

TABLE IV

DATA FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF ETHYL BROMIDE WITH BENZENE IN 1,2,4-TRICHLOROBENZENE AT 18.9°<sup>a</sup>

Time, min.	Pressure, mm.	$\log \left( \frac{P_\infty - P_0}{P_\infty - P} \right)$	$10^3 k_1$ , sec. <sup>-1</sup>
0	27.20	....	...
3	30.20	0.0140	0.178
6	32.95	.0273	.175
9	35.55	.0400	.170
12	38.35	.0546	.175
17	43.10	.0803	.182
25	50.15	.121	.185
∞	111.60	....	...
			Av. 0.178

<sup>a</sup> ArH = 9.026 mmoles, GaBr<sub>3</sub> = 0.187 mmole, EtBr = 0.939 mmole, C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub> = 6.926 g.

experiments utilizing excess aromatic as the solvent.<sup>6</sup> In other words, the values of the rate constants for the gallium bromide-catalyzed reactions of methyl and ethyl bromides with toluene at low temperatures, determined by the present experimental technique in a high vacuum system, agreed closely with the values calculated from the rate constants<sup>5</sup> obtained at higher temperatures by standard kinetic methods utilizing titration techniques. In order to establish the validity of the manometric technique for systems containing 1,2,4-trichlorobenzene, the reaction in this solvent of ethyl bromide with benzene under the influence of gallium bromide was also studied at 18.9° by the standard titrimetric determination of hydrogen bromide. The results provided a value of  $2.41 \times 10^{-3}$  l.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> for the third-order rate constant for the reaction (Table I). This value agrees fairly well with the average value obtained above by the kinetic measurement with the manometric technique. Therefore, it is concluded that any errors arising from the assumptions involved in the pressure technique for the kinetic studies appear to be no greater than the experimental error.

**Kinetic Measurements by Titrimetric Determination of Hydrogen Bromide.**—The procedure for kinetic measurements by the

titrimetric determination of hydrogen bromide was reported previously.<sup>3</sup> Data of a typical run are summarized in Table V.

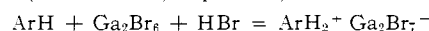
TABLE V

DATA FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF METHYL BROMIDE WITH BENZENE IN 1,2,4-TRICHLOROBENZENE AT 25°<sup>a</sup>

Time, min.	Base, ml.	$\log \left( \frac{a}{a-x} \right)$	$10^3 k_1$ , sec. <sup>-1</sup>
0	9.350	....	...
60	9.820	0.00903	0.578
120	10.350	.0195	.623
180	10.880	.0302	.643
300	11.780	.0489	.625
			Av. .617

<sup>a</sup> ArH = 1.80 moles/l., GaBr<sub>3</sub> = 0.0458 mole/l., MeBr = 0.334 mole/l.

In the present study, a rapid decrease in rate was observed in the latter stages of each run of the experiment, as was observed previously in the related reactions.<sup>3-6</sup> The decrease in rate was faster than any reasonable order would predict. In the hope of clarifying the reason for the rapid decrease in rate, the effect of the added hydrogen bromide on the rate was examined. The gallium bromide-catalyzed reaction of ethyl bromide with toluene in 1,2,4-trichlorobenzene was started after the addition of hydrogen bromide and followed by the present pressure technique. The observed third-order rate constant at 18.9° was  $5.18 \times 10^{-3}$  l.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> (Table I). This value is much smaller than the corresponding value obtained without the addition of hydrogen bromide. Thus the addition of hydrogen bromide retards the reaction. The decrease in rate is attributed to the decrease in effective concentration of the catalyst due to the formation of  $\sigma$ -complexes of gallium bromide-hydrogen bromide with aromatics (reactant and/or product).



Consequently, only kinetic data in the initial stages of the alkylation reactions were utilized for the determination of the rate constants in both the manometric and titrimetric procedures (Tables IV and V).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASH.]

## Neighboring Boron in Nucleophilic Displacement<sup>1a</sup>

BY DONALD S. MATTESON AND RAYMOND W. H. MAH<sup>1b</sup>

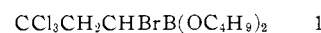
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Displacement of bromide ion from the  $\alpha$ -haloalkaneboronic ester, dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate, by nucleophiles such as iodide, butoxide, and butyl mercaptide ion is greatly facilitated by the neighboring boron atom. Butoxide evidently attacks the boron atom first to form the tetravalent boron anion, which then rearranges with expulsion of bromide ion. Strong support for this mechanism is furnished by the behavior of butyl B-aryl- and B-alkyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinates, which upon mild base treatment expel bromide ion with migration of the B-aryl or B-alkyl group from boron to carbon.

### Introduction

Neighboring-group effects of metallic atoms have not been studied extensively with the exception of elimination reactions. Elimination of a metal cation, often coordinated with a base, together with a halide ion or other leaving group from an  $\alpha$ -,<sup>2</sup>  $\beta$ -,<sup>3</sup> or  $\gamma$ -position<sup>4</sup> often proceeds so readily that it excludes all other possible reactions. However, if the carbon-metal

bond is strong enough, attack of a nucleophile on an  $\alpha$ -haloalkylmetallic compound may result in displacement of halide ion. Trimethylsilylmethyl chloride behaves in this fashion, apparently with some facilitation of attack of iodide ion by a vacant d-orbital of silicon.<sup>5,6</sup> The familiar example of such neighboring-group activation occurs in  $\alpha$ -halocarbonyl compounds.<sup>6,7</sup> These are closely related to the present series of boron compounds, boronic and carboxylic acids being iso-electronic. Investigation of the reactivity of  $\alpha$ -haloalkylboron compounds was made possible by the availability of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (1) from dibutyl ethyleneboronate and bromotrichloromethane.<sup>8</sup>



(1) (a) Supported by National Science Foundation Grant G 19906. (b) National Science Foundation Cooperative Predoctoral Fellow, 1961-1962; abstracted in part from the Ph.D. thesis of R. W. H. M.

(2) Examples include the reaction of iodomethylzinc iodide with olefins (H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959)) and the formation of *t*-butylmethylene from phenylsodium and neopentyl chloride (L. Friedman and J. G. Berger, *ibid.*, **83**, 492, 500 (1961)).

(3) Among numerous examples are: debromobromination, B. M. Mikhailov and P. M. Aronovich, *Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk*, 927 (1961); *Chem. Abstr.*, **55**, 24541 (1961); desilochlorination, L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948); and deoxymercuration, M. M. Kreevoy and G. B. Bodem, *J. Org. Chem.*, **27**, 4539 (1962), and references cited therein.

(4) An example is cyclopropane formation by debromochlorination, M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 1886 (1960).

(5) C. Eaborn and J. C. Jeffrey, *J. Chem. Soc.*, 4266 (1954).

(6) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

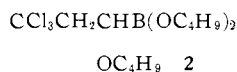
(7) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958).

(8) D. S. Matteson, *ibid.*, **82**, 4228 (1960).

### Results

The bromoalkaneboronic ester **1** reacts rapidly with sodium iodide in acetone to yield the corresponding iodo compound, dibutyl 1-iodo-3,3,3-trichloropropane-1-boronate. This displacement is 1.5–2 times faster than that of allyl bromide, measured in competition experiments. The activating effect of the dibutoxyboryl group may be fully appreciated by comparison with the corresponding carbethoxy compound, ethyl  $\alpha$ -bromo- $\gamma,\gamma,\gamma$ -trichlorobutyrate, which reacts only 0.2–0.3 times as fast as *n*-butyl bromide. Since allyl bromide reacts 65–70 times as fast as *n*-butyl bromide with potassium iodide in acetone,<sup>9</sup> the bromoalkaneboronic ester **1** reacts 300–700 times as fast as the analogous carboxylic ester. The deactivating effect of the trichloromethyl group is severe, as might be predicted.<sup>10a</sup>

Sodium butoxide in butanol displaces bromide from **1** to yield dibutyl 1-butoxy-3,3,3-trichloropropane-1-boronate (**2**).



The butoxy compound **2** also results when the bromide **1** is treated with other bases in butanol such as *t*-butylamine and dibutyl sodiomalonate. Even sodium *t*-butoxide in *t*-butyl alcohol converts **1** to **2**. Similar displacement occurs on treatment of **1** with ethanolic sodium acetate or potassium hydroxide to yield what we judged by infrared examination to be a mixture of **2** and the analogous ethoxy derivative. The product of dehydrobromination of **1**, reported elsewhere,<sup>11</sup> was not detected in any of the above experiments. This behavior is in striking contrast to that of 1,1,1-trichloro-3-bromopropane<sup>12</sup> and ethyl  $\alpha$ -bromo- $\beta$ -methyl- $\gamma,\gamma,\gamma$ -trichlorobutyrate,<sup>13</sup> both of which are dehydrobrominated by potassium hydroxide in ethanol, while sodium acetate dehydroborinates the latter. Qualitative observation of the time of appearance of potassium bromide precipitate indicated that the bromoalkaneboronate **1** reacts a number of times faster than allyl bromide with potassium hydroxide in ethanol but that the dehydrobromination of ethyl  $\alpha$ -bromo- $\gamma,\gamma,\gamma$ -trichlorobutyrate is much faster than the displacement of bromide from **1**. Thus the dibutoxyboryl group markedly accelerates displacement of bromide by alkoxide at the expense of dehydrobromination, but model systems with which to compare the acceleration are unavailable.

That base catalysis occurs in the conversion of the bromide **1** to the butoxy derivative **2** was demonstrated by refluxing **1** in butanol 17 hr., which resulted in the conversion of only 5% of it to **2**, verified by infrared comparison with an authentic mixture. Resistance to uncatalyzed solvolysis has also been found with the boronic acid corresponding to **1**, which was purified by recrystallization from water.<sup>5</sup>

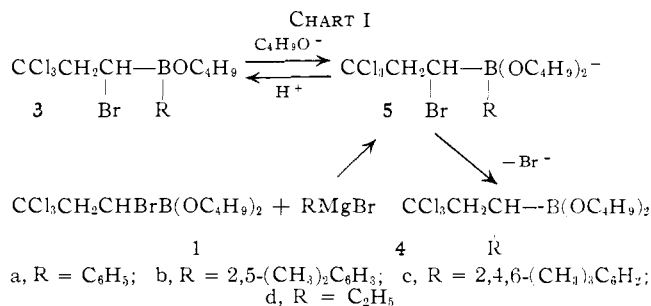
Several attempts to isolate the 1-hydroxyalkaneboronic acid or ester corresponding to **2**, which should have been a by-product of the ethanolic potassium hydroxide treatment of **1** and the major product of treatment of the corresponding boronic acid with aqueous base, failed. The boronic acid would not crystallize and attempted distillation of its butyl ester led to decomposition, presumably through polymerization by transesterification with the  $\alpha$ -hydroxy group.

The acetoxy derivative analogous to **2**, dibutyl 1-acetoxy-3,3,3-trichloropropane-1-boronate, was prepared in moderate yield by heating **1** with sodium acetate in glacial acetic acid followed by re-esterification. The odor of butyl acetate in the product and the contrast to the result with sodium acetate in ethanol suggest that these conditions may have converted the ester **1** to the  $\beta$ -diacetoxy derivative before the displacement took place.

One nucleophile was found which could compete effectively with butoxide ion. Sodium butyl mercaptide with an excess of butyl mercaptan in butanol converted the bromide **1** to dibutyl 1-butylthio-3,3,3-trichloropropane-1-boronate. Although the concentration of butoxide ion in this solution must have been far below that of the butyl mercaptide ion and the mercaptide is normally several times more nucleophilic toward carbon than the alkoxide,<sup>10a</sup> about 5% of the crude reaction product was the butoxy compound **2**.

From the above results it appears that basicity toward boron is a more important factor than nucleophilicity toward carbon in determining which competing base will displace bromide ion from **1**. To elucidate the role of the boron atom we have studied the behavior of some B-aryl- and B-alkyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinates toward bases. The synthesis of these compounds is described elsewhere.<sup>14</sup>

Shaking an ethereal solution of butyl B-phenyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinate (**3a**, Chart I) and butanol with excess aqueous sodium bicarbonate until effervescence ceases yields the displacement with rearrangement product, dibutyl 1-phenyl-3,3,3-trichloropropane-1-boronate (**4a**). The corresponding B-*p*-xylyl (**4b**) and B-mesityl (**4c**) borinates rearrange under similar conditions. Butyl B-ethyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinate (**4d**) resisted aqueous bicarbonate but rearranged with sodium butoxide in butanol. These displacements with rearrangement evidently must proceed through an intermediate anion (**5**) formed by attack of a base, which is represented as butoxide ion for convenience but may include hydroxide, bicarbonate, or others, on the boron atom of the borinic ester **3**.



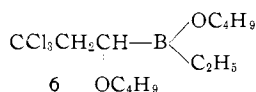
Another route to the anion **5** is provided by the addition of a Grignard reagent to dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (**1**) at  $-70^\circ$ . Because of the well-known lability of alkoxy groups on boron, the equilibration of the anion **5** with the corresponding borinic ester **3** and magnesium butoxide is probably rapid. The position of this equilibrium is unknown; a clear solution is obtained in ether or ether and tetrahydrofuran. Immediate treatment of this solution at  $-70$  to  $-40^\circ$  with aqueous acid yields borinic ester **3**, but at room temperature magnesium bromide separates and rearrangement of the anion **5** to the boronic ester **4** occurs. Infrared examination of the reaction products indicated that when the group R is mesityl (**5c**) rearrangement to boronic ester **4c** is extensive even at

(9) P. D. Bartlett and L. J. Rosen, *J. Am. Chem. Soc.*, **64**, 543 (1942).  
 (10) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (a) pp. 157–185, (b) p. 32.  
 (11) D. S. Matteson and R. W. H. Mah, *J. Org. Chem.*, **28**, 2174 (1963).  
 (12) (a) R. N. Haszeldine, *J. Chem. Soc.*, 3371 (1953); (b) J. R. Shelton and L. H. Lee, *J. Org. Chem.*, **23**, 1876 (1958).  
 (13) R. L. Huang, *J. Chem. Soc.*, 1749 (1956).

(14) D. S. Matteson and R. W. H. Mah, *J. Org. Chem.*, **28**, 2171 (1963).

–70° in ether–THF. The xylyl compound **5b** does not rearrange extensively until kept at 25° an hour or two. The phenyl compound **5a** in ether–THF or ether rearranges little in 2 hr., but yields mostly the boronic ester **4a** after 22 hr. in ether at 25°. The ethyl compound **5d** in ether yields about half borinic ester **3d** and half boronic ester **4d** after 22 hr. at 25°.

The following evidence for the structures of the boronic esters **4** was obtained. The n.m.r. spectrum of butyl 1-phenyl-3,3,3-trichloropropane-1-boronate (**4a**) was examined at 60 and 100 Mc. in deuteriochloroform with tetramethylsilane as the internal standard.<sup>15</sup> The phenyl protons appeared at 7.24 p.p.m. The –OCH<sub>2</sub>– triplet centered at 3.87 p.p.m. and partially overlapped one of the two nonequivalent –CH<sub>2</sub>CCl<sub>3</sub> protons. These were separated by 0.7 p.p.m. and showed a 15 c.p.s. coupling with each other, 10 c.p.s. with the –CH–B proton, which overlapped the second –CH<sub>2</sub>CCl<sub>3</sub> proton in the 2.65–3.0 p.p.m. region. The remaining protons of the butyl groups appeared as expected and the total integrated to the required 26 protons. The corresponding xylyl (**4b**) and mesityl (**4c**) boronic esters, not examined in detail, had infrared spectra in accord with the assigned structures. The corresponding "ethyl" boronic ester, dibutyl 1,1,1-trichloropentane-3-boronate (**4d**), was shown by infrared to be free of its isomer, butyl B-ethyl-B-(1-butoxy-3,3,3-trichloro-1-propyl)-borinate (**6**),<sup>14</sup> the product which would result if butoxy migration occurred in the anion **5d**.



### Discussion

It is evident that the displacement of bromide ion from an  $\alpha$ -bromoalkylborinic ester (**3**) must proceed in no less than two steps. The first is the addition of a Lewis base (butoxide or other) to form the anion **5** or an analogous species. Second, expulsion of bromide and migration of the aryl or alkyl group from boron to carbon occurs to yield the boronic ester **4**. (If the initially attacking base is other than butoxide ion, the isolable ester **4** will result from the subsequent well-known rapid interchange of ligands bonded through oxygen or nitrogen to boron.) Essentially the same process should occur when a base displaces bromide ion from dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (**1**) (e.g., Chart I, R = OC<sub>2</sub>H<sub>5</sub>, **3** → **5** → **4**). This mechanism is in accord with the observations that butoxide ion is much more nucleophilic relative to the competing bases than would be expected in ordinary displacement reactions, as well as the fact that displacement is accelerated far more than dehydrohalogenation. Where the attacking base is the mercaptide anion it becomes less certain that an anion analogous to **5** is an intermediate. The situation is conveniently discussed in terms of the qualitative, generalized energy diagram shown in Fig. 1. The energy of the intermediate anion (**5** or analogous species) at **A** may fall below that of the starting materials if the attacking nucleophile is basic enough or rise to the point where it is doubtful that point **A** is an energy minimum or even on the route to product, as when the attacking nucleophile is iodide ion.

If loss of bromide ion and rearrangement of anion **5** are concerted, the transition state (Fig. 1, point **B**) may be represented by the general structure **7**. The partial bonds may vary widely in strength and covalent *vs.* ionic character, depending on the nature of the migrating

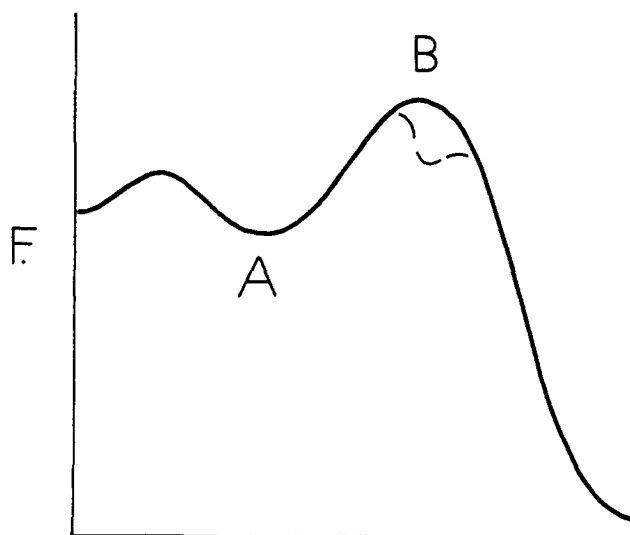
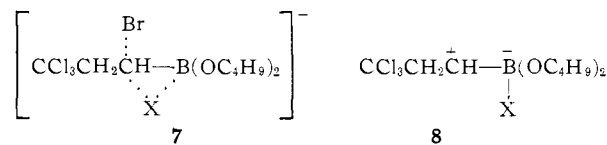


Fig. 1.—Generalized plot of *F* *vs.* reaction coordinate for displacement reactions of  $\alpha$ -bromoalkylboron compounds: point **A**, intermediate anion **5**; **B**, solid curve, transition state **7**; broken line curve, hypothetical ylid intermediate **8**.

group **X** and the reaction medium. The limiting case of ionization of bromide prior to migration of **X** may be represented by structure **8**, a "boron ylid."<sup>16</sup>



Structure **7** implies that the carbon atom on which displacement is occurring will have some electron deficiency. For structure **8** to be truly meaningful it must represent an energy minimum (Fig. 1, broken line under **B**) with a significant barrier to its rearrangement, a highly exothermic process (see below). No evidence for this has been found by us or by others<sup>16,17</sup> who have suggested analogous intermediates, although the somewhat analogous borane–carbon monoxide complex (for which rearrangement may be much less exothermic) is well known.<sup>17</sup> The absence of the borinic ester **6** in the boronic ester **4d** from rearrangement of **3d** implies that **8** (X = C<sub>2</sub>H<sub>5</sub>), if it be an intermediate, is unable to capture butanol or butoxide ion before rearranging. That the rearrangements occur in ether implies no great charge separation in transition state, although it does appear that water greatly accelerates these rearrangements and partial ionic character in the transition state (**7**) may be the cause. More doubt is cast on the ylid **8** where X is phenyl by the observation that ionization and phenyl migration are concerted in the solvolysis of 3-phenyl-2-butyl tosylate,<sup>18</sup> where the classical carbonium ion should be much less prone to rearrange than the phenylboron ylid. The situation is not as clear-cut in the reactions of the  $\alpha$ -bromoalkaneboronic ester **1** with butoxide and mercaptide ions, where the observations hardly require but do not rule out the intermediacy of the ylid **8** with X = OC<sub>2</sub>H<sub>5</sub> or SC<sub>2</sub>H<sub>5</sub>. We plan further investigation of this question.

It is not surprising that the alkyl or aryl group in the anion **5** migrates faster than a butoxy group. The boronic ester **4** contains a C–C and a B–O bond where the isomeric borinic ester **6** has a C–O and a B–C bond. The C–C and C–O bonds should differ in energy by only

(16) H. Jäger and G. Hesse, *Ber.*, **95**, 345 (1962).

(17) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962).

(18) D. J. Cram, *ibid.*, **71**, 3863 (1949).

(15) N. S. Bhacca, Varian Associates, Palo Alto, Calif.

1 or 2 kcal.<sup>10b</sup> but the B-O bond appears to be favored over the B-C bond by 30-40 kcal.<sup>19</sup> This drastically higher stability of the boronic ester **4** should also be partially reflected in the transition state leading to its formation (point **B**, Fig. 1), inasmuch as any B-X bond breaking in transition state **7** tends to make the structure more closely related to the product and will result in a general relative lowering of the energy curve leading to the boronate (Fig. 1, point **A** to products).

An isolated example of a rearrangement analogous to that of borinic ester **3** to boronic ester **4** has been found in the carbonyl series, the conversion of 1-chlorocyclohexyl phenyl ketone to sodium 1-phenylcyclohexanecarboxylate by solid sodium hydroxide.<sup>20</sup>

Although iodide ion attack on the  $\alpha$ -bromoalkaneboronic ester **1** does not necessarily involve an intermediate anion **5** with R = I, the facilitation of the displacement by the neighboring boron is rationalized adequately by transition state **7** with X = I. There is good evidence that an  $\alpha$ -carbonyl group facilitates displacement by essentially the same mechanism.<sup>7,21</sup> Though the inductive effect of the boron atom should be in the right direction to facilitate the displacement,<sup>10a</sup> from the slight rate enhancement found in the reaction of dibutyl  $\beta$ -bromoethaneboronate with iodide<sup>22</sup> it seems unlikely that this is more than a minor factor in the reactivity of the  $\alpha$ -bromoalkaneboronic ester **1**. The great reactivity of **1** also implies that a  $\sigma$ -bonded transition state **7** is involved, not merely allylic-type activation by the dialkoxyboryl or carbonyl group, since dialkoxyboryl groups are less effective than carbalkoxy groups in withdrawing electrons by  $\pi$ -bonding.<sup>17,23</sup>

In summary, the transition state **7** adequately rationalizes all the displacement reactions of  $\alpha$ -bromoalkylboron compounds observed so far and fits both into the general picture of alkyl and aryl migrations to electron-deficient carbon atoms and the activation of halogen adjacent to a carbonyl group.

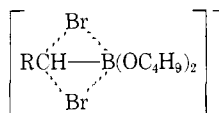
### Experimental<sup>24</sup>

**Dibutyl 1-Iodo-3,3,3-trichloropropane-1-boronate.**—A solution of 6.0 g. of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (**1**)<sup>8</sup> and 3.0 g. of sodium iodide in 50 ml. of acetone was allowed to stand in the dark at 25° for 4 hr. The organic material was taken up in ether (50 ml.), washed with water (50 ml.), treated with butanol (20 ml.), dried with magnesium sulfate, and distilled to yield 5.65 g. (84%) of dibutyl 1-iodo-3,3,3-trichloropropane-1-boronate, b.p. 95-100° (0.05 mm.), redistilled through a spinning band column, b.p. 94-95° (0.05 mm.). The stronger infrared bands appeared at 6.70, 7.01, 7.3-7.6, 7.97, 8.10, 9.05, 9.30, 9.50, 9.71, 10.29, 12.35, 13.95, 14.30, and 14.90  $\mu$ . The corresponding  $\alpha$ -bromoalkaneboronic ester **1** had all the same bands

(16) T. Charnley, H. A. Skinner, and N. B. Smith, *J. Chem. Soc.*, 2288 (1952).

(20) C. L. Stevens and E. Farkas, *J. Am. Chem. Soc.*, **74**, 5352 (1952).

(21) Bartlett and Trautenberg<sup>7</sup> have suggested that the principle of microscopic reversibility would require a symmetrical transition state whenever the displacing and leaving groups are identical (i.e., X is Br). However, microscopic reversibility does not require a symmetrical energy profile



but merely one in which the net energy change from reactants to transition state is identical in both directions. Thus, the unsymmetrical transition state **7**, which seems to us to have more favorable bonding and entropy, is permitted provided that the group X is the attacking bromide in a statistical half of the cases and the leaving bromide in the other half. More basic X groups would be much more strongly bonded to boron than would bromide; iodide might be less so.

(22) D. S. Matteson and J. D. Liedtke, *J. Org. Chem.*, **28**, 1921 (1963).

(23) D. S. Matteson, *ibid.*, **27**, 4203 (1962).

(24) Microanalyses by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were determined on neat liquids in 0.025-mm. cells with a Beckman IR-5; only the stronger bands between 5 and 16  $\mu$  are listed.

except that the 9.05 peak was shifted to 8.87, 9.30 shifted to 9.35, 9.50 absent, 12.35 shifted to 12.28 and 14.9 shifted to 14.58; minor differences in band shapes and intensities were also present.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{21}\text{BCl}_3\text{IO}_2$ : C, 30.76; H, 4.93; B, 2.52; halogen as Cl, 33.03. Found: C, 30.52; H, 4.95; B, 2.76; halogen as Cl, 32.80.

**Ethyl  $\alpha$ -bromo- $\gamma,\gamma,\gamma$ -trichlorobutyrate** was obtained by heating 30 ml. of ethyl acrylate and 100 ml. of bromotrichloroethane on the steam bath 3-4 hr. with several 0.1-g. portions of azobisisobutyronitrile at 0.5-hr. intervals; yield 15 g., b.p. 63-65° (0.05 mm.),  $n_D^{25}$  1.4936. Much telomerie by-product was obtained.

*Anal.* Calcd. for  $\text{C}_6\text{H}_9\text{BrCl}_3\text{O}_2$ : C, 24.15; H, 2.70; halogen as Cl, 47.53. Found: C, 24.40; H, 2.82; halogen as Cl, 47.29.

**Ethyl  $\alpha$ -iodo- $\gamma,\gamma,\gamma$ -trichlorobutyrate** was prepared from 2.4 g. of ethyl  $\alpha$ -bromo- $\gamma,\gamma,\gamma$ -trichlorobutyrate and 2.0 g. of sodium iodide in 20 ml. of acetone. Much iodine formation accompanied the reaction. After 48 hr. at room temperature, two simple distillations yielded 0.9 g. of the iodo ester, b.p. 65-75° (0.1 mm.),  $n_D^{25}$  1.5224. The infrared spectrum failed to show any obvious impurities (e.g., unchanged bromo ester) but a satisfactory analysis was not obtained.

*Anal.* Calcd. for  $\text{C}_6\text{H}_9\text{ICl}_3\text{O}_2$ : C, 20.86; H, 2.33; halogen as Cl, 41.06. Found: C, 21.92; H, 2.81; halogen as Cl, 42.99.

**Relative Rates.**—A solution of sodium iodide in acetone was added to a solution of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (**1**) and allyl bromide in acetone, the final concentrations being 0.25 *M* in each of the three reactants. After 2.5 hr. at 23-25° the sodium bromide was filtered and the solution was concentrated under vacuum. Infrared comparison with authentic mixtures indicated the residue contained 57 ( $\pm 3$ ) mole % dibutyl 1-iodo-3,3,3-trichloropropane-1-boronate, the rest being unchanged **1**. From the known rate constant for allyl bromide,<sup>9</sup> the time was sufficient for more than 99% reaction of the sodium iodide. The calculated rate constant for **1** is 1.5 times that of allyl bromide. At 10-fold dilution, 0.025 *M* in each reagent, after 3 hr. the product was 61 mole % iodoalkaneboronic ester, ratio of *k*'s 1.9, sodium bromide yield before concentration 72% (may be equilibrium value). As a precaution against the possibility that the above measurements reflect equilibrium constants rather than rate constants, the times of appearance of sodium bromide precipitate with **1** and with allyl bromide were compared, which again suggested a ratio of rate constants of roughly 2. Competition between ethyl  $\alpha$ -bromo- $\gamma,\gamma,\gamma$ -trichlorobutyrate and *n*-butyl bromide for sodium iodide, each at 0.33 *M*, after 46 hr. yielded 85% of sodium bromide and about 24% conversion of the bromo ester to iodo, which corresponds to a rate for the ester 0.2-0.3 (for 100% and 85% assumed completion of the reaction, respectively) times that for butyl bromide.

**Dibutyl 1-Butoxy-3,3,3-trichloropropane-1-boronate (2).**—A solution of 0.056 mole of sodium butoxide in 50 ml. of butanol was added in 10 min. under nitrogen to 20.0 g. (0.0523 mole) of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (**1**) stirred and cooled in an ice bath. After 2.5 hr. the mixture was treated with 50 ml. of ether and 50 ml. of water, the aqueous phase was washed with two 25-ml. portions of butanol, and the combined organic phase was washed with two 50-ml. portions of saturated sodium chloride. Distillation yielded 17.8 g. (90%) of dibutyl 1-butoxy-3,3,3-trichloropropane-1-boronate (**2**), b.p. 105-113° (0.02 mm.). In a convenient alternate preparation, 30 ml. of *tert*-butylamine, 30 ml. of butanol, and 8.30 g. of **1** were mixed at room temperature, refluxed 1.5 hr., filtered, the *tert*-butylamine hydrobromide was washed with ether, and the combined solution concentrated at room temperature with a water aspirator. The residue was washed with dilute hydrochloric acid, then saturated sodium chloride, dried over magnesium sulfate, and distilled to yield 6.5 g. (80%) of **2**. The analytical sample was redistilled through a spinning-band column, b.p. 100° (0.02 mm.),  $n_D^{25}$  1.4505; strong infrared bands at 6.71, 6.80, 7.02, 7.3-7.5, 7.68, 7.98, 8.10, 8.37, 9.1-9.2 (broad), 9.70, 10.29, 12.7, 13.25, 13.5, and 14.3  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{30}\text{BCl}_3\text{O}_3$ : C, 47.97; H, 8.05; B, 2.88; Cl, 28.23. Found: C, 47.78; H, 8.08; B, 2.90; Cl, 28.17.

**Dibutyl 1-Acetoxy-3,3,3-trichloropropane-1-boronate.**—A solution of 2.15 g. of sodium acetate and 10.0 g. of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (**1**) in 25 ml. of acetic acid was heated to 80-90° 25 min., after which sodium bromide precipitation began, then kept at 50-60° 17 hr. The sodium bromide (2.44 g., 90%) was filtered and washed with ether (25 ml.). The filtrate was concentrated under vacuum, treated with 6 ml. of butanol, and distilled to yield 3.3 g. (35%) of dibutyl 1-acetoxy-3,3,3-trichloropropane-1-boronate; fractionated, b.p. 96-97° (0.04 mm.),  $n_D^{25}$  1.4512; strong infrared bands at 5.77 (C=O), 6.71, 7.00, 7.26, 7.5 (broad), 7.7, 7.9-8.05, 8.37, 9.30, 9.7 (broad), 12.3, 13.55, and 14.1  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{24}\text{BCl}_3\text{O}_4$ : C, 43.20; H, 6.70; B, 2.99; Cl, 29.40. Found: C, 43.46; H, 6.67; B, 3.01; Cl, 29.16.

**Dibutyl 1-Butylthio-3,3,3-trichloropropane-1-boronate.**—A solution of sodium butyl mercaptide was prepared from 1.21 g. (0.0526 g.-atom) of sodium dissolved in 75 ml. of butanol to which 15 ml. of butyl mercaptan was subsequently added. This solution was added dropwise to 20.0 g. (0.0522 mole) of stirred dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (1) at room temperature. After 2 hr. the mixture (still slightly alkaline) was treated with 100 ml. of water and 100 ml. of ether, the aqueous phase was extracted with butanol, and the organic phase was washed with four 15-ml. portions of saturated sodium chloride and dried over magnesium sulfate. Distillation through a spinning-band column yielded a forerun containing the butoxy compound 2 (estimated to be about 5% of the crude product by infrared) and 15.5 g. of dibutyl 1-butylthio-3,3,3-trichloropropane-1-boronate, b.p. 100–101° (0.01 mm.); redistilled,  $n_D^{25}$  1.4726; strong infrared bands at 6.70, 6.80, 7.3–7.7, 7.96, 8.10, 8.79, 9.30, 9.68, 10.36, 12.1, 13.1, 13.45, and 14.4  $\mu$ .

*Anal.* Calcd. for  $C_{15}H_{30}BCl_3O_2S$ : C, 46.00; H, 7.72; B, 2.76; Cl, 27.16; S, 8.19. Found: C, 45.85; H, 7.84; B, 2.94; Cl, 27.30; S, 7.99.

**Dibutyl 1-Phenyl-3,3,3-trichloropropane-1-boronate.**—The butyl B-phenyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinate (3a),<sup>14</sup> not distilled but identified by infrared, from 11.0 g. of butyl B-phenyl-B-vinylborinate and 30 ml. of bromotrichloromethane was divided into two portions. One portion was treated with 20 ml. of triethylamine in 15 ml. of anhydrous ether, which led to no apparent reaction, followed by 20 ml. of water, which reacted exothermically. Addition of 20 ml. of butanol, acidification with dilute hydrochloric acid, and distillation yielded 7.0 g. of dibutyl 1-phenyl-3,3,3-trichloropropane-1-boronate (4a), b.p. 105–115° (0.06 mm.). The other portion of borinic ester was treated with aqueous sodium carbonate and ether until effervescence ceased, then butanol, and distilled to yield 7.2 g. of 4a (combined yield 80%). Another route to 4a began with the dropwise addition of 0.20 mole of phenylmagnesium bromide in 100 ml. of ether under nitrogen to 68.8 g. (0.18 mole) of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (1) in 200 ml. of ether stirred at –70 to –60°. After 0.5 hr. longer at –70° the mixture was acidified with 10% sulfuric acid, keeping the internal temperature below –30° until acidification was complete. At this point, it was shown in small scale runs by infrared examination that the product was butyl B-phenyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinate (3a). Addition of 100 ml. of butanol, separation, extraction of the aqueous phase with three 50-ml. portions of butanol, and washing the organic phase with six 50-ml. portions of 5% sodium chloride was followed by shaking with 50 ml. of 5% sodium chloride and increments of solid sodium bicarbonate until effervescence ceased and the aqueous phase remained basic. Distillation yielded 62.2 g. (91%) of 4a. It was also shown in 0.01-mole runs in ether (30 ml.) and in 1:1 ether-tetrahydrofuran that after 2 hr. at room temperature the solution could be cooled to –70°, acidified with dilute hydrochloric acid, washed with water, and distilled to yield some unreacted 1 and the  $\alpha$ -bromoalkylborinic ester 3a; no butanol was added to the product before distillation and yield of borinic ester was only about 50%, leaving a considerable high boiling residue (presumably borinic anhydride) which could have contained some boronate (4a) as the anhydride, but no 4a was detected by infrared in the distillate. A solution of phenylmagnesium bromide and 1 (0.5 M in each) after 4 hr. at room temperature began to deposit a second oily phase, presumably rich in magnesium bromide. After 22 hr., acidification at low temperature, washing with water, distillation of the ether, addition of a few ml. of butanol, and rapid distillation yielded 4a containing some 1 but no detectable 3a. The analytical sample of dibutyl 1-phenyl-3,3,3-trichloropropane-1-boronate (4a) was prepared by redistillation of the first sample described above through a spinning-band column, b.p. 105–106° (0.02 mm.),

$n_D^{25}$  1.4940, n.m.r. spectrum described under "Results"; medium infrared bands at 6.70, 6.86, 7.3–7.7, 7.96, 8.11, 9.32, 9.69, 10.28, 11.66, 12.8, and 14.3  $\mu$ .

*Anal.* Calcd. for  $C_{17}H_{30}BCl_3O_2$ : C, 53.79; H, 6.90; B, 2.85; Cl, 28.02. Found: C, 53.45; H, 6.76; B, 3.08; Cl, 27.84.

**Dibutyl 1-(2,5-Dimethylphenyl)-3,3,3-trichloropropane-1-boronate (4b).**—A solution of 0.024 mole of sodium butoxide in 25 ml. of butanol was added dropwise under nitrogen to 10.0 g. (0.242 mole) of butyl B-2,5-dimethylphenyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinate (3b)<sup>14</sup> with stirring. An exothermic reaction with precipitation of sodium bromide occurred. After 0.5 hr. the solution no longer gave an alkaline reaction with water and phenolphthalein. Treatment with water, ether, and butanol in the usual extraction procedure followed by distillation yielded 8.0 g. (81%) of the boronic ester 4b; fractionated, b.p. 123–124° (0.02 mm.),  $n_D^{25}$  1.4980; weak infrared band at 6.19; strong bands at 6.65, 6.72, 6.85, 7.06, 7.4–7.7, 7.97, 8.11, 9.31, 9.70, 10.28, 12.3, 13.05, and 14.45  $\mu$ . Alternately, 4b was prepared from 0.05 mole of *p*-xylylmagnesium bromide in 30 ml. of tetrahydrofuran and 18.0 g. (0.047 mole) of 1 in 30 ml. of ether. When the reaction mixture was kept cold through the acidification step as described above for the corresponding phenyl compound, the usual extraction procedure (avoiding contact with any base) followed by addition of 10 ml. of butanol and distillation yielded 7.7 g. of unchanged 1 and a second fraction, b.p. 120–135° (0.1 mm.), which appeared to be largely the borinic ester 3b with a few per cent of boronic ester 4b. Shaking this material with 15 ml. of ether, 10 ml. of butanol, 20 ml. of water, and enough solid sodium bicarbonate to raise the pH of the aqueous phase to 6–7 yielded 8.2 g. (43%) of the borinic ester 4b on distillation. A similar procedure except that the solution of xylylmagnesium bromide and 1 was kept at 25° 1.5 hr. before acidification below –40° led directly (without bicarbonate) to the boronic ester 4b; yield 11.0 g. (57%), free of any detectable amount of borinic ester 3b.

*Anal.* Calcd. for  $C_{19}H_{30}BCl_3O_2$ : C, 56.00; H, 7.41; B, 2.65; Cl, 26.09. Found: C, 56.02; H, 7.58; B, 2.80; Cl, 25.98.

**Dibutyl 1-Mesityl-3,3,3-trichloropropane-1-boronate (4c).**—Reaction of 1 with mesitylmagnesium bromide under conditions similar to those described for the *p*-xylyl compound above, keeping the reaction mixture cold through the acidification step, led to 7 g. of unchanged 1 and 6 g. of material that was mostly the boronic ester 4c but contained 10–20% borinic ester 3c. Treatment with aqueous sodium carbonate and butanol led to pure boronic ester 4c. A better yield of 4c, 64%, was obtained when the reaction mixture was allowed to warm to room temperature before acidification; the work-up procedure in this case included washing with aqueous sodium bicarbonate. The analytical sample had b.p. 129–130° (0.04 mm.),  $n_D^{25}$  1.5078; medium infrared band at 6.18, strong bands at 6.72, 6.80, 7.06, 7.4–7.7, 7.93, 8.10, 9.31, 9.70, 10.17, 11.70, 13.3, and 14.4  $\mu$ .

*Anal.* Calcd. for  $C_{20}H_{32}BCl_3O_2$ : C, 56.97; H, 7.65; B, 2.57; Cl, 25.23. Found: C, 56.71; H, 7.64; B, 2.74; Cl, 25.17.

**Dibutyl 1,1,1-Trichloropentane-3-boronate (4d).**—A solution of 0.038 mole of sodium butoxide in 40 ml. of butanol was added dropwise under nitrogen to 13.10 g. of butyl B-ethyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-borinate (3d)<sup>14</sup> with stirring and allowed to stand 1 hr. Treatment with water, ether, and butanol in the usual extraction procedure followed by distillation yielded 11.0 g. (87%) of the boronic ester 4d. The analytical sample was distilled through a small packed column; b.p. 75–76° (0.06 mm.),  $n_D^{25}$  1.4518; strong infrared bands at 6.71, 6.80, 7.03, 7.2, 7.4–7.7, 7.9, 8.09, 8.35, 9.23, 9.56, 10.22, 12.77, and 14.0  $\mu$ .

*Anal.* Calcd. for  $C_{19}H_{30}BCl_3O_2$ : C, 47.10; H, 7.91; B, 3.27; Cl, 32.10. Found: C, 47.06; H, 7.80; B, 3.40; Cl, 32.27.

[CONTRIBUTION FROM THE RESEARCH CENTER, SPRAGUE ELECTRIC CO., N. ADAMS, MASS.]

## Nucleophilic Displacement Reactions in Aromatic Systems. VII. The *ortho:para* Ratio in the Reactions of Nitrochlorobenzenes with Piperidine and with 1,4-Diazabicyclo(2.2.2)octane

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Both *o*- and *p*-nitrochlorobenzene react with two moles of 1,4-diazabicyclo(2.2.2)octane at a rate which is proportional to the product of the amine and chloride concentrations. The product from *p*-nitrochlorobenzene has been shown to be IV. The ratio,  $k_o/k_p$ , for the reactions with the above tertiary amine in benzyl alcohol at  $150 \pm 0.2^\circ$  was found to be 0.0040. For the reactions with piperidine in the same solvent at  $120 \pm 0.2^\circ$  the *ortho:para* ratio is 5.6. Values of  $k_o/k_p$  greater than one are attributed to hydrogen bonding in the transition state for the reaction with the *ortho*-substituted substrate.

It is well established that *o*-nitrohalobenzenes react with primary and secondary amines more rapidly than do *p*-nitrohalobenzenes. In contrast, those substitu-

tions, which do not at any stage involve the removal of a proton, as in reactions with alkoxides and phenoxides, proceed at a faster rate with *p*-nitrohalobenzenes.