Tetrahedron. Vol. 25, pp 1557 to 1569 Pergamon Press 1969 Printed in Great Britain

TRANSFER REACTIONS INVOLVING BORON—XVIII

THE SYNTHESIS AND CHEMICAL AND PHYSICAL CHARACTERIZATION OF MONO- AND BISBORONIC ACIDS OF THE PHENYLETHYL AND STYRYL SYSTEMS[1,2]

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(*Received in USA* 17 *July* 1968; *Received in the UK for publication* 18 *November* 1968)

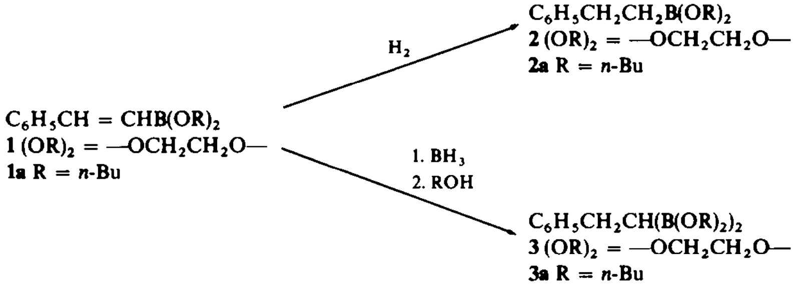
Abstract—β-Styreneboronic (**1**), 2-phenylethaneboronic (**2**), 2-phenylethane-1,1-bisboronic (**3**), α-styreneboronic (**4**), 1-phenylethaneboronic (**5**), and 1-phenylethane-1,2-bisboronic (**6**) esters have been synthesized and their chemical and physical properties have been investigated. The bisboronic esters **3** and **6** were very unreactive toward electrophilic substitution (protonolysis and oxidation) in contrast to the other boronic esters.

The unsaturated boronic esters **1** and **4** readily added bromine to give reasonably stable dibromides. The boronic esters **2** and **5** underwent facile radical bromination to give the 2-bromo-2-phenylethaneboronic (**10**) and 1-bromo-1-phenylethaneboronic (**14**) esters respectively. The bisboronic esters **3** and **6** underwent facile radical bromination to produce thermally unstable bromides which underwent elimination and subsequent addition reactions. The chemical properties of the various bromides were investigated. The electrophilic and radical hydrobrominations of **1** and **3** were investigated, producing **10** and **14** respectively. Other radical reactions of **3**, **5**, and **6** were also explored.

In an earlier investigation in our laboratories on the dihydroboration of acetylenes it was demonstrated that a number of unexpectsd oxidation products were formed.[4] In order to clarify the mode of formation of these oxidation products we have undertaken the synthesis of a series of model compounds related to the systems previously studied. This article describes the synthesis of, and the physical and chemical characterization of a series of mono- and bisboronates of the phenylethyl system (**1** through **6**).

Preparation and characterization of **1** *through* **6**. Dibutyl β-styreneboronate (**1a**), was prepared as a mixture of the *cis*- and *trans*-isomers by reaction of β-styryl magnesium bromide with trimethyl borate at −70°. Dibutyl 2-phenylethaneboronate (**2a**) was prepared by catalytic hydrogenation of **1a** in n-butanol. The ethylene esters **1** and **2** were prepared by treatment of **1a** and **2a** with ethylene glycol followed by distillation.

Hydroboration of **1a** with an excess of borane in tetrahydrofuran, folllwed by the addition of n-butanol and direct distillation, provided tetrabutyl 2-phenylethane-1,1-bisboronate (**3a**). As the hydrogens of the n-Bu groups obscured the high field resonance signals of the phenylethyl system, **3a** was converted to the diethylene ester **3** by treatment with ethylene glycol. The ^{1}H NMR spectrum of **3** displayed a triplet at $\delta = 1{\cdot}06$ (relative to TMS) corresponding to $—C\underline{H}—(B\langle)_2$, a doublet at $\delta = 2{\cdot}83$ ($—C\underline{H}_2—CH—$), a singlet at $\delta = 3{\cdot}91$ ($—OC\underline{H}_2C\underline{H}_2O—$), and a broad singlet at $\delta = 7{\cdot}11$ ($C_6\underline{H}_5—$). There was no evidence in the NMR spectrum for the presence of the other possible isomer diethylene 1-phenylethane-1,2-bisboronate (**6**). The ^{11}B NMR spectrum of **3** displayed an exceptionally broad peak, approximately 2000 Hz width at half-heighth, at −34·9 ppm (relative to boron trifluoride etherate



internal capillary) consistent with an alkyl boronate.[5] Diethylene 2-phenylethane-1,1-bisboronate (**3**) appeared to slowly undergo cross polymerization by ester exchange* as evidence by a marked increase in the viscosity of the sample on standing. Pure diethylene ester was readily regenerated by heating with a small amount of ethylene glycol followed by distillation.

Although the ^1H NMR spectrum is wholly consistent with structure **3**, it was desirable to obtain further support for the structure by chemical and physical means. Evidence for the structures of organoboron derivatives can be generally obtained by oxidation to the corresponding alkanol or carbonyl derivatives. However, the normal basic hydrogen peroxide oxidation of **3** produced a number of products, the expected normal oxidation product† phenylacetaldehyde being formed in only minor quantities.[4] Oxidation of **3** with *m*-chloroperbenzoic acid, a reagent which generally oxidizes sensitive organoboron derivatives without producing interferring side reactions,[8] produced mainly phenylacetaldehyde with only trace quantities of benzaldehyde and benzyl alcohol present.[7] Although the *m*-chloroperbenzoic acid oxidation of **3** is relatively straightforward, similar treatment of diethylene 1-phenylethane-1,2-bisboronate (**6**) produced anomalous results thus reducing somewhat the diagnostic value of the oxidation of **3** with this reagent. Attempted oxidation of **3** with pyridine N-oxide in refluxing chloroform, a reagent not expected to produce side reactions typical of peroxy reagents, leads to no observable reaction. Similar treatment of ethylene 2-phenylethaneboronate (**2**) with pyridine N-oxide produced 2-phenylethanol in excellent yield. This inertness of **3** to typical electrophilic substitution reagents appears to be quite general of these bisboronate systems.

Attempted electrophilic replacement of the two boron functional groups of **3** by hydrogen and bromine also failed. Treatment of **3** with propionic acid in diglyme for 40 hr in a sealed tube at 160° produced *no* ethylbenzene. Similar treatment of **2**

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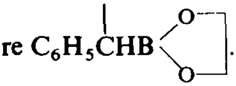
* The facile exchange of alkoxy residues between boranes has been adequately demonstrated (Ref. 6).

† See the accompanying article for a detailed description and discussion of the oxidation of the organoboron derivatives described in this article (Ref. 7).

produced a substantial yield of ethylbenzene. Attempted brominolysis of **3** with N-bromopyridinium perbromide also produced no reaction (treatment with molecular bromine in carbon tetrachloride led to radical bromination and will be discussed later in this article).

Treatment of **3** with 20% sodium hydroxide for 24 hr followed by oxidation produced only 2-phenylethanol. The facile hydrolysis of **3** to 2-phenylethaneboronic acid, which on oxidation produces 2-phenylethanol, is consistent with structure **3** and the earlier proposal by Brown and Zweifel.[9]

Final supporting evidence for structure **3** was obtained from its mass spectrum.* The most intense peak in the mass spectrum of **3** occurs at *m/e* 91 consistent with the presence of a $C_6H_5CH_2$-group. No substantial peak appears at *m/e* 160 which would be expected from a molecule containing the partial structure



$C_6H_5\overset{|}{C}HB\langle_{O}^{O}\rangle$.

Compounds **4**, **5**, and **6** were prepared in a similar manner. Dibutyl α-styreneboronate (**4a**) was prepared from α-styryl magnesium chloride and trimethylborate, and was converted to dibutyl 1-phenylethaneboronate (**5a**) by hydrogenation. The dibutyl esters **4a** and **5a** were readily converted to the ethylene esters **4** and **5** by treatment with ethylene glycol.

Hydroboration of ethylene α-styreneboronate with an excess of borane in tetrahydrofuran, followed by treatment with ethylene glycol and distillation, produced an apparent mixture of diethylene 1-phenylethane-1,2-bisboronate (**6**) and diethylene 1-phenylethane-1,1-bisboronate (**7**) in an approximate ratio of 95:5. The 1,2-bisboronate **6** was isolated in a pure state by recrystallization from carbon tetrachloride. The ^1H NMR spectrum of the diethylene ester **6** displayed an AXY system with $\delta_A = 2{\cdot}66$ ($C_6H_5C\underline{H}\langle$), $\delta_X = 1{\cdot}51$ and $\delta_Y = 1{\cdot}13$ ($—C\underline{H}_2—B\langle$) with $J_{AX} = 9{\cdot}5$ Hz, $J_{AY} = 6{\cdot}5$ Hz and $J_{XY} = 16{\cdot}0$ Hz, as well as singlets at $\delta = 4{\cdot}11$ ($—OC\underline{H}_2C\underline{H}_2O—$) and $\delta = 7{\cdot}24$ ($C_6\underline{H}_5—$). The ^{11}B NMR spectrum displayed a very broad peak at -32 ppm. The NMR spectrum of the initial hydroboration reaction mixture of ethylene α-styreneboronate displayed a singlet at $\delta = 1{\cdot}18$ in addition to the peaks ascribed to **6** above. This singlet is consistent with the presence of minor amounts of diethylene 1-phenylethane-1,1-bisboronate (**7**) as the minor component. Compound **7** has not been obtained in sufficient quantities to isolate in a pure condition.

Chemical evidence in support of structure **6** for the major hydroboration product of ethylene α-styreneboronate (**4**) is not nearly as convincing as for diethylene 2-phenylethane-1,1-bisboronate (**3**). Oxidation with basic hydrogen peroxide produced a number of products in addition to low yields of phenylethanediol.[7] Oxidation of **6** with *m*-chloroperbenzoic acid produced up to 40% yields of acetophenone with little phenylethanediol being formed. Compound **6** did not undergo oxidation with pyridine N-oxide in refluxing chloroform. Attempted protonolysis of **6** on treatment with propionic acid in diglyme at 160° for 40 hr in a sealed tube produced no observable reaction.

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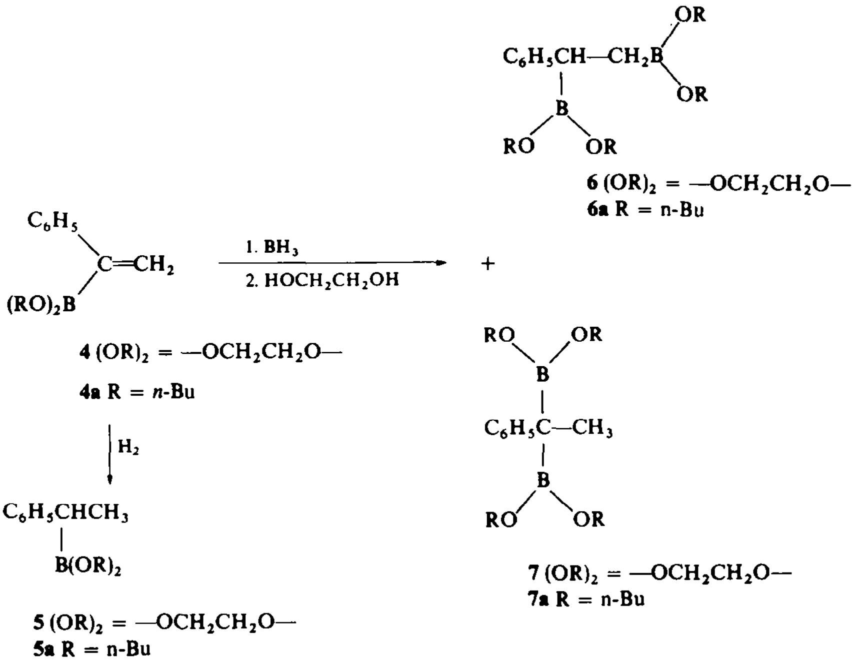
* The mass spectra of the compounds contained in this article were kindly run by Prof. T. Kinstle of Iowa State University, Ames, Iowa. A complete description of the mass spectra of these and related organoboron derivatives will be described elsewhere.



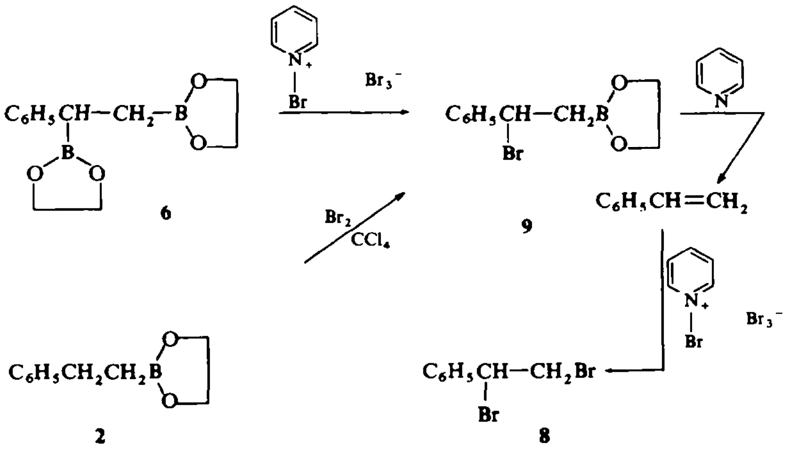
4 $(OR)_2$ = $—OCH_2CH_2O—$
4a R = *n*-Bu

5 $(OR)_2$ = $—OCH_2CH_2O—$
5a R = n-Bu

6 $(OR)_2$ = $—OCH_2CH_2O—$
6a R = n-Bu

7 $(OR)_2$ = $—OCH_2CH_2O—$
7a R = n-Bu

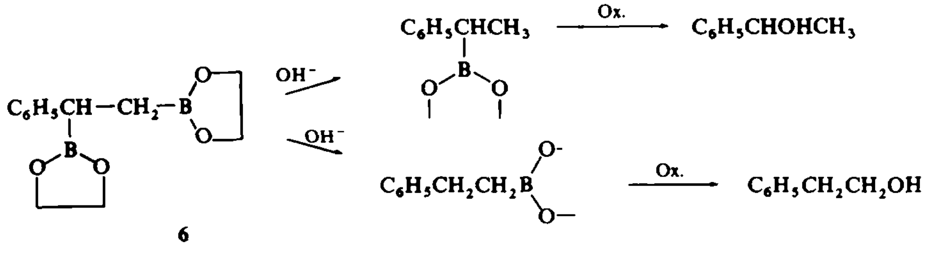
Treatment of **6** with N-bromopyridinium perbromide produced low yields of styrene dibromide (**8**). The mechanism of this transformation probably does not involve a direct brominolysis of both C—B bonds. It is believed that **6** undergoes brominolysis of the benzylic ethylenedioxyboryl functional group to produce ethylene 2-bromo-2-phenylethaneboronate (**9**) wihich undergoes a pyridine catalyzed debromoboronation[10] to produce styrene, the styrene subsequently undergoing bromination to give styrene dibromide (**8**). Evidence for this mechanistic pathway is the following. Ethylene 1-phenylethaneboronate (5) undergoes a smooth bromonolysis with N-bromopyridinium perbromide to give 1-bromo-1-phenylethane indicating



6 **9** **2** **8**

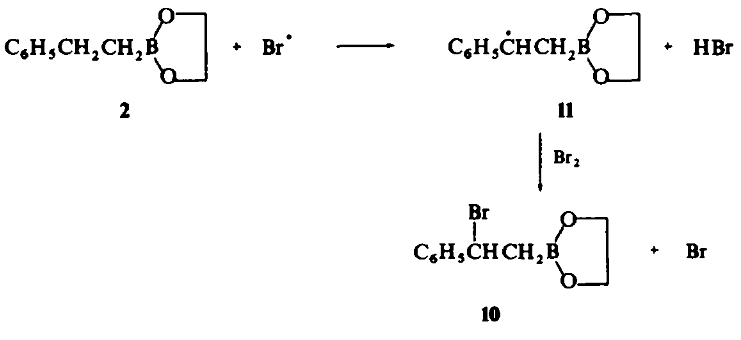
that the benzylic boron functional group is capable of being displaced in an electrophilic substitution reaction. Radical bromination of ethylene 2-phenylethaneboronate (**2**) yields ethylene 2-bromo-2-phenylethaneboronate (**9**) which undergoes a facile debromoboronation in the presence of bases to give styrene (see following paragraphs). Finally, styrene undergoes bromination with N-bromopyridinium bromide to give styrene dibromide.

Treatment of diethylene 1-phenylethane-1,2-bisboronate (**6**) with 20% sodium hydroxide for 24 hr followed by oxidation produced a mixture of 1- and 2-phenylethanols in a ratio of 8:92. It appears that **6** undergoes competitive base catalyzed hydrolysis of both carbon–carbon bonds to produce the 1- and 2-phenylethaneboronic acids[*] as proposed earlier.[4]



***Bromination reactions involving compounds* 1 *through* 6.** Preliminary studies on the basic hydrogen peroxide oxidation of the 1,1- and 1,2-bisboronates **3** and **6** indicated that the oxidation reactions were primarily radical in nature (see accompanying article[7]), and that the initial intermediates formed in these reactions underwent further reaction(s) leading to the observed product(s). It was necessary to assess the reactivity of compounds **1** through **6** in radical abstraction and addition reactions in which the initially formed product (bromo derivative) was stable.

Treatment of ethylene 2-phenylethaneboronate (**2**) with bromine in carbon tetrachloride in normal laboratory light led to a fairly rapid discharge of the bromine color with the evolution of hydrogen bromide and the formation of ethylene 2-bromo-2-phenylethaneboronate (**10**). The structure of **10** was assigned on the basis of its



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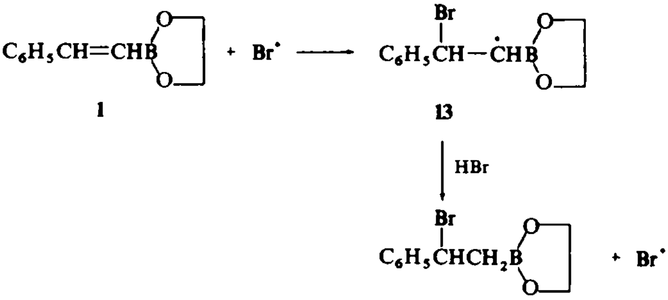
[*] On treatment with base, the ethylene boronates undoubtedly undergo hydrolysis to give boronic acids or anions. As the functional group attached to oxygen is not known, no functional group will be indicated as bonded to the oxygen.

^1H NMR spectrum, base-catalyzed debromoboronation to styrene,[10] and the thermal debromoboronation at 120° to produce styrene. No bromination of **2** occurred in the dark. The formation of **10** is readily rationalized in terms of the foregoing mechanism in which the benzylic H atom is abstracted by a bromine atom producing the chain carrying 2-ethylenedioxyboryl-1-phenyl-1-ethyl radical (**11**). No ethylene 1-bromo-2-phenylethaneboronate was formed indicating that abstraction of the β-hydrogen producing the 1-ethylenedioxyboryl-2-phenyl-1-ethyl radical (**12**) does not occur. The observed radical reactivity of **2** with Br atoms is consistent with that postulated for reactions of **2** with hydroxyl and/or hydroperoxyl radicals described in the accompanying paper.[7]

2 **12**

The electrophilic hydrobromination of ethylene β-styreneboronate (**1**) at −70° in the dark also produces ethylene 2-bromo-2-phenylethaneboronate **10**. Surprisingly, **10** is also the sole product formed in the hydrobromination of **1** under radical conditions.[*] The radical addition must proceed *via* the 1-ethylenedioxyboryl-2-bromo-2-phenyl-1-ethyl radical (**13**) in which the radical site is *alpha* to the boron instead of *alpha* to the benzene ring as in **11**. That this mode of radical attack on **1** can occur is substantiated by the fact that ethylene β-styreneboronate (**1**) must react with hydroxyl and/or hydroperoxyl radicals to give radical intermediates similar to **13**.



1 **13** **10**

The difference in the reactivity of **1** and **2** to produce the different radical intermediates **13** and **11**, respectively, may be readily rationalized on the basis of the intimate details of the mechanisms of formation of **13** and **11**. The abstraction of the benzylic hydrogen of **2** is favored by the electron withdrawing properties of the aromatic system (weaker C—H bond) and by resonance stabilization of the incipient radical center by the aromatic ring; whereas abstraction of the hydrogen on carbon

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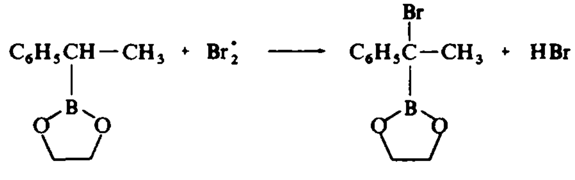
[*] The experimental conditions employed are the same as those employed by Matteson and Liedtke (Ref. 10) for the radical addition of hydrogen bromide to dibutyl ethyleneboronate. Although the conditions are ideal for radical reaction, it cannot be unambiguously ascertained that **10** is formed *via* a radical mechanism and not by an electrophilic addition reaction.

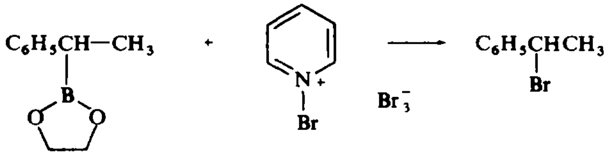
attached to boron is *disfavored* by the electron donating properties of boron but favored by resonance stabilization of the incipient radical center by the vacant p-orbital on boron* (see following paragraphs). In the radical attack on **2**, the C—H bond strength factors outlined immediately before are not present, and one is concerned only with stabilization of the incipient radical center. The known, strong interaction of a carbon–carbon double bond with the vacant *p*-orbital on boron[12] may well provide for greater stabilization of the radical center by the boron earlier along the reaction coordinate than is afforded by the aromatic system.

Radical bromination of ethylene 1-phenylethaneboronate (**5**) produced ethylene 1-bromo-1-phenylethaneboronate (**14**) undoubtedly via a mechanism very similar to that outlined for the radical bromination of **2**. None of the normal electrophilic substitution product, 1-bromo-1-phenylethane, was formed. The electrophilic and radical additions of hydrogen bromide to **4** also produced **14**. Again, the radical reactivities of **4** and **5** in these reactions parallel the reactivities of **4** and **5** with hydroxyl and hydroperoxyl radicals.[7]



5 **14**

Treatment of ethylene 1-phenylethaneboronate (**5**) with N-bromopyridine perbromide produced 1-bromo-1-phenylethane, the normal electrophilic substitution product.



5

The reactivities of ethylene 2-phenylethaneboronate (**1**) and 1-phenylethaneboronate (**5**) relative to ethylbenzene (1·00) were determined to be 0·30 and 0·63 respectively by competitive brominations. The decrease in the reactivity of **2** relative to ethylbenzene may be ascribed to the electron donating (inductive) properties of the boron thus decreasing the ease of H atom abstraction. The inductive effect of the boron should be greater in **5**, however, we might well expect an acceleration in the rate of hydrogen atom abstraction by stabilization of the incipient radical by the vacant orbital on boron. The greater reactivity of **5** over **2** indicates some stabilization

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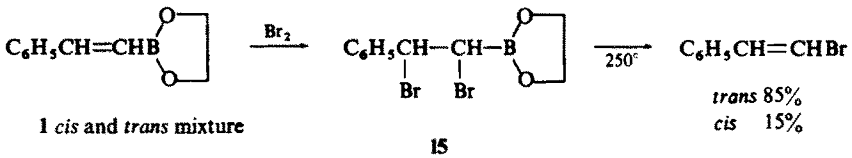
* The stabilization of free radical character by boron has been discussed by Matteson (Ref. 11).

by boron, however it is not possible to assess this on a quantitative basis. The ability of boron to stabilize radical formation on an adjacent atom will be made more apparent in the discussion of the oxidation and the mass spectra of compounds **1** through **6** in the accompanying article.[7]

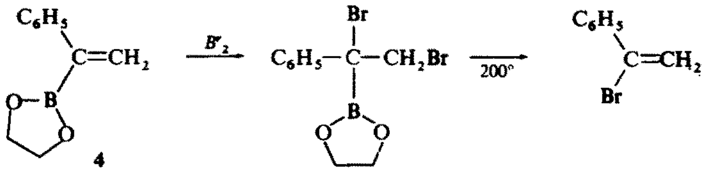
The bromination of a 56:44 mixture of *trans* and *cis* ethylene β-styreneboronate (**1**) produced what appears to be a single dibromoderivative, ethylene 1,2-dibromo-2-phenylethaneboronate (**15**). The ^{1}H NMR spectrum of the crude reaction product displayed a single set of AX doublets at $\delta = 4{\cdot}10$ and $\delta = 5{\cdot}28$ with $J = 12{\cdot}5$ Hz for the two methine hydrogens. A single, high yielding recrystallization from carbon tetrachloride gives a colorless crystalline compound with a narrow melting range. The isolation of an apparent single product makes definition the mechanism of the addition difficult. Differentiation between a radical or electrophilic process, with prior isomerization required, cannot be made. The stereochemistry of the thermal elimination cannot be used to derive the stereochemistry of **15** due to the lack of complete stereospecificity and the unknown mechanism for the elimination. The thermal debromoboronation of **17** occurs quite cleanly at 250° to give a 15:85 mixture of *cis* and *trans*-β-bromostyrene.



1 *cis* and *trans* mixture

15

The addition of bromine to ethylene α-styreneboronate produces ethylene 1,2-dibromo-1-phenylethaneboronate (**16**). The thermal debromoboronation of **16** at 200° for 4 hr in carbon tetrachloride in a sealed tube resulted in a quantitative formation of α-bromostyrene.



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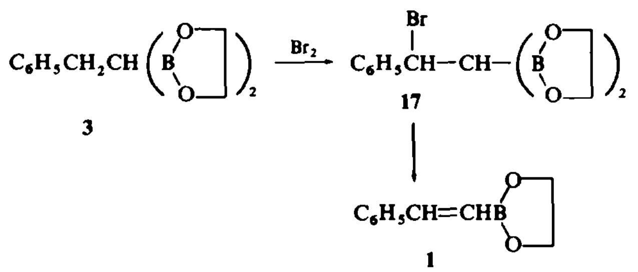
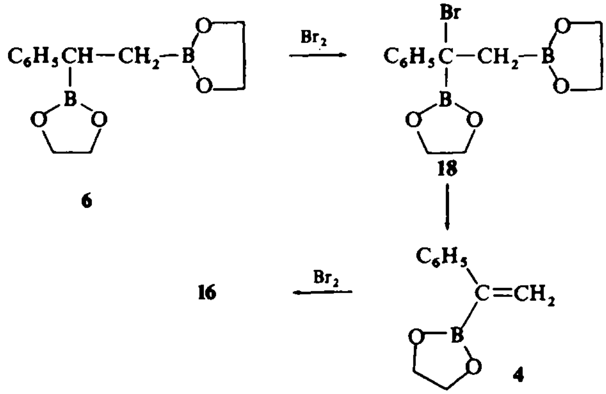
16

The radical brominaton reactions of the bisboronates **3** and **6** are somewhat more complex due to the high chemical reactivity of the intermediates formed. Radical bromination of diethylene 2-phenylethane-1,1-bisboronate (**3**) produced ethylene β-styreneboronate (**1**) and *trans*-β-bromostyrene. A rational mechanism for the formation of these products involves radical bromination of **3** to give ethylene 2-bromo-2-phenylethane-1,1-bisboronate (**17**) which is thermally unstable, undergoing elimination to generate ethylene β-styreneboronate (**1**). Further bromination of **1** followed by thermal elimination produces β-bromostyrene.



Radical bromination of **6** produces ethylene α-styreneboronate (**4**) and ethylene 1,2-dibromo-1-phenylethaneboronate (**16**) undoubtedly *via* diethylene 1-bromo-1-phenyl-1,2-bisboronate (**18**) followed by the elimination and addition reactions described above.



The radical reactivity of compounds **2**, **3**, and **6** with other radical reagents was also investigated. Decomposition of equimolar quantities of azo-bis-isobutrylnitrile, di-t-butylperoxide, benzoyl peroxide, and t-butyl hypochlorite in the presence of these compounds failed to produce any substantial amount of reaction. These reactions are in contrast to the reactivity of these compounds with bromine and Fenton's reagent.[7]

EXPERIMENTAL

Dibutyl α-styreneboronate (**4a**) *and dibutyl β-styreneboronate* (**1a**) were prepared according to the procedure of Matteson and Bowie.[13]

Dibutyl 1-phenylethaneboronate (**5a**) *and dibutyl 2-phenylethaneboronate* (**2a**) were prepared according to the procedure of Matteson and Bowie[15] by catalytic hydrogenation in butanol.

Preparation of ethylene α-styreneboronate (**4**). A mixture of 15 g of **4a** was heated with a 50% excess ethylene glycol for 2 hr and then subjected to distillation. On standing, the high boiling fraction separated into two layers which were separated. Redistillation of the upper layer gave ethylene α-styreneboronate with b.p. 68° at 0·1 mm. The NMR spectrum of the product displayed a singlet at $\delta = 4{\cdot}07$ (4H, —O—C$\underline{H}_2$—), an unresolved AB system at $\delta = 6{\cdot}14$ (2H, =C$\underline{H}$), and a complex multiplet at $\delta = 7{\cdot}2$ (5H, aromatic H).

On standing, the material slowly became more viscous, but could be readily regenerated by treatment with ethylene glycol and redistillation.

Bromination of ethylene α-styreneboronate. To a soln of 174 mg (0·001 mol) **4** in 5 ml CCl_4 was added an equimolar amount of Br_2 during which time **16** precipitated as a white powder. The CCl_4 was removed under reduced press leaving a white crystalline material (quantitative yield). All attempts at purification led to resinification.

The ^1H NMR spectrum of the crude product was very clean, displaying AB doublets at $\delta = 4{\cdot}08$ and 4·28 (—C$\underline{H}_2$Br, $J = 9{\cdot}2$ Hz), a singlet at $\delta = 4{\cdot}25$ (—O—C$\underline{H}_2$—), and a complex multiplet at $\delta = 7{\cdot}5$ (aromatic H).

Thermal debromoboronation of ethylene 1,2-dibromo-1-phenylethaneboronate. In a sealed NMR tube, 50 mg of **16** in 1 ml CCl_4 was heated at progressively higher temps for 30 min periods. No elimination was observed at 150°. At 200°, approximately half of the sample had undergone elimination in 30 min. Heating at 200° for 4 hr resulted in a quantitative debromoboronation to give α-bromostyrene (NMR : AB doublets at $\delta = 5{\cdot}70$ and 6·03 (=C$\underline{H}_2$, $J = 1{\cdot}8$ Hz)).

Electrophilic hydrobromination of ethylene α-styreneboronate. To approximately 0·75 ml liquid HBr in a blackened vessel at −70° was added 150 mg of **4**. The reaction mixture was allowed to slowly warm up during a 2 hr period. The excess HBr was removed under reduced press leaving a pale yellow crystalline residue. The NMR spectrum of the product displayed a singlet at $\delta = 2{\cdot}06$ (3H), singlet at $\delta = 4{\cdot}18$ (4H) and a multiplet centered at $\delta = 7{\cdot}27$ (5H). The NMR spectrum displayed weak peaks in the $\delta = 3$ to 4 region consistent with a small amount of HBr cleavage of the ethylene ester.* Purification for analysis in such cases was not possible.

Radical hydrobromination of ethylene α-styreneboronate. Anhydrous HBr was passed through a soln of 176 mg (0·001 mol) ethylene α-styreneboronate in 5 ml $CDCl_3$ contained in Pyrex flask irradiated by low press Hg vapor lamps.[11] The solvent was partially removed and the NMR spectrum was recorded showing the presence of only **14**. Attempts to purify the low melting material were unsuccessful. A flame test confirmed the presence of boron in the product.

Preparation of ethylene 1-phenylethaneboronate (**5**). Dibutyl 1-phenylethaneboronate was converted to the ethylene ester as described above; b.p. 67° at 1 mm. The ^1H NMR spectrum displayed a doublet at $\delta = 1{\cdot}37$ (3H, $J = 7{\cdot}5$ Hz), quartet at $\delta = 2{\cdot}46$ (1H, $J = 7{\cdot}5$ Hz), singlet at $\delta = 3{\cdot}96$ (4H) and a multiplet centered at $\delta = 7{\cdot}3$ (5H).

Radical bromination of ethylene 1-phenylethaneboronate. To a soln of 110 mg (0·63 mmol) of **5** in 5 ml CCl_4 was added 100 mg (0·63 mm) of Br_2. The color of the Br_2 was discharged almost immediately with the evolution of HBr as identified by trapping in distilled water and precipitation by Ag ion. The solvent was partially removed under reduced press. The NMR spectrum was identical with that of **14**.

Brominolysis of ethylene 1-phenylethaneboronate. The brominolysis of **5** was carried out as described by Matteson and Bowie.[15] To 110 mg (0·63 mmol) of the ester in 1 ml pyridine at Dry ice–acetone bath temp was added dropwise with stirring 0·63 mm N-bromopyridinium perbromide. During the addition the reaction mixture became solid and the temp was allowed to rise to −60° so that stirring was possible. To the reaction mixture was added 3 ml water and 3 ml hexane. The mixture was thoroughly shaken and the hexane layer was removed. Analysis of GLPC on a silicone gum rubber column indicated the formation of 1-bromo-1-phenylethane (98%).

Competitive radical bromination of ethylene 1-phenylethaneboronate (**5**) *with ethylbenzene.* A mixture of 176 mg (0·001 mol) ethylene 1-phenylethaneboronate and 106 mg (0·001 mol) ethylbenzene in 10 ml CCl_4 was treated with 0·0005 mole Br_2. Analysis of the reaction mixture by NMR indicated a ratio of ethylene 1-bromo-1-phenylethaneboronate to 1-bromo-1-phenylethane of 1 : 1·6.

Preparation of ethylene β-styreneboronate (**1**). Compound **1** was prepared as described above for ethylene *a*-styreneboronate; b.p. 67° at 0·1 mm. The ^1H NMR spectrum indicated the sample to be a mixture of *cis* (44%) and *trans* (56%) isomers: two singlets at $\delta = 4{\cdot}00$ and 4·04 (ethylene ester), doublet at $\delta = 5{\cdot}53$ (*cis* isomer, $J = 15{\cdot}9$ Hz), doublet at $\delta = 6{\cdot}10$ (*trans* isomer, $J = 18{\cdot}2$ Hz) and a complex multiplet centered at $\delta = 7{\cdot}28$ (aromatic hydrogens).

Bromination of ethylene β-styreneboronate. To a soln of 174 mg (0·001 mol) ethylene β-styreneboronate (56% *trans*) in 5 ml CCl_4 was added 0·001 mole Br_2 at room temp. The color of the Br_2 was slowly discharged during the course of 10 min during which time a white solid formed. The CCl_4 was partially removed under reduced press at room temp. The white solid was recovered by filtration giving 188 mg

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* Similar observations have been made by Matteson and Liedtke (Ref. 14).

of material. Recrystallization from CCl_4 gave **15** as colorless crystals with m.p. 150–151°. The ^1H NMR spectrum of the crude sample displayed only a single set of AX doublets at δ = 4·10 and 5·28 with J = 12·5 Hz, a singlet at δ = 4·37 and a multiplet at δ = 7·4. (Found: C, 35·47; H, 3·25; B, 3·09. Calc'd. for $C_{10}H_{11}BBr_2O_2$: C, 35·93; H, 3·30; B, 3·30%).

Thermal debromoboronation of ethylene 1,2-dibromo-2-phenylethaneboronate. A soln of 200 mg of **15** in 1 ml CCl_4 was sealed in an NMR tube and heated at progressively higher temps in a sand bath for periods of 30 min. A clean thermal debromoboronation occurred at 250° giving 85% *trans*-β-bromostyrene (AB doublets at δ = 6·81 and 7·08 with J = 14 Hz) and 15% *cis*-β-bromostyrene (doublet at δ = 6·43 with J = 8·0 Hz, the remaining doublet of the *cis* isomer being obscured by the aromatic hydrogen resonance lines).

Electrophilic addition of hydrogen bromide to ethylene β-styrylboronate. An excess of HBr was passed through a soln of 188 mg (0·00107 mol) of **1** in 5 ml $CDCl_3$ at −70° protected from all light. The sample was allowed to come to room temp and the solvent was partially removed. The ^1H NMR spectrum displayed an apparent doublet at δ = 2·03 (2H, J = 8·0 Hz), singlet at δ = 4·07 (4H), an apparent triplet at δ = 5·28 (1H, J = 8·0 Hz), and a multiplet at δ = 7·09 (aromatic H).

Radical addition of hydrogen bromide to ethylene β-styreneboronate. An excess of gaseous HBr was bubbled through a soln of 0·1752 g (0·001 mol) of **1** in 5 ml $CDCl_3$ contained in a Pyrex flask and irradiated with a bank of low press Hg arc lamps. The solvent was partially removed under reduced press and the ^1H NMR spectrum was recorded showing the presence of only **10**.

Preparation of ethylene 2-phenylethaneboronate. Ethylene 2-phenylethaneboronate was prepared by ester exchange with ethylene glycol as described above; b.p. 68° at 1 mm. The ^1H NMR spectrum displayed triplets at δ = 1·09 and 2·71 (2H each, J = 8·3 Hz), a singlet at δ = 4·00 (4H) and a broad singlet at δ = 7·09 (5H, aromatic H).

Radical bromination of ethylene 2-phenylethaneboronate with bromine in carbon tetrachloride. To 110 mg (0·00063 mol) of **2** in 5 ml CCl_4 was added dropwise and with stirring a soln of 100 mg (0·00063 mol) Br_2 in 1 ml CCl_4. The Br_2 color was rapidly discharged with the evolution of a gas which was dissolved in water; the resulting acidic soln produced a pale yellow ppt when treated with Ag ion. The ^1H NMR spectrum was identical with that described above for **10** derived by the hydrobromination of ethylene β-styreneboronate.

Thermal debromoboronation of ethylene 2-bromo-2-phenylethaneboronate. A 100 mg portion of **10** in 1 ml CCl_4 was sealed in an NMR tube. Heating the contents of the tube at 80° for 30 min did not induce elimination; however, heating at 120° for 30 min resulted in the quantitative formation of styrene.

Hydrolysis of ethylene 2-bromo-2-phenylethaneboronate. A 50 mg portion of **10** in 1 ml CCl_4 was shaken with a few drops of water. The organic layer was removed and dried over $MgSO_4$. Analysis of the extract by GLPC showed the presence of styrene.

Competitive radical bromination of ethylene 2-phenylethane boronate (**10**) *and ethylbenzene.* To a mixture of 50 mg (0·0005 mol) ethylbenzene and 88 mg (0·0005 mol) of **5** was added 40 mg (0·00025 mol) Br_2 in CCl_4. Direct analysis of the reaction mixture was not feasible. The CCl_4 soln was washed with water and dried over $MgSO_4$. Analysis by UV spectroscopy showed the presence of styrene in 30% yield. The analysis was carried out at 292 mμ where absorption due to other species in solution is neglible.

Oxidation of ethylene 2-phenylethaneboronate with pyridine N-oxide. To a soln of 1·14 g (0·012 mol) pyridine N-oxide in 4 ml $CHCl_3$ was added under a N_2 0·35 g (0·002 mol) of **2** in 3 ml $CHCl_3$. The resulting soln was refluxed for 2 hr. MeOH (4 ml) was added and the soln was concentrated until about 1 ml residue remained. Benzene (5 ml) was added and the soln, after concentration by distillation, was analyzed by GLPC on a 20 ft Carbowax on firebrick column at 200° indicating 2-phenylethanol to be present.

Hydrogenolysis of ethylene 2-phenylethaneboronate with propionic acid. Compound **2** (0·005 mol), propionic acid (0·05 mol), and 9 ml diglyme were sealed under a N_2 atm in a heavy-walled tube. The sealed tube was heated in a sand bath at 160° for 40 hr. The tube was cooled to room temp and then placed in a Dry ice–acetone bath and opened. The contents were extracted with hexane and the extract was washed successively with $NaHCO_3$ aq and water, and finally dried over $MgSO_4$. The residue, after removing the solvent, was analyzed by GLPC on a DEGS column on Chromosorb W showing ethylbenzene to be present.

Preparation of diethylene 2-phenyl-1,1-bisboronate (**3**). To a soln of **1a** (3·74 g, 0·0144 mol) in 5 ml THF was added 0·0163 mol borane in 24 ml THF. The mixture was stirred at room temp for 12 hr. BuOH (5·5 ml) was cautiously added and the resulting reaction mixture distilled giving fractions with b.p. 45–47° at 0·05 mm (tributyl borate) and 135–160° at 0·08 mm. The high boiling fraction was carefully redistilled at 135–138° at 0·05 mm giving 2·4 g (40%) of **3a**. (Found: C, 68·70; H, 10·33; B, 5·28. Calcd. for $C_{24}H_{44}B_2O_4$: C, 68·92; H, 10·60; B, 5·17%).

To the tetrabutyl ester was added 1 ml distilled ethylene glycol. Distillation of the mixture gave BuOH and a fraction boiling at 115–117° at 0·04 mm corresponding to the diethylene ester. The ^1H NMR spectrum of the diethylene ester displayed a triplet at $\delta = 1{\cdot}06$ (1H), doublet at $\delta = 2{\cdot}83$ (2H), singlet at $\delta = 3{\cdot}91$ (8H), and a singlet at $\delta = 7{\cdot}11$ (5H). The ^{11}B NMR spectrum displayed a peak at $-34{\cdot}9$ ppm (relative to boron trifluoride etherate internal capillary) with a ~2000 Hz width at half peak height.

Attempted hydrogenolysis of diethylene 2-*phenylethane*-1,1-*bisboronate*. A mixture of 0·004 mol of **3** and 0·04 mol propionic acid in 5 ml anhydrous diglyme was placed in a sealed, heavy-walled galss tube and heated at 160° for 40 hr. The reaction mixture was worked up as described above for the hydrogenolysis of **2**. An analysis by both GLPC and NMR showed that no ethylbenzene was formed.

Base-catalyzed hydrolysis of diethylene 2-*phenylethane*-1,1-*bisboronate*. A 70 mg portion of **3** in 0·5 ml THF and 0·5 ml 10% NaOH aq was allowed to stir 24 hr at room temp. The reaction mixture was oxidized by the addition of 0·3 ml 30% H_2O_2. Extraction of the reaction mixture with ether followed by GLPC analysis indicated the presence of only 2-phenylethanol (96% yield).

Attempted bromination of diethylene 2-*phenylethane*-1,1-*bisboronate with* N-*bromopyridinium perbromide*. To 154 mg (0·007 mol) **3** in 1 ml dry pyridine at Dry ice acetone bath temp (−70°) was added 160 mg (0·001 mol) Br_2 in pyridine. The reaction mixture was worked up as described above for the brominolysis of **5**. No characterizable products were detected when analyzed by NMR.

Radical bromination of ethylene 2-*phenylethane*-1,1-*bisboronate*. To 110 mg of **3** in 5 ml CCl_4 was added 100 mg (0·0006 mole) of Br_2 in CCl_4. HBr was evolved during the Br_2 addition and identified as described above in the bromination of **2**.

Direct analysis of the reaction mixture by NMR, after partial removal of the CCl_4, indicated the presence of **2**. The presence of *trans*-β-bromostyrene was confirmed by GLPC analysis employing a 4 ft silicone gum rubber on Firebrick column at 150°.

Attempted oxidation of ethylene 2-*phenylethane*-1,1-*bisboronate with pyridine* N-*oxide*. To 0·25 g (0·0002 mol) of **3** in 1 ml CCl_3 was added a 200% excess pyridine N-oxide in $CHCl_3$. The reaction mixture was refluxed for 3 hr and worked up as described above for the oxidation of **3**. Analysis by IR, NMR and GLPC demonstrated the absence of any oxidation products.

Oxidation of tetrabutyl 2-*phenylethane*-1,1-*bisboronate with* m-*chloroperbenzoic acid*. Approximately 100 mg of **3a** and 0·5 g *m*-chloroperbenzoic acid in 5 ml $CHCl_3$ was allowed to stand at room temp for 22 hr. The soln was extracted with 5 ml of acidified 5% ferrous ammonium sulfate, washed with $NaHCO_3$ aq, and was dried over $MgSO_4$. Analysis by GLPC on a Carbowax 20M on firebrick column showed the presence of phenylacetaldehyde (90%) with only trace quantities of benzaldehyde and benzyl alcohol.

Preparation of diethylene 1-*phenylethane*-1,2-*bisboronate* (**6**). Compound **4a** (8·70 g, 0·0355 mol) was treated with 0·034 mol borane in 25 ml THF for 18 hr at room temp. BuOH (10 g) was added and the reaction mixture distilled giving the **6a** (4·76 g, 32%) fraction with b.p. 138–142° at 0·1 mm. Treatment with ethylene glycol followed by distillation, approximate b.p. 120° at 0·4 mm, gave a crystalline mixture of **6** (95%) and apparently **7** (5%). The NMR spectrum of the mixture displayed a weak singlet at $\delta = 1{\cdot}30$, an XY portion of an AXY system centered at $\delta = 1{\cdot}38$ ($\Delta\delta_{XY} = 0{\cdot}15$ ppm, $J_{XY} = 16{\cdot}0$ Hz, $J_{AX} = 9{\cdot}5$ Hz, $J_{BX} = 6{\cdot}5$ Hz), the A portion of the AXY system at $\delta = 2{\cdot}69$, singlet at $\delta = 4{\cdot}13$, and a broad singlet at $\delta = 7{\cdot}2$.

Recrystallization from CCl_4 gave the pure **6** with m.p. 115–117°. (Found: C, 58·52; H, 6·82; B, 8·64. Calcd. for $C_{12}H_{16}B_2O_4$: C, 58·61; H, 6·56; B, 8·80%).

Attempted hydrogenolysis of diethylene 1-*phenylethane*-1,2-*bisboronate with propionic acid*. To 0·5 g (0·002 mol) of **6** in diglyme (3 ml) in a heavy walled glass tube was added 1·5 g (0·02 mol) propionic acid. The tube was sealed and heated for 40 hr at 140° in a sand bath and worked up and analyzed as described above for the attempted hydrogenolysis of **3**. No ethylbenzene was detected.

Base-catalyzed hydrolysis of diethylene 1-*phenylethane*-1,2-*bisboronate*. Compound **6** (70 mg) was subjected to base-catalyzed hydrolysis as described above for **3**. Analysis by GLPC indicated the formation of 1-phenylethanol (8%) and 2-phenylethanol (92%) in nearly quantitative yield.

Brominolysis of ethylene 1-*phenylethane*-1,2-*bisboronate with* N-*bromopyridinium perbromide*. The bromination was carried out as described above for **5** on 154 mg (0·0006 mol) of **6**. Analysis of the reaction product by ^1H NMR revealed the presence of styrene dibromide (XY portion of an AXY system centered at $\delta = 3{\cdot}95$ ($\Delta\delta_{XY} \sim 0{\cdot}033$ ppm, $J_{AX} = 9$ Hz, $J_{AY} = 7$ Hz, $J_{XY} \approx 11{\cdot}2$ Hz).

Radical bromination of 1-*phenylethane*-1,2-*bisboronate with bromine in carbon tetrachloride*. To 154 mg

(0·00063 mol) of **6** in 2 ml CCl_4 was added 100 mg (0·00063 mol) Br_2 in CCl_4. HBr was evolved and detected as described above. Analysis of the reaction mixture by ^1H NMR showed the presence of **4** (40%) and **16** (60%).

Attempted oxidation of diethylene 1-phenylethane-1,2-bisboronate with pyridine N-oxide. To a soln of 0·57 g distilled pyridine N-oxide in 3 ml $CHCl_3$ was added 250 mg (0·001 mol) of **6**. The reaction mixture was refluxed for 2 hr and worked up as described above for **3**. Analysis of the reaction residue by ^1H NMR showed the presence of only starting material. No oxidation products were detected by GLPC.

Oxidation of tetrabutyl 1-phenylethane-1,2-bisboronate with m-chloroperbenzoic acid. Approximately 100 mg of **6a** was oxidized with *m*-chloroperbenzoic acid as described for **3a** above. GLPC analysis showed the presence of acetophenone (40%) and phenylethane-1,2-diol with trace amounts of benzaldehyde and 1- and 2-phenylethanol present.

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