Organoboranes. XII. Hydroboration of 1,3-Butadiene with Borane in Tetrahydrofuran in a Ratio Equal to or Smaller than 1:1. Interconversion between *B*-Alkylborolanes and 1,2-Tetramethylenediboranes[1]

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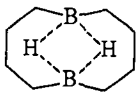
Abstract: The hydroboration product derived from 1,3-butadiene and borane in tetrahydrofuran (THF) in the 1:1 molar ratio is polymeric and has a repeating unit which can be largely represented by a pseudocyclic 1,2-tetramethylenediborane structure, **10**, while the products derived from 1,3-butadiene and borane in THF in a ratio equal to or smaller than 3:4 mainly consist of bis(1,2-tetramethylenediboryl)butanes with the excess of borane unreacted. Formation of these products involves a facile opening of the borolane rings of the 3:2 compounds, 1,3- and 1,4-bis(1′-borolyl)butanes, with borane, which appears to be a general reaction for *B*-alkylborolanes. Thus, the reaction of *B*-(*n*-butyl)borolane with borane in the 1:1 ratio yields cleanly and quantitatively 1-*n*-butyl-1,2-tetramethylenediborane which was isolated and identified as the trimethoxy derivative. With this facile opening of a borolane ring with borane as a key to understanding, the reaction of 1,3-butadiene with borane in THF is now clarified and evidently proceeds through the formation of a number of species with interesting characteristics. The nonformation of the parent borolane unit in the reaction of *B*-alkylborolanes with borane indicates that the parent borolane is evidently less stable than the pseudocyclic species in which the double-hydrogen bridge is stabilized by the tetramethylene moiety. The B–H bond of the double-hydrogen bridge in the pseudocyclic 1,2-tetramethylenediborane exhibits an unusual selectivity in that it reacts readily with water and methanol, but only sluggishly with olefins at 25°. The reaction with olefins can be greatly accelerated by refluxing the reaction mixture in THF. This treatment converts the pseudocyclic 1,2-tetramethylenediborane largely into *B*-alkylborolanes, thereby providing a simple method for the synthesis of *B*-alkylborolanes in good yields. Therefore, it is evident that, in the absence of the stabilizing double-hydrogen bridge, the borolane-containing structure is more stable than the open-chain structure.

Hydroboration of 1,3-butadiene has been extensively studied in the past 10 years and a number of highly interesting and unusual features have been revealed.[3] The oxidation products appear to be well understood. However, much remains to be clarified about the actual structures of the organoborane intermediates.



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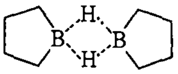

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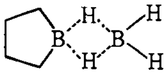
It is only recently that we were able to correct and clarify some erroneous and confusing results. Thus, it has been shown that the distillate derived from 1,3-butadiene and borane in the 1:1 molar ratio has an unusual transannularly bridged structure, 1,6-diboracyclodecane (**1**),[3i,3j] rather than the originally proposed bisborolane structure (**2**).[3b] Earlier interpretations by Köster[3b,4] of the hydroboration of 1,3-butadiene must therefore be revised. Similarly, Köster's assignment[4b–4d] of **3** to a material obtained from **1** and diborane was questioned by Young and Shore,[3j] who believe that Köster prepared **4** rather than **3**.



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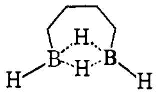

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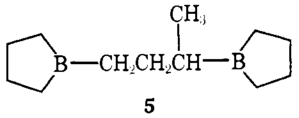
On the other hand, it has been demonstrated that the kinetically controlled products from 1,3-butadiene and borane in the 3:2 ratio largely consist of 1,3- and 1,4-bis(1′-borolyl)butanes (**5** and **6**), the ratio of the two being *ca.* 70/30.[3k] A novel result with the 3:2 products is that on thermal isomerization the major product obtained is the "*gem*-dibora" compound **7**, rather than **6**. The ratio of **7** and **6** in an equilibrium mixture is again *ca.* 70/30.[3k] Thus, in these cyclic derivatives thermal isomerization does not cause the boron atoms to move preferentially to the two ends of



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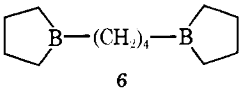

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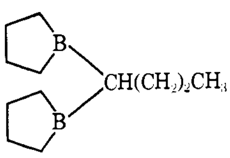
[1] For a preliminary report on some aspects of the chemistry of *B*-alkylborolanes, see H. C. Brown, E. Negishi, and P. L. Burke, *J. Amer. Chem. Soc.*, **92**, 6649 (1970).

[2] (a) Postdoctoral research associate on a research grant, DA 31-134 ADO(D) 453, supported by the U. S. Army Research Office (Durham). (b) Graduate assistant on a research grant, GM 10937, supported by the National Institutes of Health.

[3] (a) R. Köster, *Angew. Chem.*, 71, 520 (1959); (b) R. Köster, *ibid.*, 72, 626 (1960); (c) K. A. Saegebarth, U. S. Patent 3,008,997 (1961); (d) G. Zweifel, K. Nagase, and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 183 (1962); (e) H. G. Weiss, W. J. Lehmann, and I. Shapiro, *ibid.*, **84**, 3840 (1962); (f) A. E. Pope and 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**, 141 (1964); (h) B. M. Mikhailov, A. Y. Bezmenov, and L. S. Vasil'ev, *ibid.*, 167, 590 (1966); (i) E. Breuer and H. C. Brown, *Israel J. Chem.*, **2**, 238 (1964); E. Breuer and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4164 (1969); (j) D. E. Young and S. G. Shore, *ibid.*, **91**, 3497 (1969); (k) H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 2460 (1970).

[4] (a) R. Köster and G. Benedikt, *Angew. Chem.*, **75**, 346 (1963); (b) R. Köster, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Pergamon Press, New York, N. Y., 1964, p 289; (c) R. Köster, "Advances in Organometallic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1964, p 257; (d) R. Köster and Iwasaki, *Advan. Chem. Ser.*, No. **42**, 148 (1964); (e) R. Köster, G. Griasnov, W. Larbig, and P. Binger, *Justus Liebigs Ann. Chem.*, 672, 1 (1964).



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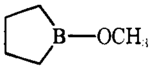
the chain, as might have been anticipated from the behavior of the simple trialkylboranes.

In the present report we describe still another class of compounds, derived from 1,3-butadiene and borane in THF, compounds with unusual properties. We also attempt to correlate the results of hydroboration of 1,3-butadiene with various reactant ratios.

Results and Discussion

Nature of the Hydroboration Product Derived from 1,3-Butadiene and Borane in THF in the 1:1 Molar Ratio. Earlier, we reported that the 1:1 hydroboration product derived from 1,3-butadiene and borane is polymeric and that neither 1-methoxyborolane (**8**) nor



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the stable dimer (**1**) was detected in any significant quantities by glpc examination after methanolysis.[3d,3i] These results have been confirmed in the present study using both borane-to-diene and diene-to-borane modes of addition.[5,6]

In an attempt to obtain further information as to the nature of the 1:1 hydroboration product, it was noted that the 1:1 hydroboration product reacted with even reactive terminal olefins, such as 1-butene and 1-octene, only sluggishly at room temperature. Thus, reaction of 1-octene with the 1:1 product was only *ca.* 15% complete in 1 hr at 25°, while methanolysis of the 1:1 product was complete within 30 min at the same temperature.

The results of the reaction with 1-octene are summarized in Table I.

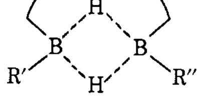
Table I. Reaction of the 1:1 Hydroboration Product[a] with the Stoichiometric Quantity[b] of 1-Octene at 25°

Time of reaction, hr	Residual 1-octene,[c] %	Active hydride,[d] %
1	84	88
3	79	81
6	75	66
24	42	34
48	25	18

[a] Obtained by addition of borane to 1,3-butadiene in THF and kept at 25° for 24 hr. [b] 1-Octene (50 mmol) was added to a 50-mmol aliquot of the 1:1 hydroboration product. [c] Glpc analysis at low block and column temperatures (50°). [d] By hydrolysis. The lower values at 24 and 48 hr compared with those for 1-octene are accounted for by the formation of the stable dimer (1).

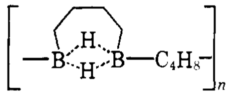
It should be noted that the reaction of 1-octene with borane in THF at 25° is complete as soon as addition is over. To our knowledge, this 1:1 hydroboration product represents the first recognized example of an organoborane which reacts readily with methanol, yet hydroborates olefins only sluggishly. Ordinary organoboranes which have hydridic hydrogens react readily both with methanol and with terminal olefins, while a few, such as **1**, do not react with either reactant at any appreciable rate at 25°.

One possible structure which could account for such unusual properties is that of the pseudocyclic tetraalkyldiborane (**9**), in which the double-hydrogen bridge is



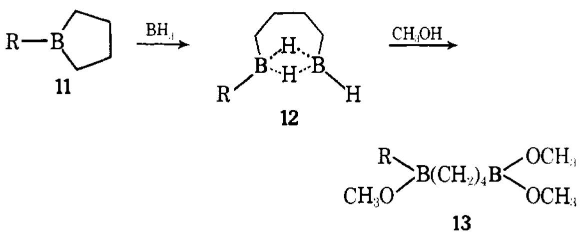
9, R = alkylene; R',R'' = alkyl or alkylene

reinforced and hence stabilized by being incorporated within a cyclic system involving the alkylene group. This assumption led us to a tentative formulation of the structure of the major portion of the 1:1 product as **10**, to be discussed later in greater detail.



10, $C_4H_8 = (CH_2)_4$ or $(CH_2)_2\overset{CH_3}{\overset{|}{C}}H$; n = integers

Reaction of *B*-Alkylborolanes with Borane. Facile Conversion of *B*-Alkylborolanes into Pseudocyclic 1,2-Tetramethylenediboranes. Our earlier results[3k] indicated that the 3:2 hydroboration products consist largely of nonpolymeric "dumbbell" compounds **5** and **6**. Consequently, it was quite puzzling that the 1:1 hydroboration product appeared to be almost entirely polymeric and essentially free from the 3:2 compounds (**5** and **6**), even when borane was added to 1,3-butadiene. Since the hydroboration in the 1:1 molar ratio with the borane-to-diene mode of addition should largely go through the 3:2 stage, it was thought that the 3:2 products **5** and **6** must have been destroyed by the borane or by some other species present in the reaction mixture. This led us to explore the reaction of *B*-alkylborolane (**11**) with borane.



(1)

a, R = n-C_4H_9
b, R = n-C_8H_{17}

When *B*-(*n*-butyl)borolane (**11a**) was treated with an equimolar quantity of borane in THF at 25° (eq 1), essentially complete reaction of borane was observed within 15 min, as indicated by the disappearance of the

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(5) It was essential to use low block and column temperatures (both *ca.* 50°) in the glpc analysis of **8** in order to prevent decomposition of polymeric methanolysis products into **8**. On the other hand, the stable dimer (**1**) was shown to be inert toward methanol and olefins even when block and column temperatures were kept at 150°.

(6) Upon standing the 1:1 hydroboration product was slowly transformed into **1** (10–15% at 24–72 hr).

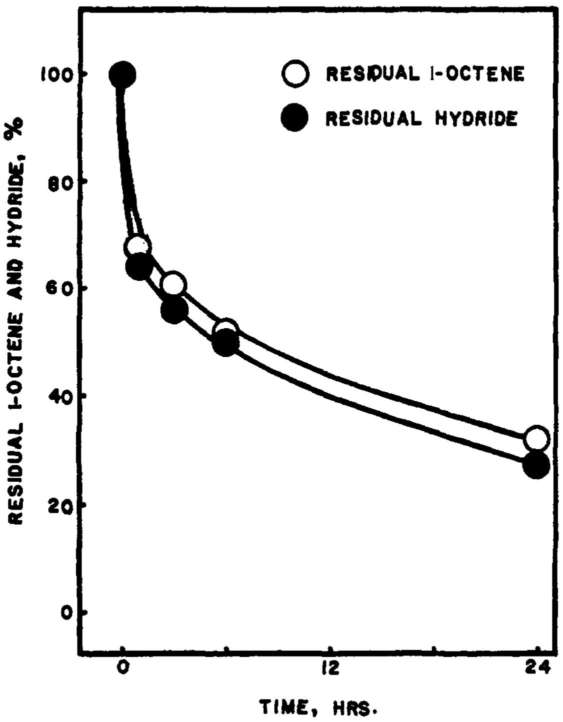
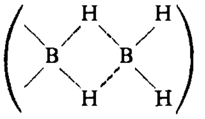
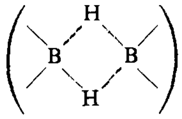


Figure 1. Hydroboration of 1-octene with 1-*n*-octyl-1,2-tetramethylenediborane in the stoichiometric molar ratio at 25°.

strong band at 2400 cm^{-1} of borane in THF[7a] in the infrared spectrum of the reaction mixture. A peak near 2600 cm^{-1} due to the double terminal B–H bonds of a substituted diborane[7]



was also absent. An extensive formation of the double-hydrogen bridge



was apparent from the presence of a strong band[7] at 1570 cm^{-1}, which was totally absent in the spectrum of either **11a** or borane in THF. A medium absorption at 2510 cm^{-1} for a single terminal B–H bond[7] was also observed.

Glpc examination of the reaction mixture after methanolysis at 1 hr indicated the presence of essentially one peak with a retention time which was longer than that of tetramethyl butane-1,4-diboronate or tributylborane. Upon distillation of the methanolysis product, 1-(*n*-butyl)methoxyboryl-4-dimethoxyborylbutane (**13a**) was obtained in 85% yield (94% by glpc) and identified by elemental analysis and ir and pmr spectroscopy.

It became clear from these results that *B*-(*n*-butyl)-borolane (**11a**) reacts with borane (eq 1) to form 1-*n*-butyl-1,2-tetramethylenediborane (**12a**). The alternative reaction path to form bisborolane (**2**) and *n*-butylborane does not take place. A similar result was obtained also with *B*-(*n*-octyl)borolane (**11b**), although no attempt was made to isolate the methanolysis product **13b** in this case.

Quite interestingly, the hydroboration of 1-octene with **12b** in the 3:1 molar ratio at 25° is rapid up to *ca.* 33% reaction, but is considerably slower thereafter, as is clearly shown in Figure 1. This result is in agreement with our earlier assumption that the B–H bond incorporated in the pseudocyclic moiety is less reactive toward olefins than the ordinary B–H bridges of *sym*-tetraalkyldiboranes. The rapid uptake of 1-octene up to *ca.* 33% reaction is attributed to the greater reactivity of the terminal B–H bond of **12**.

An attempt was made to transform **12a** into the parent 1,2-tetramethylenediborane (**4**) by treatment with excess borane in THF. Apparently the usually rapid exchange reactions of organoboranes with borane does not occur with **12a**, since an insignificant change was observed by glpc as well as by ir in 24 hr at 25°. Possibly the internal bridge provides **12** with an unusual stability toward the action of borane.

Structure of the 1:1 Hydroboration Product Derived from 1,3-Butadiene and Borane in THF in the 1:1 Molar Ratio. As was pointed out in the preceding section, hydroboration in the 1:1 molar ratio with the borane-to-diene mode of addition would be expected to go largely through the 3:2 products. Indeed, when two-thirds of the borane had been added to the 1,3-butadiene, the presence of the 3:2 compounds could readily be demonstrated by infrared and glpc analyses of the hydroboration mixture. In light of the results presented in the previous section, it was clear that a study of the action of borane with the 3:2 compounds might help to resolve the problem of the structure of the 1:1 hydroboration product.

When a 70:30 mixture of distilled **5** and **6** was treated with an equimolar quantity of borane at 25°, immediate loss of the borane was observed, as indicated by the total disappearance of the strong band at 2400 cm^{-1} of borane in THF.[7a] Moreover, a strong band at 1570 cm^{-1} and a relatively weak band at 2510 cm^{-1} appeared just as in the reaction of *B*-alkylborolanes with borane. Failure to detect 1-methoxyborolane (**8**), tetramethyl 1,4-butanediboronate, or its 1,3-isomer[8] in the glpc analyses after methanolysis again indicated that the borolane ring moiety rather than the chain moiety had selectively reacted with borane.

Furthermore, the infrared band at 2510 cm^{-1}, indicative of the presence of terminal hydrogens,[7] slowly diminished on standing, strongly suggesting that the terminal hydrogens were consumed in a slow reaction followed the initial rapid reaction with borane.

These results not only support structure **10** for the 1:1 product proposed in the earlier discussion, but also permit us to depict the path of its formation as shown by eq 2.[9]

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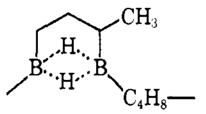
[7] (a) G. J. Klender, Ph.D. Thesis, Purdue University, 1961; (b) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, 17, 396 (1961).

[8] An authentic sample of the 1,3-isomer was not prepared. However, there was no peak in the general region expected from the retention time of 13.

[9] In view of the presence of 20–25% of 1-methyltrimethylene unit in the distilled 3:2 product, an isomeric pseudocyclic moiety, 16, may arise



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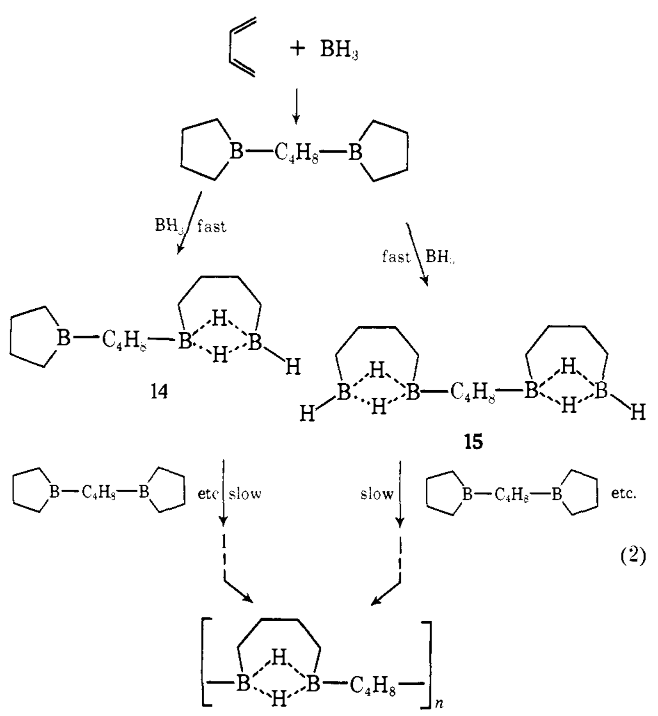
in the slow polymerization process. However, this moiety has been



(2)

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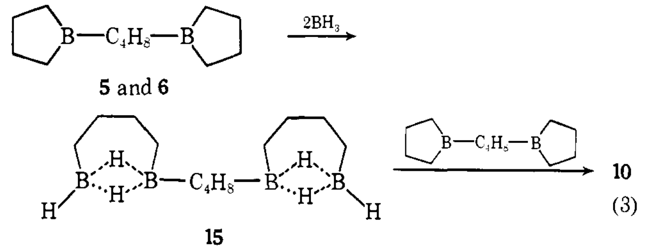
It was possible to obtain the 1:1 polymeric product (**10**) exclusively *via* **15** by reacting the 3:2 products (**5** and **6**) with 2 mol equiv of borane to form **15**, which will be discussed later in detail, followed by the addition of an equimolar quantity of a mixture of **5** and **6** to **15** (eq 3). In this experiment, it was clearly established that the reaction of the 3:2 compounds (**5** and **6**) with **15** is considerably slower than their reaction with borane itself. Thus, the disappearance of 90% of the 3:2 compounds in the second step (eq 3) required *ca.* 24 hr at 25°, whereas that in the first step was complete within 15 min at the same temperature. Therefore, the reaction of the 3:2 compounds (**5** and **6**) with an equimolar quantity of borane should largely yield a statistical mixture of **14** (50%), **15** (25%), and the starting mixture of **5** and **6** (25%) as an initial product. This is in agreement with an observation that the 1:1 hydroboration mixture with the borane-to-diene mode of addition, immediately following completion of the addition, contained *ca.* 20–25% of the 3:2 compounds observed by glpc after methanolysis.



(3)

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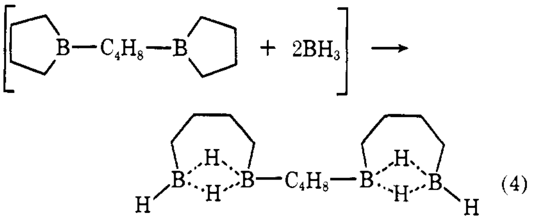
The reaction path for hydroboration in the 1:1 molar ratio with the diene-to-borane mode of addition is somewhat less certain. However, the final product is essentially indistinguishable from that which is obtained with the borane-to-diene mode of addition. Thus, the same structural moiety **10** may be assigned tentatively in this case also. Absence of the stable dimer (**1**) in the initial product seems to exclude the intermediacy of 1,2-tetramethylenediborane (**4**), since Young and Shore[3j] have reported that **4** reacts with 1,3-butadiene to form **1** as the sole product in THF and since our own result has indicated that the stable dimer does not react either with borane or with 1,3-butadiene at any appreciable rate at room temperature.

Structure of the Hydroboration Product Derived from 1,3-Butadiene and Borane in THF in a Molar Ratio Equal to or Smaller than 3:4. Based upon the foregoing discussion, it may be argued that the hydroboration of 1,3-butadiene with borane in THF in the 3:4 molar ratio with the borane-to-diene mode of addition would yield **15** as a distinct product *via* the 3:2 compounds (**5** and **6**) (eq 4) and that use of any excessive quantity of borane would not significantly affect the nature of the reaction. Thus, the hydroboration in the 1:2 molar ratio would also yield **15** leaving the excess of borane unreacted (eq 5).

$3CH_2{=}CHCH{=}CH_2 + 4BH_3 \longrightarrow$



(4)

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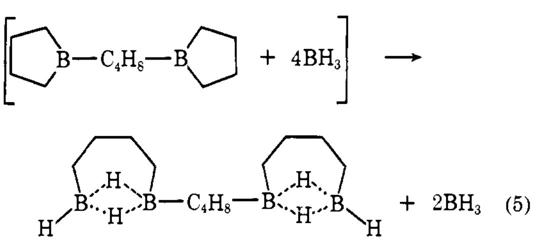
$3CH_2{=}CHCH{=}CH_2 + 6BH_3 \longrightarrow$



(5)

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The above formulations are strongly supported again by the results of a study of the reaction of **5** and **6** with borane. Immediate and complete loss of borane was observed by infrared examination, when a distilled mixture of **5** and **6** was treated with 2 molar equiv of borane. The borolane ring and borane must have reacted in a 1:1 manner. Although we have not so far been successful in isolating either **15** or its derivatives, absence of borane, bisborolane (**2**), 1,2-tetramethylenediborane (**4**), the stable 1:1 dimer (**1**), or the 3:2 compounds (**5** and **6**), in either infrared or glpc (after methanolysis) examination, is in agreement with the formulation shown by eq 4. Unlike the 1:1 cases, neither the infrared spectrum nor the active hydride content changed over 72 hr, excluding the slow polymerization process and the slow formation of the 1:1 stable dimer (**1**) observed in the 1:1 cases.

Our assumption that the excess of borane beyond the quantity required for the formation of the 3:4 product (**15**) would remain practically unreacted was supported by the fact that 1,2-tetramethylenediborane (**4**) was not formed in any appreciable quantity even after 72 hr at 25°. This result is in agreement with our earlier ob-

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omitted from the discussion for simplicity, since it could account for only a minor portion of the 1:1 hydroboration product. Moreover, no positive evidence for the presence of **16** is presently available.

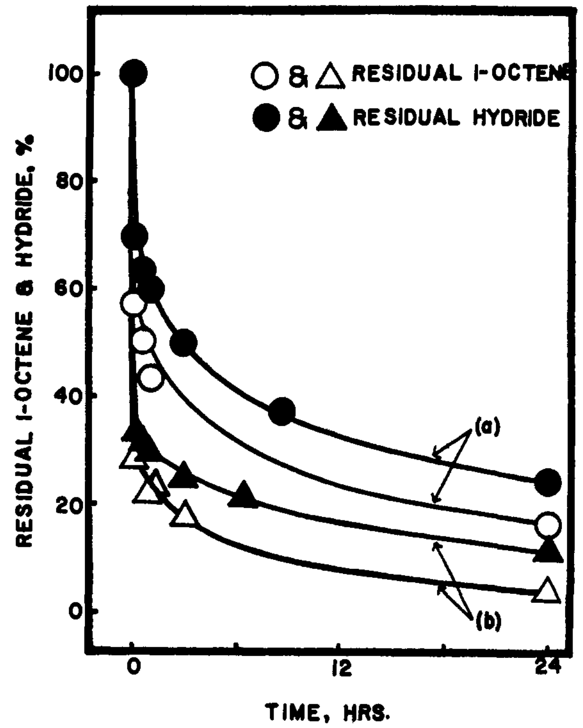
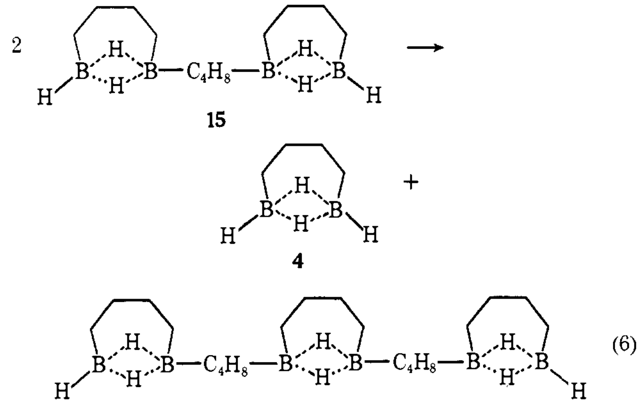


Figure 2. Reaction at 25° of a stoichiometric quantity of 1-octene with the 3:4 and 1:2 hydroboration products obtained by the borane-to-diene mode of addition: (a) 3:4 hydroboration product + 1-octene; (b) 1:2 hydroboration product + 1-octene.

servation that 1-alkyl-1,2-tetramethylenediborane (**12**) is stable to borane at 25°.

Another possible reaction of **15** is its disproportionation, as indicated in eq 6. However, such a reaction must also be extremely slow, if it can occur at all, since it should also yield 1,2-tetramethylenediborane (**4**) as it proceeds, and this is not observed.



(6)

Furthermore, the experimental results for the reaction of 1-octene with both the 3:4 product and the 1:2 product, summarized in Figure 2, are in excellent agreement with the above formulations of these products.

The reaction path for hydroboration with the diene-to-borane mode of addition in these ratios is less clear. It is noteworthy, however, that the hydroboration even in the 1:2 molar ratio yields only a minor quantity (*ca.* 20%) of the expected 1,2-tetramethylenediborane (**4**). In view of the fact that Young and Shore[3j] successfully prepared **4** in good yields in noncoordinating solvents such as dibutyl ether, the selection of a suitable solvent must be an important factor in determining the course of hydroboration of 1,3-butadiene.

Just as in the 1:1 cases, the 1:2 products obtained with the two different modes of addition are surprisingly similar except for the minor difference in the quantity of 1,2-tetramethylenediborane (**4**). Thus, the two products gave quite similar ir spectra and active hydride analyses. The two results of hydroboration of 1-octene were also similar. Furthermore, the amount of unreacted borane (*ca.* 28%) was in excellent agreement with an assumption that all of the C_4H_8 moiety except for that present in 20% **4** is incorporated in **15**. This requires the presence of 27% of unreacted borane. Therefore, it appears that the same structure, **15**, assigned to the major product in the 1:2 case with the borane-to-diene mode of addition, may be assigned to the major product produced in this case also.

Conversion of the 1:1 Hydroboration Product into *B*-Alkylborolanes. A Simple Synthesis of *B*-Alkylborolanes. A synthetically useful consequence of the present study is the formation of *B*-alkylborolanes in the hydroboration of olefins with the 1:1 hydroboration mixture. Although the hydroboration is slow at 25°, it is greatly accelerated by refluxing the reaction mixture. At this temperature, the hydroboration is usually complete within several hours and the usual distillation after evaporation of the solvent readily yields *B*-alkylborolanes. The yields realized are in the range of 55–65%, presumably a result of the presence of considerable amounts of the 1-methyltrimethylene moiety as well as a minor amount of the 1:1 dimer (**1**) in the hydroboration product. Nevertheless, it represents one of the simplest methods for the preparation of *B*-alkylborolanes, obtainable in the past either with difficulty or with limited alkyl groups on the boron atom.[10]

The experimental results for the preparation of *B*-alkylborolanes are summarized in Table II.

Table II. Synthesis of *B*-Alkylborolanes by the Reaction of the 1:1 Hydroboration Product Derived from 1,3-Butadiene and Borane in THF with Olefins[a]

Olefin	Product[b]	Yield,[c] %	Bp (mm), °C
1-Butene	*B*-(*n*-Butyl)borolane	63	62–65 (50)
1-Pentene	*B*-(*n*-Pentyl)borolane	56	65–68 (12)
1-Octene	*B*-(*n*-Octyl)borolane	53	104–105 (5)
Cyclopentene	*B*-Cyclopentylborolane	58	87–88 (30)
Cyclohexene	*B*-Cyclohexylborolane	57	96–97 (20)

[a] Refluxed in THF. [b] *B*-(*n*-Butyl)borolane and *B*-cyclopentylborolane were identified by glpc analyses of the oxidation products, boron analysis, and conversion into the corresponding cyclopentanols in high yields *via* carbonylation–oxidation. The other products were identified by glpc analyses of the oxidation products and boron analysis. [c] By isolation.

Glpc analysis using a block temperature of 50° indicated the presence of a considerable quantity (~40%)

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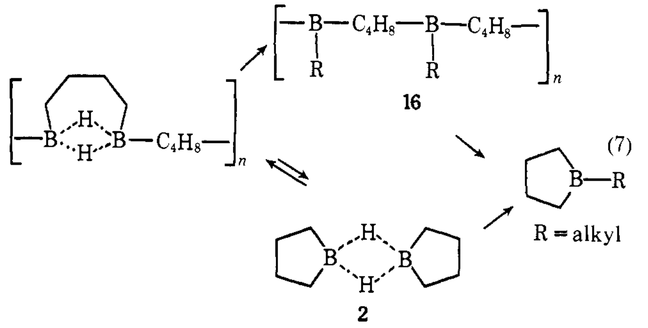
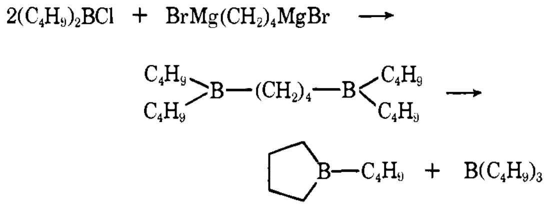
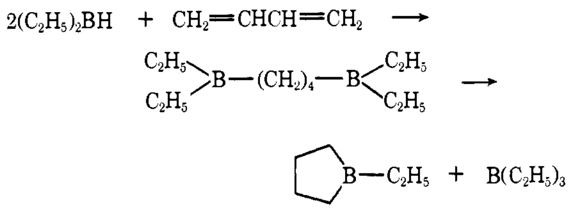
[10] (a) K. Torssell, *Acta Chem. Scand.*, **8**, 1779 (1954); (b) S. L. Clark, J. R. Jones, and H. Stange, *Advan. Chem. Ser.*, **No. 32**, 228 (1961); (c) B. M. Mikhailov and V. A. Dorokhov, *Dokl. Akad. Nauk SSSR*, **133**, 119 (1960); (d) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **83**, 2541 (1961); (e) R. Köster and G. W. Rotermund, *Angew. Chem.*, **72**, 138 (1960); R. Köster, W. Larbig, and G. W. Rotermund, *Justus Liebigs Ann. Chem.*, **682**, 21 (1965); (f) T. J. Logan and T. J. Flautt, *J. Amer. Chem. Soc.*, **82**, 3446 (1960); (g) R. Köster, G. Griaznov, W. Larbig, and P. Binger, *Justus Liebigs Ann. Chem.*, **672**, 1 (1964); (h) H. C. Brown and C. D. Pfaffenberger, *J. Amer. Chem. Soc.*, **89**, 5475 (1967); (i) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967).

of *B*-(*n*-butyl)borolane in the hydroboration mixture, even when the hydroboration of 1-butene was carried out at room temperature. The result indicates that formation of *B*-alkylborolanes does not require either heating at higher temperatures or distillation. It is not clear, however, which of the two possible paths indicated in eq **7** is preferred. Intermediacy of **16** is reasonable in the light of results reported by Clarke, *et al.*,[10b] as well as by Köster, *et al.*[10g] (eq 8 and 9).





(8)[10b]



(9)[10g]

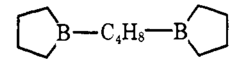
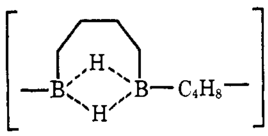
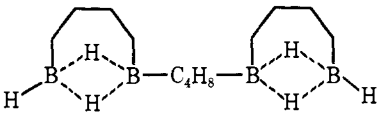
Conclusions

B-Alkylborolanes react readily with borane to form the corresponding substituted pseudocyclic 1,2-tetramethylenediboranes. With this facile opening of the borolane ring as a key to understanding, the reaction pathway and the structures of the hydroboration products from 1,3-butadiene and borane in THF in ratios equal to or smaller than 1:1 have been clarified. Integrated with the information available from our earlier study,[3k] the course of the reaction of 1,3-butadiene with borane in THF at 25° with the borane-to-diene mode of addition may be summarized as shown in Table III.

It has also been demonstrated that the B–H bond of the double-hydrogen bridge in the pseudocyclic 1,2-tetramethylenediborane possesses unique reactivity in that it reacts readily with protic solvents such as water and methanol and yet reacts only sluggishly with olefins at 25°. The reaction with olefins can be greatly accelerated by refluxing the reaction mixture in THF and it converts a pseudocyclic 1,2-tetramethylenediborane largely into *B*-alkylborolanes, thereby providing a simple method for the synthesis of *B*-alkylborolanes.

Finally, the high stability of the bridges in the pseudocyclic 1,2-tetramethylenediborane units apparently causes the parent borolane structure to be unstable relative to conversion into the polymeric species containing these bridges. On the other hand, the facile conversion of the pseudocyclic species into *B*-alkylborolanes in the reaction with olefins indicates that, in the absence of this stabilizing double-hydrogen bridge, the borolane-containing structure is more stable than the open-chain structure.

Table III. Products of Hydroboration of 1,3-Butadiene with Borane in THF with the Borane-to-Diene Mode of Addition

1,3-Butadiene–BH_3	Major products[b]	Other components
≥3/2[a]		$(CH_2=CHCH=CH_2)$[c]
1/1	 [d]	
≤3/4		(BH_3)[c]

[a] Even when the ratio was 3:1, the ratio of the 3:2 dumbell compounds to *B*-butenylborolane was *ca.* 20:1 by glpc. [b] $-C_4H_8-$ = $-(CH_2)_4-$ or $-(CH_2)_2CHCH_3$. [c] Unreacted starting compound. [d] *n* = integers.

Experimental Section

Materials. The purification of reagents and solvents and preparation of borane solutions in tetrahydrofuran were carried out as described previously.[11] 1,3-Butadiene (Matheson) and 1-butene (Phillips) were used from cylinders without further purification. Commercially available 1-pentene, 1-octene, cyclopentene, cyclohexene, and methanol were used without additional treatment. The organoboranes were always handled under nitrogen with careful exclusion of oxygen and water vapor.

Infrared spectra were obtained on a Perkin-Elmer Model 137B spectrometer and pmr spectra were obtained on a Varian T-60 spectrometer.

Hydroboration of 1,3-Butadiene with Borane in the Ratio of 1:1. (a) Borane-to-Diene Mode of Addition. 1,3-Butadiene (8.1 g, 150 mmol) was condensed, weighed, then allowed to evaporate slowly and the gas conducted into 81.0 ml of tetrahydrofuran cooled to −10° in a three-necked flask fitted with a dropping funnel capped with a large serum stopple, a Dry Ice condenser, a thermometer well, and a serum stopple inlet for removal of samples by syringe. The top of the Dry Ice condenser was fitted with a connecting tube attached to a dry nitrogen source. When the transfer of the diene was completed, 61.5 ml (150 mmol) of 2.44 *M* borane in tetrahydrofuran was introduced to the dropping funnel by syringe and added dropwise at a rate such that the temperature of the reaction remained at 5° or below. When 50 mmol of the borane had been added, a 1-μl aliquot was examined by glpc. The 3:2 compounds (**5** and **6**) and *B*-butenylborolane were observed in a molar ratio of *ca.* 20:1. The ratio was essentially unchanged when 100 mmol of borane had been added. When the addition of the borane was completed, the reaction was kept at 0.5° for 3 hr and then allowed to warm to room temperature (*ca.* 25°). At 0 hr[12] a 4.0-ml sample of the reaction mixture was hydrolyzed in a 1:1:1 mixture of water, tetrahydrofuran, and glycerol and the hydrogen evolved measured by displacement of water. The analyses indicated the presence of 107% of the theoretical amount of residual active hydride[13] (150 mmol) in the reac-

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(11) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

(12) Throughout this paper 0 hr implies only that the indicated samples were taken within *ca.* 5 min of completing the addition of reagent.

(13) The term active hydride is used to distinguish boron–hydrogen bonds which undergo ready hydrolysis by water at 25° from that present in the 1:1 stable dimer (1) which is unreactive toward water and olefins at 25°.[3i] Calculations for residual active hydride ignore relatively small changes (*ca.* 2%) in concentration over the temperature ranges at which the experiments were conducted.

tion mixture. Additional samples were treated similarly at intervals for a period of 72 hr. At 48 hr the value had decreased to 94%.[14] In a similar manner a 5.0-ml sample of the reaction mixture was removed at 0 hr and treated with 0.4 ml (10 mmol, 100% excess) of anhydrous methanol, and the hydrogen evolved measured. The quantity of hydrogen evolved (130 ml at 24.5° and 743 mm) indicated 101% of the theoretical residual hydride present. At 48 hr the value had decreased to 96%. The methanolyzed samples were also analyzed by glpc. After the evolution of hydrogen was complete (*ca.* 30 min) *n*-nonane was added to the sample and the mixture analyzed for *B*-methoxyborolane (**8**) on a 6-ft column of 10% SE-30 and 0.5% Armac on Chromosorb W. The injection block and column were kept at 50° to avoid thermal breakdown of polymeric species to *B*-methoxyborolane. Tetramethyl butane-1,4-diboronate (the methanolysis product of 1,2-tetramethylenediborane (**4**)), 1,6-diboracyclodecane (**1**), and the 3:2 compounds (**5** and **6**) were analyzed for using a 2-ft column of 10% SE-30 and 0.5% Armac on Chromosorb W programmed from an initial temperature of 100° at 10°/min. The injection block was kept at *ca.* 150°. *n*-Hexadecane was employed as an internal standard for analysis of all three compounds. Analysis of the methanolyzed sample at 0 hr indicated the presence of only traces of *B*-methoxyborolane, tetramethyl butane-1,4-diboronate, and 1,6-diboracyclodecane. Approximately 10 mmol (20% based on 1,3-butadiene) of the 3:2 compounds and small amounts of unidentified compounds were observed. After 48 hr, traces of *B*-methoxyborolane and tetramethyl butane-1,4-diboronate, *ca.* 6 mmol (8%) of 1,6-diboracyclodecane, and traces of the 3:2 compounds were found present.

The infrared spectrum (tetrahydrofuran reference solvent) of the reaction mixture at 0 hr showed weak bands at 2510 cm^{-1} (BH stretching for single terminal hydrogen[15]) and *ca.* 2400 cm^{-1} (BH stretching of borane in tetrahydrofuran solution[7a]). A broad, strong band appeared at *ca.* 1570 cm^{-1} (double-hydrogen bridge of the type in diborane[15]). After 5 hr, the band at 2400 cm^{-1} was absent, implying the complete reaction of borane.[16] After 24 hr the band at 1570 cm^{-1} remained as a broad, strong peak; however, the 2510-cm^{-1} band had decreased to one of very weak intensity. A shoulder band of moderate intensity at 1610 cm^{-1} was also clearly evident at 24 hr implying the presence of 1,6-diboracyclodecane in the reaction mixture.[3i] The spectrum remained essentially unchanged at 48 hr.

At 24 hr a 50.0-ml sample (50 mmol of $-C_4H_8-$ moiety) of the reaction mixture was treated at *ca.* 25° with 25.0 ml (50 mmol) of a 2 *M* solution of 1-octene in tetrahydrofuran also containing *n*-nonane as an internal standard. The 1-octene solution was added all at once by syringe. The hydroboration of 1-octene was then followed by periodic hydrolysis of a sample of the reaction mixture and measurement of the hydrogen evolved. The amount of hydride present at 24 hr in the 50-ml sample (48.4 mmol) utilized for the hydroboration of 1-octene was taken as the 100% residual active hydride value for the 1-octene reaction. The 1-octene hydroboration was also simultaneously followed by direct glpc analysis for residual 1-octene on a 6-ft column of 10% SE-30 and 0.5% Armac on Chromosorb W. The temperature of the injection block and column was 50°. The results of the hydride and 1-octene uptakes are summarized in Table I.

(b) **Diene-to-Borane Mode of Addition.** The apparatus employed for this experiment was the same as described above except for the dropping funnel which was not required. The reaction flask was charged with 84.0 ml (200 mmol) of 2.38 *M* borane in tetrahydrofuran and cooled to −10°. 1,3-Butadiene (10.8 g, 200 mmol) was condensed in a tube, then allowed to evaporate slowly and the gas was conducted by means of a syringe needle below the surface of the borane solution. Magnetic stirring was maintained throughout the reaction phase of the experiment. The final volume of the reaction mixture was 94 ml. Treatment of a 5.0-ml sample of the reaction mixture at 0 hr[12] indicated the presence of 131% of the theoretical quantity of residual hydride (200 mmol). The value slowly decreased and was 83% at 72 hr. Glpc analysis of the methanolyzed samples, as described in the previous experiment, indicated the presence of only traces of *B*-methoxyborolane (**8**), 1,6-diboracyclodecane (**1**), and the 3:2 compounds (**5** and **6**) at 0 hr. At 72 hr a trace of *B*-methoxyborolane, 10% (based on 1,3-butadiene) of 1,6-diboracyclodecane, and only traces of 3:2 compounds were observed. Tetramethyl butane-1,4-diboronate was not observed.

The infrared spectrum of the reaction mixture showed the same bands and change with time as described for the experiment employing the borane-to-diene mode of addition.

At 24 hr, a 23.5-ml sample of the reaction mixture (50 mmol of $-C_4H_8-$ moiety; 37.2 mmol of active hydride) was treated at 25° with 25 ml (50 mmol) of a 2 *M* solution of 1-octene and the hydroboration of 1-octene was followed as described in the previous experiment. The results of the hydride and 1-octene uptakes are shown in Table IV. The initial quantity of hydride in the 23.5 ml sample (37.2 mmol) is taken as the 100% residual hydride value.

Table IV. Reaction of a Stoichiometric Quantity of 1-Octene[a] with the 1:1 Hydroboration Product[b] at 25°

Time of reaction, hr	Residual 1-octene,[c] %	Residual active hydride,[d] %
0	94	96
0.5	90	93
1	91	89
3	81	79
6	70	69
24	51	38
48	39	23

[a] 1-Octene (50 mmol) was added to a 50-mmol aliquot of the 1:1 hydroboration product. [b] Obtained by the addition of 1,3-butadiene to borane in THF. [c] See footnote *c*, Table I. [d] See footnote *d*, Table I.

Hydroboration of 1,3-Butadiene with Borane in the Ratio of 3:4. Borane-to-Diene Mode of Addition. 1,3-Butadiene (8.1 g, 150 mmol), dissolved in 60.5 ml of tetrahydrofuran, was hydroborated with 82 ml (200 mmol) of 2.44 *M* borane in tetrahydrofuran using the borane-to-diene mode of addition as described previously for the 1:1 ratio. The final reaction volume was 150 ml. Hydrolysis of a sample at 0 hr[12] indicated 105% of the theoretical residual hydride (300 mmol) present in the reaction. This value had decreased to 98% at 77 hr. Similarly methanolysis of samples at the same times indicated 100 and 95% residual hydride. Glpc examination of the methanolyzed sample at 0 hr showed the presence of traces of *B*-methoxyborolane (**8**) and 1,6-diboracyclodecane (**1**), 5% tetramethyl butane-1,4-diboronate, and *ca.* 19% of the 3:2 compounds (**5** and **6**). At 77 hr traces of **8** and **1**, a minor quantity of either the 3:2 compounds (**5** and **6**) or some unidentified compounds, and 7% tetramethyl butane-1,4-diboronate were observed.

An infrared spectrum of the reaction mixture at 0 hr showed bands at 2510 cm^{-1} (m), 2400 cm^{-1} (m), and 1570 cm^{-1} (s).[7,15] After 24 hr the band at 2400 cm^{-1} had decreased to one of negligible intensity but was still observed at 77 hr. No change in the intensity of the other bands was noted over the 77-hr period.

At 24 hr, a 25.0-ml sample (25 mmol of $-C_4H_8-$ moiety, 50 mmol of active hydride) of the reaction mixture was treated at 25° with 50 mmol of 1-octene and the reaction was followed as previously described. The results are presented in Figure 2.

Hydroboration of 1,3-Butadiene with Borane in the Ratio of 1:2. (a) Borane-to-Diene Mode of Addition. 1,3-Butadiene (8.1 g, 150 mmol), dissolved in 19.5 ml of tetrahydrofuran, was hydroborated by the addition of 123 ml (300 mmol) of 2.44 *M* borane in tetrahydrofuran in a manner analogous to that described for the 1:1 ratio of reactants. The final volume of the reaction mixture was 150 ml. At 0 hr[12] both hydrolysis and methanolysis indicated the uptake of the theoretical quantity of hydride (300 mmol). The quantity of residual active hydride remained essentially constant for at least 72 hr at 25°. Glpc analysis of the 0 hr methanolyzed sample indicated the presence of traces of *B*-methoxyborolane (**8**) and 1,6-diboracyclodecane (**1**), *ca.* 3% tetramethyl butane-1,4-diboronate, and *ca.* 14% of the 3:2 compounds (**5** and **6**). After

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[14] The decrease to a value of less than the theoretical amount is considered primarily due to the slow formation of small amounts of 1:1 stable dimer (1) (10–15% in 72 hr).

[15] Weiss and coworkers[3e] have reported the terminal B–H stretching frequency of 1,2-tetramethylenediborane (4) to be 2510 cm^{-1} and that of the double-hydrogen bridge to be 1580 cm^{-1}.

[16] In the hydroboration mixture in tetrahydrofuran, borane can exist either as a complex with tetrahydrofuran or as a moiety of monoalkyldiboranes or unsymmetric dialkyldiboranes which exhibit a doublet[7] at *ca.* 2500 and 2600 cm^{-1}. The absence of a band at 2400 cm^{-1} indicates the absence of the borane tetrahydrofuran complex and the presence of only a single band at 2510 cm^{-1} in the terminal BH stretching region excludes the latter two possibilities.

72 hr the quantity of the tetramethyl ester had risen to *ca.* 7% and **1**, **8**, **5**, and **6** were found only in trace amounts.

The infrared spectrum of the reaction mixture at 0 hr[12] showed bands at 2510 cm^{-1} (m), 2400 cm^{-1} (s), and 1570 cm^{-1} (s). The spectrum remains unchanged in these regions for at least 72 hr.

At 24 hr a 25.0-ml sample of the reaction mixture (25 mmol of $-C_4H_8-$ moiety, 100 mmol of active hydride) was treated at 25° with 100 mmol of 1-octene and the reaction followed as previously described. The results of the uptake of reactants are shown in Figure 2.

(b) **Diene-to-Borane Mode of Addition.** 1,3-Butadiene (8.1 g, 150 mmol) was hydroborated in a manner analogous to that described for the hydroboration in the ratio of 1:1 using 128 ml (300 mmol) of 2.34 *M* borane in tetrahydrofuran. Hydrolysis and methanolysis indicated the presence of 99% of the theoretical residual hydride (400 mmol) at 0 hr.[12] This value remained essentially constant for at least 72 hr (96% at 72 hr). Glpc analysis of the methanolysis sample at 0 hr indicated the virtual absence of *B*-methoxyborolane (**8**), 1,6-diboracyclodecane (**1**), and the 3:2 compounds (**5** and **6**). Tetramethyl butane-1,4-diboronate was found in the amount of *ca.* 20%.

The infrared spectrum of the reaction mixture was virtually the same as that described for the 1:2 hydroboration mixture formed using the borane-to-diene mode of addition. No change in the spectrum was observed over a 96-hr period.

At 24 hr a 22.5-ml sample (25 mmol of $-C_4H_8-$ moiety, 98.1 mmol of active hydride) of the reaction mixture was treated at 25° with 100 mmol of 1-octene and the reaction of 1-octene followed as previously described. The results of the reactant uptakes are shown in Figure 3.

(c) **Determination of the Unreacted Borane.** A 1-hr old, 22.5-ml sample (25 mmol of $-C_4H_8-$ moiety; 100 mmol of active hydride) of the hydroboration mixture prepared in the previous experiment was placed in a separate flask and 25 mmol of *n*-decane was added as an internal standard. The sample was then treated at 0°, with 110 mmol of 1-butene. After the addition of 1-butene was completed (*ca.* 20 min) a sample was withdrawn and quenched in a mixture of hexane and water and the hexane phase was analyzed for tributylborane on a 6-ft column of 10% SE-30 and 0.5% Armac on Chromosorb W. The analysis indicated the presence of 13.7 mmol of tributylborane. This corresponds to 27.5% of the initial amount of borane (50 mmol).

In a second experiment, 150 mmol of 1,3-butadiene was hydroborated with 128 ml (300 mmol) of 2.34 *M* borane in tetrahydrofuran employing the diene-to-borane mode of addition. After the addition was complete, the reaction was kept at 0° for 2 hr, then treated with 19.6 g (612 mmol) of anhydrous methanol while keeping the reaction at 0–5°. A quantitative yield of hydrogen (600 mmol) was obtained, 97% being evolved as rapidly as the methanol was added (*ca.* 1.5 hr). The volatile components of the methanolyzed reaction mixture were distilled off at room temperature and *ca.* 100 mm and trapped in a receiver at −78°. The pressure was lowered to 10 mm toward the end of the distillation for *ca.* 5 min to remove the last traces of volatile material. After diluting the distillate to 250.0 ml with water, aliquots (15 ml) of the resulting boric acid solution were titrated with 0.2 *M* sodium hydroxide after addition of *ca.* 2 g (*ca.* 100% excess) of mannitol using phenolphthalein as an indicator. The results indicated the presence of 82.4 mmol of boric acid in the total solution, which corresponded to 27.5% of the initial borane remaining unreacted.

(d) **Oxidation of the 1:2 Hydroboration Mixture.** Oxidation of 1 hr and 1 week old samples of the 1:2 hydroboration product in the usual manner[11] using 3 *N* sodium hydroxide and 30% hydrogen peroxide yielded a mixture of 1,3- and 1,4-butanediols in the ratio of 36:64 in both cases. The combined yields of diols at each time were 88 and 94%, respectively. These figures are in agreement with those reported earlier for experiments employing the diene-to-borane mode of additions.[3d]

Reaction of *B*-(*n*-Butyl)borolane (11a) with Borane in THF in the Molar Ratio of 1:1 at 25°. To a solution of *B*-(*n*-butyl)borolane (**11a**) (2.48 g, 20 mmol) prepared by the method described later in this section in 5 ml of THF and 1.14 g (10 mmol) of *n*-octane was added 9.7 ml (20 mmol) of 2.06 *M* borane in THF at 25°. The total volume was *ca.* 20 ml. At 15 min the infrared spectrum of the reaction mixture indicated nearly complete consumption of borane as evidenced by the nearly complete disappearance of a band at 2400 cm^{-1}. The fact that borane did not exist even as a moiety of substituted diboranes was clearly demonstrated by the absence of a band near 2600 cm^{-1}. A sharp and medium band at 2510 cm^{-1} was present in addition to a strong band at 1570 cm^{-1}. At 1 hr the infrared spectrum was essentially the same as that at 15 min. At 2 hr a 2-ml aliquot was added to 0.5 ml of absolute methanol at 25°. After the theoretical quantity (160 ml) of hydrogen was evolved, the methanolysis products were analyzed by glpc using 2-ft SE-30 columns. One analysis was made using the block and column temperatures of 50° to detect primarily *B*-methoxyborolane (**8**) and the remaining *B*-(*n*-butyl)borolane (**11a**). The other analysis was made at the block temperature of 150°. The starting compound **11a** completely disappeared in 2 hr. Essentially one peak, which was identified below as 1-(*n*-butyl)methoxyboryl-4-dimethoxyborylbutane (**13a**), was present (94%).

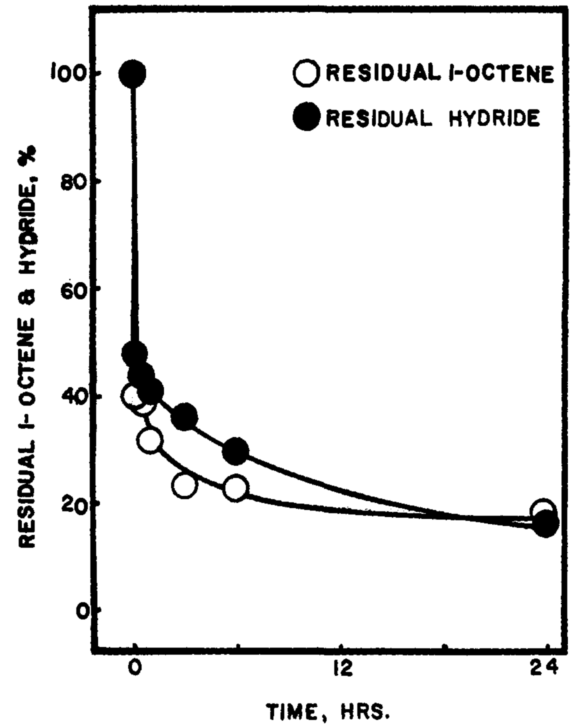

Figure 3. Reaction at 25° of a stoichiometric quantity of 1-octene with the 1:2 hydroboration product obtained by the diene-to-borane mode of addition.

Reaction of 1-*n*-Butyl-1,2-tetramethylenediborane (12a) with Borane in THF in the Molar Ratio of 1:1 at 25°. To the remainder of the reaction mixture (17.5 ml) was added 8.5 ml (17.5 mmol) of borane in THF at 25° at 2 hr. One hour later, a 3-ml aliquot was added to 1 ml of absolute methanol and 310 ml of hydrogen was evolved at 25° (747 mm). Glpc examination of the methanolysis product revealed the presence of **13a** (90%). No other volatile compounds were present in any significant quantities. Under these conditions expected *B*-methoxyborolane (**8**), 1,6-diboracyclodecane (**1**), tetramethyl butane-1,4-diboronate, dimethyl *n*-butaneboronate, methyl dibutaneborinate, and tributylborane were observable. The infrared spectrum indicated the presence of a strong band at 2400 cm^{-1} in addition to the bands at 2510 and 1570 cm^{-1} mentioned in the previous experiment. Neither glpc nor infrared spectrum showed any appreciable change over a period of 72 hr.

Preparation of 1-(*n*-Butyl)methoxyboryl-4-dimethoxyborylbutane (13a). The same experiment as described above was repeated on the same scale except that *n*-octane was not added. Two hours after the addition of borane, the entire reaction mixture was added to 6 ml (150 mmol) of absolute methanol and the resultant mixture was subjected to distillation, after completion of hydrogen evolution, to yield 3.85 g (85%) of **13a**: bp 74–75° (0.5 mm); n^{20}D 1.4285; ir (neat) 1330 (s) and 1360 cm^{-1} (s); pmr (CCl_4, TMS) δ 0.6–1.1 (multiplet, 9 H), 1.1–1.6 (multiplet, 8 H), 3.50 (singlet, 6 H), and 3.68 ppm (singlet, 3 H).

Anal. Calcd for $C_{11}H_{26}B_2O_3$: C, 57.96; H, 11.50; B, 9.48. Found: C, 58.03; H, 11.48; B, 9.23.

Reaction of *B*-(*n*-Octyl)borolane (11b) with Borane in THF in the Molar Ratio of 1:1 at 25°. To a solution of *B*-(*n*-octyl)borolane (**11b**) (3.6 g, 20 mmol) prepared by the method described later in this section in 4 ml of THF and 1.28 g (10 mmol) of *n*-nonane was added 9.7 ml (20 mmol) of 2.06 *M* borane in THF at 25°. The

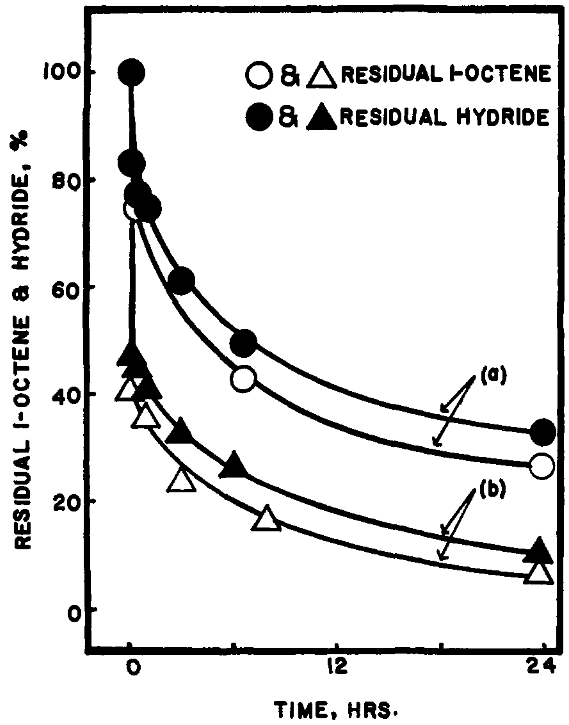

Figure 4. Reaction at 25° of a stoichiometric quantity of 1-octene with the 3:4 and 1:2 exchange products: (a) 3:4 exchange product + 1-octene; (b) 1:2 exchange product + 1-octene.

infrared spectra taken at appropriate times showed the same features as were observed in the reaction of B-(*n*-butyl)borolane (**11a**) with borane. Glpc examination after methanolysis at 2 hr failed to detect any volatile peak in any significant quantity.

Hydroboration of 1-Octene at 25° with the Stoichiometric Quantity of the Exchange Product Derived from B-(*n*-Octyl)borolane (11b) and Borane in the Molar Ratio of 1:1. To one-half (*ca.* 10 ml, 10 mmol in **12b**) of the 3 hr old reaction mixture obtained in the preceding experiment was added at 25° 10 ml of a 3 *M* solution of 1-octene (3.36 g, 30 mmol) in THF. At appropriate times 2-ml aliquots were treated with 0.25 ml of absolute methanol at 25° and the resultant mixture, after completion of gas evolution, was analyzed for 1-octene by glpc. The residual active hydride was calculated from the amount of gas evolution. The results of residual active hydride and 1-octene analyses are summarized in Figure 1.

Reaction of the 3:2 Compounds (5 and 6) with Borane in the Ratio of 1:1. A mixture of the distilled 3:2 compounds[17] (**5** and **6**) (4.75 g, 25 mmol) was dissolved in 58.7 ml of tetrahydrofuran and cooled to 0–5°. To this solution was added 10.7 ml (25 mmol) of 2.34 *M* borane in tetrahydrofuran all at once. The final ratio of $-C_4H_8-$ moiety to boron was thus 1:1. The reaction mixture was kept at 0.5° with rapid stirring for 3 hr and then allowed to warm to room temperature. Hydrolysis of a sample of the reaction at 0 hr[12] indicated the presence of 98% of the theoretical quantity of active hydride (75 mmol). After 72 hr the value had decreased to 74%.

An infrared spectrum of the reaction mixture at 0 hr showed bands at 2510 (m), 2400 (w), and 1570 cm^{-1} (s).[15] After 1 hr the band at 2400 cm^{-1} was absent. The band at 2510 cm^{-1} decreased to one of only weak intensity after 24 hr. The 1570-cm^{-1} band remained strong in intensity even at 72 hr. A shoulder peak at 1610 cm^{-1} was evident at 6 hr and had increased to moderate intensity after 24 hr indicating the formation of some 1,6-diboracyclodecane.

At 24 hr a 25-ml sample (25 mmol of $-C_4H_8-$ moiety, 21.0 mmol of active hydride) of the reaction mixture was removed and treated at 25° with 25 mmol of 1-octene and the reaction of 1-octene followed as previously described. The results of the hydride and 1-octene uptakes are shown in Table V.

Table V. Reaction of a Stoichiometric Quantity of 1-Octene[a] with the 1:1 Exchange Product[b] at 25°

Time of reaction, hr	Residual 1-octene,[c] %	Residual active hydride, %
0	78	98
0.5	79	92
1	71	89
3	58	65
6	50	59
24	36	35
48	26	26

[a] 1-Octene (25 mmol) was added to a 25-mmol aliquot of the 1:1 exchange product. [b] Formed by the addition of borane in THF to the 3:2 compounds (**5** and **6**). [c] *Cf.* footnote *c*, Table I. [d] *Cf.* footnote *d*, Table I.

Glpc examination of the methanolysis products using *n*-nonane and *n*-hexadecane as internal standards at 30 min indicated the virtual absence of B-methoxyborolane (**8**), 1,6-diboracyclodecane (**1**), and tetramethyl butane-1,4-diboronate. The 3:2 compounds were the major observable compounds (*ca.* 20% of the original quantity). At 72 hr 15% of 1,6-diboracyclodecane was present (based on C_4H_8 moiety). A minor quantity of either **5** or some unidentified compound was also present. After 1 month the amount of **1** increased to *ca.* 30%.

Reaction of the 3:2 Compounds (5 and 6) with Borane in the Ratio of 1:2. Distilled 3:2 compounds[17] (**5** and **6**) (4.75 g, 25 mmol) in 66 ml of tetrahydrofuran were allowed to react at 0° with 21.4 ml (50 mmol) of 2.34 *M* borane in tetrahydrofuran. The final ratio of $-C_4H_8-$ moiety to boron was 3:4. Hydrolysis of an aliquot at 0 hr[12] indicated 100% (150 mmol) of the theoretical quantity of active hydride present. The quantity remained essentially constant for at least 72 hr (98% at 72 hr).

Infrared analysis of the reaction product at 15 min showed bands at 2510 (m), 2400 (w), and 1570 cm^{-1} (s). After 2 hr the band at 2400 cm^{-1} decreased to one of negligible intensity. No additional change of the spectrum in these regions was observed for at least 1 week except for the appearance of a band at 1610 cm^{-1} (m) implying the formation of some 1,6-diboracyclodecane (**1**).

At 24 hr, a 25-ml sample (23.2 mmol of $-C_4H_8-$ moiety; 45.8 mmol of active hydride) of the reaction mixture was treated at *ca.* 25° with 50 mmol of 1-octene in the usual manner. The results of the hydride and 1-octene uptakes are shown in Figure 4.

Glpc examination of the methanolysis products using *n*-nonane and *n*-hexadecane as internal standards at 2 hr did not detect any volatile compounds in any appreciable quantities.

Reaction of the 3:4 Product (15) with the 3:2 Compounds (5 and 6) in the Molar Ratio of 1:1 at 25°. The 3:4 product (**15**) was prepared as described above by the reaction of the 3:2 compounds (**5** and **6**) (1.9 g, 10 mmol) dissolved in 18 ml of tetrahydrofuran with 2.06 *M* borane in tetrahydrofuran (9.7 ml, 20 mmol) at 25°. Two hours later the 3:2 compounds (1.9 g, 10 mmol) dissolved in 25 ml of tetrahydrofuran, 0.64 g (5 mmol) of *n*-nonane, and 1.13 g (5 mmol) of *n*-hexadecane were added at 25°. The total volume of the reaction mixture was *ca.* 60 ml. The reaction was followed by infrared spectroscopy, active hydride analysis, and glpc analysis of the residual 3:2 compounds. The amount of active hydride at 24 hr decreased to 89% of that at 0 hr. The intensity of the band at 2510 cm^{-1} in the infrared spectrum decreased with time. At 6 hr a shoulder at 1612 cm^{-1} became clearly observable and its intensity increased with time. Characteristic features of the infrared spectrum at 24 hr were quite similar to those of the 1:1 hydroboration mixture at 24 hr. The results of the residual 3:2 compounds' analysis are summarized in Table VI. At 24 hr the only other significant compound observed by glpc was 1,6-diboracyclodecane (**1**) (9%).

Reaction of the 3:2 Compounds (5 and 6) with Borane in the Ratio of 1:4. In a manner analogous to the experiment described for the reaction of the 3:2 compounds with borane in the 1:1 ratio, 25 mmol of the distilled 3:2 compounds[17] (**5** and **6**) in 26.6 ml of tetrahydrofuran was allowed to react with 42.8 ml (100 mmol) of 2.34 *M* borane in tetrahydrofuran at 0°. The final ratio of $-C_4H_8-$ moiety to boron was 1:2. Hydrolysis of a sample of the reaction mixture at 0 hr[12] indicated the presence of 100% (300 mmol) of the theoretical quantity of active hydride. After 72 hr the value had decreased to 97%.

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(17) The 3:2 compounds utilized were freshly prepared in 80% yield by the method previously described.[3k] The ratio of isomers was approximately 70% 1,3-bis(1′-boracyclopentyl)butane to 30% of the 1,4-isomer. Small amounts of other positional isomers were also present.

Table VI. Glpc Analysis of the Residual 3:2 Compounds (**5** and **6**) in the Reaction of the 3:4 Product (**15**) with the 3:2 Compounds in the Molar Ratio of 1:1 at 25°

Time of reaction, hr	Residual 3:2 compounds, %
0	100
1	62
3	45
6	32
24	8

An infrared spectrum of the reaction mixture at 0 hr showed bands at 2510 (m), 2400 (s), and 1570 cm^{-1} (s). The spectrum remained unchanged in these regions for up to 72 hr.

At 24 hr a 25-ml sample (25 mmol of $-C_4H_8-$ moiety, 100 mmol of active hydride) was treated at *ca.* 25° with 100 mmol of 1-octene and the hydroboration of the olefin was followed as described previously. The results of the reactant uptakes are shown in Figure 4.

Attempted Reaction of 1,6-Diboracyclodecane (1) with Borane in Tetrahydrofuran at 25°. 1,6-Diboracyclodecane[18] (**1**) (3.4 g, 25 mmol) was dissolved in 73.6 ml of tetrahydrofuran and 22.4 ml (50 mmol) of 2.23 *M* borane in tetrahydrofuran was added all at once. At periodic intervals beginning 1 hr after the borane addition, 5.0 ml samples were methanolyzed using 0.6 ml (15 mmol, 50% excess) of anhydrous methanol and analyzed by glpc on a 2-ft column of 10% SE-30 and 0.5% Armac on Chromosorb W. After 48 hr at *ca.* 25°, no apparent loss of 1,6-diboracyclodecane was observed. In addition, an infrared spectrum of the reaction mixture showed bands at 2400 (s) and 1610 cm^{-1} (s) with no indication of bands at 2510 or 1570 cm^{-1}.[15]

Refluxing the mixture (*ca.* 65°) for 24 hr affected the formation of only traces of 1,2-tetramethylenediborane (**4**) as indicated by infrared and glpc analyses. No significant loss of **1** was observed.

Preparation of *B*-Alkylborolanes by the Hydroboration of Appropriate Olefins with the Hydroboration Mixture Derived from 1,3-Butadiene and Borane in the Ratio of 1:1. The following procedure for the preparation of *B*-cyclopentylborolane is representative. The other products listed in Table II may be prepared in an analogous manner.

To the 1 hr old 1:1 hydroboration mixture prepared in a 300-ml flask equipped with a stirring magnet, a thermometer well, a septum inlet, and a series of water and Dry Ice condensers connected to a nitrogen source by the addition of 50 ml (103 mmol) of 2.06 *M* borane to 5.4 g (100 mmol) of 1,3-butadiene dissolved in 50 ml of tetrahydrofuran at 25° was added 6.8 g (100 mmol) of cyclopentene. The resultant mixture was refluxed for 2-3 hr. After evaporation of the solvent, the residue was transferred to a smaller distilling apparatus by means of a syringe and fractionally distilled to give 7.9 g (58%) of *B*-cyclopentylborolane, bp 75-78° (20 mm).

The distilled *B*-cyclopentylborolane (1.36 g, 10 mmol) was oxidized with 3 *N* sodium hydroxide (5 ml) and 30% hydrogen peroxide (5 ml). After an usual work-up, glpc examination using *n*-tridecane as a standard indicated the presence of 10.2 mmol of cyclopentanol and 9.6 mmol of 1,4-butanediol. The aqueous layer was acidified to methyl orange with 3 *N* hydrochloric acid and titrated with 0.5 *N* sodium hydroxide using phenolphthalein as an indicator after the addition of 3.64 g (20 mmol) of mannitol. The result indicated the presence of 10.2 mmol of boric acid.

Conversion of *B*-Cyclopentylborolane into 1-Cyclopentylcyclopentanol *via* Carbonylation-Oxidation. *B*-Cyclopentylborolane (2.72 g, 20 mmol) was dissolved in 50 ml of tetrahydrofuran. Immediately after addition of 1.8 ml (*ca.* 30 mmol) of ethylene glycol,[19] the resultant mixture was carbonylated in a 250-ml autoclave at 70 atm and 150° for 3 hr during which time the pressure reading reached to a constant value at 150°. After cooling the mixture was oxidized at 30-40° with 10 ml of 3 *N* sodium hydroxide, 10 ml of 30% hydrogen peroxide, and 10 ml of 95% ethanol followed by heating at 50° for 1 hr. After saturating the organic layer with potassium carbonate, the organic layer was separated. A 15-mmol aliquot was distilled to give 1.87 g (81%) of 1-cyclopentylcyclopentanol: bp 73-75° (1 mm) (lit.[20] bp 85-87° (3 mm)); ir (neat) 3430 (s), 1000 cm^{-1} (m); pmr (CCl_4, TMS) δ 1.2-2.2 (broad singlet centered at 1.6, 17 *H*), 2.35 (singlet, 1 *H*). The remaining 5-mmol aliquot was analyzed by glpc using *n*-dodecane as a standard (yield by glpc 93%).

Glpc Examination of the Reaction of 1-Butene with the Hydroboration Mixture Derived from 1,3-Butadiene and Borane in the Ratio of 1:1. 1-Butene (5.6 g, 100 mmol) was hydroborated at 25° with the 1:1 hydroboration mixture prepared by the addition of 50 ml (103 mmol) of 2.06 *M* borane in tetrahydrofuran to 1,3-butadiene (100 mmol) in 50 ml of tetrahydrofuran. The uptake of active hydride was *ca.* 90% over in 72 hr. After methanolysis, glpc analysis on a 2-ft SE-30 column using block and column temperatures of 50° revealed the presence of 38 mmol (38%) of *B*-(*n*-butyl)borolane (**11a**).

Preparation of *B*-Methoxyborolane (8). The compound was prepared essentially by the method of Mikhailov and coworkers[21] by the reaction of the distilled mixture of **5** and **6** obtained above with methyl borate using borane in THF as a catalyst: yield 60%; bp 46-48° (103 mm) (lit.[21] 41° (83 mm)); pmr (CCl_4) δ 0.73 (triplet, 4 H), 1.60 (quintetlike multiplet, 4 H), and 3.70 (singlet, 3 H).

Preparation of Tetramethyl Butane-1,4-diboronate. Tetramethyl butane-1,4-diboronate was obtained essentially by the method of Mikhailov and coworkers.[21] Freshly distilled *B*-methoxyborolane (**8**) was treated with a 50% excess of trimethyl borate and 2.5 mol % of borane in tetrahydrofuran. Addition of a small amount of methanol and distillation gave a 65% yield (based on *B*-methoxyborolane) of tetramethyl butane-1,4-diboronate free of isomeric side products: bp 83-86° (6-7 mm); n^{20}D 1.4168 (lit.[21] 53-53.5° (2 mm), n^{20}D 1.4175); pmr (CCl_4, TMS) δ 0.73 (multiplet, 4 H), 1.35 (multiplet, 4 H), 3.50 (singlet, 12 H).

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(18) Prepared by the method of Breuer and Brown;[3i] bp 65° (4 mm), n^{20}D 1.4824 (lit.[3i] bp 59-60° (5 mm), n^{20}D 1.4886).

(19) *B*-Alkylborolanes react with ethylene glycol. Therefore, use of a large excess of ethylene glycol or prolonged standing of *B*-alkylborolanes in contact with ethylene glycol should be avoided. In the previous paper[3k] we reported a procedure which involves a two-stage carbonylation. However, we have found that the one-stage carbonylation presently described gives equally good results.

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