procedure described, except that the reaction mixture was not allowed to warm above −40° before acidification. Although the product survived treatment with a small amount of sodium bicarbonate during the work-up procedure, this possibly risky step[3] is probably unnecessary. The borinate was distilled through a spinning-band column; yield, 27.8 g. (84%); b.p. 65–67° (0.01 mm.); strong infrared bands at 6.81, 7.10, 7.3–7.4, 7.65, 7.95, 9.32, 9.70, 10.70, 12.3, 13.35, and 14.1 μ. The analytical sample was fractionated again to remove unchanged starting boronic ester, which boiled about 5–10° higher than borinate product.

Anal. Calcd. for $C_9H_{17}BBrCl_3O$: C, 31.95; H, 5.07; B, 3.20; halogen as Cl, 41.91. Found: C, 32.06; H, 5.21; B, 3.29; halogen as Cl, 41.85.

Butyl *B*-(3-Methyl-1-butyl)-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate.—By essentially the same procedure, keeping the reaction mixture cold until acidification, 0.1 mole of isoamylmagnesium bromide in 100 ml. of ether and 38.0 g. (0.0954 mole) of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate, in 100 ml. of ether, yielded 31.5 g. (84%) of the borinate after one simple distillation. The analytical sample was redistilled twice through a spinning-band column; b.p. 78–79° (0.01 mm.); $n^{24}D$ 1.4738; strong infrared bands appeared at 6.71, 8.86, 9.32, 9.70, and 13.2 μ.

Anal. Calcd. for $C_{12}H_{23}BBrCl_3O$: C, 37.89; H, 6.09; B, 2.84; halogen as Cl, 37.28. Found: C, 37.58; H, 6.19; B, 3.08; halogen as Cl, 37.60.

Neighboring Boron in SN2′ Displacements on a Trichloropropeneboronic Ester[1a]

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Dehydrobromination of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate has been accomplished with anhydrous *t*-butylamine. The product, dibutyl 3,3,3-trichloropropene-1-boronate, readily undergoes SN2′ displacement of chloride ion by nucleophilic reagents, including phenylmagnesium bromide.

In the course of our investigation of the chemistry of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (1),[2] we attempted the dehydrobromination of this compound to yield dibutyl 3,3,3-trichloropropene-1-boronate (2).

$$\underset{1}{CCl_3CH_2CHBrB(OC_4H_9)_2} \longrightarrow \underset{2}{CCl_3CH{=}CH{-}B(OC_4H_9)_2}$$

This dehydrobromination proved to be surprisingly difficult to accomplish. As has been noted in the preceding paper of this series,[2b] reagents such as alcoholic potassium hydroxide, alcoholic sodium acetate, sodium butoxide, and even sodium *t*-butoxide cause displacement of bromide ion by alkoxide with no detectable dehydrohalogenation. Quinoline has been used for the dehydrobromination of a boronic acid in which the bromine atom was remote from the boron,[3] but this reagent converted the α-bromoalkaneboronic ester 1 to intractable black tar, as did a more hindered heterocycle, 2,6-lutidine, and a secondary amine, piperidine (tried with the hope of displacing bromide).

The dehydrohalogenation was accomplished by treating the α-bromoalkaneboronic ester 1 with excess triethylamine. The conditions for the best use of triethylamine were not explored, since in early experiments less tar formation and higher yields of the trichloropropeneboronic ester 2 were obtained with *t*-butylamine as the dehydrohalogenating agent. This reagent combines the advantages of high basicity toward hydrogen and sufficient steric hindrance to reduce its basicity toward boron so that side reactions involving base attack on boron are minimized. The dehydrohalogenation product 2 also proved to be very sensitive to attack by bases other than hindered amines. This sensitivity complicated the work-up procedure. If the *t*-butylammonium bromide was filtered and the solution distilled directly, the product 2 was contaminated with sublimable solids. After vacuum distillation of the *t*-butylamine the residue of 2 contained dissolved material which absorbed in the N–H region near 2.9 μ. It is possible that a small proportion of the butoxy groups in the boronic ester was replaced with the *t*-butylamino group, or that some boron–amine complex was present and the unknown material underwent decomposition to amine salt during the subsequent distillation. It was not desirable to use an extraction procedure directly on the crude reaction mixture, since contact with water in the presence of amine decomposed the product 2. The problem was circumvented by distilling the *t*-butylamine, dissolving the residue in ether, and adding it to an excess of dilute hydrochloric acid. After separation and addition of a little butanol to ensure complete esterification, the distillation of 2 then proceeded without difficulty.

The structure of the trichloropropeneboronic ester 2 was proved by its reaction with hydrogen peroxide in the presence of 2,4-dinitrophenylhydrazine to yield the 2,4-dinitrophenylhydrazone of β,β,β-trichloropropionaldehyde.[2a] The *trans* isomer of 2 would be expected to be favored thermodynamically and, provided the usual stereochemistry of eliminations prevails in its formation, kinetically.

$$2 \longrightarrow CCl_3CH_2CH{=}N{-}NHC_6H_3(NO_2)_2$$

However, there remains the possibility that some of the *cis* isomer is present also. In different batches of 2 the infrared band at 10.95 μ varied from moderately weak to moderately strong and the C=C band at 6.11 μ varied slightly in width, the rest of the spectrum remaining constant. There is also the possibility that the impurity is a structural isomer, $CCl_2{=}CH{-}CHClB(OC_4H_9)_2$, but it seems unlikely that this isomerization would occur without concurrent introduction of bromine into the product, which seems to be precluded by the analytical data. The presence of this isomer is rendered even more unlikely by the observation that 2 survived thirteen hours with lithium chloride in refluxing acetone without undergoing any change.

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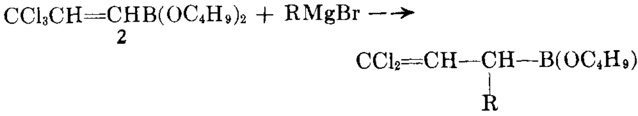
[1] (a) Supported by National Science Foundation grant G 19906; (b) National Science Foundation Cooperative Predoctoral Fellow, 1961–1962; abstracted from the Ph. D. thesis of R. W. H. M.

[2] (a) D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1962); (b) D. S. Matteson and R. W. H. Mah, *ibid.*, **85**, 2599 (1963); (c) D. S. Matteson and R. W. H. Mah, *J. Org. Chem.*, **28**, 2171 (1963).

[3] A. K. Hoffman and W. M. Thomas, *J. Am. Chem. Soc.*, **81**, 530 (1959).

Phenylmagnesium bromide in ether reacted with dibutyl 3,3,3-trichloropropene-1-boronate (**2**) to yield the product of formal S$_N$2′ displacement of chloride ion by phenyl, dibutyl 1,1-dichloro-3-phenylpropene-3-boronate (**3a**). The structure is supported by the

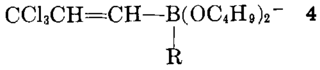


$$\underset{\mathbf{2}}{CCl_3CH{=}CHB(OC_4H_9)_2} + RMgBr \longrightarrow CCl_2{=}CH{-}\underset{R}{\underset{|}{C}}H{-}B(OC_4H_9)_2 \quad \mathbf{3}$$

a, R = C_6H_5; b, R = $CH_2CH_2CH(CH_3)_2$

n.m.r. spectrum in deuteriochloroform with tetramethylsilane as internal standard, which shows the expected peaks due to phenyl and butoxy group protons, as well as a doublet centered at 6.25 p.p.m. due to the olefinic proton, and another doublet at 3.58 p.p.m. due to the adjacent methine proton.[4] Further evidence for the structure is provided by deboronation with hydrogen peroxide to 1,1-dichloro-3-phenylpropen-3-ol, $CCl_2{=}CH{-}CH(OH)C_6H_5$.[5] A similar product, dibutyl 1,1-dichloro-6-methylhept-1-ene-3-boronate (**3b**), was obtained by the addition of isoamylmagnesium bromide to the trichloropropeneboronic ester **2**. Its structure was not rigorously proved, but the general similarity of its infrared spectrum to that of **3a** leaves little doubt.

It seems unlikely that direct S$_N$2′ displacement of chloride ion by a Grignard reagent would occur. We postulate that the anion **4** is an intermediate and the over-all mechanism is vinylogous to that of displacement of bromide ion from the α-bromoalkaneboronic ester **1**.[2b] However, we have been frustrated in attempts to obtain the borinic ester that would result from loss of butoxide ion from **4**. Where R is phenyl, the rearrangement to the boronic ester **3a** is evidently complete at −70° within fifty minutes. Attempts to dehydrobrominate butyl *B*-phenyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate[2c] with *t*-butylamine resulted in formation of the expected *t*-butylammonium bromide, but the boron-containing product seemed to be a mixture and no sample yielding good elemental analyses for butyl *B*-phenyl-*B*-(3,3,3-trichloropropenyl)borinate could be obtained.



$$CCl_3CH{=}CH{-}\underset{R}{\underset{|}{B}}(OC_4H_9)_2^- \quad \mathbf{4}$$

Treatment of the trichloropropeneboronic ester **2** with sodium butoxide or *t*-butylamine in butanol led to dibutyl 1,1-dichloro-3-butoxypropene-3-boronate (**3c**, R = OC_4H_9). Again it appears likely, but has not been proved, that anion **4** (R = OC_4H_9) is an intermediate in this displacement with rearrangement. The assigned structure is supported by the infrared spectrum plus the difficulty in imagining any stable, reasonable alternative.

The foregoing reactions of the trichloropropeneboronic ester **2** contrast with those of *B*,*B*-dialkyl-*B*-(3-chloro-1-propenyl)boranes, which recently have been reported[6] to react with bases such as sodium hydroxide or sodium tetraalkylborons to undergo an elimination (deborochlorination) reaction, which yielded allene and methylacetylene.

Experimental[7]

Dibutyl 3,3,3-Trichloropropene-1-boronate (2).—A mixture of 60 ml. of *t*-butylamine (dried by distillation from calcium hydride) and dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (1) was refluxed for 1 hr. under nitrogen. The *t*-butylammonium bromide (7.65 g., 94%) was filtered and washed with ether, and the combined filtrate was concentrated under reduced pressure. The residue was dissolved in 25 ml. of ether and shaken with 60 ml. of 0.2 *M* hydrochloric acid. The aqueous phase was extracted with two 10-ml. portions of butanol. The combined organic phase was washed with portions of saturated sodium chloride solution until the final wash was neutral, dried over magnesium sulfate, and distilled to yield 11.5 g. (68%) of dibutyl 3,3,3-trichloropropene-1-boronate (2), b.p. 70–80° (0.05 mm.) The analytical sample, originally prepared with triethylamine as the dehydrobrominating agent (24 hr. at 60–70°), was redistilled twice through a spinning-band column; b.p. 71–72° (0.05 mm.); strong infrared bands at 6.11, 6.70, 6.82, 7.0, 7.3–7.7, 7.89, 8.08, 8.25, 9.28, 9.70, 10.16, 10.95 (medium, variable intensity in different samples), 11.63, 12.2, and 13.7 (very strong and broad) μ.

Anal. Calcd. for $C_{11}H_{20}HCl_3O_3$: C, 43.82; H, 6.69; B, 3.59; Cl, 35.28. Found: C, 43.79, 43.96; H, 6.70, 6.87; B, 3.77, 3.80; Cl, 35.26, 35.43.

Dibutyl 1,1-Dichloro-3-phenylpropene-3-boronate (3a).—Twenty-four milliliters of 3 *M* phenylmagnesium bromide (Arapahoe Chemical Co.) in ether was added in 15 min. to a solution of 20.0 g. of dibutyl 3,3,3-trichloropropene-1-boronate (2) in 100 ml. of ether stirred at −60° under nitrogen. The mixture was allowed to warm to 10° over a period of 1 hr., then cooled below −40°, and treated with a solution of 2 ml. of sulfuric acid in 100 ml. of water. After warming to room temperature the phases were separated, the aqueous phase was washed with two 15-ml. portions of butanol, and the combined organic phase was washed with four 20-ml. portions of saturated sodium chloride. Enough solid sodium bicarbonate was added to the last washing to bring the pH of the aqueous phase to 6. (In another run, freshly prepared phenylmagnesium bromide was used, the reaction mixture was not permitted to warm above −40° until acidified, and the sodium bicarbonate treatment was omitted. The same product was obtained in about the same yield.) Distillation yielded 12.1 g. (60%) of dibutyl 1,1-dichloro-3-phenylpropene-3-boronate, b.p. 100–109° (0.05 mm.). The analytical sample was redistilled through a spinning-band column; b.p. 105° (0.05 mm.); medium infrared band at 6.20; strong bands at 6.70, 6.86, 7.04, 7.3–7.8, 8.10, 9.33, 9.72, 11.1 (with shoulder, 10.95), and 14.28 μ.

Anal. Calcd. for $C_{17}H_{25}BCl_2O_2$: C, 59.51; H, 7.34; B, 3.18; Cl, 20.67. Found: C, 59.35; H, 7.38; B, 3.47; Cl, 21.21.

1,1-Dichloro-3-phenylpropen-3-ol.—The reaction of 1.95 g. of dibutyl 1,1-dichloro-3-phenylpropane-3-boronate (**3a**) with 3 ml. of 30% hydrogen peroxide was exothermic. Extraction of the product with ether and concentration followed by crystallization from ligroin at −50° yielded 0.42 g. (36%) of 1,1-dichloro-3-phenylpropen-3-ol, m.p. 53–54°; twice sublimed, m.p. 57–57.5° (lit.[5] m.p. 57°); strong infrared bands at 6.17, 9.75, 11.1, 11.7, 13.1, and 14.3 μ.

Anal. Calcd. for $C_9H_8Cl_2O$: C, 53.24; H, 3.97; Cl, 34.92. Found: C, 53.21; H, 3.86; Cl, 34.93.

Dibutyl 1,1-Dichloro-6-methylhept-1-ene-3-boronate (3b).—By essentially the same procedure described for the preparation of the phenyl compound **3a**, 15.0 g. of the trichloropropeneboronic ester 2 and 0.5 mole of isoamylmagnesium bromide yielded 13.8 g. of crude dibutyl 1,1-dichloro-6-methylhept-1-ene-3-boronate (**3b**); b.p. 83–87° (0.05 mm.); fractionated with a spinning-band column to remove unchanged 2, 8.1 g. (48%), b.p. 88–90° (0.05 mm.), again redistilled for analysis; medium infrared band at 6.18, strong bands at 6.72, 6.80, 7.04, 7.3–7.8, 8.10, 8.43, 9.10, 9.31, 9.72, 11.2, and 11.5 μ.

Anal. Calcd. for $C_{16}H_{31}BCl_2O_2$: C, 57.00; H, 9.27; B, 3.21; Cl, 21.03. Found: C, 56.75; H, 9.25; B, 3.38; Cl, 20.95.

Dibutyl 1,1-Dichloro-3-butoxypropene-3-boronate (3c).—A solution of 0.027 mole of sodium butoxide in 50 ml. of butanol

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[4] Spectrum and interpretation by N. S. Bhacca, Varian Associates, Palo Alto, Calif.

[5] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Dokl. Akad. Nauk, SSSR*, **99**, 781 (1954); *Chem. Abstr.*, **49**, 15797e (1955).

[6] P. Binger and R. Köster, *Angew. Chem.*, **74**, 652 (1962).

[7] Microanalyses were by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were taken on neat liquids in 0.025-mm. cells with a Beckman IR-5. Only the stronger bands between 5 and 16 μ are listed.

was added in 15 min. to 8.0 g. (0.027 mole) of the trichloropropeneboronic ester **2** stirred under nitrogen. After 3 hr. the slurry was treated with ether and water, and the organic phase was washed with saturated sodium chloride and dried over magnesium sulfate. Distillation yielded 5.5 g. (61%) of dibutyl 1,1-dichloro-3-butoxypropene-3-boronate (**3c**), b.p. 88–90° (0.05 mm.). A 56% yield of **3c** also was obtained by warming 5.0 g. of **2** with 10 ml. of butanol and 5 ml. of *t*-butylamine for 5 min. at 35–40°. The analytical sample was redistilled through a spinning-band column; b.p. 84–85° (0.01 mm.); strong infrared bands at 6.18, 6.72, 6.80, 7.0, 7.3–7.7, 7.95, 8.09, 8.35, 8.90, 9.1 (broad), 9.6, 9.70, 9.3–9.4, 11.17, and 11.6 μ.

Anal. Calcd. for $C_{15}H_{29}BCl_2O_3$: C, 53.13; H, 8.62; B, 3.19; Cl, 20.91. Found: C, 53.27; H, 8.81; B, 3.39; Cl, 20.99.

Reactions of 1,1-Dichloro-2,2-diphenylethene and 1,1,1-Trichloro-2,2-diphenylethane with Nucleophilic Reagents. A New Method for Certain Allenes[1]

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1,1,1-Trichloro-2,2-diphenylethane (Ia) underwent dehydrohalogenation with potassium amide in liquid ammonia to form 1,1-dichloro-2,2-diphenylethene (IIa), which reacted further with this reagent to give diphenylacetonitrile. The latter reaction presumably involved nucleophilic substitution, followed by dehydrohalogenation. Dichloroethene IIa and its *p*-chloro derivative IIb reacted with potassium diphenylmethide in liquid ammonia to afford 1,1,3,3-tetraphenylallene (VIa) and its *p*-chloro derivative VIb, respectively. These reactions also presumably involved nucleophilic substitution, followed by dehydrohalogenation. However, IIa was converted by potassium triphenylmethide slowly in liquid ammonia and faster in refluxing tetrahydrofuran to tolane. This product presumably arose through displacement on halogen, followed by rearrangement. IIa was converted to tolane by phenyllithium in ether.

It is well known that the 1,1,1-trichloro-2,2-diarylethanes (Ia,b) readily undergo dehydrohalogenation with refluxing, ethanolic potassium hydroxide to form the 1,1-dichloro-2,2-diarylethenes (IIa,b),[2] which are relatively stable towards this reagent.[3]

$$(p\text{-Y-}C_6H_4)_2CHCCl_3 \qquad (p\text{-Y-}C_6H_4)_2C{=}CCl_2$$
$$\text{Ia, Y = H} \qquad \text{IIa, Y = H}$$
$$\text{b, Y = Cl} \qquad \text{b, Y = Cl}$$

However, dichloroethene IIa has been converted to diphenylacetic acid by treatment with alcoholic potassium hydroxide at 150° (under pressure)[4] and by treatment with sodium ethoxide at 180° followed by hydrochloric acid.[5] In the latter reaction, the twofold nucleophilic substitution product III was assumed to be an intermediate.[5]

$$\underset{\text{III}}{(C_6H_5)_2C{=}C(OC_2H_5)_2}$$

In the present investigation a study was made of the reactions of Ia and, especially, those of IIa,b with some, more strongly nucleophilic reagents.

Like potassium hydroxide and sodium ethoxide, potassium amide in liquid ammonia readily effected dehydrohalogenation of Ia to form IIa. However, in contrast to the two former nucleophiles, potassium amide reacted further with IIa at the same temperature to give diphenylacetonitrile (IV) (equation 1, Table I).

$$\text{Ia} \xrightarrow[\text{liq. NH}_3]{\text{KNH}_2} \text{IIa} \xrightarrow[\text{liq. NH}_3]{3\text{KNH}_2} \underset{\text{IV}}{(C_6H_5)_2CHCN} \qquad (1)$$

TABLE I

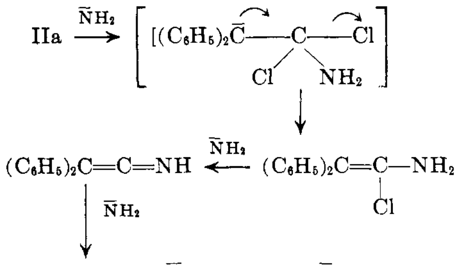
REACTIONS OF HALIDES Ia AND IIa WITH POTASSIUM AMIDE IN LIQUID AMMONIA

Halide	Mol. equiv. of reagent	Mode of addition	Product	Yield, %
Ia	1	Inverse	IIa	98
Ia	4	Direct	IIa	10[a]
			IV	87[a]
IIa	1	Direct	IV	33[b]
IIa	3	Direct	IV	88[c]
IIa	3.7	Direct	IV	90 (98)[a]

[a] Determined by v.p.c. [b] 66% of IIa was recovered. [c] 10% of IIa was recovered (by v.p.c.).

Table I shows that an excellent yield of IIa was obtained from Ia employing molecular equivalents of the reactions by the inverse addition procedure, and that excellent yields of IV were obtained from Ia and IIa with excess of the reagent. The conversion of IIa to the anion of IV may be accounted for by nucleophilic substitution, followed by dehydrohalogenation and, finally, by ionization (Scheme A). The nucleophilic substitution presumably involves an addition–elimination mechanism.

SCHEME A



In agreement with Scheme A, three molecular equivalents of the reagent appear to be involved in the conversion of IIa to IV, since the yield was only 33% with

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[1] Supported by the Army Research Office (Durham) and the National Science Foundation.

[2] See, for example, K. Brand and A. Busse-Sundermann, *Ber.*, **75**, 1819 (1942); S. J. Cristol, *J. Am. Chem. Soc.*, **67**, 1494 (1945).

[3] In contrast to trichloroethane Ia, the corresponding trifluoroethane is converted to diphenylacetic acid and its ethyl ester even by refluxing ethanolic potassium hydroxide; see R. Mechoilam, S. Cohen, and A. Kaluszyner, *J. Org. Chem.*, **21**, 801 (1956).

[4] F. E. Sheibley and C. F. Prutton, *J. Am. Chem. Soc.*, **62**, 840 (1940); O. Grummett, A. Buck, and A. Jenkins, *ibid.*, **67**, 156 (1945); F. Gatzi and W. Stanbach, *Helv. Chim. Acta*, **29**, 563 (1946).

[5] E. E. Harris and G. B. Frankforter, *J. Am. Chem. Soc.*, **48**, 3144 (1926).