[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. VII. Dialkylchloroboranes from the Reaction of Boron Chloride with Trialkylboranes. Disproportionation of Dialkylchloroboranes[1,2]

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Boron chloride reacts quite rapidly with trialkylboranes at temperatures above 100° to give nearly quantitative yields of dialkylchloroboranes. Several new dialkylchloroboranes have been prepared by this method and characterized. Substantially no reaction occurs when the reactants are mixed in stoichiometric proportions at 25 or 50°. The dialkylchloroboranes can be distilled under vacuum at temperatures below 100° without disproportionation. At higher temperatures the equilibrium, $2R_2BCl \rightleftarrows RBCl_2 + R_3B$, exists with all but a very small proportion of the material in the form of the dialkylchloroborane. By slow fractional distillation at atmospheric pressure the alkyldichloroborane can be removed and the disproportionation reaction thus made to go to completion. No tendency for disproportionation of dialkylchloroboranes into trialkylboranes and boron chloride has been observed. Mixtures of trialkylboranes and alkyldichloroboranes are converted on refluxing to dialkylchloroboranes. A possible mechanism for the reaction of boron chloride with trialkylboranes is discussed. Di-*sec*-butylchloroborane can be obtained from the reaction of tri-*sec*-butylborane with boron chloride, but when this α-branched dialkylchloroborane is disproportionated, tri-*n*-butylborane is formed. Dialkylchloroboranes, in contrast to alkyldichloroboranes, can be separated readily from ether on distillation.

While a number of methods have been used[3] for the preparation of dialkylchloroboranes, the only method described in the literature which appears to be generally applicable involves the reaction of hydrogen chloride with trialkylboranes at elevated temperatures.[4] Trimethylborane has been treated with boron chloride in a closed tube at 320°[5] and by a flow process at 350 to 400°[6] and has been reported to yield dimethylchloroborane and methyldichloroborane. A study of the liquid phase reaction between boron chloride and some higher trialkylboranes has now been carried out and the results are reported in the present paper.

Experimental

Attempted Reaction between Boron Chloride and Tri-*n*-butylborane at 25 and 50°.—In separate experiments boron chloride was passed into tri-*n*-butylborane, at 25° and again at 50°, until the boron chloride–tri-*n*-butylborane ratio reached 1 to 2. Upon distillation of the product the boron chloride was evolved completely, and the tri-*n*-butylborane was recovered unchanged.

Preparation of Di-*n*-butylchloroborane from Boron Chloride and Tri-*n*-butylborane.—Tri-*n*-butylborane (93 g., 0.4 mole) was placed in a 200-ml. flask, fitted with a Claisen-type distilling head, water-cooled condenser, a 300-ml. receiver, with adapter leading to a solid carbon dioxide-cooled trap and bubbler bottles. Boron chloride was passed through mercury bubbler bottles into the tri-*n*-butylborane. Absorption of boron chloride occurred at room temperature. When the liquid appeared to be saturated with boron chloride, it was heated to 160° with continued addition of boron chloride. Distillation began at once, and in a 45-minute period, 110 g. of distillate was obtained in the receiver and an additional 15 g. in the cold trap. The product was redistilled through a 60-cm. packed column under vacuum to give 112 g. (91% yield) of di-*n*-butylchloroborane, b.p. 47–48° at 7 mm.; calcd. Cl, 22.1, obsd. Cl 22.0. Rapid distillation of the product through a packed column at atmospheric pressure and with total take-off gave essentially complete recovery of material, b.p. 173–174° at 747 mm. The infrared spectrum of the product was recorded.

Diisobutylchloroborane.—Triisobutylborane (1 mole) was treated with boron chloride in the same manner as above and similarly distilled at 7 mm. and at atmospheric pressure. A nearly quantitative yield of diisobutylchloroborane was obtained, b.p. 33.0° at 7 mm., 156° at 747 mm., $n^{25}\text{D}$ 1.4160, d^{25} 0.8251; calcd. Cl 22.1, obsd. Cl 22.0. The infrared spectrum was recorded.

Di-*sec*-butylchloroborane.—Tri-*sec*-butylborane, which had been distilled only under vacuum and whose infrared spectrum had been checked to ensure[1] the isomeric identity of the material, was allowed to react as above with boron chloride. An 82% yield of product, b.p. 36–39° at 7 mm., was obtained. This was redistilled in a packed column at total take-off without appreciable loss of material to give a product, b.p. 160–161° at 747 mm., $n^{25}\text{D}$ 1.4230; calcd. Cl 22.1, obsd. Cl 22.2. The infrared spectrum was recorded and found to be different from the spectrum of di-*n*-butylchloroborane and from that of diisobutylchloroborane.

Reaction of the Tributylborane from *t*-Butylmagnesium Chloride with Boron Chloride.—One mole of tributylborane produced from the reaction of *t*-butylmagnesium chloride with boron chloride[1] (b.p. 64° at 7 mm., $n^{25}\text{D}$ 1.4215, d^{25} 0.7390) was treated in the same manner as above with boron chloride. The principal product obtained had the following constants, b.p. 34° at 7 mm., $n^{25}\text{D}$ 1.4167, d^{25} 0.8255, which are in agreement with the constants for diisobutylchloroborane listed above. The infrared spectrum of this product was identical with that of diisobutylchloroborane.

Reaction of the Tripropylborane from Isopropylmagnesium Bromide with Boron Chloride.—A tripropylborane was prepared by the reaction of boron chloride with isopropylmagnesium bromide to give a product with b.p. 148–154°, in agreement with the value reported in the literature.[7] Repeated distillations in a 60-cm. column did not decrease the boiling range. This product (52 g., 0.36 mole) was treated, as in the cases described above, with boron chloride. The reaction product was fractionally distilled in a 100-cm. column at 7 mm. The principal fraction had a boiling range from 26–36° at 7 mm. Three separate fractions in this boiling range were collected and analyzed for chlorine. Each fraction gave essentially the same chlorine analysis which was in agreement with the value calculated for dipropylchloroborane. A higher boiling fraction was redistilled at atmospheric pressure and gave the same boiling point as the original tripropylborane.

Reaction of Tri-*n*-butylborane with *n*-Butyldichloroborane.—Tri-*n*-butylborane (0.3 mole) and *n*-butyldichloroborane (0.3 mole) were heated at reflux under nitrogen for 48 hr. Distillation in a 60-cm. column at 6 mm. gave an 80% yield of di-*n*-butylchloroborane and 12% unreacted tri-*n*-butylborane. No butyldichloroborane was recovered.

Disproportionation Studies on Dialkylchloroboranes.—These studies were carried out in general by subjecting the dialkylchloroboranes to fractional distillation at atmospheric pressure in a 60- or 100-cm., glass-helix packed column of the total reflux, partial take-off type. A very slow rate of take-off, determined by the lowering of the head temperature to the boiling point of the alkyldichloroborane, was used. In some cases it was necessary to reflux for some time, without take-off, until a sufficient quantity of alkyldichloroborane was formed to permit its separation.

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[1] Previous paper, THIS JOURNAL, **79**, 5190 (1957).

[2] From the dissertation submitted by Eugene C. Ashby in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Notre Dame, 1957. Presented in part at the Atlantic City Meeting of the American Chemical Society, September, 1956.

[3] M. F. Lappert, *Chem. Revs.*, **56**, 1049 (1956).

[4] R. B. Booth and C. A. Kraus, THIS JOURNAL, **74**, 1415 (1952).

[5] E. Wiberg and B. Bolz, *Fiat Review, Inorganic Chemistry*, Part I, 238 (1948).

[6] H. J. Becher, *Z. anorg. allgem. Chem.*, **271**, 243 (1953).

[7] E. Krause and P. Nobbe, *Ber.*, **64**, 2112 (1931).

Partial Disproportionation of Di-*n*-butylchloroborane.—Distillation of 180 g. of di-*n*-butylchloroborane at atmospheric pressure in a packed column at a 5-to-1 reflux ratio gave 28 g. of butyldichloroborane, b.p. 105–109°, and 30 g. of an intermediate fraction, b.p. 109–170°. The column was then adjusted for total take-off, and 96 g. of material, b.p. 170–174°, was collected. A final fraction (32 g.), b.p. 210–215°, identified as tri-*n*-butylborane, was also obtained.

Disproportionation of the Dibutylchloroborane Originating with *t*-Butylmagnesium Chloride.—The dibutylchloroborane (90 g., 0.56 mole), originating from *t*-butylmagnesium chloride, as described above, was subjected to a very slow fractional distillation at atmospheric pressure in a 100-cm. column. Operating conditions were adjusted so that the upper column temperature did not exceed the boiling point of diisobutylchloroborane. Over a 4-day period, 34 g. of a lower boiling fraction, b.p. 95–96° was collected. Chlorine analysis showed this compound to be a butyldichloroborane, and its boiling point identified it as isobutyldichloroborane.[8] The higher boiling fraction was distilled rapidly to give 40 g. of product, b.p. 188–189°, $n^{25}\text{D}$ 1.4190 and d^{25} 0.7304. These constants are in agreement with those of triisobutylborane.

Disproportionation of Di-*sec*-butylchloroborane.—By exactly the same procedure as described above, di-*sec*-butylchloroborane was disproportionated by a slow fractionation over a three-day period. An 80% yield of two products was obtained. The lower boiling product had b.p. 99–100°, the boiling point of *sec*-butyldichloroborane,[8] and analyzed correctly for chlorine, thus identifying it as *sec*-butyldichloroborane. The higher boiling fraction had the same b.p. and infrared spectrum as tri-*n*-butylborane.

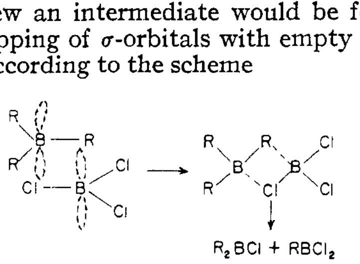
Separation of Di-*n*-butylchloroborane from Ether.—To 150 ml. of ether was added, under a nitrogen atmosphere, 70 g. of freshly distilled di-*n*-butylchloroborane. There was no evidence of heat evolution during the addition. Rapid distillation of the liquid from a Claisen flask resulted in complete separation of the ether and recovery of the di-*n*-butylchloroborane.

Physical Measurements and Analyses.—Densities, refractive indexes, chlorine analyses and infrared spectra were obtained as described previously.[1,8]

Discussion

As a method of preparation for the higher dialkylchloroboranes, the reaction of boron chloride with trialkylboranes has several advantages over previously reported methods. The reaction is readily carried out with ordinary laboratory apparatus, the yields are high and the starting materials are either available or readily prepared by well established methods. While the percentage of the theoretical yield obtainable from the reaction of trialkylboranes with hydrogen chloride[4] may be high, the effective yield is much less than in the boron chloride–trialkylborane reaction because of the loss of an alkyl group as hydrocarbon in the hydrogen chloride reaction.

The mechanism suggested in the preceding paper[1] for the disproportionation reaction of trialkylboranes may also be applicable to the reaction of boron chloride with trialkylboranes. According to this view an intermediate would be formed by the overlapping of σ-orbitals with empty p-orbitals of boron according to the scheme



Cleavage of the bridge dimer would then result in the formation of one mole of dialkylchloroborane and one mole of alkyldichloroborane. Since this reaction actually produces dialkylchloroborane almost exclusively, a second rapid reaction between alkyldichloroborane and trialkylborane must then occur in the presence of excess trialkylborane. It is essential to this mechanism that the second reaction occur more rapidly than the first to account for the formation almost exclusively of dialkylchloroborane. We have shown that refluxing of tributylborane with butyldichloroborane results in complete conversion to dialkylchloroborane. Thus the feasibility of this sequence of reactions to explain the results obtained is established.

One important difference between the reaction of boron chloride with trialkylboranes and the disproportionation of unsymmetrical trialkylboranes is immediately evident. The disproportionation of unsymmetrical trialkylboranes occurs very rapidly and at much lower temperatures than the boron chloride–trialkylborane reaction. A possible explanation for this difference is provided by the fact that in the boron chloride there is some degree of double bonding, $\overset{\ominus}{B}=\overset{\oplus}{Cl}$, which would tend partially to saturate the boron atom and make the p-orbital less readily available for dimer formation. The fact that the boron in boron chloride is more electrophilic than the boron in trialkylboranes would further suggest that electrostatic factors are not important in this mechanism.

It is clear from the results of the disproportionation studies that there is no tendency for the reaction by which the dialkylchloroboranes are formed to be reversed. In no case did we observe any formation of boron chloride and trialkylborane from the disproportionation of the dialkylchloroboranes. Apparently in the temperature range up to about 180° the chloroboranes once formed are much more stable than the starting materials. This is in contrast to the usual course of the disproportionation reactions of organoboron compounds which in many cases have been shown to form symmetrical products.

The manner in which the disproportionation of dialkylchloroboranes occurs and the products formed indicate that the following equilibrium exists between dialkylchloroborane and the disproportionation products: $2R_2BCl \rightleftarrows RBCl_2 + R_3B$. The equilibrium is so far to the left at temperatures up to 180° that a rapid distillation, even in a packed column, gives no evidence of the formation of disproportionation products. When the distillation is carried out under vacuum, pure dialkylchloroboranes are obtained without contamination with disproportionation products. This suggests that the equilibrium point is shifted even farther to the left as the temperature is lowered. The presence of the two disproportionation products in very small amounts is shown by the ability to bleed off very slowly (by fractional distillation) the lowest boiling equilibrium species, $RBCl_2$, and bring about in this manner the complete disproportionation of the dialkylchloroboranes.

The reason for the greater stability of the dialkylchloroboranes than of the other possible products

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(8) P. A. McCusker, E. C. Ashby and H. S. Makowski, THIS JOURNAL, **79**, 5182 (1957).

of the disproportionation reaction is not clear. The alkyldichloroboranes can be distilled up to about 180° with no sign of disproportionation, but in the presence of trialkylborane are rapidly converted to dialkylchloroboranes. Dialkylchloroboranes are apparently not converted to alkyldichloroboranes in the presence of excess boron chloride in this temperature range. The most stable molecule in this case appears to be the one with one atom of chlorine per boron rather than two or none. It would appear that this stability is fundamental in nature and that the formation of the dialkylchloroborane rather than the other products is not a result of a favorable route to reaction.

The factors which make for great stability in the dialkylchloroboranes apparently are not effective for the corresponding fluorine compounds. While the alkyldifluoroboranes have been shown to be stable to disproportionation,[9] less is known about the disproportionation tendencies of dialkylfluoroboranes. Only one such compound, dimethylfluoroborane, has been reported.[10] Although this compound has been reported to be stable to disproportionation at room temperature, it has been suggested[11] that in the presence of certain reaction products it may have disproportionated. Preliminary[12] work in these laboratories has indicated that the higher dialkylfluoroboranes are not readily obtainable from the reaction of boron fluoride with the anhydrides of dialkylborinic acids. They can be obtained by the fluorination of dialkylchloroboranes but appear to be much more readily disproportionated to alkyldifluoroboranes and trialkylborane than the corresponding chloro compounds.

The dibutylchloroborane produced in the reaction of boron chloride with the tributylborane from *t*-butylmagnesium chloride has the same physical constants and infrared spectrum as the product from triisobutylborane. This constitutes further evidence of the identity of the two tributylboranes. If one tertiary alkyl group was present in the starting tributylborane, it apparently isomerized during the reaction.

The results obtained from the reaction of boron chloride with the trialkylborane obtained from isopropylmagnesium bromide and distilled at atmospheric pressure at 153–155° are consistent with the assumption that the trialkylborane consisted of a mixture of tri-*n*-propylborane and tri-isopropylborane. A product boiling over a ten degree range was collected in three approximately equal fractions. Each fraction had, within the limits of experimental error, the same chlorine content. A mixture of di-*n*-propylchloroborane and diisopropylchloroborane would show exactly this behavior.

The isolation of di-*sec*-butylchloroborane from the reaction of tri-*sec*-butylborane with boron chloride shows that the reaction may take place without isomerization of the dialkylchloroborane formed. During the high temperature disproportionation reaction, however, the trialkylborane formed does undergo isomerization. It appears that two α-branched alkyl groups may be retained on a boron atom at moderately elevated temperatures, but when three such groups are present isomerization occurs more readily.

The expected reduced electrophilic character of the boron in dialkylchloroboranes, as compared to alkyldichloroboranes, results in easy separation of dialkylchloroboranes from ether in contrast to the cleavage which results from attempts to separate alkyldichloroboranes from ether.

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[9] P. A. McCusker and L. J. Glunz, This Journal, **77**, 4253 (1955).

[10] A. Burg, *ibid.*, **62**, 2228 (1940).

[11] A. Burg and J. Banus, *ibid.*, **76**, 9303 (1954).

[12] P. A. McClusker, G. F. Hennion and A. J. Rutkowski, unpublished work.

[Contribution from the Chemical Laboratories of the University of Notre Dame]

Organoboron Compounds. VIII. The Reaction of Triorganoboranes with Boric Oxide[1]

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Trialkylboroxines, $(RBO)_3$, containing primary alkyl groups, tricyclohexylboroxine and triphenylboroxine, are easily prepared by the reaction of triorganoboranes with anhydrous boric oxide. Reaction occurs slowly at atmospheric pressure and reflux temperature and affords yields of 70% and higher. α-Branched trialkylboranes are isomerized in the process and give the corresponding primary alkylboroxines. Thus tri-*n*-butylboroxine is produced in this way with both tri-*n*-butylborane and tri-*sec*-butylborane.

Discussion

Previous papers[3] in this series included brief discussions of the mechanism of disproportionation and rearrangement reactions of triorganoboranes. Specifically, it was proposed that the vacant p-orbital of one boron atom may overlap σ-orbitals of another boron atom (or σ-orbitals of other types) leading to bridged-dimers which cleave to yield products which are (usually) thermodynamically more stable. This notion, while not amenable to rigid proof, suggests that triorganoboranes should undergo a considerable variety of reactions with substances which are sterically and electronically capable of such interaction. A number of such reactions are now being studied in this Laboratory. In this paper we report the reaction of tri-

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[1] Previous paper, This Journal, **79**, 5192 (1957).

[2] Abstracted in part from the Ph.D. Dissertations of E.C.A. and A.J.R.

[3] G. F. Hennion, P. A. McCusker, *et al.*, papers VI and VII, This Journal, **79**, 5190, 5192 (1957).