Organoboranes. VIII. Structure of the Thermally Isomerized Organoborane from the Reaction of Borane and 1,3-Butadiene in a 1:1 Molar Ratio. Evidence for an Exceptionally Stable Transannular Boron–Hydrogen Bridge[1]

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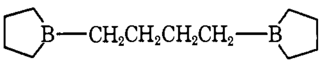
Abstract: Distillation of the largely polymeric product produced in the reaction of equimolar quantities of borane and 1,3-butadiene produces a material, $C_8H_{16}B_2H_2$, with extraordinary properties for a tetrasubstituted diborane (dimer of a dialkylborane). Thus this material is stable to water and methanol at room temperature, and fails to hydroborate simple olefins without heating. It is not oxidized by cold alkaline hydrogen peroxide, and this treatment can be used to prepare the pure material, free of the usual small amounts of more reactive impurities. These characteristics do not appear to be compatible with the proposed formulation as bisborolane, $(CH_2)_4BH_2B(CH_2)_4$. Accordingly, the alternative formulation as 1,6-diboracyclodecane, with a transannular boron–hydrogen bridge, was investigated. Reaction with methanol occurs slowly in refluxing tetrahydrofuran, liberating hydrogen, and forming methoxy derivatives. However, glpc examination of the reaction mixture revealed the essential absence of B-methoxyborolane, $(CH_2)_4BOCH_3$, in the initial phases of the reaction. Similarly, protonolysis with acetic acid forms 1,4-butanediboronic acid, isolated and identified as the bisdiethanolamine derivative, mp 261–263°. Both of these observations are compatible with the formulation of the compound as 1,6-diboracyclodecane, but not with the bisborolane structure. Finally, it is pointed out that the highly unusual characteristics of the compound are readily understood in terms of the formulation as 1,6-diboracyclodecane, where the transannular structure could greatly stabilize the boron–hydrogen bridge and render this moiety relatively inert toward reagents which usually attack it with ease.

The hydroboration of 1,3-butadiene has a number of highly interesting and unusual features which have encouraged its study in several laboratories.[4]

Under the usual mild conditions, such as ether solvents and 0–25°, the hydroboration evidently proceeds to the formation of relatively low molecular weight polymers containing approximately 75% of 1,4- and 25% of 1,3-diborabutane units.[4d] Distillation of the polymeric material yields a product, $C_{12}H_{24}B_2$, formulated by Köster[4a] as 1,1′-tetramethylenebisborolane (**1**). This structure has been accepted by Saegebarth[4c] and, in part, by Mikhailov and his coworkers[4g] for the products they have obtained.[5] However, we have been unable to find any experimental evidence for this proposed structure.[6]



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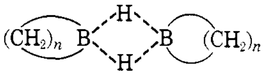
Hydroboration of 1,3-butadiene with borane in a 1:1 molar ratio in ether solvents likewise produces a polymeric material.[4d] The excess boron–hydrogen bonds exhibit the usual reactivity of such bonds and undergo rapid hydrolysis with water and methanolysis with methanol at 0°. This treatment does not depolymerize the product, since vacuum distillation of the methanolized product at room temperature gives almost none of the highly volatile B-methoxyborolane.[4d]

On the other hand, Köster has reported that the reaction of equimolar amounts of borane with dienes results in the formation of bisboracyclanes (**2**).[4b] He indicated that these bisboracyclanes, with n = 4, 5, and 6, are unusually stable materials, exhibiting unusual stability toward water and oxidizing agents, as well as an unusual infrared spectrum. However, in more recent publications these unusual properties were claimed only for the bisborolane (**2**, n = 4).[7]



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Initially we were puzzled by the vast difference in the nature of the products formed in our hydroboration experiments[4d] and those reported by Köster.[4a,b] However, it now appears that the products obtained by Köster are produced at relatively high temperature, presumably as a result of depolymerization of the polymer formed under the usual conditions.[4d] It appeared desirable to study the transformation of the initially formed polymer into the material described by

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[1] A preliminary report of this study was communicated to the 31st Meeting of the Israel Chemical Society, Dec 26–28, 1964, at Jerusalem, Israel; E. Breuer and H. C. Brown, *Israel J. Chem.*, 2, 238 (1964).

[2] Postdoctorate Research Associate on Grant 19878 provided by the National Science Foundation and Grant GM 10937 from the National Institutes of Health.

[3] Department of Pharmaceutical Chemistry, The Hebrew University, Jerusalem, Israel.

[4] (a) R. Köster, *Angew. Chem.*, 71, 520 (1959); (b) R. Köster, *ibid.*, 72, 626 (1960); (c) K. Saegebarth, *J. Am. Chem. Soc.*, 82, 2081 (1960); K. A. Saegebarth, U. S. Patent 3,008,997 (1961); *Chem. Abstr.*, 51, 12534*i* (1962); (d) G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, 84, 183 (1962); (e) H. G. Weiss, W. J. Lehmann, and I. Shapiro, *ibid.*, 84, 3840 (1962); (f) A. E. Poper and H. A. Skinner, *J. Chem. Soc.*, 3704 (1963); (g) B. M. Mikhailov, A. Y. Bezmenov, L. S. Vasil'ev, and V. G. Kiselev, *Dokl. Akad. Nauk SSSR*, 155 (1), 141 (1964); *Chem. Abstr.*, 60, 13263 (1964).

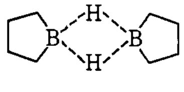
[5] Mikhailov and his coworkers[4g] believe that the alkyl chain linking the two borolane units may have considerable branching.

[6] We are currently studying the carbonylation of these intermediates in the hope of establishing their true structure. Research is in progress with Dr. E. Negishi.

[7] (a) R. Köster, *Progr. Boron Chem.*, 1, 289 (1964); (b) R. Köster and K. Iwasaki, "Boron-Nitrogen Chemistry," Advances in Chemistry Series No. 42, American Chemical Society, Washington, D. C., 1964, p 148.

Köster as "bisborolane."[4d] Consequently, we decided to undertake a detailed study of the structure of this product.

Our results for this "1:1 dimer" appear to be in far better agreement with the structure, 1,6-diboracyclodecane (**4**), than with the previously proposed structure, bisborolane (**3**).



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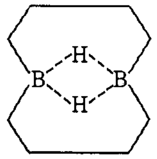

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Results

Depolymerization–Distillation of the 1,3-Butadiene–Borane 1:1 Product. An equimolar amount of 1,3-butadiene was added to a solution of borane in tetrahydrofuran at 0°. After 1 hr, the solution was subjected to distillation and the solvent removed at atmospheric pressure, leaving an oily residue of low volatility. This residue was then subjected to thermal depolymerization and distillation under vacuum. There was obtained an oily distillate, bp 88° (16 mm), $n^{20}\text{D}$ 1.4793, with approximately 10% of a nonvolatile residue. The distillate was washed with cold (0°) dilute alkaline hydrogen peroxide, extracted with petroleum ether (bp 30–60°), and distilled. The product, bp 59–60° (5 mm), $n^{20}\text{D}$ 1.4886, is evidently identical with the 1:1 dimer (bisborolane) of Köster.[4b] The infrared spectrum was identical with that reported.[7a]

The elementary analysis and molecular weight agreed with the molecular formula, $C_8H_{16}B_2H_2$. The product was stable to oxygen, water, and methanol, as described by Köster.[7a,b]

Mass spectral determination of the molecular weight at low voltage (15 eV) to minimize fragmentation gave parent peaks at *m/e* 134, 135, and 136, corresponding to the undissociated 1:1 dimer. No peaks were observed at *m/e* 67 and 68 corresponding to the 1:1 monomer.

In contrast, *sym*-tetrasiamyldiborane underwent complete dissociation under these conditions, exhibiting parent peaks only at *m/e* 82 and 83, corresponding to the monomeric disiamylborane species. No peaks at *m/e* 164–166 were observed in this case.

The question arose as to whether the 1:1 dimer was present as such in the initial hydroboration product. Accordingly, the initial 1,3-butadieneborane product was subjected to glpc examination. There was found 16% of the 1:1 dimer. Since depolymerization could have occurred in the heated injection port of the instrument, this 16% must be considered to represent an upper limit of the amount of Köster product present in the hydroboration stage. In actual fact, the amount present is probably far less. (The methanolysis experiments described later indicate the amount to be far less, not more than 1%.)

Oxidation of the initial hydroboration product (predominantly polymer) with alkaline hydrogen peroxide gave 75% 1,4-, 22% 1,3-, and 3% 1,2-butanediol. Oxidation of the distilled 1:1 dimer gave 100% 1,4-butanediol. On the other hand, oxidation of the relatively nonvolatile residue yielded 30% 1,4-, 65% 1,3-, and 5% 1,2-butanediol. These results are summarized in Table I.

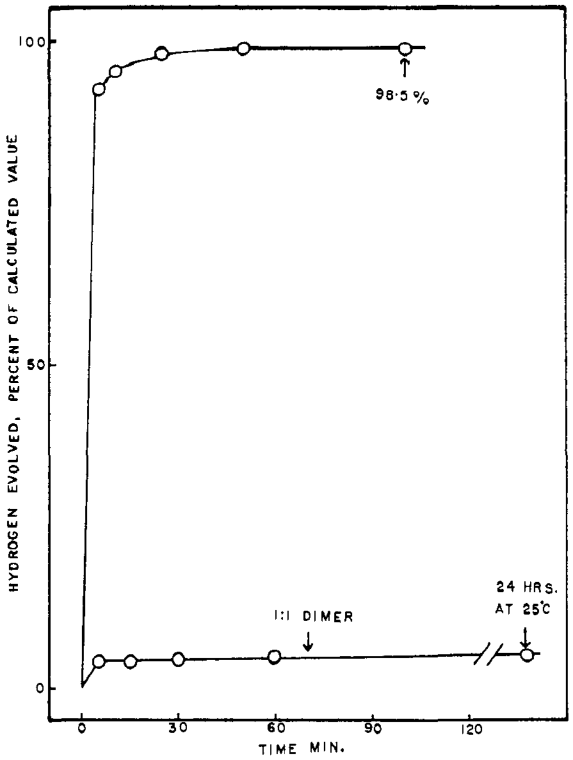


Figure 1. Reaction of methanol at 0° with the polymeric 1:1 hydroboration product of 1,3-butadiene and the depolymerized distillate.

Table I. Distribution of Butanediol Isomers Formed in the Oxidation of the Fractions from the Hydroboration–Distillation of 1,3-Butadiene

Fraction	Butanediol, % 1,4	1,3	1,2
Hydroboration product	75	22	3
Depolymerization-distilled product[a]	100	0	0
Nonvolatile residue	30	65	5

[a] 1:1 dimer, **3** or **4**.

Methanolysis of the 1,3-Butadiene–Borane 1:1 Products. It was previously reported that the product produced in the reaction of equimolar amounts of borane and 1,3-butadiene at 0° reacts rapidly and quantitatively with methanol to liberate the theoretical quantity of hydrogen (eq 1).[4d]

$$n(\text{CH=CH}_2)_2 + n\text{BH}_3 \longrightarrow [(\text{C}_4\text{H}_8)\text{BH}]_n \xrightarrow{\text{CH}_3\text{OH}} [(\text{C}_4\text{H}_8)\text{BOCH}_3]_n + n\text{H}_2 \quad (1)$$

This result was checked. 1,3-Butadiene, 120 mmol, was added to 120 mmol of borane in tetrahydrofuran at 0°. Addition of 122 mmol of methanol at 0° produced an almost immediate evolution of 92.8% of hydrogen, rising to 98.5% in 2 hr at 25°. These results are shown in Figure 1. Since the 1:1 dimer does not react with methanol under these conditions, as shown by the results shown graphically in Figure 1, it is evident that the initial polymeric product cannot contain any significant quantity of the 1:1 dimer.

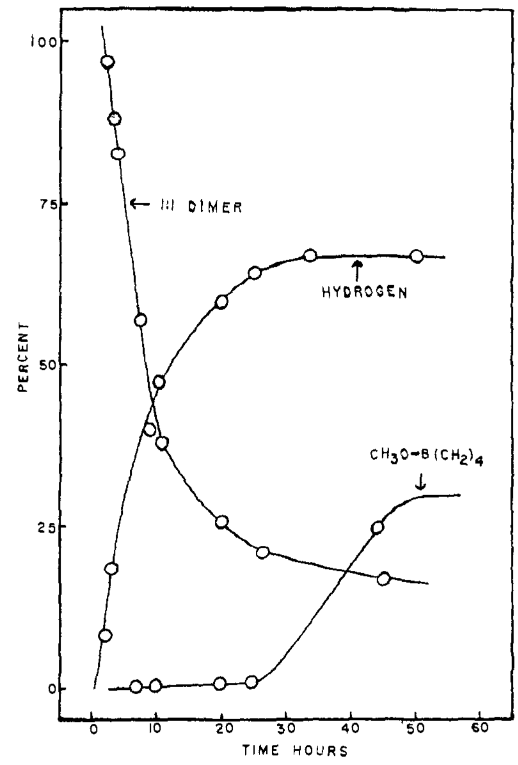
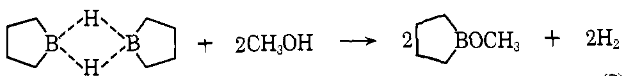


Figure 2. Reaction of methanol at 70° with the 1:1 dimer.

The reaction product produced by treatment of the initially produced polymer with methanol was subjected to detailed examination. Evacuation at room temperature failed to produce any B-methoxyborolane. Subjection to glpc (cold injection port) failed to show more than traces of B-methoxyborolane. However, depolymerization–distillation at elevated temperatures gave 50% of B-methoxyborolane, along with some higher boiling products, possibly dimeric species.

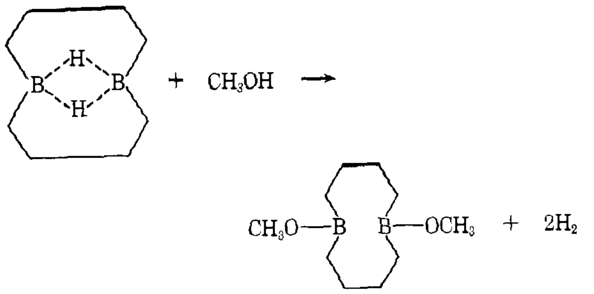
Köster previously noted that the 1:1 dimer exhibits a remarkable stability toward alcoholysis at room temperature, undergoing a slow reaction only at temperatures of 70–100°.[4b] Indeed, we confirmed that this product exhibited almost no reaction with methanol in 24 hr at room temperature (Figure 1).

It appeared that the reaction with methanol at higher temperatures might provide a basis for deciding between the alternative structures, 3 and 4. The reaction of 3 with methanol must produce B-methoxyborolane in an amount corresponding to the number of moles of hydrogen produced (eq 2). On the other hand, the 1,6-diboracyclodecane structure 4 could liberate hydrogen without necessarily undergoing depolymerization to B-methoxyborolane (eq 3).



(2)

Accordingly, a solution of 42 mmol of the 1:1 dimer and 122 mmol of methanol in 15 ml of tetrahydrofuran was refluxed for 24 hr. The hydrogen collected corresponded to 73% methanolysis. Distillation of this material at atmospheric pressure failed to give any significant quantity of B-methoxyborolane. However, by heating the product under vacuum, depolymerization evidently occurred and B-methoxyborolane was obtained.



(3)

In a second experiment the 1:1 dimer was heated with methanol in refluxing tetrahydrofuran with an internal standard present. The hydrogen evolved was measured and the solution was periodically examined by glpc for the decrease in the quantity of the 1:1 dimer and the presence of B-methoxyborolane. It was observed that in 3 hr the hydrogen evolved corresponded to the reaction of 20% of the 1:1 dimer and there was actually present, by glpc analysis, 82% of residual dimer. Yet at this time only trace quantities of the B-methoxyborolane were present. At 10 hr the hydrogen evolved corresponded to the reaction of 47% of the initial dimer introduced. Again the analysis indicated the presence of only traces of B-methoxyborolane. The reaction was continued and B-methoxyborolane slowly appeared, evidently formed in a subsequent reaction from the initially produced ester. The results are shown graphically in Figure 2.

The liberation of hydrogen[8] without the concurrent formation of B-methoxyborolane appears to be incompatible with the proposed bisborolane structure for the depolymerized distillate. The results are consistent with the 1,6-diboracyclodecane structure, provided it is assumed that the initial product is the dimethoxy derivative which then undergoes a slow conversion to B-methoxyborolane.

Protonolysis of the 1:1 Dimer with Acetic Acid. Organoboranes undergo ready protonolysis with acetic acid.[9] In refluxing diglyme, all three groups of organoboranes undergo protonolysis. However, in glacial acetic acid the reaction proceeds readily to the removal of two of the three groups and only slowly beyond.[10] Accordingly, we undertook to examine the behavior of the 1:1 dimer toward refluxing anhydrous acetic acid.

Ten mmoles of the 1:1 dimer was dissolved in 10 ml of acetic acid and the solution heated under reflux for 4 hr. From the reaction mixture there was obtained the known bisdiethanolamine ester 1,4-butanediboronic acid, mp 261–263°,[11] in a yield of 11%.[12]

The formation of *n*-butane was also demonstrated. *n*-Butylboronic acid is presumably also formed. However, we did not identify it. Unless one postulates a rearrangement, the formation of 1,4-butanediboronic acid is incompatible with the bisborolane structure (3), but is compatible with the alternative 1,6-diboracyclodecane structure (4).

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[8] A quantitative recovery of hydrogen was not achieved. However, the apparatus had some rubber connections and we have since noted that while hydrogen recoveries are quite satisfactory for the usual fast reactions, they are low for slow reactions, such as the present one.

[9] H. C. Brown and K. Murray, *J. Am. Chem. Soc.*, 81, 4108 (1959).

[10] K. J. Murray, Ph.D. Thesis, Purdue University Library.

[11] W. R. Bamford and S. Fordham, *Soc. Chem. Ind.* (London) (Monograph), 13, 320 (1961); *Chem. Abstr.*, 56, 5991 (1962).

[12] In a repetition of this experiment Dr. D. N. Butler later obtained a 14% yield of this salt. If the protonolysis were to proceed in a purely statistical manner the optimum yield would be 25%.

Discussion

Previously it had been reported from this laboratory that the hydroboration of butadiene in an ether solvent produces an organoborane polymer of low molecular weight.[4d] This observation was confirmed in the present study. Moreover, glpc examination of the product revealed the presence of no more than 16% of the 1:1 dimer (Köster's bisborolane). Since depolymerization could have occurred in the hot injection port, this provides only an upper limit to the amount of the 1:1 dimer that can be present. Actually, the methanolysis experiments indicate that the amount of the 1:1 dimer present cannot exceed 1%.

Thermal depolymerization–distillation of the initial polymeric hydroboration product of 1,3-butadiene gave a 75% yield of the 1:1 dimer, which exhibited identical physical properties and a superimposable infrared spectrum with the substance described by Köster as bisborolane.[7]

Oxidation of the initial hydroboration product gave a mixture of 1,4-, 1,3-, and 1,2-butanediols (Table I). However, oxidation of the 1:1 dimer gave only the 1,4 isomer. On the other hand, the residue (approximately 10%) gave a butanediol mixture containing 30% 1,4, 65% 1,3, and 5% 1,2.

If all of the 1,4-borabutane moieties in the initial polymer had gone to form the 1:1 dimer, the 75% yield realized would represent a quantitative recovery. However, it is probable that some isomerization of the boron linkages to the butane chain occurs at the temperature required for the depolymerization stage.[13] The results suggest that the 1,4-borabutane moieties cyclize readily to form the 1:1 dimer, whereas the 1,3 and 1,2 moieties fail to cyclize and thereby produce a less volatile material, presumably polymeric, which accumulates in the residue.

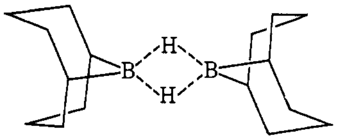
Mass spectral determination of the molecular weight at low voltages gave a value of 136, corresponding to the dimeric formula, $C_8H_{16}B_2H_2$, with no peak at *m/e* 67–68. On the other hand, *sym*-tetrasiamyldiborane, under the same conditions, exhibited only peaks for the monomer.

Similarly, the infrared spectrum of the 1:1 dimer exhibits the bridge hydrogen absorption at 1612 cm^{-1}. This compares to the usual value at 1550–1570 cm^{-1} for *sym*-tetraalkyldiboranes.[14,15]

The 1:1 dimer is stable to air and inert to water, methanol, and even acetic acid at room temperature. It fails to hydroborate olefins. It can be purified by treatment with cold dilute alkaline hydrogen peroxide solution.

Thus both the physical and chemical properties are in sharp contrast to those exhibited by the simple *sym*-tetraalkyldiboranes. One possible explanation, in terms of the bisborolane structure, is to assume that the formation of the five-membered ring gives the system unusual stability.

Indeed, it has recently been reported that cyclic hydroboration of 1,5-cyclooctadiene with an equimolar quantity of borane gives 9-borabicyclo[3.3.1]nonane (**5**).[16] This borane, 9-BBN, is indeed unusually stable toward dissociation into the monomer, attributed to resistance by the strained boron atom to undergo a change in hybridization with an increase in the preferred angle at the bridging boron atom.[16]



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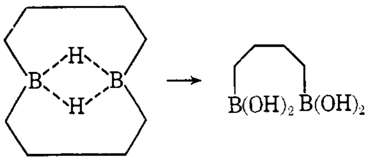
However, 9-BBN exhibits the normal infrared absorption of the $>BH_2B<$ bridge at 1560 cm^{-1}. Moreover, the molecule is highly reactive in hydroboration[16] and in methanolysis.[17]

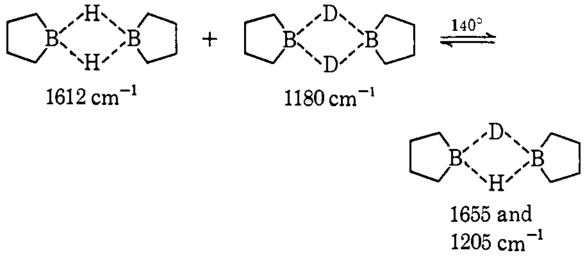
The reaction of the 1:1 dimer with methanol is not only exceedingly slow at room temperature, it is also very slow in refluxing tetrahydrofuran, requiring many hours to go to completion (Figure 1). Moreover, in this methanolysis a considerable portion of the available boron–hydrogen bonds react, generating hydrogen, without the simultaneous formation of B-methoxyborolane. The product of the methanolysis could be converted relatively rapidly into B-methoxyborolane only by heating it under vacuum.

Finally, protonolysis of bisborolane to form 1,4-butanediboronic acid is impossible, without assuming a rearrangement during the protonolysis stage. On the other hand, it is consistent with the 1,6-diboracyclodecane structure (eq 4).



(4)

Köster has reported[7a,b] that the 1:1 dimer with isotopically different bridges fails to undergo exchange at room temperature or even 100°. At 140° exchange does occur as evidenced by the appearance of new absorption bands in the infrared spectrum (eq 5).



(5)

Again, this remarkable resistance to exchange at the usually highly labile boron–hydrogen bridge is difficult to understand in terms of Köster's bisborolane structure (**3**), but it is readily explicable in terms of the alternative (**4**).

Shapiro and his coworkers previously studied the reaction of 1,3-butadiene with excess diborane at 100° in the gas phase.[4e] They obtained two products. The major product of the reaction was formulated as the cyclic organoborane (**6**) on the basis of the oxidation

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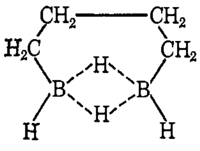
[13] For a review of such isomerizations, see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[14] H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

[15] I. Shapiro, C. O. Wilson, Jr., and W. J. Lehmann, *J. Chem. Phys.*, **29**, 237 (1958); W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *ibid.*, **32**, 1088 (1960); **32**, 1786 (1960); **33**, 590 (1960).

[16] E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 5280, 5281, 5283 (1968).

[17] Unpublished research with N. M. Yoon.



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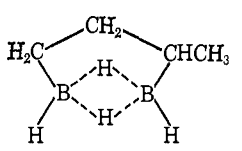

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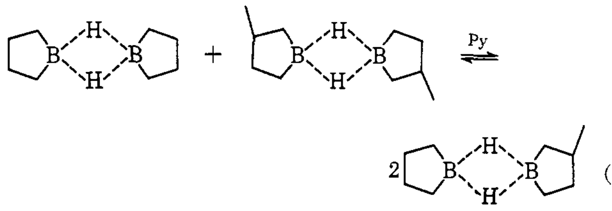
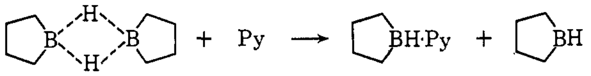
product, as well as the infrared and the ^{11}B and H nuclear magnetic resonance spectra. The minor product of the reaction was unstable, with a tendency to yield polymeric products. It was formulated as the cyclic organoborane (**7**). These results, in our opinion, likewise support the proposed formulation of the 1:1 dimer as 1,6-diboracyclodecane (**4**).

Köster has argued that his proposed formulation is supported by his observations of the ability of various amines to "catalyze" reactions of the 1:1 dimer.[7b] For example, the exchange reaction of tagged borolanes, which as previously discussed requires elevated temperatures, can be made to proceed at room temperature in the presence of pyridine (eq 6).



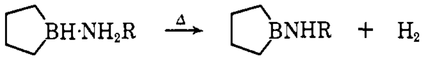
(6)

The reaction is not truly catalytic, since the amount of mixed 1:1 dimer formed corresponds to the amount of pyridine added to the mixture. It has been suggested that the pyridine forms an addition compound with one-half of the dimer, liberating a molecule of bisborolane. The free bisborolane entities then combine (eq 7).



(7)

The 1:1 dimer also reacts with primary amine to form addition compounds which are stable at room temperature, but liberate hydrogen at elevated temperatures.[18] The reaction is considered to be that shown (eq 8).



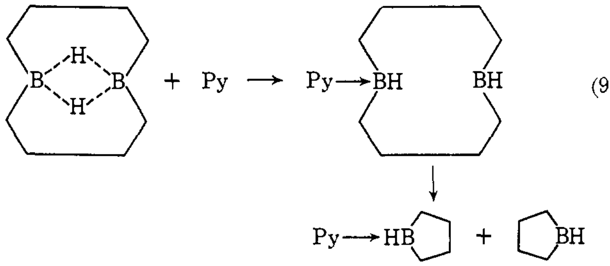
(8)

These reactions were considered by Köster[7b] to provide compelling evidence against the proposed 1,6-diboracyclodecane structure. However, the observed reactions are readily accommodated by this structure.

The available evidence is that medium rings with eight, nine, and ten members are highly strained, with a maximum in the strain appearing in the ten-ring system, cyclodecane.[19]

Boron–carbon bonds are quite labile, undergoing relatively rapid exchange, especially in the presence of boron–hydrogen bonds.[20] Consequently, it might be thought that a molecule with the 1,6-diboracyclodecane structure would be exceedingly unstable, rapidly undergoing conversion to a polymer, or to a bisborolane derivative, relieving the strain. However, this conclusion ignores the stabilizing influence of the proposed transannular boron–hydrogen bridge (**4**).[21]

The addition of an amine to the bridged 1,6-diboracyclodecane structure would be expected to open the bridge (eq 9). With loss of the stabilization afforded by the transannular system, the strained ten-ring system would be expected to undergo rapid conversion either to the less strained five-ring system, or to a polymer.



(9)

If all of the evidence is considered, it would appear that the bridged 1,6-diboracyclodecane structure (**4**) provides the most consistent interpretation of the reactions of the 1:1 dimer and the highly unusual physical and chemical properties of the boron–hydrogen bridge. This appears to be the first molecule containing such a transannular boron–hydrogen bridge. However, it is apparent that it should be possible to synthesize many other ring systems with such bridges.

Experimental Section

Materials. The purification of reagents and solvents and the preparation of borane solutions in tetrahydrofuran were carried out as described previously.[22] 1,3-Butadiene (Matheson) was used from the cylinder without further purification.

Hydroboration of 1,3-Butadiene. All operations were carried out under nitrogen. 1,3-Butadiene was condensed and 20.7 ml of the liquid (250 mmol) was allowed to evaporate slowly and the gas conducted into 158 ml of 1.58 *M* borane in tetrahydrofuran (250 mmol of BH_3) maintained at 0°. After 1 hr, a sample was removed and subjected to glpc examination, utilizing a 1-m column of 10% silicone rubber SE-30 on Firebrick (injection port 150°; initial column temperature, 50°; programmed at 3.3°/min). By comparison with a pure sample of the 1:1 dimer, there was present a maximum of 16% of this species.

The tetrahydrofuran was removed by distillation at atmospheric pressure, leaving 14.5 g of an oily residue (calculated for 100% yield, 16.9 g). An aliquot was removed and oxidized with alkaline hydrogen peroxide, giving a mixture of butanediols (Table I).

The remaining 13.7 g of the product was depolymerized by subjecting it to vacuum distillation, yielding 10.13 g of distillate, bp 88° (13 mm), $n^{20}\mathrm{D}$ 1.4793, and 1.40 g of residue. An aliquot of the distillate and the residue were separately oxidized by alkaline hydrogen peroxide. The butanediols were recovered and analyzed by glpc as previously described.[4d]

The distillate was washed with a cold alkaline solution of diluted hydrogen peroxide and extracted with petroleum ether. After drying over sodium sulfate, the solvent was removed and the pure 1:1 dimer obtained by distillation, bp 59–60° (5 mm), $n^{20}\mathrm{D}$ 1.4886 (lit.[7a,b] bp 76–77° (10 mm), $n^{20}\mathrm{D}$ 1.4894).

Anal. Calcd for $C_8H_{18}B_2$: C, 70.58; H, 13.23; mol wt, 136. Found: C, 70.52; H, 13.22; mol wt by osmometry, 142; by mass spectrometry, 134, 135, 136.

Reaction of the 1:1 Polymeric Product with Methanol. 1,3-Butadiene, 120 mmol, was hydroborated with borane in tetrahydrofuran as described in the previous experiment. After removal of the solvent 6.5 g of oily residue was obtained. This was dis-

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(18) Indeed, we have observed that treatment of the 1:1 dimer with β-dimethylaminoethanol causes immediate liberation of the theoretical quantity of hydrogen at room temperature, in contrast to the very slow reaction with methanol.

(19) For a fascinating review with literature references, see V. Prelog, *J. Chem. Soc.*, 420 (1950).

(20) R. Köster and G. Schomburg, *Angew. Chem.*, **72**, 567 (1960); R. Köster, G. Bruno, and P. Binger, *Ann.*, **644**, 1 (1961).

(21) Other types of transannular bridges are well known and can even lead to bond formation between groups which do not bond in the parent molecules. See, for example, N. J. Leonard, *Record Chem. Progr.*, **17**, 243 (1956).

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solved in 20 ml of tetrahydrofuran, the mixture was cooled to 0°, and 5.0 ml of methanol (122 mmol) was slowly introduced. There was a vigorous reaction and 92.5% of the theoretical hydrogen was evolved by the time the addition had been completed. The solution was stirred at room temperature for 2 hr. The total hydrogen evolved increased to 98.5% of the calculated quantity.

The flask was immersed in an oil bath and the temperature raised to 165° as the tetrahydrofuran and possible B-methoxyborolane was collected. However, glpc examination of the distillate revealed only traces of B-methoxyborolane.

The flask containing the product was connected to a vacuum and heated. At 85–90° bath temperature and a pressure of 15 mm, distillation of a volatile product was observed and 2.82 g was collected in a trap cooled to −78°. Glpc analysis showed the presence of solvent (15%) and two peaks with retention times of 3.8 and 6.2 min. By raising the bath temperature to 180–200°, a larger fraction was collected, 3.58 g. Glpc analysis showed the presence of B-methoxyborolane, 62%, retention time 2.0 min, and the previous two peaks of longer retention time, 3.8 and 6.2 min.

Reaction of the 1:1 Dimer with Methanol. Freshly distilled 1:1 dimer, 5.73 g, 42.1 mmol, was dissolved in 15 ml of tetrahydrofuran at 0° and 5.0 ml of methanol (122 mmol) added. There was an initial evolution of 80 ml of hydrogen (3.57 mmol, 4.25%). Further evolution was very slow, the total being 97 ml (5.13%) after 24 hr. The solution was then refluxed for 24 hr, causing the slow liberation of 1380 ml of hydrogen (61 mmol, 73% of theory[8]). Glpc analysis showed the presence of 18% unreacted 1:1 dimer.

The tetrahydrofuran was removed at atmospheric pressure. Depolymerization with vacuum distillation gave two fractions: 3.62 g, with one major peak (70%) on glpc examination, exhibiting a retention time of 2.5 min, and three minor peaks with retention times of 5.2, 8.2, and 14 min, and 2.42 g, with glpc showing the presence of six peaks. Redistillation of the larger first fraction at atmospheric pressure, bp 92–96° (747 mm), yielded 2.14 g. However, glpc analysis showed no improvement in apparent purity. Nevertheless mass spectral examination of this fraction showed one parent peak at low voltage (15 eV) at *m/e* 97 and 98, in accordance with that expected for B-methoxyborolane.

In another experiment, *n*-dodecane was added as an internal standard and the reaction followed by glpc analysis, as well as by hydrogen evolution. The 1:1 dimer, 1.33 g (9.8 mmol), freshly distilled in 4.0 ml of tetrahydrofuran containing 0.725 g of *n*-dodecane. Then 1.0 ml (24 mmol) of methanol was added, causing the liberation of 18 ml of hydrogen (0.80 mmol, 4.1%) in 85 min. The solution was brought to a gentle reflux and the evolution of hydrogen was observed as samples were removed with a syringe for glpc examination. The results are shown in Figure 2.

Protonolysis of the 1:1 Dimer. Freshly distilled dimer, 1.44 g, was dissolved in 10 ml of glacial acetic acid at room temperature. No gas was evolved. The solution was brought to reflux temperature and maintained there for 4 hr. There was evolved 490 ml of gas. The solution was evaporated to dryness *in vacuo* and 5.0 ml of diethanolamine added, followed by the addition of *n*-octane. The *n*-octane was distilled until the distillate showed no trace of acetic acid (1:1 *n*-octane–acetic acid azeotrope boils at 109°). The residue was treated with acetone, precipitating 338 mg (1.08 mmol) of 1,4-butanediboronic acid bisdiethanolamine ester, mp 244–250°. Four recrystallizations from Cellosolve gave the analytically pure sample, mp 261–263° (lit.[11] 245–247°).

Anal. Calcd for $C_{12}H_{26}B_2N_2O_6$: C, 50.74; H, 9.22; N, 9.86. Found: C, 50.91; H, 9.43; N, 9.60.

The 60-Mcps nmr spectrum in D_2O shows two distinctive multiplets centered at δ 3.0 (8 H) and 3.82 (8 H), two broad peaks centered at 0.6 (4 H) and 1.3 (4 H), and an enlarged water peak resulting from the exchange of the NH hydrogens. The infrared spectrum shows a band at 3144 cm^{-1}, characteristic of the NH grouping in diethanolamine esters of boronic acids.[23]

Reaction of the 1:1 Dimer with β-Dimethylaminoethanol. The freshly distilled 1:1 dimer, 0.711 g (5.22 mmol), was dissolved in 4.0 ml of dry tetrahydrofuran and 0.930 g (10.45 mmol) of β-dimethylaminoethanol was introduced with a syringe. There was an immediate evolution of hydrogen corresponding to 85% of the calculated amount. Removal of the solvent gave an oil which could not be crystallized.

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Intramolecular Triplet–Triplet Energy Transfer between Nonconjugated Chromophores with Fixed Orientation[1]

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Abstract: Efficient but not total triplet–triplet energy transfer is reported between tetralin-1,4-dione and fluorene chromophores held together by a rigid molecular frame at known separation distance and mutual orientation. The exchange mechanism is compared with the alternative resonance-type interaction of admixed singlet character in the lowest triplets. An order-of-magnitude calculation of the exchange-transfer probability gives a result compatible with the observed transfer efficiency.

Triplet–triplet energy transfer is a basic process in both photochemistry and molecular spectroscopy. It was first observed in rigid solutions in which the donor and acceptor molecules were present as cosolutes at 77°K, when selective excitation of the donor led to phosphorescence emission from the acceptor.[2,3] Later, flash spectroscopy allowed observation of the phenomenon in fluid solution at room temperature by determination of the T–T absorption of the acceptor.[4] Other efficient ways to investigate the migration of triplet energy in solution were provided by the use of α-diketones[5,6] or lanthanide-ion acceptors,[7-9] which exhibit quantitatively measurable luminescence in fluid solution corresponding to transitions involving a change of multiplicity of two.

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