greatly different from the corresponding value of 0.6% observed in the acetolysis of *threo*-3-phenyl-2-butyl tosylate (II-OTs).[3,15] Consequently, this result removes the reported discrepancy in solvolytic behavior of these two closely related systems,[2] and, in turn, no longer required is the theory which postulates that a process involving the formation of solvated open species could lead to predominantly retained product.[2,4] We are currently exploring the question of from which of the two pathways, the k_Δ and k_s, this small but significant amount of active retained product arises.

Experimental Section

Materials. The syntheses were carried out according to the procedure described by Cram and his coworkers.[11] The observed physical constants of the compounds are in good agreement with the reported values (Table III). The resolved alcohols are essentially optically pure, judging from the result of the following experiment. $(-)$-*O*-methylmandelic acid was prepared by the method of Jacobus and Raban,[16] mp 66.5–67.5°, $[\alpha]^{25}$D -163.5 (*c* 1.5, H_2O). This was converted to the acid chloride by the action of thionyl chloride, and this acid chloride was allowed to react with L(+)-*threo*-4-phenyl-3-hexanol ($[\alpha]$D $+20.8$) in pyridine–benzene for 12 hr at room temperature. The ester was purified by preparative glpc and examined by pmr. The methine and the methoxy protons of the acid moiety appear as singlets (δ 4.70 and 3.37, respectively), showing the presence of a single diastereomeric isomer.

Kinetic Procedure. The titrimetric and polarimetric rates of acetolysis were determined by the previously described procedure.[17]

Product Studies. The procedure is similar to that reported previously.[6] Isolation of retained product from the reaction mixture was performed by preparative glpc separation. A controlled experiment showed that no significant amount of racemization takes place during this isolation process.

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[15] The expected amount of active retained product in the absence of internal return becomes *ca.* 3.3% (1 × 3.3) for I-OTs and *ca.* 2.6% (0.6 × 4.4) for II-OTs.

[16] J. Jacobus and M. Raban, *J. Chem. Educ.*, **46**, 351 (1969); mp 66–67°, $[\alpha]^{25}$D -164 (*c* 1.5, H_2O).

[17] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1147 (1952).

Hydroboration. XXXIII. Cyclic Hydroboration of 1,4-Pentadiene with Borane in Tetrahydrofuran. Thermal Behavior of the Organoborane Derivatives and a Simple Synthesis of Bisborinane and *B*-Alkylborinanes

Ei-ichi Negishi,[1a] Patrick L. Burke,[1b] and Herbert C. Brown*

Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907. *Received March 10, 1972*

Abstract: The hydroboration of 1,4-pentadiene with borane in tetrahydrofuran in the 3:2 molar ratio produces in 72% yield a mixture of at least six 3:2 compounds. Oxidation of the product provides 1,5- and 1,4-pentanediols in a ratio of 42:58. Thermal treatment of the 3:2 product at 170°, followed by oxidation, yields 1,5- and 1,4-pentanediols and 1-pentanol in a ratio of approximately 80:10:10. The reaction of the thermally treated 3:2 product with an equimolar quantity of borane in tetrahydrofuran provides bisborinane in 80% yield. The hydroboration of olefins with bisborinane represents a simple convenient synthesis of *B*-alkylborinanes in excellent yields. The two major components of the thermally treated 3:2 product have been identified as 1,5- and 1,1-bis(1′-borinyl)pentanes by utilizing the carbonylation technique. A set of empirical rules predicting the thermal behavior of the dumbbell-shaped 3:2 compounds derived from dienes is proposed. The hydroboration of 1,4-pentadiene with borane in tetrahydrofuran in the 1:1 molar ratio followed by heating at 70–100° cleanly transforms the pentamethylene and 1-methyltetramethylene moieties into bisborinane (~45% yield) and 2,7-dimethyl-1,6-diboracyclodecane (~50% yield), respectively. Physical and chemical properties of the latter substance closely resemble those of the parent compound, 1,6-diboracyclodecane. At or below 100° both bisborinane and 2,7-dimethyl-1,6-diboracyclodecane are stable. Neither interconversion of the ring systems nor isomerization of the individual pentamethylene and 1-methyltetramethylene moieties takes place. At higher temperatures (>100°) both compounds undergo decomposition without evidence of interconversion.

Hydroboration of 1,4-pentadiene with borane in tetrahydrofuran (THF), followed by oxidation, yields 38% of 1,5- and 62% of 1,4-pentanediols.[2] Simple hydroboration–oxidation of this diene had been expected to yield predominantly the 1,5-diol. The unusual distribution which was realized led to the suggestion that in this case hydroboration must involve the formation of cyclic organoborane species.[2] However, no attempt was made to isolate and characterize these products. Until recently[3] these had been the only results available on the hydroboration of 1,4-pentadiene with borane in THF.

Recently we have developed experimental procedures for studying such cyclic organoboranes. Applied to the hydroboration of 1,3-butadiene, these methods clarified the course of the reaction and the nature of the products obtained.[4]

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[1] (a) Postdoctoral Research Associate on a research grant, DA 31-134 ARO(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.

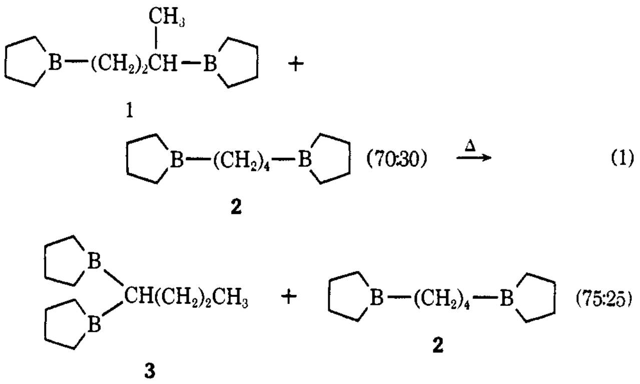
[2] G. Zweifel, K. Nagase, and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 183 (1962).

[3] H. C. Brown, E. Negishi, and P. L. Burke, *ibid.*, **94**, 3561 (1972).

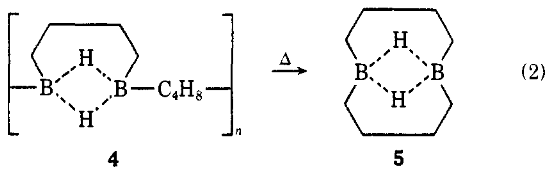
[4] (a) E. Breuer and H. C. Brown, *ibid.*, **91**, 4164 (1969); (b) H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 2460 (1970); (c) H. C. H. C. Brown, E. Negishi, and P. L. Burke *ibid.*, **93**, 3400 (1971).

This study revealed a number of unexpected, fascinating features, among which the following are pertinent here.

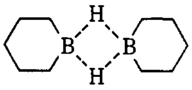
(1) The reaction of 1,3-butadiene with borane in THF in the stoichiometric ratio produces in 70% yield a 70:30 mixture of 1,3- and 1,4-bis(1'-borolyl)butanes (**1** and **2**). Thermal treatment of the initial product produces a 75:25 mixture of **3** and **2**[4b] (eq 1).



(2) The 1:1 kinetic product, on the other hand, is a polymer largely represented by **4**.[4c] Its thermal treatment provides a remarkably stable dimer **5**, isolated in 64% yield[4a] (eq 2).



The success of this approach in the study of the hydroboration of 1,3-butadiene encouraged us to undertake a similar study of 1,4-pentadiene. We hoped to establish the nature of the organoborane products. We also wished to examine the thermal behavior of these products for comparison with the corresponding behavior of the butadiene derivatives.[4] Finally, we hoped to establish conditions for a simple synthesis of bisborinane (**6**) and its derivatives.[5]



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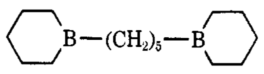
Results and Discussion

Nature of the Initial 3:2 Hydroboration Product. The hydroboration of 1,4-pentadiene with borane in THF in the 3:2 molar ratio with the borane-to diene mode of addition was carried out in a manner analogous to the case of 1,3-butadiene.[4b] When the addition of borane was over, the uptake of hydride was essentially complete. After oxidation, 1,5- and 1,4-pentanediols were obtained in a ratio of 45:55, roughly similar to the values previously reported.[2] Glpc examination of the hydroboration mixture using a 2-ft 10% SE-30 column[4b] revealed the presence of six peaks in the region for the 3:2 compounds (5:10:21:27:24:13 in the order of elution). The overall yield of the 3:2 compounds was 72% by glpc (65% by isolation). The last peak had the same retention time as an authentic sample of 1,5-bis(1'-borinyl)pentane (**7**), identified in the thermally isomerized product, as described later.



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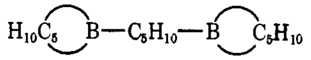
From the similarities in the glpc retention times and in boiling behavior, the other peaks must be isomeric substances. Therefore, it is not unreasonable to assume that the remaining five peaks correspond to five or more of the 3:2 compounds[6] (**8**), made of borinane and 2-methylborolane rings and pentamethylene and 1-methyltetramethylene connecting chains.



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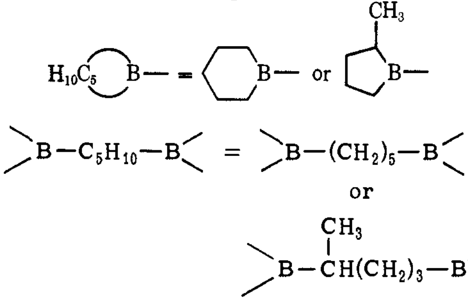
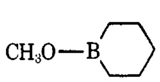


Although no further attempts have been made to identify each of these compounds, it has been clearly established that the hydroboration of 1,4-pentadiene with the stoichiometric quantity of borane in THF at 0° with the borane-to-diene mode of addition produces largely a mixture of 3:2 compounds rather than higher polymers.

Nature of the Initial 1:1 Product. Addition of borane in THF to 1,4-pentadiene in the 1:1 molar ratio at 0° gave a reaction product which, after 1 hr, contained 1 equiv of active hydride per mole of boron atoms. After destroying the active hydride with methanol, glpc examination[7] of the reaction mixture revealed the presence of 25-30% of *B*-methoxyborinane (**10**) along with a minor amount (5%) of *B*-methoxy-2-methylborolane (**11**).



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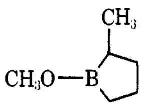

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Except for a minor quantity of the unreacted 3:2 compounds, no other compounds were detected, even when the temperature of the injection port was raised to 150°. Oxidation of the methanolyzed reaction mixture revealed the presence of 1,5- and 1,4-pentanediols in a ratio of 42:58. There-

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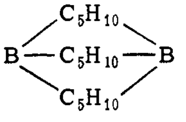
(5) H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971).

(6) Cage structures represented by **9** are not excluded on a rigorous basis. However, such cage structures have not yet been established to be present in such hydroboration reaction mixtures.



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(7) At 50° on a 2-ft SE-30 column.

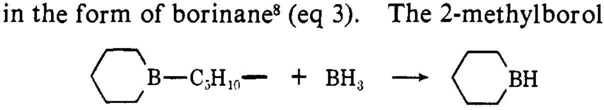
Table I. Thermal Treatment at 70° of the 1:1 Hydroboration Mixture Derived from 1,4-Pentadiene and Borane in THF

Time of refluxing,[a] hr	Active hydride,[b] %	Glpc yield of methanolysis product,[c] %				Glpc yield of pentanediol,[d] %		
		10	11	1:1 dimer	Total	1,5-	1,4-	Total[e]
0	100	24	5	0	29	37	50	87
1	77	33	2	26	63	39	56	95
3		39	Trace	34	73			
6	58	45	Trace	41	86	38	57	95
24	54	43	Trace	46	89	45	56	101
48	54	46	Trace	46	92	41	52	93

[a] At ~70°. [b] By methanolysis. [c] Glpc analysis on a 2-ft 10% SE-30 column (Chromosorb W as solid support). Glpc analysis of **10** and **11** at 50° (injection block, column, and detector). Glpc analysis of the 1:1 dimer at 150°. [d] Glpc analysis of the trimethylsilyl derivatives on an SE-30 column. [e] No other alcoholic products obtained.

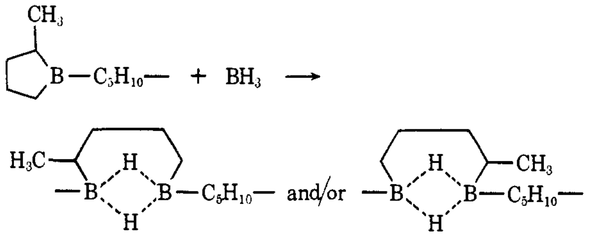
fore, little or no isomerization had occurred under these conditions.

We believe that these observations can be accounted for as follows. Addition of the first two-thirds of the borane rapidly transforms 1,4-pentadiene largely into the isomeric 3:2 dumbbell-shaped molecules (**7** and **8**). Addition of the last third of the borane results in a relatively fast reaction of **7** and **8** with the borane. This reaction takes two different pathways. The borinane moiety is removed from the 3:2 compounds in the form of borinane[8] (eq 3). The 2-methylborolane



(3)

moiety reacts by ring opening (eq 4), as previously established for the parent borolane structure.[8]

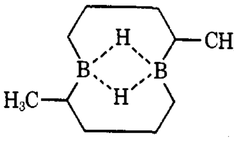


(4)

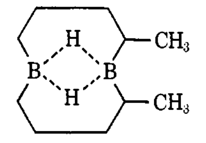
The experimental results obtained above are quite analogous to those obtained recently by hydroborating 1,4-pentadiene using the diene-to-borane mode of addition.[3] Consequently, this supports the earlier interpretation that the reaction *via* the addition of the 1,4-pentadiene to borane must largely proceed through the fast prior formation of the 3:2 compounds, followed by the reaction with residual borane to form bisborinane (**6**) and polymeric product.

Thermal Treatment of the 1:1 Product. Since the simple 1:1 hydroboration failed to yield the desired bisborinane in satisfactory yield, a study of the effect of heat on the initial reaction product was initiated. First, the 1:1 hydroboration mixture was refluxed (~70°), and the reaction was followed by ir, active hydride analysis, and glpc examinations of the methanolysis products as well as of the oxidation products. The experimental results are summarized in Table I. After 24 hr of refluxing, the ir spectrum of the reaction mixture showed the presence of two strong bands for the B---H---B stretching at 1595 and 1560 cm^{-1} and essentially no absorption in the 2600–2400-cm^{-1} region for the terminal B–H stretching. These observations strongly indicated that the product contained a mixture of tetraalkyldiboranes. Glpc examination of the oxidation products revealed the formation of 1,5- and 1,4-pentanediols in a ratio of 45:55. Therefore, little or no position isomerization had taken place. Determination of active hydride by methanolysis indicated that the thermally treated mixture retained only 54% of the initial quantity of active hydride. Glpc examination of the methanolyzed product revealed the presence of *B*-methoxyborinane (**10**) (43% yield) and a new product. Distillation of the methanolyzed mixture yielded **10** in 39% yield. The second product, bp 89–90° (6 mm), $n^{20}D$ 1.4872, was identified as dimethyl-1,6-diboracyclodecane (**12**) by the correct elemental analyses, glpc analysis of the oxidation product (1,4-pentanediol in 101% yield), ir (1595 (s) cm^{-1}), pmr, and mass spectrometry. The yield was 49% by isolation. As in the case of the parent substance, 1,6-diboracyclodecane[4a] (**5**), this product (**12**) is stable to methanol at 25°.

Except for a very minor shoulder on the side of longer retention time, only a single peak was observed by glpc. Therefore, the apparently more stable **12a**



12a

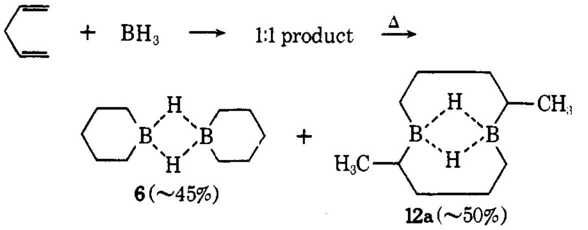


12b

may tentatively be assigned as the structure of the 1:1 stable dimer, although a more rigorous examination is necessary to establish this point.

The thermal treatment of the concentrated 1:1 hydroboration product at 100° gave quite similar results except for a faster rate of reaction (Table V in the Experimental Section).

These results clearly indicate the following. (1) The thermally treated (≤100°) products are essentially cyclic and consist of bisborinane (**6**) and 2,7-dimethyl-1,6-diboracyclodecane (**12a**) in comparable quantities (eq 5). (2) No detectable position isomerization takes place, the ratio of 1,5- and 1,4-pentanediols remaining essentially constant. Thus, no intercon-



(5)

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(8) H. C. Brown, E. Negishi, and P. L. Burke, *J. Amer. Chem. Soc.*, **92**, 6649 (1970).

Table II. Thermal Treatment at 170° of the 1:1 Hydroboration Product Derived from 1,4-Pentadiene and Borane

Time of heating,[a] hr	Glpc yield of methanolysis product,[b] %				Glpc yield of oxidation product,[c] %			
					Pentanediol			
	10	11	12a	Total	1,5-	1,4-	1-Pentanol	Total
0					46	57	Trace	103
0.5	33	Trace	44	77	43	51	5	99
1	20	Trace	51	71	33	51	9	93
3	11	Trace	10	22	38	22	28	88
6	5	Trace	4	9	34	10	35	79

[a] At 170°. [b] See footnote *c* of Table I. [c] The diol analysis was performed on an SE-30 column after silylation. The analysis of 1-pentanol was performed on a Carbowax 20M column.

version of **6** and **12a**, which must be accompanied by position isomerization, occurs under these conditions (≤ 100°).[9] (3) Finally, both **6** and **12a** are quite stable and do not undergo decomposition for at least 24 hr at or below 100°.

In an attempt to cause position isomerization, the concentrated 1,4-pentadiene-borane reaction mixture was heated at 120, 140, and 170°. At these temperatures, rather unexpected changes took place. The results of thermal treatment at 170° are summarized in Table II.

As is clear from Table II, the amounts of both **10** and **12a** decreased with time after reaching the maximum values within 1 hr. At 6 hr only 5% of **10** and 4% of **12a** were present. No other compounds were detected in any significant quantities by glpc (maximum temperature 250°). Thus, no evidence for the interconversion of **6** and **12a** was obtained. The amounts of both 1,5- and 1,4-pentanediols decreased monotonously with time. The loss was largely compensated for by the formation of 1-pentanol. However, the total yield of monool and diols appeared to decrease slowly with time. The results were quite analogous at 140 and 120°, except the rate of change was slower. Under no circumstances was an increase observed in the amount of 1,5-pentanediol.

Thermal Treatment of the 3:2 Product. With the hope of isomerizing the 1-methyltetramethylene moiety to pentamethylene, the 3:2 product derived from 1,4-pentanediene was subjected to thermal treatment. The same technique as employed in the thermal treatment of the corresponding butadiene derivatives[4b] was adopted. Thus, the 3:2 product **8** was heated at 170° (bath temperature) under nitrogen after evaporation of the solvent. After heating for the scheduled period of time, the thermally treated mixture was cooled and oxidized in the usual manner. A major increase in the amount of 1,5-pentanediol was observed. Consequently, under these conditions an isomerization of the 1,4-diborapentane moiety to the 1,5- is occurring. The results of these studies are summarized in Table III.

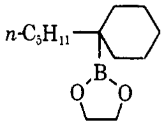
Table III. Thermal Isomerization of the 3:2 Hydroboration Product Derived from 1,4-Pentadiene and Borane. Glpc Analyses of Alcohols Produced after Oxidation

Time of heating,[a] hr	Pentanediol,[b] % 1,5-	1,4-	1-Pentanol,[b] %	Total yield, %
0	37	58	Trace	95
2	72	13	6	91
6	77	13	8	98
12	75	10	8	93

[a] At 170°. [b] See footnote *c* of Table II.

Glpc examination of the thermally treated (3 hr) product indicated the presence of two major peaks in the ratio of approximately 3:4 along with several other minor peaks.

In order to determine the exact structures of the two major components, a weighed quantity (50 mmol) of the thermally treated (3 hr) product was carbonylated in the presence of ethylene glycol.[4b,10] Glpc examination of the carbonylation product on a SE-30 column revealed the presence of 12.5 mmol (25%) of **13** and 20.5 mmol (41%) of **14**. Upon distillation of the carbonylation product after the usual work-up,



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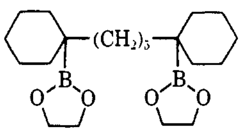

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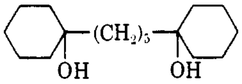
14 was isolated in 41% yield. Oxidation of the purified **14** yielded quantitatively 1,1′-pentamethylenedicyclohexanol (**15**).



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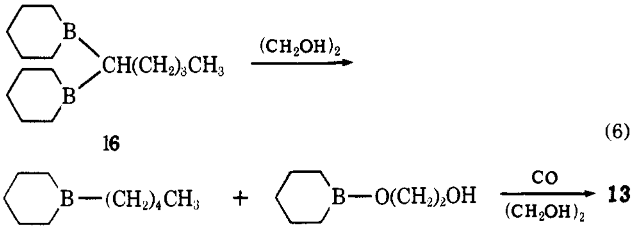
These results clearly support **7** as the structure of one of the two major products obtained by the thermal treatment. As in the case of 1,3-butadiene,[4b] it is reasonable to assign **16** to the other major product and to depict the formation of **13** from **16** as shown by eq 6.



(6)

We conclude, therefore, that under these isomerizing conditions the mixture of 3:2 dumbbell-shaped molecules **8** are transformed largely into 1,5-bis(1-borinyl)pentane **7**, with a somewhat smaller amount of the 1,1 isomer **16**. Perhaps even more significant is the observation that the thermal treatment provides the pentamethylene moiety in a yield of 80%.

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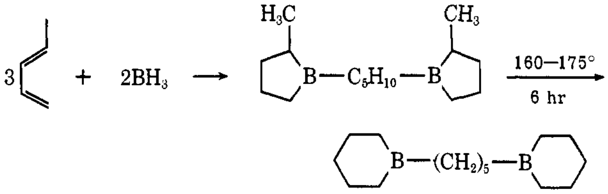
(9) At 100° a purified sample of **12a** was heated. No appreciable change was observed by glpc at least for 12 hr at this temperature.

(10) H. C. Brown, *Accounts Chem. Res.*, 2, 65 (1969).

In 1960 Saegebarth[11] reported the following thermal transformations (eq 7 and 8). As mentioned earlier,



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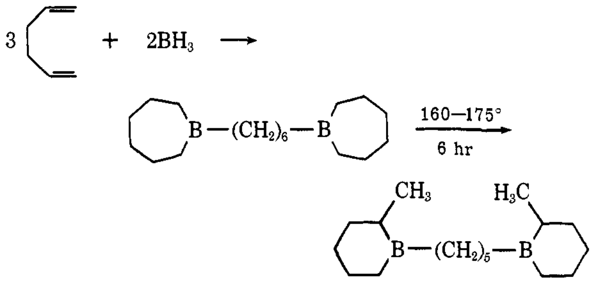
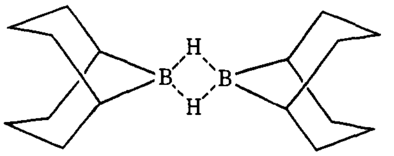


(8)

we recently reported a novel isomerization of the chain moieties of dumbbell compounds[4b] (eq 1). These earlier data, together with the results of the present study, permit us to postulate a set of empirical rules to predict the thermal behavior of the 3:2 dumbbell compounds derived from dienes. (1) The thermal isomerization of the ring moieties present in the 3:2 dumbbell compounds proceeds to form predominantly six-membered rings, when possible. (2) The thermal isomerization of the chain moieties present in the 3:2 dumbbell compounds proceeds to form predominantly α,α- and α,ω-diboraalkane moieties.

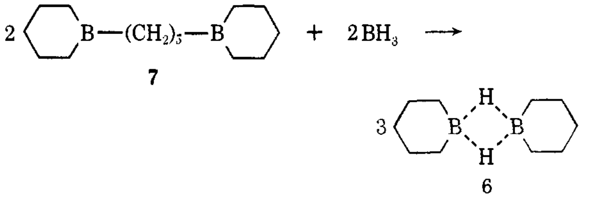
A Simple Synthesis of Bisborinane and *B*-Alkylborinanes.[5] The hydroboration of 1,5-cyclooctadiene provides a convenient route to 9-borabicyclo[3.3.1]-nonane (9-BBN) (**17**);[12] this substance has proven very valuable in applying the new chemistry of organoboranes for synthetic requirements.[13] Certain new developments in our laboratories made it desirable to have bisborinane **6** readily available as a reagent for certain reactions where 9-BBN was not applicable.[14]



17

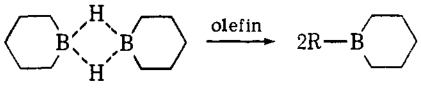
Köster[15] briefly mentions the synthesis of bisborinane by the hydroboration of 1,4-pentadiene. Unfortunately, no details have been reported. Based on this investigation, it is clear that simple hydroboration is unsatisfactory as a route to bisborinane, providing only ~45% of **6** even after thermal treatment. It occurred to us that the thermally isomerized 3:2 product might provide a more favorable route to the desired compound.

Indeed, this proved to be the case. On treatment of the thermally treated (3 hr at 170°) 3:2 product with an equimolar quantity of borane in THF at 25°, a rapid exchange reaction took place, as indicated by the disappearance of the strong band at 2400 cm^{-1} ($BH_3\cdot THF$) as well as by the appearance of a strong band at 1560 cm^{-1} (B---H---B). The reaction reached a steady state in 3 hr, and no further detectable change was observed for at least 72 hr at 25°. Glpc examination of a methanolyzed aliquot indicated the formation of *B*-methoxyborinane (**10**) in 80% yield. Evidently, all of the pentamethylene moiety present in the 3:2 product was converted into **6**. Therefore, the chain moiety of **7** must have also cyclized (eq 9). Evaporation of the solvent yielded a crystalline material. Pure bisborinane was obtained by sublimation, mp 52-54°. The substance was identified by analyses of the oxidation products (1,5-pentanediol (94%) and boric acid (101%)), analysis of active hydride by methanolysis (95%) and glpc analysis of the resultant *B*-methoxyborinane (97%), and ir (1560 cm^{-1} (s)).



(9)

No difficulty was encountered in preparing various *B*-alkylborinanes in excellent yields by the hydroboration of olefins with bisborinane at 25° (eq 10). The results of preparation of *B*-alkylborinanes are summarized in Table IV.



(10)

Table IV. Synthesis of *B*-Alkylborinanes

Alkyl group of *B*-alkylborinane	Yield,[a] % Glpc	Yield,[a] % Isolated	Bp, °C (mm)
n-Butyl	90	79	78-81 (18)
n-Pentyl	93	81	92-95 (20)
sec-Butyl	88	73	64-67 (20)
Cyclopentyl	91	75	97-100 (19)
Cyclohexyl	93	90	115-118 (20)
exo-Norbornyl	91	76	128-130 (20)

[a] Based on olefins.

In cases in which *B*-alkylborinanes are required as intermediates, isolation of neither bisborinane nor *B*-alkylborinanes is necessary. Although the crude bisborinane contained approximately 20% of impurities, loss of olefin through side reactions with these impurities was practically avoided by using a modest excess (25-50%) of the solution containing bisborinane. Evidently, the hydrides in the impurities were less reactive, so that the olefins reacted preferentially with bisbo-

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(11) K. A. Saegebarth, *J. Amer. Chem. Soc.*, **82**, 2081 (1960). In the light of our previous[2,4b] and present studies as well as that by Mikhailov and his coworkers [A. Ya. Bezmenov, L. S. Vasil'ev, and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2111 (1965)], Saegebarth's results appear to be considerably oversimplified. Nevertheless, his conclusion that the thermal isomerization of the ring moieties present in the 3:2 dumbbell compounds proceeds to form preferentially the six-membered rings appears valid.

(12) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968).

(13) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281, 5283 (1968); H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, **91**, 2144 (1969); H. C. Brown and M. M. Rogić, *ibid.*, **91**, 2146 (1969); H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969); H. C. Brown and S. P. Rhodes, *ibid.*, **91**, 2149 (1969).

(14) H. C. Brown and E. Negishi, *ibid.*, **93**, 3777 (1971).

(15) R. Köster, *Angew. Chem.*, **72**, 626 (1960).

Table V. Thermal Treatment at 100° of the 1:1 Hydroboration Product Derived from 1,4-Pentadiene and Borane in THF

Time of heating,[a] hr	Active hydride,[b] %	Glpc yield of methanolysis product,[c] %				Glpc yield of pentanediols,[d] %		
		10	**11**	1:1 dimer	Total	1,5-	1,4-	Total
0	100	29	10	0	39	39	54	93
1	50	41	Trace	47	88			
3	48	44	Trace	51	95			
6	47	44	Trace	53	97			
24	48	46	Trace	50	96	39	52	91

[a] At 100°. [b-d] See the corresponding footnotes in Table I.

rinane to form the corresponding *B*-alkylborinanes in nearly quantitative yields based on the olefins without being contaminated with the isomeric impurities. Excess reagent is conveniently destroyed with water or alcohol prior to isolation or further use of the *B*-alkylborinanes.

The present simple synthesis of bisborinane not only permits a convenient and general synthesis of *B*-alkylborinanes but provides the basis for a further study as to its utility as a valuable new reagent for syntheses *via* hydroboration[14] and for selective reduction.

Conclusion

The present study has established the structures of the thermally treated 1:1 and 3:2 products derived from 1,4-pentadiene and borane in THF. The nature of the initial 1:1 and 3:2 products has also been clarified to some extent. These results are highly consistent with our earlier findings with 1,3-butadiene and with *B*-alkylboracyclanes. A set of empirical rules predicting the thermal behavior of the dumbbell-shaped 3:2 compounds derived from dienes has been proposed. Finally, a simple convenient synthesis of bisborinane and *B*-alkylborinanes has been established.

Experimental Section

The organoboranes were always handled under nitrogen with careful exclusion of oxygen and moisture. Pmr, ir, and mass spectra were obtained with a Varian T-60, a Perkin-Elmer 137B, and a Hitachi RMU-6A, respectively. Melting points were uncorrected.

Materials. The preparation of borane solutions in THF was carried out as described previously.[16] Commercially available 1,4-pentadiene, 1-butene, 2-butene, 1-pentene, cyclopentene, cyclohexane, norbornene, and methanol were used without additional purification after checking the refractive indices.

Hydroboration of 1,4-Pentadiene with Borane in THF in the Molar Ratio of 3:2. A 300-ml three-necked flask fitted with a septum inlet, a magnetic stirring bar, a thermometer well, and a condenser, the tip of which was connected to a mercury bubbler, was flushed with nitrogen, cooled at 0°, and charged with 93.9 ml (100 mmol) of a 1.07 *M* solution of 1,4-pentadiene in THF. To this was added 27.9 ml (66.7 mmol) of a 2.44 *M* solution of borane in THF at 0–5°. The total volume was adjusted to 133 ml. The reaction mixture was kept at 0° for 3 hr and then allowed to warm to 25°. Immediately following the completion of addition of borane, a 4.0-ml aliquot was hydrolyzed in a 1:1:1 mixture of water, glycerol, and THF, and the hydrogen evolved was measured. The analysis indicated that only 5% of the active hydride was remaining. The amount of active hydride decreased to less than 1% in 3 hr. Glpc examination[17] of the reaction mixture at 3 hr on a 2-ft column of SE-30 on Chromosorb W using tridecane as an internal standard revealed the presence of at least six peaks in the region for the 3:2 compounds. The overall glpc yield was 72%. Minor quantities (5–10%) of more volatile products (three peaks) were also present. The ratio of the six peaks for the 3:2 compounds in one examination was 5:10:21:27:24:13 in the order of elution. The last peak had the same retention time as 1,5-bis(1′-borinyl)pentane. No appreciable change in the yield or product distribution was observed by the glpc examination for at least 48 hr.

Oxidation of 20-ml (10 mmol in boron) aliquots at 3 and 48 hr with 4 ml each of 30% hydrogen peroxide and 3 *N* sodium hydroxide yielded, after the usual work-up, 1,5- and 1,4-pentanediols in the ratio of 45:55 in both cases (92 and 94% overall yields, respectively).[18]

A 20-mmol (40 mmol in boron and 60 mmol in 1,4-pentadiene) aliquot of the 3:2 hydroboration mixture was distilled after evaporation of the solvent to yield 3.0 g (65%) of a mixture of the 3:2 compounds, bp 105–107° (1 mm).

Hydroboration of 1,4-Pentadiene with Borane in THF in the Molar Ratio of 1:1. The experiment was carried out in a manner similar to the one described above for the hydroboration in the 3:2 molar ratio except that the molar ratio of 1,4-pentadiene to borane was 1:1. After the addition of borane at 0° (1 hr), an active hydride analysis by the usual hydrolysis indicated the presence of 105% of the theoretical quantity of hydride ($^1/_3$ of the initial quantity being 100%). At this time the ir spectrum of the 1:1 hydroboration mixture indicated the presence of bands at 2600, 2500, and 2400 cm^{-1} as well as a broad strong band at 1560 cm^{-1} with minor shoulders. Glpc examination[7] after methanolysis at 1 hr indicated the presence of 25–30% of *B*-methoxyborinane along with ~5% of *B*-methoxy-2-methylborolane. Except for a minor quantity of the 3:2 compounds, no other compounds were detected in any appreciable quantities, even when higher temperatures (~150°) were used for glpc. The usual oxidation of the methanolyzed mixture yielded 1,5- and 1,4-pentanediols in 93% yield in the ratio of 42:58. No *n*-pentanol was observed.

Thermal Treatment of the 1:1 Kinetic Products. (a) At the Refluxing Temperature of the Hydroboration Mixture. A 1:1 hydroboration mixture obtained as described above was refluxed at ~70°. At a scheduled time, an aliquot was withdrawn and analyzed for the amount of active hydride by methanolysis and/or hydrolysis. The methanolysis products were analyzed by glpc.[7] The remainder of the methanolysis product was oxidized and the oxidation products analyzed by glpc after silylation.[18] The experimental results were summarized in Table I. Examination of the thermally treated mixture by ir after refluxing for 1 hr indicated a very minor peak at 2510 cm^{-1} as an only peak in the 2600–2400-cm^{-1} region and two strong bands at 1595 and 1560 cm^{-1}. The band at 2510 cm^{-1} disappeared after 3 hr. The intensity of the band at 1595 cm^{-1} relative to that at 1560 cm^{-1} increased with time.

(b) At 100°. The 1:1 hydroboration mixture was heated at 100° (bath temperature) after removing the solvent below 30° under diminished pressure. Examination of the thermally treated mixture was carried out as described in the previous experiment. The experimental results were summarized in Table V.

(c) At 120, 140, and 170°. These experiments were carried out in a manner similar to that described for the experiment at 100°. The experimental results of the thermal treatment at 170° were summarized in Table II. The results obtained by the thermal treatment at 120 or 140° were similar to those obtained at 170° except that the changes were slower. At no time the yield of either 1,4- or 1,5-pentanediol exceeded the initial quantity. A slow formation of 1-pentanol was observed at these temperatures (6% in 10 hr at 120° and 14% in 6 hr at 140°).

Preparation of 2,7-Dimethyl-1,6-diboracyclodecane (12a). A 100-mmol aliquot of the 1:1 hydroboration mixture in THF was

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

(17) The injection block temperature was kept at 100° and the column temperature was programmed from 50 to 100°.

(18) By glpc analysis of the trimethylsilyl ethers on a 6-ft SE-30 column.

refluxed for 24 hr at *ca.* 68°. After cooling the mixture under nitrogen, it was treated with 6.4 g (200 mmol) of methanol at 25°. The excess of methanol and THF was evaporated and the residue distilled. Two fractions were collected. The more volatile fraction was essentially pure *B*-methoxyborinane,[19] 4.4 g (39%), bp 47–48° (27 mm). The higher boiling fraction was identified as 2,7-dimethyl-1,6-diboracyclodecane (**12a**): 4.0 g (49%); bp 89–90° (6 mm); n^{20}D 1.4872; ir (neat) 1800 (w), 1595 (s), 1460 (m), 1420 (m), 1320 (m), 1180 (m), 1165 (m), 1070 (m), 1010 (m), 945 (m), 810 (m), 790 (m), 770 cm^{-1} (m); pmr (CCl_4, TMS) δ 2.0–1.2 (broad multiplet with a peak at *ca.* 1.75, *ca.* 8 H) and 1.2–0.6 ppm (broad multiplet with a sharp peak and a small shoulder at 0.9 and 1.04, respectively, *ca.* 12 H); mass spectrum (70 eV, 75°) *m/e* (rel intensity) 164 (100), 163 (48), 162 (6).

Anal. Calcd for $C_{10}H_{22}B_2$: C, 73.27; H, 13.53; B, 13.20. Found: C, 73.22; H, 13.39; B, 13.40.

Glpc examination on a 12-ft SE-30 column exhibited only a single peak with a very minor shoulder on the side of longer retention time. Oxidation of 0.33 g (2 mmol) of **12a** yielded 2.02 mmol of 1,4-pentanediol (101% by glpc). 2,7-Dimethyl-1,6-diboracyclodecane (0.82 g, 5 mmol) was dissolved in 10 ml of THF. After adding 0.8 ml (20 mmol) of methanol, the resultant mixture was stirred at 25° for 24 hr. No detectable amount of hydrogen was evolved.

2,7-Dimethyl-1,6-diboracyclodecane (**12a**) (1.64 g, 10 mmol) was heated at 100° (bath temperature) in the presence of *n*-tridecane (internal standard). No detectable loss of **12a** was observed by glpc at least for 12 hr.

Thermal Isomerization of the 3:2 Hydroboration Products. An aliquot of the 3:2 hydroboration mixture was concentrated at 30° under diminished pressure. After removing the volatile substance thoroughly, the residue was heated at 170° (bath temperature) for a scheduled period of time. After cooling under an atmosphere of nitrogen, the thermally treated product was oxidized with 3 *N* sodium hydroxide and 30% hydrogen peroxide in the usual manner and the oxidation products were analyzed by glpc after silylation.[18] The results were summarized in Table III. Glpc examination of the thermally treated mixture (3 hr) indicated the presence of two major peaks in the ratio of *ca.* 3:4 along with several other minor peaks.

Carbonylation of the Thermally Treated 3:2 Products. The thermally treated 3:2 product (11.6 g, 50 mmol) obtained above (170°, 3 hr) was dissolved in 100 ml of THF and carbonylated overnight with carbon monoxide at 1000 psi and 150° in the presence of 9.3 g (150 mmol) of ethylene glycol.[4b,10] Glpc examination of the carbonylation products on an SE-30 column using *n*-dodecane as an internal standard revealed the presence of 12.5 mmol (25% based on the stoichiometry shown by eq 6) of **13** and 20.5 mmol (41%) of **14**. Several other minor peaks were also observed. The substance **13** was identified by comparing the glpc retention time and ir and pmr spectra with those of an authentic sample obtained earlier by the carbonylation of *B*-(*n*-pentyl)borinane:[19] ir (neat) 2950 (s), 1390 (s), 1230 (s), 1210 (s), 1020 cm^{-1} (s); pmr (CCl_4, TMS) δ 0.6–2.2 (multiplet, 21 H), 4.13 ppm (singlet, 4 H). Upon distillation of a 40-mmol aliquot of the carbonylated reaction mixture after the usual work-up (extraction with pentane followed by washing with water and drying), 7.7 g (41%) of **14** was obtained, bp 152–156° (0.02–0.025 mm). The product, which spontaneously crystallized on standing, was purified by recrystallization from pentane: mp 67–70°; ir (Nujol) 1395 (s), 1240 (s), 1220 (s), 1020 cm^{-1} (s); pmr (CCl_4, TMS) δ 0.6–2.0 (broad multiplet with a relatively sharp peak at 1.18 ppm, 30 H), 4.17 ppm (singlet, 8 H).

Anal. Calcd for $C_{21}H_{38}B_2O_4$: C, 67.05; H, 10.18; B, 5.75. Found: C, 66.77; H, 10.35; B, 5.89.

Preparation of 1,1′-Pentamethylenedicyclohexanol 15 by the Oxidation of 14. The purified diboronate **14** (1.88 g, 5 mmol) was dissolved in 10 ml of THF and oxidized at 30–40° with 5 ml each of 6 *N* sodium hydroxide and 30% hydrogen peroxide after addition of 10 ml of ethanol. The oxidation mixture was then heated at 50° for 1 hr. After the usual work-up, evaporation of the solvent provided 1.30 g (97%) of 1,1′-pentamethylenedicyclohexanol (**15**): mp 84–85° after recrystallization from pentane; ir (Nujol) 3300, 3230, 1390 cm^{-1}; pmr ($CDCl_3$, TMS) δ 1.1–1.7 (two peaks at 1.4 and 1.5 ppm, 30 H), 3.73 ppm (exchangeable with D_2O, 2 H). A 1:1 mixture of the product with an authentic sample of **15** obtained in the following experiment melted at 83–84°.

Preparation of 1,1′-Pentamethylenedicyclohexanol (15) by the Reaction of Cyclohexanone with the Grignard Reagent Derived from 1,5-Dibromopentane. An authentic sample of **15** was prepared by the method reported in the literature[20] (yield 23%), mp 85.5–86.5° (lit.[20] mp 77–78°).

Preparation of Bisborinane. In a distillation setup with a 300-ml three-necked flask with a septum inlet, a magnetic stirring bar, and a thermometer well were placed 21 g (300 mmol) of 1,4-pentadiene and 100 ml of THF. Borane in THF (2.2 *M*, 91 ml, 200 mmol) was under over 30 min at 0°. One hour later the solvent was evaporated under diminished pressure, and the residue heated at 170° (bath temperature) for 3 hr. After cooling 45.5 ml of 2.2 *M* borane (100 mmol) was added at room temperature, and the concentration was adjusted to 2.0 *M* in active hydride by the addition of THF. The resultant solution was used as a stock solution of bisborinane in THF.

An aliquot of the above-obtained bisborinane solution was evaporated first at 20 mm and then at 1 mm and 25°. The resultant crystalline solid was sublimed at 0.5 mm to yield pure bisborinane: mp 52–54°; ir (CCl_4) 1560 cm^{-1} (s); pmr[21] (CCl_4, TMS) δ 0.95 (broad singlet, 8 H), 1.52 ppm (broad singlet, 12 H).

Anal. Calcd for $C_{10}H_{22}B_2$: B, 13.20. Found: B, 13.33.

The substance was further identified by analysis of active hydride by methanolysis (95%) and by glpc analyses of the resultant *B*-methoxyborinane (97%) and of 1,5-pentanediol (94%) obtained by the usual oxidation of the methanolysis product.

Preparation of *B*-Alkylborinanes by the Hydroboration of Appropriate Olefins with Bisborinane. The following procedure for the preparation of *B*-cyclohexylborinane is representative. To 20 ml of 2.0 *M* (in active hydride) bisborinane solution in THF was added 2.46 g (30 mmol) of cyclohexene in 30 ml of THF at 20–25°. After stirring the reaction mixture at 25° for 2 hr, the residual hydride was quenched with 0.18 ml (10 mmol) of water. A glpc examination indicated the presence of 28 mmol (93% based on cyclohexene) of *B*-cyclohexylborinane which was essentially free from isomeric impurities. Distillation provided 4.4 g (90%) of *B*-cyclohexylborinane, bp 115–118° (20 mm).[19] The experimental results with other olefins are summarized in Table IV.

Acknowledgment. The authors are indebted to Mr. William E. Baitinger for assistance in obtaining the mass spectra.

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(19) The compound was identified by the comparison of glpc retention times and spectral data with those of an authentic sample: H. C. Brown, E. Negishi, and S. K. Gupta, *J. Amer. Chem. Soc.*, 92, 6648 (1970).

(20) J. Colonge and R. David, *Bull. Soc. Chim. Fr.*, 1248 (1959).

(21) Minor peaks at 0.2 and 2.3 ppm were also observable. However, no rigorous attempt was made to locate all peaks due to the hydridic hydrogens.