounds (Goubeau, F.I.A.T. Review of German Science 1939—1946, Inorganic Chemistry, Part I, 1948, p. 215). However, it would be overhasty to ascribe this to slight association in the liquid state (as Goubeau does for the ethyl compounds), since the boiling points of compounds R_2BX are all below those of the corresponding compounds R_2CHX. Furthermore, the Trouton constant for tri-*n*-propylborine, which is generally believed to be non-associated, is similar to those for the di-*n*-propylhalogenoborines: its value, calculated from the vapour-pressure data of Krause and Nitsche (*Ber.*, 1921, **54**, 2784) is 23·5. The progressive increase in the Trouton constant observed on passing from the methyl through the ethyl to the *n*-propyl compounds requires explaining. Vapour-density measurements have established the monomeric formulæ for both di-*n*-propyl-bromoborine and -chloroborine, while the liquid densities are $1·095 \pm 0·005$ and $0·848 \pm 0·003$ respectively.

Di-*n*-propyl-bromoborine and -chloroborine resemble the corresponding iodo-compound (see Part II). The chloro-compound is, however, spontaneously inflammable, igniting more readily even than tri-*n*-propylborine. The ease of self-ignition is not entirely a question of relative volatility, since the bromo- (though not the iodo-)compound is also more volatile than tri-*n*-propylborine, but does not ignite spontaneously. Rather, the slight general reduction in reactivity on passing from the chloro- to the bromo- and the iodo-compound is probably largely to be associated with a more pronounced steric factor which noticeably restricts the reactivity.

The boiling points of the known dialkylhalogenoborines are compared in the accompanying Table. The value for dimethylfluoroborine has been taken from Burg (*J. Amer. Chem. Soc.*, 1940, **62**, 2228), those for the remaining dimethyl- and diethyl-halogenoborines from Goubeau (*loc. cit.*), those for the di-*n*-propylhalogenoborines from the present work and Part II of this series, and that for di-*n*-butylchloroborine from Booth and Kraus (*J. Amer. Chem. Soc.*, 1952, **74**, 1415).

Boiling points of dialkylhalogenoborines.

R	BR_2F	BR_2Cl	BR_2Br	BR_2I
Me	−42°	5°	31°	69°
Et	—	79	101	—
Pr^{n}	—	127	145	174
Bu^{n}	—	173	—	—

The Table shows the general gradation expected, but the increment in boiling point per CH_2 is everywhere larger than for the corresponding alkyl halides CHR_2X. In addition, the increment in boiling point on substitution of one halogen for another tends to be larger. For example, the difference between the boiling points of BMe_2Br and BMe_2I is 38° compared with 30° for $CHMe_2Br$ and $CHMe_2I$. Further, the boiling points do not everywhere exhibit a strict proportionality. For example, the values predicted for the di-*n*-propylhalogenoborines on a basis of strict proportionality from the values for the boron halides on the one hand and tri-*n*-propylborine on the other are 108°, 134°, and 174° for the chloro-, bromo-, and iodo-compounds respectively. However, only the iodo-compound has the predicted boiling point. The methylchlorosilanes (Gilliam, Liebhafsky, and Winslow, *J. Amer. Chem. Soc.*, 1941, **63**, 801) exhibit a similar irregularity.

EXPERIMENTAL

Di-*n*-propyliodoborine was prepared as described in Part II. In general, material with the boiling range 168—180° was used.

*Reactions of Di-*n*-propyliodoborine.—With antimony tribromide.* Preliminary experiments indicated that halogen-exchange occurred with the separation of the dark-red antimony triiodide. In order to ensure complete reaction, the antimony tribromide was used in approx. 20% excess. Thus 53 g. of the anhydrous compound were placed in a nitrogen-filled Kon flask and 82 g. of di-*n*-propylmonoiodoborine allowed to run in. No noticeable amount of heat was liberated in the cold, but the reaction appeared to take place rapidly at 100°. This temperature was maintained in a water-bath for 2½ hours, during which time nothing condensed in a liquid-oxygen trap attached to the system. The water-bath was replaced by an oil-bath and the liquid product (50 g.) distilled over. On refractionation through a column packed with Fenske single-turn glass helices it was observed to distil mostly in the range 126—148°. Further fractionations yielded 20 g. of a material boiling at 143—146° (corr.) which was shown (see below) by analysis to be practically pure *di-*n*-propylbromoborine*.

With antimony trichloride. In this case an exothermic reaction was observed to commence in the cold. The same technique with a 20% excess of antimony trihalide was employed as in the preceding experiment. Again nothing was observed to condense in the liquid-oxygen trap. From 36 g. of antimony trichloride and 84 g. of di-*n*-propyl monoiodoborine 36 g. of distillate were obtained. On refractionation, most of this distilled in the range 94—129°. After a number of fractionations 10 g. of a liquid boiling at 127° and giving correct analytical data (see below) for *di-*n*-propylchloroborine* were obtained.

With antimony trifluoride. Again a certain amount of heat was liberated in the cold, but in this case, in spite of maintaining the starting material for 2½ hr. at 100° with a 20% excess of antimony fluoride, unchanged di-*n*-propyliodoborine was found among the products. A little unidentified volatile material (liquid at −40°) collected in the liquid-oxygen trap. This contained boron and iodine but no fluorine. The main volatile product from 16 g. of antimony trifluoride and 50 g. of di-*n*-propyliodoborine was 22 g. of a distillate obtained with the subsequent use of an oil-bath. The distillate boiled mostly in the range 161—167° and had the properties of a mixture of tri-*n*-propylborine and unchanged di-*n*-propyliodoborine. It was fluorine-free while the liquid density was 0·924, *i.e.*, intermediate between the values for the two compounds (0·72 and 1·521 respectively).

With lead fluoride. Di-*n*-propyliodoborine (25 g.) was treated with plumbous fluoride (16·5 g.) under the same conditions as above. There were no indications of reaction and 18 g. of di-*n*-propylmonoiodoborine (b. p. 168—178°) were subsequently distilled off unchanged. The distillate gave a negative test for fluorine.

With silver fluoride. Argentous fluoride was prepared by dissolving freshly precipitated, washed silver carbonate in the minimum quantity of aqueous hydrogen fluoride and evaporation to dryness in a platinum dish.

Preliminary tests showed that silver fluoride reacts immediately with di-*n*-propyliodoborine in the cold, but that no di-*n*-propylfluoroborine was obtained by subsequent distillation at atmospheric pressure. The experiment was therefore repeated with a modified technique designed to keep the temperature as low as possible.

Di-*n*-propyliodoborine (23 g.) was added slowly during 1¼ hr. to silver fluoride (20 g., 50% excess) in a Kon flask filled with nitrogen. The exothermic reaction was moderated by cooling with water. After 48 hr. at room temperature during which gaseous material condensed in the liquid-oxygen trap, the pressure was reduced to 25 mm.; more gaseous material was then evolved. The last of the volatile material was distilled over by gentle warming in a water-bath. About 1 g. of liquid distillate was collected, the material in the liquid-oxygen trap amounting to about 7 ml. (in the liquid state). The only other volatile product was a small quantity of a white solid which collected in the condenser and became yellowish in air. This behaved as *n*-propylboronic acid, and had apparently been formed through the presence of traces of moisture and oxygen. Its m. p. was 109° [Krause and Nitsche, *loc. cit.*, report m. p. 107° (uncorr.)].

The solid remaining in the reaction flask contained fluorine and iodine but no boron. The liquid distillate was fluorine-free but contained boron and non-ionisable iodine. Decomposition with nitric acid was necessary to reveal the presence of iodine. On fractional distillation *n*-propyl iodide, b. p. 104°, was isolated; a less volatile portion was shown to be tri-*n*-propylborine.

The contents of the liquid-oxygen trap were fractionated in high-vacuum apparatus into two portions (nearly equal in volume), one volatile and the other involatile at −50°. The latter was liquid at atmospheric pressure and on fractionation in nitrogen boiled at 72—160°; the first portion was identified as ethyl iodide (b. p. 72°) by its vapour density (Found: 78·7. Calc. for C_2H_5I: 77·99) and content of non-ionisable iodine (decomposition with nitric acid); the less volatile material yielded only tri-*n*-propylborine and *n*-propyl iodide.

The fraction volatile at −50° (*ca.* 3 ml.) was liquid at −78° and contained boron, fluorine, and iodine. It was pink in colour, apparently through iodine. It was almost entirely volatile at −100° *in vacuo*. It was again divided into two roughly equal fractions by fractional condensation at −130° in a high-vacuum apparatus. The fraction involatile at −130° attained a vapour pressure of 1 atm. at approximately −5°, close to the boiling point of *n*-propyl fluoride (−3°) and was mostly insoluble in water, burning with a luminous green flame. That it consisted mainly of *n*-propyl fluoride is further confirmed by vapour-density measurements (Found: 31·5, 31·4, 31·2. Calc. for C_3H_7F: 31·03). The fraction which did not condense at −130° attained a vapour pressure of 1 atm. at about −50° and had the properties of a mixture of boron trifluoride and hydrogen iodide plus a little *n*-propyl fluoride. A number of vapour-density determinations were carried out on samples of material in this fraction. Each sample was subsequently dissolved as far as possible in water, the volume of gas not dissolving being measured. The aqueous solution was analysed for iodine (silver iodide) and fluorine (Ryss's method, *Zavodskaya Lab.*, 1946, **12**, 651). In this way the contents of *n*-propyl fluoride, hydrogen iodide, and boron trifluoride were calculated from each sample (see Table). The agreement between the calculated and the observed vapour densities indicates absence of other components.

Sample	C_3H_7F (wt.%)	HI (wt.%)	BF_3 (wt.%)	Total (%)	Vapour density calc. from composition	Vapour density (obs.)
1	6·02	8·21	87·18	101·41	35·05	34·99
2	9·22	22·81	70·21	102·24	37·53	37·78
3	13·43	40·00	48·34	101·77	40·98	41·20

Analysis of Di-n-*propylbromoborine*.—Samples were treated as in the analysis of di-*n*-propyliodoborine (see Part II). The hydrogen bromide liberated was titrated with sodium hydroxide, and the boron was estimated as boric acid in the presence of excess of glycerol after oxidation with nitric acid followed by distillation as trimethyl borate and subsequent hydrolysis. The results were: Found: Br, 45·7, 45·8, 45·1; B, 6·03, 6·11, 6·10% ($C_6H_{14}BrB$ requires Br, 45·2; B, 6·12%). The foregoing figures refer to the main fraction boiling at 143—146°. A more volatile fraction (b. p. 126—139°) gave on analysis: Br, 60·7, 60·7, 61·2%; this suggests that it contained *n*-propyldibromoborine.

Analysis of Di-n-*propylchloroborine*.—Similar analysis, except that the chloride was also estimated gravimetrically as silver chloride, gave: Found: Cl (by NaOH), 26·4, 26·4; (as AgCl) 26·3, 26·4; B, 8·07, 7·99, 8·14, 7·99% ($C_6H_{14}ClB$ requires Cl, 26·8; B, 8·17%). The foregoing figures refer to the liquid boiling at 127°. A more volatile fraction (boiling at 94—115°) contained 46·7% of chlorine, so that *n*-propyldichloroborine was presumably present in this fraction.

Physical Properties.—Except where otherwise stated, the methods used were those described in Part II.

Vapour pressure. Pressure–temperature readings over a wide pressure range were recorded for the liquid and vapour of each compound while undergoing distillation in a nitrogen atmosphere. No deviationary trends were observed which pointed to disproportionation. The readings are well represented by the equations: (for BPr^n_2Br) $\log p_{mm.} = -2120/T + 7{\cdot}9549$; (for BPr^n_2Cl) $\log p_{mm.} = -2056/T + 8{\cdot}0146$. These correspond to b. p. 145° and 127° respectively.

Melting point. The values observed for the bromo-compound were (pentane thermometer): −96° to −95°, −94° to −92°, −95° to −94°, −95° to −94°. From these the m. p. may be taken as −94° with an absolute accuracy not better than ±2°. The m. p. of the chloro-compound was too low to be measured conveniently. Although solid at the temperature of liquid oxygen (−183°), the compound liquefies not very far above that temperature, and was observed to melt immediately in a bath at −125°.

Liquid density. The second of the two methods used for di-*n*-propyliodoborine was adopted. The values obtained for the bromo-compound after correction for buoyancy were 1·098, 1·090, 1·102, 1·092 (mean 1·095 ± 0·005); and for the chloro-compound 0·852, 0·844, 0·847 (mean 0·848 ± 0·003), both at 20°.

Vapour density. The following values were obtained by Dumas's method for the molecular weight of the bromo-compound (bulbs previously filled with nitrogen):

Obs. mol. wt.	195·0	200·0	187·7	194·9
Deviation (%) from that required for BPr_2Br	+10·2	+13·1	+6·1	+10·2

Since this method gives results a few units % high, the values indicate a monomeric vapour. In the case of the chloro-compound the ordinary Dumas technique broke down because of the extreme inflammability of the vapour and the attendant difficulty of sealing off the bulbs. It was, however, feasible to substitute the conventional type of Dumas bulb by a glass globe fitted with a glass tap lubricated with silicone vacuum-grease, which was found to withstand a temperature of 160° without difficulty. The following results were obtained:

Obs. mol. wt.	142·0	139·0	142·6
Deviation (%) from that required for BPr_2Cl	+7·2	+5·0	+7·7

Again the results are those to be expected for the monomeric compound.

Chemical Properties.—The chloro-compound was observed to ignite spontaneously in air, while the bromo-compound merely fumed at room temperature. Like the iodo-compound (Part II), both are immediately hydrolysed, the relative vigour with which they attack water appearing to be: $BPr^n_2Cl > BPr^n_2Br > BPr^n_2I$. The first product in each case is a liquid less dense than water, but in an oxidising atmosphere *n*-propylboronic acid is obtained (cf. Krause and Nitsche, *loc. cit.*). The products from the bromo- and the chloro-compound both had m. p. 109°.

The authors gratefully acknowledge the loan of platinum apparatus by Imperial Chemical Industries Limited, and one of them (D. D.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

UNIVERSITY COLLEGE, EXETER. [*Received, June 29th*, 1953.]