# ORGANOBORON COMPOUNDS-XVIII

## ALKYLBROMOBORANES AND RELATIVE DISPROPORTIONATION TENDENCIES OF ALKYLHALOBORANES\*

## P. A. MCCUSKER and J. H. BRIGHT

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

## (Received 10 February 1966)

Abstract—The disproportionation tendencies of alkylbromoboranes are significantly different from those of the corresponding alkylchloro and alkylfluoro compounds. Alkyldibromoboranes undergo slow thermal disproportionation to boron bromide and trialkylboranes on fractional distillation while alkyldichloro- and diffuoroboranes are completely resistant to disproportionation under the same conditions. Dialkylbromoboranes are completely resistant to thermal disproportionation in contrast to the slow disproportionation of dialkylchloroboranes and the more rapid disproportionation of dialkylfluoroboranes. That these differences in disproportionation tendencies are the result of thermodynamic rather than kinetic factors has been shown by equilibration experiments. Primary aklyldibromoboranes, dialkylbromoboranes or mixtures thereof are conveniently prepared in high yields by the reaction of appropriate stoichiometric amounts of boron bromide with primary trialkylboranes at 140° or above. Tri*iso*propylborane, even in the presence of diborane, does not react with boron bromide until extensive isomerization of *iso*propyl to *n*-propyl groups has occurred. Tri-sbutylborane reacts with only partial isomerization to give appreciable yields of pure di-s-butylbormoborane.

## INTRODUCTION

PREVIOUS studies in these laboratories on alkylchloro- and alkylfluoroboranes have shown that alkyldifluoroboranes<sup>(1)</sup> and alkyldichloroboranes<sup>(2)</sup> are completely resistant to thermal disproportionation (up to 180°), while dialkylchloroboranes<sup>(3)</sup> undergo slow disproportationation on fractional distillation. It has also been observed that dialkylfluoroboranes undergo disproportionation more readily than do dialkylchloroboranes. The differences in the disportionation tendencies of these alkylhaloboranes was tentatively attributed to mechanistic factors involving the ease of formation of a presumed dimeric intermediate. The possibility that the disproportionation reactions might be thermodynamically controlled, however, could not be excluded on the basis of the available data. In order to obtain more information as to the factors affecting the relative disproportionation tendencies of the alkylhaloboranes, disproportionation studies have been carried out on the alkylbromoboranes and equilibrium data have been obtained for all three alkylhaloborane systems. A convenient method has been developed for the preparation of the alkylbromoboranes and the preparative reaction studied in some detail. A comparison has also been made of the reaction of boron bromide with primary and secondary trialkylboranes.

\* Contribution from the Department of Chemistry and Radiation Laboratory, University of Notre Dame. The Radiation Laboratory of the University of Notre Dame is operated under contract with the U.S. Atomic Energy Commission. This is AEC Document COO-38-383. Previous paper, M. A. MOLINARI and P. A. MCCUSKER, J. org. Chem. 29, 2094 (1964).

<sup>&</sup>lt;sup>(1)</sup> P. A. MCCUSKER and L. J. GLUNZ, J. Am. chem. Soc. 77, 4253 (1955).

<sup>&</sup>lt;sup>(2)</sup> P. A. MCCUSKER, E. C. ASHBY and H. S. MAKOWSKI, J. Am. chem. Soc. 79, 5182 (1957).

<sup>&</sup>lt;sup>(8)</sup> P. A. MCCUSKER, C. F. HENNION and E. C. ASHBY, J. Am. chem. Soc. 79, 5192 (1957).

#### EXPERIMENTAL

All operations were carried out in closed apparatus under an atmosphere of dry nitrogen. The preparation of trialkylboranes, measurements of physical properties and alkyl group and elemental analyses were carried out as described in previous papers of this series.<sup>(4)</sup>

#### Reaction of boron bromide with triisobutylborane in a 1:1 mole ratio

To 0.16 mole of triisobutylborane was added over a period of 1 hr 0.17 mole of boron bromide at reflux temperature (175° falling to 146°). Heating was continued for a further 6-hr period. Distillation of the resulting mixture through a spinning-band column gave 0.09 mole (55 per cent yield) of pure isobutyldibromoborane, b.p.  $33\cdot1-33\cdot2^{\circ}$  (13 mm),  $n_{25}^{25}$  1.4652,  $d^{25}$  1.552;  $MR_{\rm D}$  calc. 40.39, obsd. 40.60. (Found: Br, 69.8%. Calc. for C<sub>4</sub>H<sub>4</sub>BBr<sub>2</sub>: Br, 70.2%.) Alkaline oxidation gave only isobutyl alcohol by GLC. As a higher boiling function there was also obtained 0.09 mole (55 per cent yield) of pure diisobutylbromoborane, b.p. 45·8-46·0° (5·5 mm)  $n_{25}^{25}$  1.4340,  $d^{25}$  1.040;  $MR_{\rm D}$  calc. 51·5, obsd. 51·3. (Found: Br, 38·8%. Calc. for C<sub>8</sub>H<sub>18</sub>BBr: Br, 39·0%.)

#### Simultaneous preparation of other alkyldibromo- and dialkylbromoboranes

By an entirely similar procedure in the temperature range 156–128° there was obtained (1) a 55 per cent yield of *n*-propyldibromoborane, b.p. 32·3–32·8 (19 mm),  $n_D^{25}$  1·4679,  $d^{25}$  1·656;  $MR_D$  calc. 35·82, obsd. 35·88. (Found: Br, 76·3%. Calc. for  $C_3H_7BBr_2$ ; Br, 74·8%.) Also a 75 per cent yield of di-*n*-propylbromoborane b.p. 47·8–48·2° (14·5 mm),  $n_D^{25}$  1·4373,  $d^{25}$  1·107;  $MR_D$  calc. 42·1, obsd. 42·0. (Found: Br, 45·3%. Calc. for  $C_8H_{14}BBr$ : Br, 45·2%.) In the temperature range, 192–175° there was obtained by a similar procedure (1) an 85 per cent yield of *n*-amyldibromoborane, b.p. 49·6–49·8°, (6·6 mm),  $n_D^{25}$ 1·4658,  $d^{25}$ 1·4578;  $MR_D$  calc. 45·0, obsd. 48·2. (Found: Br, 63·7%. Calc. for  $C_8H_{14}BBr$ : Br, 64·1%.) Also a 28 per cent yield of di-*n*-amylborane, b.p. 57·9–60·4° (2·1 mm),  $n_D^{25}$ 1·4494,  $d^{25}$ 1·053;  $MR_D$  calc. 60·58, obsd. 59·45. (Found: Br, 34·0%. Calc. for  $C_{10}H_{22}BBr$ : Br, 33·9%.)

#### Preparation of dialkylbromoboranes

When 0.12 mole of boron bromide was heated for a  $4\frac{1}{2}$ -hr period with 0.24 mole of triisobutylborane at the reflux temperature (167–145°) there was obtained a 73 per cent yield of pure diisobutylbromoborane with the properties described above. In a similar manner, when 0.11 mole of boron bromide was heated at reflux with 0.20 mole of tri-*n*-butylbromoborane, there was obtained a 56 per cent yield of di-*n*-butylbromoborane b.p. 65·2–65·7° (6·4 mm),  $n_D$  1·447,  $d^{25}$  1·006;  $MR_D$  calc. 51·5, obsd. 51·1. (Found: Br, 39·4%. Calc, for C<sub>8</sub>H<sub>18</sub>BBr: Br, 39·0%.)

When trissobutylborane (0.14 mole) was heated with boron bromide (0.07 mole) for  $\frac{1}{2}$  hr at 129– 141° there was obtained on distillation 0.06 mole of unreacted trissobutylborane, 0.09 mole of dissobutylbromoborane and 0.05 mole of isobutylbromoborane. No boron bromide was recovered. Heating for a 5 hr period of mixture containing 0.12 mole of isobutyldibromoborane and 0.12 mole of trissobutylborane gave a nearly quantitive (97 per cent) yield of pure dissobutylbromoborane with the properties cited above.

#### Preparation of alkyldibromoboranes

When 0.35 mole of boron tribromide was heated at  $180-130^{\circ}$  with 0.18 mole of tri*iso*butylborane for a 5-hr period there resulted a 73 per cent yield of pure *iso*butyldibromoborane with the properties cited above. Similarly there was obtained a 45 per cent yield of pure *n*-butyldibromoborane.

When 0.18 mole of boron bromide and 0.18 mole of dissobutylbromoborane were heated at reflux (164°) for 5-hr there was obtained at 89 per cent yield of pure *iso*butyldibromoborane. Di-*n*-butylbromoborane and boron bromide similarly gave a 36 per cent yield of pure *n*-butylbromoborane.

#### Preparation of di-s-butylbromoborane

When 0.08 mole of boron bromide was heated with 0.16 mole of pure tri-s-butylborane for 1 hr at 170° a high yield of a wide-boiling fraction analysing for dibutylbromoborane was obtained. Oxidation of the product showed that the butyl groups were 7 per cent normal and 93 per cent secondary. On fractionation of the crude product a 13 per cent yield of pure di-s-butylbromoborane was obtained

(4) P. A. MCCUSKER, J. V. MARRA and G. F. HENNION, J. Am. chem. Soc. 83, 1924 (1960).

b.p.  $50.0-50.1^{\circ}$  (5 mm),  $n_D^{25}$  1.444,  $d^{25}$ , 1.070;  $MR_D$  calc. 51.5, obsd. 50.9. (Found: Br, 38.8%. Calc. for  $C_8H_{18}BBr$ ; Br, 39.0%.) From the same mole ratio of reactants, heated for  $\frac{3}{4}$  hr at 191°, there was obtained a 95 per cent yield of a mixture of dibutylbromoboranes whose butyl groups were 85 per cent normal and 15 per cent secondary.

#### Attempted preparation of isopropylbromoboranes

Reaction between boron bromide and *triisopripylborane* was attempted in the temperature range  $101-145^{\circ}$  with reaction times up to 5 hr. When dipropylbromoboranes were obtained the wide boiling fractions were found to contain only small percentages of *isopropyl* groups and correspondingly high percentages of *n*-propyl groups. No pure di*isopropylbromoborane* could be isolated from the reactions mixtures. Attempts were made to catalyse the reaction with diborane.<sup>(3)</sup> Addition of 0.003 mole of diborane to a mixture containing 0.24 mole of boron bromide and 0.24 mole of tri*isopropylbromoborane* at 60° with reaction times of more than 1 hr gave no more than traces of propylbromoboranes.

#### Disproportionation of alkyldibromoboranes

The general procedure followed in the disproportionation experiments involved refluxing of pure starting materials under a spinning-band column with periodic bleeding off of low-boiling disproportionation products. When *iso*butyldibromoborane (0.22 mole) was so treated at a pot temperature of 95–99° (160 mm) for a 21 hr period, 0.05 mole of boron bromide was obtained. Further heating at 123–137° for an additional 38 hr resulted in the collection of an additional 0.03 mole of boron bromide. Fractional distallation of the residue at low pressure resulted in the recovery of 0.06 mole of unreacted *iso*butyldibromoborane and 0.06 mole of di*iso*butylbromoborane. These results correspond to a 73 per cent disproportionation of *iso*butyldibromoborane based on the equation:

## $2RBBr_2 \rightarrow BBr_3 + R_2BBr$

Similar treatment of *n*-propyldibromoborane (0.03 mole) at  $125-128^{\circ}$  over a 4-hr period yielded boron bromide (0.007 mole), *n*-propyldibromoborane (0.019 mole) and di-*n*-propylbromoborane (0.006 mole). These results correspond to a 44 per cent disproportionation.

#### Attempted disproportionation of dialkylbromoboranes

When diisobutylbromoborane (0.14 mole) was refluxed under a spinning-band column for 33 hr at  $175-180^{\circ}$  the total yield of low boiling product was less than 1 g. The low boiling product had a bromine content of 51.0 per cent. The expected disproportionation products, *iso*butyldibromoborane or boron bromide, have bromine contents of 70.2 and 95.7 per cent respectively.

Similar treatment of di-*n*-propylbromoborane (0.09 mole) at 151° for a 4-hr period resulted in the formation of a few drops of low boiling material which had a much lower bromine content than calculated for the disproportionation products.

When di-s-butylbromoborane (0.09 mole) was similarly treated at  $183-190^{\circ}$  for 4 hr the few drops of low boiling material again analysed relatively very low in bromine. Distillation of the residue gave a high yield of wide-boiling material with the proper bromine content for a dibutylbromoborane but having a *n*-butyl group to s-butyl group ratio of 7:3.

## Equilibrium in the disproportionation of disobutylchloroborane

Dissobutylchloroborane (0.25 mole) was heated at reflux (155°) under dry nitrogen for 16 hr. Distillation through a spinning-band column at 9.1 mm gave a 90 per cent recovery of dissobutylchloroborane an 8.1 per cent yield of triisobutylborane and an 8.9 per cent yield of isobutyldichloroborane.

In a separate experiment triisobutylborane (0.12 mole) and isobutyldichloroborane (0.12 mole) were heated at reflux (156°) for 16 hr. Distillation at 9.9 mm gave an 89 per cent yield of diisobutylchloroborane, an 8.8 per cent recovery of triisobutylborane, and an 8.2 per cent recovery of isobutyldichloroborane.

#### Equilibrium in the disproportionation of disobutylfluoroborane

Dissobutylfluoroborane (0.11 mole) was heated at reflux  $(136-132^\circ)$  with 26 g or redistilled *n*-decane in an apparatus having a cold-finger at dry ice temperature. The condenser was connected to a

<sup>(5)</sup> R. KOSTER, Angew. Chem. 73, 66 (1961).

cold trap also at dry ice temperature. Reflux at atmospheric pressure was maintained for 4 hr. No material was found in the cold trap, indicating that efficient condensation had occurred. *Iso*butyldifluoroborane (0.02 mole) was removed at room temperature and reduced pressure. Distillation of the residue at 45 mm gave 25 g of *n*-decane, 0.02 mole of tri*iso*butylborane, and 0.07 mole of unreacted di*iso*butylfluoroborane. These results indicate a 36 per cent disproportionation at equilibrium.

## DISCUSSION

Since it had been observed in previous work that dialkylchloroboranes were more resistant to disproportionation than dialkylfluoroboranes, it was anticipated that the stability order would be  $R_2BBr > R_2BCl > R_2BF$ . The results of studies on the disproportionation of the dialkylbromoboranes confirmed this expectation qualitatively although the *complete* resistance of the dialkylbromoboranes to disproportionation could not have been anticipated.

If mechanistic factors involving the relative ease of formation of a dimeric intermediate were responsible for the difference in the disproportionation tendencies, it could reasonably be postulated that decreased ease of formation of intermolecular  $p-\pi$  bonds in going from the fluorine to the bromine compounds was responsible for the differences in disproportionation tendencies. From general observations on these reactions, however, little difference could be noted in the times required for equilibrium to be reached. This suggested that equilibrium differences might be controlling in these cases.

The equilibrium data obtained showed that the proportion of dialkylhaloborane present at equilibrium increases from 64 per cent for dialkylfluoroborane, to 90 per cent for dialkylchloroborane and to 100 per cent for dialkylbromoborane It thus appears that thermodynamic rather than kinetic factors determine the relative disproportionation tendencies. A larger proportion of alkyldihaloborane and trialkylborane at equilibrium permits more facile separation of the products of the disproportionation reaction. The reactions appear to occur at similar rates.

The reasons for the differences in the stabilities of the three dialkylhaloboranes are not immediately evident. In all three cases entropy factors would favour the disproportionation products to a like extent. The observed results thus require that enthalpy factors be responsible for the differences in the stabilities of the three dialkylhaloboranes. The common feature of the three disproportionation reactions is the pronounced tendency for boron to be bonded preferentially to one halogen atom. This results in the equilibria lying far in the direction of the disproportionation products in all three cases. Difference in the equilibrium compositions may well be due to a reverse tendency which involves resonance stabilization of  $RBX_2$  to a degree which varies significantly with the halogen concerned. Such resonance stabilization, dependent on

p- $\pi$  bonding between halogen and boron, as in R- $\overline{B}$  would be expected to be

 $X^+$ 

maximal for the fluorine compounds, intermediate for the chlorine compounds and minimal for the bromine compounds. The equilibrium data are consistent with the assumption that such a factor is important in these systems.

While, of the three dialkylhalo compounds, the dialkylbromoboranes show the smallest tendency toward disporportionation, alkyldibromoboranes alone of the three alkyldihalo compounds undergo disproportionation to any observable extent up to about 180°. In the cases of the alkyldihaloboranes mechanistic factors do not appear to be controlling since it would be anticipated that formation of a dimeric intermediate would be least likely with the bromine compounds both for steric and electronic reasons. It would appear that the net resonance stabilization of RBX<sub>2</sub> as compared to BX<sub>3</sub> plus R<sub>2</sub>BX is great enough in the case of the fluorine and chlorine compounds to keep the equilibrium all the way to the left and insufficient in the case of the bromine compounds to prevent the presence of a small proportion of disproportionation products at equilibrium.

The results obtained in the preparations of the primary alkylbromoboranes indicate that the three possible exchange reactions

$$BBr_3 + R_3 B \rightarrow RBBr_2 + R_2 BBr \tag{1}$$

$$RBBr_2 + R_3B \rightarrow 2R_2BBr \tag{2}$$

$$BBr_3 + R_2 BBr \to 2RBBr_2 \tag{3}$$

take place and that in all cases the equilibrium point lies far to the right. When 1:1 mole ratios of trialkylborane and boron tribromide are used, approximately equal yields of alkyldibromoborane and dialkylbromoborane are obtained. When 2:1 mole ratios of trialkylborane to boron bromide are used and sufficient time allowed for the completion of the reactions, the product is almost exclusively dialkylbromoborane resulting from reaction (1) followed by reaction (2). With a 0.5:1 ratio of trialkylborane to boron bromide the product is almost exclusively alkyldibromoborane resulting from reaction (1) followed by reaction (3). That reaction (1) occurs more rapidly than reaction (2) may be concluded from the fact that when a reaction mixture containing a 2:1 mole ratio of trialkylborane to boron bromide is heated for periods of time insufficient for complete reaction the yield of alkyldibromoborane is nearly as high as that of dialkylbromoborane and unreacted trialkylborane is recovered.

As to the mechanism of the exchange reaction, it would appear that the simple formation of a bridged dimer between the reactants may not be sufficient for the exchange of alkyl groups. The temperatures required for these exchange reactions are of the order of magnitude at which isomerization of alkyl groups occurs. Work in this Laboratory<sup>(6)</sup> has shown that the isomerization of alkyl groups involves the formation of B—H compounds and olefin. Furthermore KOSTER<sup>(5)</sup> has reported that, in the presence of compounds containing B—H bonds, the exchange reaction between boron halides and trialkylboranes occurs rapidly at room temperature. The high temperature requirement for the exchange reaction suggests that the mechanism of exchange involves the formation of  $R_2BH$  and olefin from the trialkylborane and that a bridged dimer involving the B—H compound and boron bromide is then formed to initiate the following series of reactions:

$$\mathbf{R}_{2}\mathbf{B} \rightleftharpoons \mathbf{R}_{2}\mathbf{B}\mathbf{H} + \text{olefin} \tag{4}$$

$$R_{2}BH + BBr_{3} \rightleftharpoons B B B \rightleftharpoons R_{2}BBr + HBBr_{2}$$
(5)  
$$R Br Br Br$$

**B**r

$$HBBr_2 + olefin \rightleftharpoons RBBr_2 \tag{6}$$

<sup>(8)</sup> F. M. ROSSI, P. A. MCCUSKER and G. F. HENNION, Abstracts, 145th Nat. Meeting Am. Chem. Soc. New York, New York, September 1963, p. 9-Q.

D

u

While a significant yield (13 per cent) of di-s-butylbromoborane could be obtained by the reaction (at minimum temperatures and times) of boron bromide with tri-sbutylborane without complete isomerization of secondary groups to primary groups, no diisopropylbromoborane could be obtained from boron bromide and triisopropylborane. This relative behaviour of the two secondary trialkylboranes toward boron bromide parallels their behaviour toward trimethoxyboroxine.<sup>(7)</sup> If the formation of some B—H compound is necessary for the reactions to proceed it may be that such species form more readily from secondary butyl groups than from *iso*propyl groups. Even in the presence of diborane, however, tri*iso*propylborane fails to react with boron bromide at 60°. This result suggests that some other factors are responsible for the low reactivity of tri*iso*propylborane toward boron bromide and trimethoxyboroxine.

<sup>(7)</sup> P. A. MCCUSKER and J. H. BRIGHT, J. org. chem. 29, 2093 (1964).