resulting solution was extracted with three 10-ml. portions of cold saturated ammonium sulfate solution. The bulk of the solvent was removed under reduced pressure and the residue was dissolved in chloroform and titrated iodometrically. Titration indicated that approximately 30% of the anhydride had been converted to peroxidic materials. The reaction was followed by taking infrared spectra of the carbonyl region (5 to 6 μ) at intervals. At the end of 6 hr. there were bands at 1730, 1775, and 1800 cm.$^{-1}$ attributable to peroxide, peracid, acid, and anhydride groups.

Repetition of this reaction in the absence of the urea afforded the same result—a 30% conversion of anhydride to peroxidic products.

D. **Benzoic Anhydride and Perbenzoic Acid in the Presence of a Trace of Benzoic Acid.**—To 290 mg. (0.00128 mole) of benzoic anhydride and 15.7 mg. (0.000128 mole) of benzoic acid in a mixture of 4 ml. of methylene chloride and 2 ml. of ether, stirred and cooled to 2°, was added 3 ml. of an ethereal solution containing 58.2 mg./ml. of perbenzoic acid (177 mg., 0.00128 mole). The resulting solution was stirred for 3 hr. At the end of this period 25 ml. of cold ether was added and the solution was extracted with three 10-ml. portions of cold saturated sodium bicarbonate (acidification with concentrated hydrochloric acid, extraction with ether, drying, and evaporation of the solvent gave 130.4 mg. of benzoic acid, m.p. 121.5–122.5°), three 10-ml. portions of cold sodium carbonate solution, and two 10-ml. portions of saturated sodium chloride solution. Combination of the latter washings and treatment as indicated previously gave 55.6 mg. of benzoic acid, m.p. 119–121°. The washed ethereal solution was dried over calcium sulfate. Filtration and evaporation of the solvent gave 290 mg. of a solid, 62% benzoyl peroxide by titration. Crystallization of a portion of the crude solid from chloroform–methanol gave benzoyl peroxide, m.p. 104–104.5°, infrared spectrum superimposable with that of authentic sample.

Repetition of this experiment in the presence of dicyclohexylurea (288 mg.) afforded the same result—61% conversion of benzoic anhydride to benzoyl peroxide.

Phthaloyl Peroxide.—To a cold (2°), stirred solution of 2.64 g. (0.0128 mole) of dicyclohexylcarbodiimide in 20 ml. of ether was added 4.7 ml. of an ethereal solution of hydrogen peroxide containing 265 mg./ml. (1.25 g., 0.0366 mole). To the resulting solution was added over a 4-hr. period a solution of 1.8 g. (0.0122 mole) of phthalic anhydride (recrystallized from chloroform) in 25 ml. of methylene chloride. The total reaction time was 8 hr. The resulting mixture was filtered and the precipitate was triturated with three 20-ml. portions of cold methylene chloride (yield of urea, 2.38 g., m.p. 231–233°). The combined filtrates were washed with three 20-ml. portions of cold saturated ammonium sulfate solution and one 10-ml. portion of cold saturated sodium chloride solution. The solution was dried over calcium sulfate and the solvent was evaporated giving a residual solid. The solid was crystallized from ethyl acetate–pentane giving 1.55 g. of a yellow solid, m.p. 95–100°. The solid was redissolved in ethyl acetate and the solution was extracted with two 10-ml. portions of cold saturated sodium bicarbonate solution and 10 ml. of saturated sodium chloride solution. Treatment of the resulting material as indicated previously gave 0.81 g. of phthaloyl peroxide[16] in the form of off-white granular crystals, m.p. 112–113° (exploded at 114°), titrimetric purity 99%. The infrared spectrum of the solid (chloroform) is the same as that of an authentic sample.

Reaction of Bicyclo[2.2.2]octane-1,2-dicarboxylic Anhydride[6] with Hydrogen Peroxide and Dicyclohexylcarbodiimide.—Several reactions were attempted varying the time of addition of the anhydride and the quantity of hydrogen peroxide. In all cases the only materials isolated were colorless oils of varying peroxide content (30–60%). Attempts to crystallize or resolve the oils on cellulose pulp or Florisil (Floridin Co.) were unsuccessful.[17]

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(16) F. D. Greene, *J. Am. Chem. Soc.*, **78**, 2246 (1956).

(17) Further details may be found in the Ph.D. thesis of J. Kazan, Ph.D. thesis in chemistry, Massachusetts Institute of Technology, February, 1963.

Vinylborinic and α-Bromoalkylborinic Esters[1]

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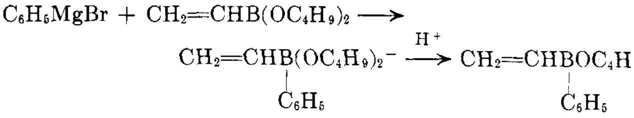
B-Aryl-*B*-vinylborinic esters have been prepared by the addition of aryl Grignard reagents to dibutyl ethyleneboronate. Light-initiated addition of bromotrichloromethane to the vinyl group yielded the corresponding *B*-aryl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinic esters. *B*-Alkyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinic esters were prepared by addition of the alkyl Grignard reagent to dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate.

We undertook the synthesis of some α-bromoalkylborinic esters with the expectation that their behavior toward nucleophiles would clarify the role of boron in assisting the displacement of the neighboring halogen atom[3] and the hope that they might be useful synthetic intermediates. The radical-catalyzed addition of bromotrichloromethane to dibutyl ethyleneboronate[4] suggested possible synthetic routes to compounds of this class. The extraneous trichloromethyl group introduced concurrently in the synthesis does not interfere with essential behavior of α-bromoalkylboron function.

B-Aryl-*B*-vinylborinates were prepared to serve as precursors of the corresponding *B*-aryl-*B*(1-bromo-3,3,3-trichloro-1-propyl)borinates as well as a logical extension of our studies of the properties of vinylboron compounds. Butyl *B*-phenyl-*B*-vinylborinate[5] was synthesized by the addition of phenylmagnesium bromide to dibutyl ethyleneboronate.



$$C_6H_5MgBr + CH_2{=}CHB(OC_4H_9)_2 \longrightarrow \underset{C_6H_5}{CH_2{=}CHB}(OC_4H_9)_2^- \xrightarrow{H^+} CH_2{=}CH\underset{C_6H_5}{B}OC_4H_9$$

The yield was almost insensitive to the temperature of addition between −70 and +40°, although at the higher temperature, 12% of the dibutyl ethyleneboronate was converted to dibutyl benzeneboronate. Since early experiments seemed to indicate that addition of vinylmagnesium bromide to dibutyl benzeneboronate gave lower yields, addition of the aryl Grignard to dibutyl ethyleneboronate was adopted as the standard method. However, subsequently observed erratic

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(1) Supported by National Science Foundation grants G 9916 and G 19906.

(2) National Science Foundation Cooperative Predoctoral Fellow, 1961–1962; abstracted in part from the Ph.D. thesis of R. W. H. M.

(3) D. S. Matteson and R. W. H. Mah, *J. Am. Chem. Soc.*, **85**, 2599 (1963).

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

(5) Under the customary nomenclature of borinic esters [*Chem. Abstr.*, **56**, 46N (1962)], this would be called butyl phenylvinylborinate. We have inserted *B*'s to clarify which groups are attached to boron, names such as butyl 3-methyl-1-butyl-(1-bromo-3,3,3-trichloro-1-propyl)borinate being almost incomprehensible.

variations in yields make this conclusion questionable.

The erratic yields were traced to the instability of the *B*-aryl-*B*-vinylborinates to prolonged exposure to warm butanol at the end of the distillation of the solvents under reduced pressure. Decompositions of both the *B*-*o*-tolyl- and *B*-*p*-xylyl-*B*-vinylborinic esters to dibutyl ethyleneboronate at this point were observed by infrared examination of the solutions. Dearylation was avoided by using ether to extract the borinate, and adding no butanol beyond that formed in the reaction; there turned out to be insufficient water present to require added butanol for its azeotropic removal.

Freshly prepared phenylmagnesium bromide turned out to be essential. Commercial material from two sources led to low yields and formation of a considerable amount of biphenyl.

Butyl *B*-phenyl-*B*-vinylborinate polymerizes very readily and is difficult to store even at −15° in the presence of phenothiazine. A sample which did not polymerize, presumably because exposure to oxygen was minimized, appeared to have disproportionated after several months. Distillation yielded a forerun, evidently phenyldivinylborane and other boranes, which ignited spontaneously on cotton in air, as well as dibutyl benzeneboronate, confirmed by infrared comparison with an authentic sample.

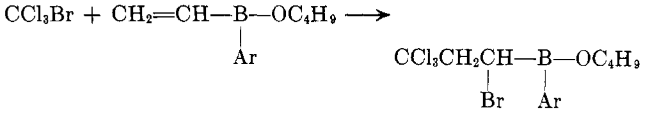
The reactivity of butyl *B*-phenyl-*B*-vinylborinate toward free radicals is qualitatively in accord with simple molecular orbital calculations, which yield essentially the same free valence and radical stabilization energy[4] found for butyl divinylborinate.[6] For example, when α_B was chosen as $\alpha_C - 1.0\ \beta_{C-C}$ and the phenyl bonds as 0.84 $\beta_{C=C}$, the radical stabilization was 0.141 β compared to 0.139 β for butyl divinylborinate[6], and 0.098 β for dibutyl ethyleneboronate,[4] while the free valence was 0.780 for both borinates and 0.770 for dibutyl ethyleneboronate. The trends on changing parameters are such that the use of improved parameters[7] would not alter the relative results. That the phenylvinylborinate is isolable, while butyl divinylborinate is not[6], may be attributed to dilution of vinyl group concentration by the phenyl group as well as some steric hindrance.

Butyl *B*-*o*-tolyl-, *B*-*p*-xylyl-, and *B*-mesityl-*B*-vinylborinate were prepared in the same manner as the phenyl compound. These showed better stability on storage than the phenyl compound, and butyl *B*-mesityl-*B*-vinylborinate failed to polymerize when heated with azobisisobutyronitrile. Steric hindrance would tend to shield the boron atom from attack by oxygen and would force the aryl group out of coplanarity with the vinyl, which, according to simple molecular orbital calculations, should reduce the susceptibility of the vinyl group to radical attack. Direct steric interference with chain propagation also would be expected.

The question of possible conjugate addition of arylmagnesium bromide to the double bond of dibutyl ethyleneboronate was examined briefly. None would be expected on the basis of simple molecular orbital calculations[7] unless there were severe steric hindrance to normal addition and, even then, the Grignard reagent might not be sufficiently active to lead to formation of the hypothetical intermediate $\mathrm{ArCH_2CH{=}BX_2^-}$. No dibutyl 2-phenylethaneboronate could be detected by infrared examination of the higher boiling fractions from the butyl phenylvinylborinate preparation in refluxing ether; the principal by-product was dibutyl benzeneboronate. Addition of mesitylmagnesium bromide to di-*t*-butyl ethyleneboronate[8] gave an excellent yield of mesitylvinylborinic ester and only a small amount of higher boiling residue. The effectiveness of the steric hindrance to addition of the mesityl group to boron in the *t*-butyl ester depends on the size of the boron atom, which may become relatively large and not severely hindered as it acquires a negative charge.

8-Quinolinol has been reported to form useful solid derivatives of borinic acids.[9] Butyl *B*-phenyl-*B*-vinylborinate yielded a crystalline derivative, but the more hindered *B*-aryl-*B*-vinylborinates did not.

Light-initiated addition of bromotrichloromethane to butyl *B*-phenyl-*B*-vinylborinate proceeded readily, but initial attempts to isolate the product, butyl *B*-phenyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate, failed because of its instability. Treatment of this product with aqueous sodium bicarbonate led to an isolable substance which proved to be a rearrangement product, dibutyl 1-phenyl-3,3,3-trichloropropane-1-boronate, reported in detail elsewhere.[3] However, no difficulty was encountered in the addition of bromotrichloromethane to butyl *B*-*p*-xylyl- or *B*-mesityl-*B*-vinylborinate. Subsequently, butyl *B*-phenyl-*B*-vinylborinate was freed of lower boiling borane contaminants by careful distillation; the bromotrichloromethane addition then proceeded without difficulty.



$$\mathrm{CCl_3Br} + \mathrm{CH_2{=}CH{-}\underset{\displaystyle Ar}{\underset{|}{B}}{-}OC_4H_9} \longrightarrow \mathrm{CCl_3CH_2\underset{\displaystyle Br}{\underset{|}{CH}}{-}\underset{\displaystyle Ar}{\underset{|}{B}}{-}OC_4H_9}$$

The alternate possible route to these *B*-aryl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinates is the addition of the aryl Grignard reagent to dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate.[4] This route has not been fully investigated. It does appear to be a satisfactory method for preparing the phenyl compound provided the temperature of the reaction mixture is kept at −70° until after the addition of aqueous acid is complete. Exposure to higher temperatures may result in some rearrangement to dibutyl 1-phenyl-3,3,3-trichloropropane-1-boronate.[3] It appeared that considerable rearrangement occurred even at −70° with the mesityl compound, possibly some with the xylyl, making this route unsatisfactory for these compounds. Another drawback to this route is the small separation in boiling points between the starting boronic ester and the product borinate.

The choice of routes is altered in the aliphatic series, where our experience with one unstable *B*-alkyl-*B*-vinylborinate[6] did not encourage any attempt to synthesize compounds of this class as precursors to the bromotrichloromethane adducts. The addition of the alkyl Grignard reagent to dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate at low temperature was used for the successful preparation of butyl *B*-ethyl- and *B*-(3-methyl-1-butyl)-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate.[3]

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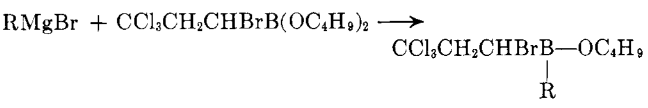
(6) D. S. Matteson, *J. Org. Chem.*, **27**, 275 (1962).

(7) Ref. 6, p. 4293.

(8) Ref. 6, p. 3712.

(9) J. E. Douglass, *ibid.*, **26**, 1312 (1961).



$$\mathrm{RMgBr + CCl_3CH_2CHBrB(OC_4H_9)_2 \longrightarrow \underset{\displaystyle R}{\overset{}{CCl_3CH_2CHBrB}}{-}OC_4H_9}$$

This synthesis was extended to the corresponding α-butoxy compound. Treatment of dibutyl 1-butoxy-3,3,3-trichloropropane-1-boronate[3] with ethylmagnesium bromide yielded butyl *B*-ethyl-*B*-(1-butoxy-3,3,3-trichloro-1-propyl)borinate, $CCl_3CH_2CH(OC_4H_9)B(C_2H_5)OC_4H_9$. This compound appeared to oxidize readily in air.

Experimental[10]

Butyl *B*-2,5-Dimethylphenyl-*B*-vinylborinate.—A solution of 0.20 mole of 2,5-dimethylphenylmagnesium bromide in 100 ml. of tetrahydrofuran was added dropwise under nitrogen over a period of 0.5 hr. to a vigorously stirred solution of 36.0 g. (0.19 mole) of dibutyl ethyleneboronate in 100 ml. of anhydrous ether kept at −70°. The mixture was allowed to warm to 0° over a period of 2 hr. After addition of 0.1 g. of phenothiazine, the mixture was cooled to −40° and acidified with 230 ml. of 1.5 *M* hydrochloric acid. After warming to 5° the phases were separated, the aqueous phase was extracted with ether and the combined organic phase was washed with two 100-ml. portions of saturated sodium chloride solution, followed by 50 ml. of saturated salt and enough solid sodium bicarbonate to raise the pH of the aqueous phase to 6. Removal of the solvents with the water aspirator, addition of 20 ml. of butanol to ensure complete esterification, and rapid removal of the butanol, followed by distillation through a 15-cm. column packed with Podbielniak nichrome helices, yielded 5 ml. of unchanged dibutyl ethyleneboronate and 28.5 g. (70%) of butyl *B*-2,5-dimethylphenyl-*B*-vinylborinate, b.p. 59–61° (0.05 mm.). The material was stored at −15° with a trace of phenothiazine as an inhibitor. Strong infrared bands appeared at 6.22, 7.48, 7.72, 7.81, 8.05, 8.15, 8.50, 10.30, and 12.30 μ. The analytical sample was redistilled.

Anal. Calcd. for $C_{14}H_{21}BO$: C, 77.80; H, 9.79; B, 5.01. Found: C, 77.68; H, 9.60; B, 5.07.

Butyl *B*-*o*-Tolyl-*B*-vinylborinate.—By essentially the procedure just described, 0.10 mole of *o*-tolylmagnesium bromide in 50 ml. of tetrahydrofuran added to 18.0 g. (0.098 mole) of dibutyl ethyleneboronate in 50 ml. of ether at −60° yielded 15.1 g. (76%) of butyl *o*-tolylvinylborinate, b.p. 50–52° (0.05 mm.); $n^{25}\text{D}$ 1.4945; strong infrared bands at 6.22, 7.47, 7.73, 7.81, 8.22, 8.33, 10.29, 13.27, and 13.60 μ.

Anal. Calcd. for $C_{13}H_{19}BO$: C, 77.25; H, 9.49; B, 5.35. Found: C, 77.44; H, 9.63; B, 5.25.

Butyl *B*-Mesityl-*B*-vinylborinate.—Addition of 0.05 mole of mesitylmagnesium bromide in 30 ml. of tetrahydrofuran to 9.0 g. of dibutyl ethyleneboronate in 25 ml. of ether at −60° led to 8.2 g. (73%) of butyl mesitylvinylborinate, b.p. 74–76° (0.05 mm.). This substance was also obtained from 0.05 mole of mesitylmagnesium bromide in 25 ml. of tetrahydrofuran and 9.20 g. of di-*t*-butyl ethyleneboronate[8] in 75 ml. of ether kept at room temperature 2 days, followed by the usual work-up, including treatment with 1-butanol, in 71% yield. Strong infrared bands appeared at 6.20, 7.06, 7.50, 7.81, 8.25, 8.62, 10.30, 11.75, and 13.92 μ.

Anal. Calcd. for $C_{15}H_{23}BO$: C, 78.28; H, 10.08; B, 4.70. Found: C, 78.63; H, 10.34; B, 4.99.

Butyl *B*-Phenyl-*B*-vinylborinate.—By essentially the same procedure as described, 0.20 mole of freshly prepared phenylmagnesium bromide in 100 ml. of ethyl ether added to 33.8 g. (0.183 mole) of dibutyl ethyleneboronate in 200 ml. of ether at −60° yielded 24.5 g. (75%) of butyl phenylvinylborinate, b.p. 45–48° (0.05 mm.); $n^{21.5}\text{D}$ 1.5045. Strong infrared bands appeared at 6.23, 6.92, 7.02, 7.50, 7.80, 8.07, 8.23, 10.3, and 14.2 μ.

Anal. Calcd. for $C_{12}H_{17}BO$: C, 76.63; H, 9.11; B, 5.75. Found: C, 76.45; H, 9.31; B, 5.70.

Addition of 0.1 mole of phenylmagnesium bromide in 100 ml. of ether to 19.3 g. (0.105 mole) of dibutyl ethyleneboronate in 50 ml. of refluxing ether over a period of 10 hr., followed by refluxing 14 hr. and the usual isolation procedure, yielded 11.2 g. (60%) of butyl phenylvinylborinate and 2.87 g. (12%) of dibutyl benzeneboronate, b.p. 88–110° (0.08 mm.), confirmed by infrared comparison with an authentic sample.[11] A sample of dibutyl 2-phenylethaneboronate was prepared by the usual boronic ester synthesis from 2-phenylethylmagnesium iodide and methyl borate, b.p. 105–112° (0.1 mm.), not fully characterized.[12] The infrared spectrum of the higher boiling part of the dibutyl benzeneboronate showed no evidence of the presence of phenylethaneboronate. That the benzeneboronate could only have arisen from ethyleneboronate was shown by the infrared spectrum of the starting material, which contained no detectable (0.5%) butyl borate.

8-Quinolinol Derivative of Phenylvinylborinic Acid.—A solution of 3.24 g. of butyl phenylvinylborinate in 10 ml. of 95% ethanol was added to 2.5 g. of 8-hydroxyquinoline in 10 ml. of ethanol. The product crystallized immediately; yield, 1.68 g. (63%); recrystallized, m.p. 142–143°.

Anal. Calcd. for $C_{17}H_{14}BNO$: C, 78.80; H, 5.45; B, 4.18; N, 5.41. Found: C, 78.52; H, 5.49; B, 4.40; N, 5.50.

Butyl *B*-Phenyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate.—Butyl phenylvinylborinate was freshly redistilled, with care being taken to remove any borane contamination with the forerun. A solution of 13.0 g. (0.069 mole) of butyl phenylvinylborinate in 100 ml. of bromotrichloromethane (Eastman practical grade) in a Vycor flask was irradiated about 12 hr. with a 60-w. mercury vapor lamp ("Mineralight" near ultraviolet) at room temperature under nitrogen. Bromotrichloromethane was distilled at 20 mm., the adduct at 110–115° (0.1 mm.); yield, 13.5 g. (51%). The adduct turned purple after brief exposure to air. The analytical sample was distilled through a short Vigreux column; b.p. 112–114° (0.1 mm.); $n^{24}\text{D}$ 1.5355; a medium infrared band at 6.25, strong bands at 6.96, 7.10, 7.4, 7.67, 8.22, 10.68, 12.30, 13.22, and 14.2 μ.

Anal. Calcd. for $C_{13}H_{17}BBrCl_3O$: C, 40.41; H, 4.43; B, 2.80; halogen as Cl, 36.71. Found: C, 40.59; H, 4.66; B, 2.89; halogen as Cl, 36.51.

Butyl *B*-2,5-Dimethylphenyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate.—Irradiation of 16.3 g. of butyl *B*-2,5-dimethylphenyl-*B*-vinylborinate in 100 ml. of bromotrichloromethane according to the foregoing procedure yielded 29.5 g. (95%) of the adduct; b.p. 127–134° (0.1 mm.); weak infrared bands at 6.20 and 6.32, strong bands at 7.06, 7.45, 7.67, 8.04, 8.52, 10.50, 12.30 and 14.1 μ.

Anal. Calcd. for $C_{15}H_{21}BBrCl_3O$: C, 43.47; H, 5.11; B, 2.61; halogen as Cl, 34.22. Found: C, 43.40; H, 5.20; B, 2.72; halogen as Cl, 34.06.

Butyl *B*-Mesityl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate.—Irradiation of 8.1 g. of butyl mesitylvinylborinate in 75 ml. of bromotrichloromethane according to the foregoing procedure yielded 11.1 g. (75%) of the adduct; b.p. 129–130° (0.02 mm.); strong infrared bands at 6.20, 7.1, 7.46, 8.12, 8.63, 11.75, 12.50, and 14.10 μ.

Anal. Calcd. for $C_{16}H_{23}BBrCl_3O$: C, 44.86; H, 5.41; B, 2.52; halogen as Cl, 33.10. Found: C, 45.16; H, 5.60; B, 2.70; halogen as Cl, 32.91.

Butyl *B*-Ethyl-*B*-(1-butoxy-3,3,3-trichloro-1-propyl)borinate.—A solution of 0.05 mole of ethylmagnesium bromide prepared in 40 ml. of tetrahydrofuran was added in about 0.5 hr. to a stirred solution of 18.0 g. (0.048 mole) of dibutyl 1-butoxy-3,3,3-trichloropropane-1-boronate in 25 ml. of ether at −60° under nitrogen, then kept at −60° 0.5 hr. longer. After warming to 0°, the work-up procedure previously described for arylvinylborinates was followed, except that the washing with saturated sodium chloride was carried out without the addition of any sodium bicarbonate. Simple distillation yielded 11.4 g. (72%) of the borinate, b.p. 90–92° (0.05 mm.). The analytical sample was redistilled twice; $n^{25}\text{D}$ 1.4532; broad and strong infrared band attributed to the ether linkage at 9.1–9.2 μ; other strong bands at 6.82, 7.10, 7.40, 12.75, and 14.2 μ.

Anal. Calcd. for $C_{13}H_{26}BCl_3O_2$: C, 47.10; H, 7.91; B, 3.27; Cl, 32.10. Found: C, 46.85; H, 7.95; B, 3.09; Cl, 31.98.

Butyl *B*-Ethyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinate.—A solution of 0.1 mole of ethylmagnesium bromide in 100 ml. of ether was added to 38.1 g. (0.099 mole) of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate in 100 ml. of ether according to the

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(10) 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.

(11) Benzeneboronic acid [R. M. Washburn, E. Levens, C. F. Albright, and F. A. Billig, *Org. Syn.*, **39**, 3 (1959)] was esterified with butanol.

(12) 2-Phenylethaneboronic acid: D. L. Yabroff, G. E. K. Branch, and B. Bettman, *J. Am. Chem. Soc.*, **56**, 1850 (1934).

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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(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).