to room temperature, helium added to increase the pressure to slightly above atmospheric, and the flasks were vigorously shaken. The gases were then analyzed by gas chromatography. Mixtures of known volumes of products and reference gases were analyzed under reaction conditions to obtain calibration factors.

After the gas analysis, a reference ester was added to the reaction solution and the solution brought to a volume of 50 cc with glacial acetic acid. A 15-ml aliquot of the solution was then added to 15 ml of diethyl ether. The ether solution was washed three times with water and three times with saturated sodium bicarbonate solution to remove the excess carboxylic acid. The ether solution was analyzed for ester products by gas chromatography. Solutions containing known concentrations of product and reference esters were analyzed in the same manner to obtain calibration factors.

Gas chromatographic analyses of gaseous products were performed on instruments equipped with thermal conductivity detectors. Carbon dioxide was analyzed on a 2-ft Poropak Q column at room temperature using ethane as a reference gas. Propane, propene, isobutane, and isobutene were analyzed on a 15-ft 30% Dowtherm on firebrick column at room temperature using *n*-butane as a marker.

Esters were analyzed on instruments employing flame-ionization detectors (Varian Aerograph, Model 1200, and Varian Aerograph, Model 200). An 8-ft DEGS column was used to analyze *n*-propyl *n*-butyrate, isopropyl *n*-butyrate, isopropyl isobutyrate, and isopropyl acetate with *n*-butyl acetate as the marker. A 6-ft Morflex column was used to analyze *t*-butyl pivalate and *t*-butyl acetate with *n*-butyl acetate as the marker.

Kinetic Procedure. Kinetics were followed on a Beckmann DB-G spectrophotometer equipped with a Sargent Model SRLG recorder. Temperature control was within ±0.4° in the thermostated compartment. The manganese(III) acetate concentrations were determined spectrophotometrically at 462 nm (shoulder).

Stock solutions of *ca.* 1.3×10^{-2} *M* manganese(III) acetate in pivalic acid were used and diluted by a factor of 5 with pivalic acid for the kinetic studies. Added acids and bases were dissolved in pivalic acid and added as required.

After the reaction solution had been made up, a portion was transferred to a 1-cm cell which was sealed with a rubber septum. The solution was then degassed with helium introduced through a hypodermic needle for 10–15 min. The cell was preheated with shaking to within 10° of the desired temperature before being placed in the spectrophotometer.

Epr Method. All spectra were run on a Varian E-3 epr spectrometer. The same sample tube was used for the sample Mn^{III} and standard Mn^{II} solutions. The temperature was controlled to within 1.0°.

Acknowledgment. We wish to thank the National Science Foundation for generous financial support of this work, Dr. Sheldon Lande for the study of the autoxidative decarboxylations catalyzed by Mn^{III}, and Professor E. C. Kooyman for kindly sending us copies of the theses of Drs. W. J. DeKlein, R. E. Van der Ploeg, R. W. de Korte, and L. W. Hessel.

Organoboranes. IX. Structure of the Organoboranes Formed in the Reaction of 1,3-Butadiene and Diborane in the Stoichiometric Ratio. An Unusual Thermal Isomerization of These Organoboranes

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Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907. *Received August 5, 1969*

Abstract: The hydroboration of 1,3-butadiene with diborane in the stoichiometric ratio at 0° produces predominantly the dumbbell-shaped structures, 1,3- and 1,4-bis(1-boracyclopentyl)butanes. Although the ratio of the two major isomers varies somewhat with the reaction conditions, the 1,3 isomer is the preferred product, ~70%, under kinetically controlled conditions. Under isomerization conditions (140–170°), this isomer rapidly vanishes and the product is converted into 75% 1,1- and 25% 1,4-bis(1-boracyclopentyl)butanes. Independent syntheses of 1,1- and 1,4-bis(1-boracyclopentyl)butanes was achieved by treating 1-butyne and 1,3-butadiene with B-methoxyboracyclopentane and lithium aluminum hydride. The structure of the 1,4 isomer was confirmed by treatment with carbon monoxide to form 1,1′-tetramethylenedicyclopentanol. In marked contrast to the behavior of simple trialkylboranes, the boracyclopentane ring is readily opened by solvolysis with water or alcohol. Deuterolysis with heavy water, followed by oxidation, provides a convenient synthesis of 1-butanol-4-d_1. The present understanding of the reaction products and the chemistry of "bisborolane" permits postulation of a reaction mechanism for the hydroboration of 1,3-butadiene.

The cyclic hydroboration of dienes with thexylborane[2] followed by carbonylation provides a convenient new synthetic route to cyclic and polycyclic ketones.[3,4] Hydroboration with diborane, followed by carbonylation, has been successfully applied to trienes[5] and to one diene, 1,5-cyclooctadiene.[6] However, extension of this promising new synthetic approach to dienes generally has been handicapped by the confused state of our knowledge as to the structure of the products formed from the reaction of diborane with dienes.[7]

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[1] Postdoctorate Research Associate on a research grant, DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

[2] H. C. Brown and C. D. Pfaffenberger, *J. Amer. Chem. Soc.*, **89**, 5475 (1967).

[3] H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967); H. C. Brown and E. Negishi, *Chem. Commun.*, 594 (1968).

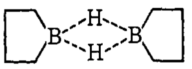
[4] For a general review of this development with complete literature references, see H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

[5] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **89**, 5478 (1967); H. C. Brown and W. C. Dickason, *ibid.*, **91**, 1226 (1969); H. C. Brown and E. Negishi, *ibid.*, **91**, 1224 (1969).

[6] E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280, 5281, 5283 (1968).

[7] The hydroboration–oxidation of dienes has been subjected to detailed study. However, for such production of enols or diols, the precise structure of the boron intermediates is not of major importance and

Consider the situation with respect to the simplest conjugated diene, 1,3-butadiene.[8] In 1960 Köster reported that the reaction of 1,3-butadiene with either diborane or triethylamine–borane yielded a distillable organoborane which exhibited highly unusual stability toward alcohols, olefins, and oxidizing agents for a substance containing residual boron–hydrogen bonds.[8b] Köster proposed the structure to be that of "bisborolane" (**1**). While we could confirm these unusual properties for the 1:1 product,[9] the structure **1** did not appear to be compatible with these unusual properties. Therefore, we proposed the alternative structure, 1,6-diboracyclodecane (**2**).[8d]



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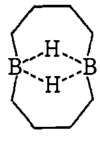

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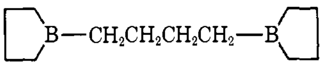
Subsequent study enabled us to conclude that **2** was indeed the structure of the thermally isomerized 1:1 compound.[10] This conclusion was recently confirmed by Young and Shore utilizing a totally independent approach.[11] Consequently, we may now consider the question of the structure of the thermally isomerized 1:1 product as resolved.[12]

Köster also reported, without giving any details, that the hydroboration of 1,3-butadiene with diborane or triethylamine–borane yielded as the 3:2 product the substance 1,4-bis(1-boracyclopentyl)butane (**3**).[8a] Similar results were realized by Saegebarth and he also assigned structure **3** to the product obtained by distillation of the reaction mixture.[8c]



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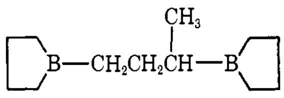
On the other hand, Mikhailov and his coworkers reported that in this reaction they obtained a mixture of three isomers in a ratio of 55:39:6, to which they assigned the structures **3**, **4**, and **5**.[8g] The latter workers based their conclusions largely on the identification of the products formed in the oxidation of the distilled mixture of organoboranes. Indeed, their results are far more consistent with our early identification of the diols from the hydroboration–oxidation of 1,3-butadiene,[8d] than are those of Köster[8a] and Saegebarth.[8c]



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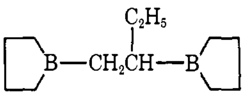

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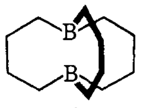
None of these earlier workers considered the possibility of utilizing the reaction for the possible synthesis of cage structures, such as **6** and **7**, nor the possibility that such structures might actually be present in the reaction mixtures.



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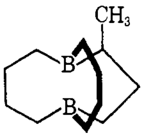

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It is quite clear that to rely entirely upon identification of the oxidation products for characterization of the intermediates could be misleading. Accordingly, we decided to undertake an investigation of the structures of the 3:2 products utilizing less ambiguous methods.

Results and Discussion

Hydroboration of 1,3-Butadiene and Glpc Examination of the Product. In the initial studies we utilized the hydroboration procedure described by Saegebarth.[8c] Köster's experimental procedure has not yet been described and Mikhailov utilized a considerable excess of 1,3-butadiene in his study, which led to the formation of a considerable quantity of volatile by-products. This appeared to be undesirable for our objectives.

Accordingly, diborane was passed into a solution of 1,3-butadiene in a mixture of ether and pentane maintained at 2–10°, utilizing amounts of the two reactants to correspond to the stoichiometric ratio (1,3-butadiene: B_2H_6 = 3:1). After the addition was complete, the reaction product was permitted to stand at room temperature for 24 hr, and then subjected to glpc examination. The chromatogram revealed two major peaks, I and II, in the expected region for the 3:2 products, with some quite minor peaks both in the same region and in a more volatile region (corresponding to a 2:1 reaction product). The total area of I and II corresponded to a yield of approximately 70–80%. The ratio of I to II varied slightly from experiment to experiment, with II being present in a considerably larger amount, approximately 30% I to 70% II.[13]

As it was much more convenient to use a solution of borane in tetrahydrofuran (THF), rather than gaseous diborane, we examined the possibility of substituting this reagent. To a solution of 1,3-butadiene (1.2 mol) in THF at 0° was added an ~2 *M* solution of borane (0.8 mol) in THF over a period of 1–2 hr. Glpc examination of the reaction mixture indicated the presence of the same two products, I and II, in a comparable yield and in a similar ratio. Consequently this procedure was adopted as the standard method of hydroboration for all subsequent work.

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little attention was paid to the isolation and characterization of the intermediates: H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 15.

(8) (a) R. Köster, *Angew. Chem.*, **71**, 520 (1959); (b) R. Köster, *ibid.*, **72**, 626 (1960); (c) K. A. Saegebarth, *J. Amer. Chem. Soc.*, **82**, 2081 (1960); 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 H. A. Skinner, *J. Chem. Soc.*, 3704 (1963); (g) B. M. Mikhailov, A. Y. Bezmenov, L. S. Vasil'ev, and V. G. Kiselev, *Dokl. Akad. Nauk SSSR*, **155**, 141 (1964); *Chem. Abstr.*, **60**, 13263 (1964).

(9) It is convenient to refer to the reaction product from 1,3-butadiene and borane in a 1:1 ratio as the 1:1 compound, although the isolated product is actually the dimer, containing two 1,3-butadiene and borane moieties. Likewise the product produced from the two reactants in the stoichiometric ratio will be referred to as the 3:2 compound.

(10) 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).

(11) D. E. Young and S. G. Shore, *ibid.*, **91**, 3497 (1969).

(12) We are currently exploring the nature of the 1:1 product under nonisomerization conditions.

(13) The fact that we have been able to observe pure isomers as single peaks and that the glpc analysis proved to be highly reproducible appears to support the conclusion that no extensive isomerization takes place during the analysis.

Thermal Isomerization of the 3:2 Product. As will be seen subsequently, we have identified I as 1,4-bis(1-boracyclopentyl)butane (**3**), and II as the 1,3 isomer (**4**). Consequently, we were puzzled by the discrepancy between our results, which indicated the 1,4 isomer to be the minor product, with the reports of Köster[8a] and of Saegebarth,[8e] which indicated this isomer to be the sole product, and the report of Mikhailov and his coworkers,[8g] which indicated this isomer to be the preferred product. It appeared that this difference in results might arise from a thermal isomerization[14] of the initially formed organoboranes, either during distillation or some other thermal treatment during the work-up. Accordingly, we undertook to study the effect of distillation and thermal treatment on the composition of the 3:2 product.

Heating the reaction product in THF under reflux for 24 hr did not result in any appreciable change in composition.

Simple distillation under vacuum of the hydroboration mixture from the above synthesis in THF gave a liquid, bp 66–68° (1 mm), in a yield of 77%. (This material is much more reactive toward air than simple organoboranes and must be handled with complete exclusion of oxygen.) Glpc analysis of the distillate indicated the presence of I and II in essentially the original ratio of 30:70, with two minor peaks present in the same region. Evidently, no significant change occurs in the course of distillation under these mild conditions.

The distilled reaction product was then maintained at 140° under nitrogen and aliquots removed at appropriate time intervals for glpc analysis. Here isomerization was quite rapid. The amount of II decreased monotonously. At first I increased, but it later decreased, and a peak III, originally present as one of the minor by-product peaks in this region, became the dominant product. The results are summarized in Table I.

Table I. Thermal Isomerization of the Distilled 3:2 Product at 140°

Time of heating, hr	Isomer distribution, %[a]			
	I[b]	II[c]	III[d]	Total
0	29	68	3	100
0.5	43	50	6	99
1	51	41	9	101
2	56	32	13	101
4	56	21	20	97
6	54	16	27	97
8	55	10	32	97
12	40	3	55	98
16	37	3	60	100
20	33	3	62	98
24	30	3	60	93

[a] Based on I + II + III = 100% at 0 hr. [b] 1,4 Isomer (**3**). [c] 1,3 Isomer (**4**). [d] 1,1 Isomer (**14**).

Similar treatment of the hydroboration product, without prior isolation of the 3:2 compound by distillation, gave similar results, with one exception. In this case the total yield rose with time to above 100%, indicating that nonvolatile polymeric species present in the reaction mixture had undergone some depolymerization. These results are summarized in Table II.

Table II. Thermal Isomerization of the 3:2 Hydroboration Product at 140°

Time of heating, hr	Isomer distribution, %[a]			
	I[b]	II[c]	III[d]	Total
0	28	70	2	100
0.5	33	49	18	100
1	40	32	22	94
2	45	21	33	99
4	50	17	39	106
6	50	13	45	108
8	49	11	48	108
12	47	5	53	105
16	46	5	54	105
20	41	4	60	105
24	40	2	60	102

[a–d] See corresponding footnotes in Table I.

The thermal isomerization was greatly accelerated at 170°. At this temperature, an apparent equilibrium mixture of 25% I:75% III was obtained in less than 6 hr. The isomer II was essentially absent within 2 hr (Table III).

Table III. Thermal Isomerization of the 3:2 Hydroboration Product at 170°

Time of heating, hr	Isomer distribution, %[a]			
	I[b]	II[c]	III[d]	Total
0	28	70	2	100
2	38	Trace	76	114
6	28	Trace	84	112
12	26	Trace	84	110

[a–d] See corresponding footnotes in Table I.

One important conclusion to be drawn from these experiments is that no single product is obtained at any stage of the thermal treatments. Consequently, these results argue strongly against the positions taken by Köster[8a] or Saegebarth,[8c] who claimed the formation of only a single product **3** in the hydroboration of 1,3-butadiene.

Identification of the Compound I. We were unable to separate I and II in the distilled 3:2 product, either by fractional distillation in a highly efficient spinning band column or by preparative gas chromatography. However, I and III in the thermally isomerized product were readily separated and purified by distillation through the spinning band column: I, bp 76–78° (1 mm); III, bp 64–65° (1 mm). The individual isomers, I and III, as well as the distilled 3:2 product (30% I:70% II) were then oxidized with alkaline hydrogen peroxide and the alcohols and diols produced were analyzed by glpc. The results are summarized in Table IV.

Isomer I exhibited the absence of any methyl peak in its pmr spectrum. Moreover, the oxidation of **I** yielded essentially pure 1,4-butanediol in nearly quantitative yield. It follows that the structure of I can only be either **3** or **6**, for these two are the only structures for a compound with two boron atoms and three tetramethylene moieties.

That the structure of I must be that of **3** is indicated by its carbonylation to form 1,1′-tetramethylene-

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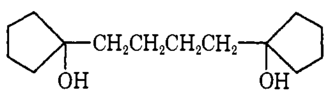
[14] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **88**, 1433 (1966).

Table IV. Oxidation Products from Isomers I, II, and III

Compd	Oxidation products, %			
	1-Butanol	1,3-Butanediol[a,b]	1,4-Butanediol[a]	Total yield, %
I	2	Trace	96	98
III	30	Trace	65	95
30% I + 70% II	Trace	22	68	90
II		(35)[c]	(65)[c]	

[a] Analyzed as the corresponding trimethylsilyl derivatives. [b] The amount of 1,3-butanediol includes a small quantity (≤3%) of 1,2-butanediol. It was necessary for us to acetylate the butanediols in order to observe separate peaks for the 1,2- and 1,3-diols. However, as we were primarily interested in establishing the structures of the major components, we adopted the much simpler silylation technique in the present study. [c] Calculated from the results for the mixture, by correcting for the 30% I present and normalizing.

dicyclopentanol (**8**). Although the yield of **8** is low (20–30% by glpc), the fact that **8** is the only major



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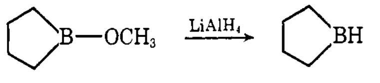
product observable by glpc in the expected region seems to favor **3** over **6**. The carbonylation product was identified by comparing its mp, ir and pmr spectra, and glpc retention time with an authentic sample of **8** prepared with the Grignard reagent from 1,4-dibromobutane and cyclopentanone.

The structural assignment was further confirmed by an independent synthesis of I by an unambiguous procedure. B-Methoxyboracyclopentane[15] was treated with lithium aluminum hydride in the presence of 1,3-butadiene. Apparently, the reactive boracyclopentane (or its dimer **1**) is produced *in situ* and hydroborates the 1,3-butadiene (eq 1 and 2) before it is converted into the inert isomeric form **2**.[16]



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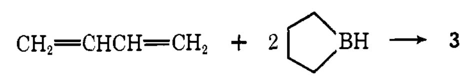

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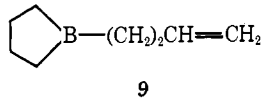
A significant by-product in this reaction was a more volatile species, which we believe to be **9**. This has



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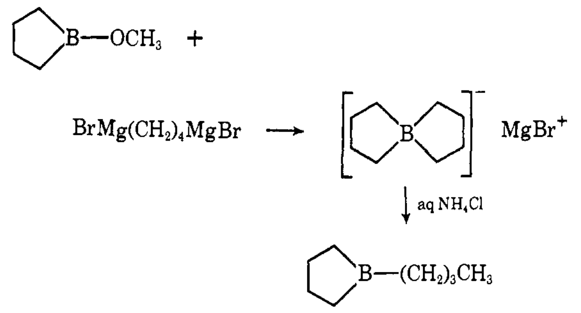
a number of interesting implications which we propose to explore.[16]

An earlier attempt to synthesize I by the reaction of B-methoxyboracyclopentane with the Grignard reagent from 1,4-dibromobutane was less successful. Following treatment of the reaction mixture with aqueous ammonium chloride, the major product indicated by glpc examination proved to be B-(1-butyl)boracyclopentane (**10**). At this point we do not know the reason for the failure. Possibly the di-Grignard reagent undergoes cyclization (eq 3), instead of reacting in the



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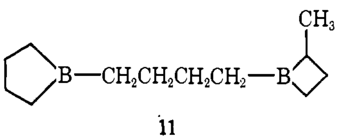
(3)

desired direction. An authentic sample of **10** was prepared in 70% yield from the reaction of B-methoxyboracyclopentane and lithium aluminum hydride in the presence of 1-butene.[16]

Identification of the Compound II. As is shown in Table IV, the oxidation of a 30:70 mixture of I and II yielded 1,3- and 1,4-butanediols in a ratio of 24:76 (normalized from 22:68). Since I yields only 1,4-butanediol on oxidation, it follows that II yielded 1,3- and 1,4-butanediols in a ratio of 24:46, very close to 1:2.

This indicates that II has one of three possible structures, **4**, **7**, or **11**.



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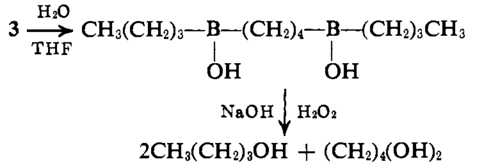
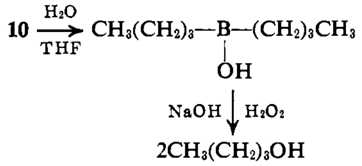
We have recently observed that the boracyclopentane structure is remarkably more sensitive to hydrolysis than are ordinary trialkylboranes. Thus in 24 hr I (or **3**) is converted into an intermediate which is oxidized into 2 mol of 1-butanol and 1 mol of 1,4-butanediol. The reaction presumably takes the indicated course (eq 4).



$$\begin{gathered} 3 \xrightarrow[\text{THF}]{H_2O} CH_3(CH_2)_3—\underset{\substack{|\\ OH}}{B}—(CH_2)_4—\underset{\substack{|\\ OH}}{B}—(CH_2)_3CH_3 \\ \Big\downarrow \text{NaOH}\ H_2O_2 \\ 2CH_3(CH_2)_3OH + (CH_2)_4(OH)_2 \end{gathered} \qquad (4)$$

Applied to B-(1-butyl)boracyclopentane we observed that the peak of the original organoborane disappeared in 3 hr. Whereas oxidation of the original material yielded 95% of 1-butanol and 90% of 1,4-butanediol, the hydrolyzed product corresponded to 182% of 1-butanol and only traces of the diol (eq 5).



$$\begin{gathered} 10 \xrightarrow[\text{THF}]{H_2O} CH_3(CH_2)_3—\underset{\substack{|\\ OH}}{B}—(CH_2)_3CH_3 \\ \Big\downarrow \text{NaOH}\ H_2O_2 \\ 2CH_3(CH_2)_3OH \end{gathered} \qquad (5)$$

This hydrolytic instability of the boracyclopentane system can be used to eliminate **7** and **11** from consideration for the structure of II. The usual 30:70 mixture of I and II was subjected to hydrolysis. At appropriate time intervals aliquots were removed and oxidized. The products were then examined by glpc. The results are summarized in Table V.

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(15) B. M. Mikhailov, L. S. Vasil'ev, and E. N. Safonova, *Dokl. Akad. Nauk SSSR*, **149**, 630 (1962).

(16) A detailed study of this approach to reactive boracyclopentane and its application to make B-substituted boracyclopentanes is under way.

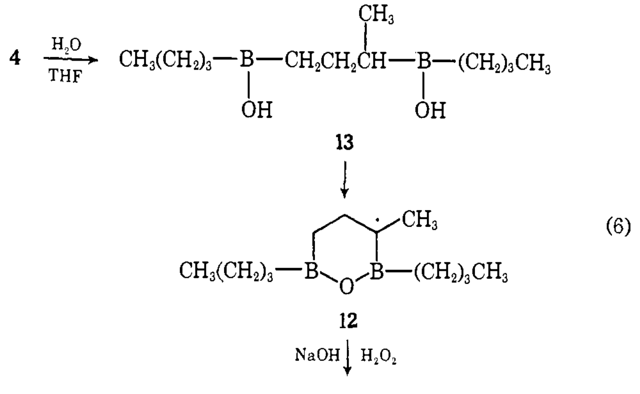
Table V. Hydrolysis of the Distilled 3:2 Product in THF at 25°

	Oxidation products, %			
Time, hr	1-Butanol	1,3-Butanediol[a,b]	1,4-Butanediol[a]	Total yield, %
0	Trace	22	68	90
1	14	23	62	99
2	36	22	40	98
6	49	21	29	99
24	60	23	17	100
48	60	24	16	100
96	60	22	18	100

[a,b] See the corresponding footnotes in Table IV.

As is clear from Table V, the results reveal the following. First, 1,4-butanediol is the only compound which is lost as a result of the hydrolysis. Second, the loss of 1,4-butanediol is compensated by an increase in the formation of 1-butanol. Third, the maximum amount of 1-butanol obtained (60%) is not far from the 66.7% expected for a mixture of **3** and **4**. Fourth, the amount of 1,3-butanediol remained essentially constant. Finally, no butanes were formed. These results are in full agreement with the assignment of **4** to the compound II. On the other hand, it is difficult to explain the results on the basis of **7** or **11**.

When the hydrolysis of the mixture of I and II was followed by glpc, it was observed that a new peak grew as I and II disappeared. Consequently, the hydrolysis mixture was distilled and a clear, pyrophoric liquid, bp 70° (1 mm) was obtained. It was purified by distillation through a spinning band column, bp 46° (0.1 mm). After oxidation it yielded 66% of 1-butanol and 33% of 1,3-butanediol. The mass spectrum showed a strong peak (20%) for the molecular ion at *m/e* = 208. The ratio of *m/e* 208:207:206 was the expected 16:8:1, indicating the presence of two boron atoms. These data coupled with the correct elemental analysis suggest a cyclic borinic anhydride **12** which may either be present in the reaction product, or readily formed from the diborinic acid intermediate **13** (eq 6).



(6)

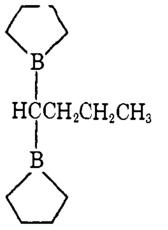
One synthetically useful application of the ready hydrolysis of the boracyclopentane unit is a simple and convenient preparation of 1-butanol-4-d_1. The 3:2 hydroboration product was refluxed with D_2O for several hours. After oxidation, 1-butanol-4-d_1 was isolated in a yield of 40% by preparative glpc. The pmr spectrum indicated the isotopic purity was ~95%.

Identification of the Compound III. One of the highly unexpected results of this investigation is the discovery that the isomer III, present in only trace amounts (if at all[17]) in the initial hydroboration product, becomes the major reaction product as a result of the isomerization procedure. As was mentioned earlier, pure III was readily isolated as a pure substance by distillation of the isomerized product through the spinning band column.

Oxidation of III by alkaline hydrogen peroxide (Table IV) yielded 30% of 1-butanol and 65% of 1,4-butanediol. This production of approximately 33 mol % of 1-butanol from a product with the composition of a 3:2 isomer was initially highly puzzling. However, in attempting to carbonylate the isomer in the presence of ethylene glycol, we noted that the peak corresponding to III disappeared almost immediately following the addition of the glycol.

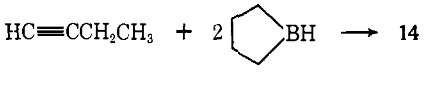
This behavior was reminiscent of that of the dihydroboration products of terminal acetylenes.[18] These 1,1-diborane compounds undergo hydrolysis so rapidly that the oxidation yields the alcohols, instead of the expected aldehydes.

Indeed, when III was treated with an equimolar quantity of methanol, in the presence of a catalytic quantity of sodium methoxide, glpc examination revealed the disappearance of the peak associated with III and the appearance of peaks identified as B-methoxyboracyclopentane and B-(1-butyl)boracyclopentane(**10**). Carbonylation of the reaction mixture gave a 70% yield of 1-(1-butyl)cyclopentanol, confirming the presence of B-(1-butyl)boracyclopentane. On this basis, we assign the structure of 1,1-bis(1-boracyclopentyl)butane (**14**) to III.



14

Finally, the assignment of the structure to III was confirmed by an independent synthesis of III in 53% yield by the reaction of B-methoxyboracyclopentane with lithium aluminum hydride[16] in the presence of 1-butyne (eq 1, 7).



(7)

We believe that the thermal isomerization of **3** and/or **4** into **14** represents a new type of thermal isomerization of the organoboranes derived from dienes and polyenes. If this isomerization proves general, it should provide a convenient route to proceed from many other dienes to the 1,1-diborane derivatives.[19]

Mechanism of Hydroboration of 1,3-Butadiene. Young and Shore report that in solvents in which di-

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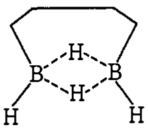
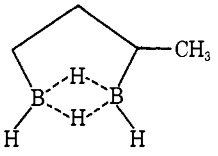
(17) We cannot eliminate the possibility at this time that the minor peak corresponding to III, observed in the glpc analysis of the 3:2 hydroboration product, actually arises as a consequence of the thermal treatment inherent in the analytical procedure.

(18) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 3834 (1961); G. Zweifel and H. Arzoumanian, *ibid.*, **89**, 291 (1967).

(19) A detailed study on this type of thermal isomerization is under way.

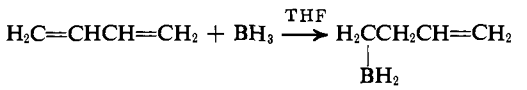
borane is not dissociated, such as di-*n*-butyl ether, the reaction can be directed to give the 1:2 products **15** and **16**.[11] Since they allowed the initial reaction products to remain in contact with a slight excess of diborane for 3–7 days, it is not clear whether these are the initial reaction products or the equilibrated products.


15



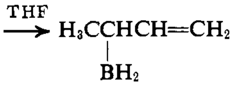
16

In the dissociating solvent, THF, diborane exists as the monomer, BH_3. It is probable that the initial reaction involves an addition to a single double bond of the 1,3-butadiene molecule at both the 1 and 2 positions[8d] (eq 8, 9).



$$H_2C{=}CHCH{=}CH_2 + BH_3 \xrightarrow{THF} \underset{BH_2}{H_2C}CH_2CH{=}CH_2 \qquad (8)$$

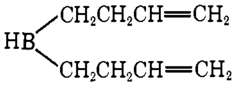
17

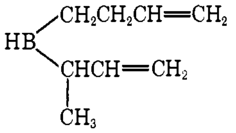


$$\xrightarrow{THF} H_3C\underset{BH_2}{CH}CH{=}CH_2 \qquad (9)$$

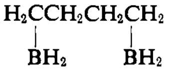
18

Isolated double bonds are more reactive than conjugative double bonds in the hydroboration reaction.[8d] Consequently, the intermediates **17** and **18** should disappear rapidly. However, formation of the 2:1 products such as **19** and **20**, which was proposed by Mikhailov and his coworkers,[8g] does not appear to be the predominant path, because this involves the preferential consumption of a less reactive conjugated double bond in the presence of the more reactive isolated double bonds. From the present results, the dominant reaction of **17** must be cyclization to produce boracyclopentane.[20] Cyclization of **18** to produce a four-membered ring is ruled out, since such a ring was not formed in any of the identified products.


19

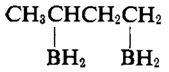

20

Addition of borane to the terminal double bonds of **17** and **18**[21] would give the diborane derivatives, **21** and **22**. These are merely the unbridged forms of **15** and **16**. These molecules could react with 1,3-butadiene through cyclic hydroboration to yield the 3:2 products, **3** and **4**.



$$\underset{BH_2}{H_2C}CH_2CH_2\underset{BH_2}{CH_2}$$

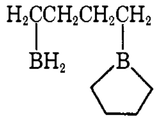
21

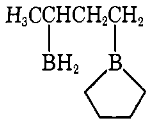


$$CH_3\underset{BH_2}{CH}CH_2\underset{BH_2}{CH_2}$$

22

Alternatively, **17** and **18** could react with boracyclopentane to yield the intermediates **26** and **27**. Cyclic hydroboration of 1,3-butadiene with the free BH_2 groups would again lead to **3** and **4**.


26


27

Then there is the possibility that boracyclopentane will react with 1,3-butadiene to give **3** *via* **9**. This is essentially the synthetic route which we utilized for the preparation of pure **3**.

Conclusions

The present study has established the structures of the initial reaction products produced in the 3:2 stoichiometric reaction of 1,3-butadiene with borane to be **3** and **4**. The mechanism of the reaction has been clarified. The ready thermal isomerization of the initial reaction products **3** and **4** into the new product, 1,1-bis(1-boracyclopentyl)butane (**13**), has been demonstrated. The *in situ* formation of reactive boracyclopentane in the reaction of B-methoxyboracyclopentane with lithium aluminum hydride in the presence of unsaturated hydrocarbons has been demonstrated. This reactive boracyclopentane has been utilized to synthesize authentic samples of B-(1-butyl)boracyclopentane, 1,4- and 1,1-bis(1-boracyclopentyl)butanes. Finally, carbonylation of these intermediates offers a promising synthetic route to tertiary cyclopentanols.

Experimental Section

Materials. The purification of reagents and solvents and the preparation of borane solution in tetrahydrofuran were carried out as described previously.[22] 1,3-Butadiene (Matheson), 1-butene (Phillips), 1-butyne (Farchan), and carbon monoxide (Matheson) were used from the cylinders without further purification.

The organoboranes were always handled under nitrogen with the careful exclusion of oxygen.

Glpc Analyses. Boron-containing compounds were analyzed on SE-30 (5%) columns (column length 1 m and 2 m, injection block and detector temperature 200°, column temperature 50–230° programmed after 3 min at 10–15° per min). Monools were analyzed on a 2-m 5% Carbowax 20M column at 50° (injection block and detector temperature 200°). Diols were analyzed after silylation with adequate quantities of Tri-Sil (Pierce Chemical Co.) on a 2-m 5% SE-30 column using the same conditions specified above for the analysis of boron-containing compounds. 1,1′-Tetramethylene-

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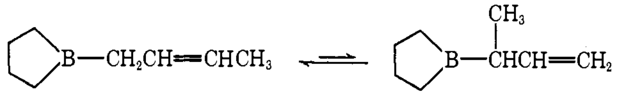
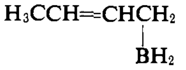
(20) Mikhailov and his coworkers ruled out from consideration the possibility of a cyclization of **17** to boracyclopentane[8g] on the basis of Köster's conclusion that boracyclopentane (as the dimer **1**) was inert to further hydroboration.[8b] However, it is now apparent that this conclusion refers only to the thermally isomerized dimer **2**, and can no longer be used to argue against the formation of boracyclopentane as an intermediate.

(21) B. M. Mikhailov, A. Y. Bezmenov, and L. S. Vasil'ev (*Dokl. Akad. Nauk SSSR*, **167**, 590 (1966)) have examined the hydroboration–oxidation of B-crotylboracyclopentane **23**. Their results appear to require a rapid transformation of the allylic isomer **24** into **23** which is competitive with the rate of hydroboration. On this basis it is necessary to consider the possibility that **18** may undergo isomerization into the crotyl derivative **25**, providing another possible intermediate in the reaction mechanism. This would be the intermediate responsible for the presence of small quantities of the 1,2 isomer in the butanediol product.[8d,g] In the present study, we did not attempt to analyze for the small amounts of this isomer (~3%)[8d,g] produced in the hydroboration–oxidation of 1,3-butadiene.



23 **24**



$$H_3CCH{=}CH\underset{BH_2}{CH_2}$$

25

(22) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

dicyclopentanol was also analyzed without silylation on the SE-30 column under the same conditions.

Hydroboration of 1,3-Butadiene with Borane in a 3:2 Ratio. 1,3-Butadiene (72 g, 1.32 mol) was distilled into tetrahydrofuran (THF) (800 ml) maintained at −10°. The hydroboration was achieved at 0° by the dropwise addition of a THF solution of borane (2.00 *M*, 400 ml, 0.8 mol) in 1-2 hr with efficient stirring. The clear solution after 2 hr of stirring at 25° was allowed to stand for 24 hr. A residual hydride analysis at this point indicated the completion of the reaction. Glpc analysis for the organoboranes showed about 5% of the more volatile species, and the less volatile 3:2 boranes in the following ratio: I (22%): II (56%); III (2%).

Distillation of the 3:2 Hydroboration Product. The 3:2 hydroboration product (100 mmol) was concentrated at 30° and distilled to give 14.6 g (77%) of organoboranes, bp 66–68 (1 mm), lit.[8g] bp 75.5–81° (2 mm). Glpc analysis of the distillate indicated the following organoborane composition: more volatile components (5%); 3:2 organoboranes, I (27%), II (65%), and III (3%).

Attempted Isolation of II from the 3:2 Hydroboration Product. A careful distillation of the 3:2 hydroboration product (15 g) through a Teflon spinning band column (10:1 reflux ratio) gave 9.2 g of a constant boiling fraction during 8-hr distillation period, bp 51° (0.2 mm). Glpc analysis revealed it to be about 90% pure organoborane III. Evidently, thermal isomerization had occurred during the slow distillation process. When the distillation was carried out at a faster rate, the distillate was a mixture of I, II, and III.

Attempts at the separation through preparative glpc were similarly not successful.

Thermal Isomerization of the Organoboranes. The 3:2 hydroboration product was concentrated at 30° and the residue containing the mixture of the isomeric boranes was heated at 140° or 170° in the presence of *n*-dodecane as an internal standard. Aliquots were withdrawn at intervals and analyzed by glpc for the isomeric organoborane composition. The data are presented in Table I and III.

In another experiment, the distillated mixture of the organoboranes was subjected to the identical treatment. The data are presented in Table II.

Isolation of 1,1- and 1,4-Bis(1-boracyclopentyl)butanes (3) and (14). Two hundred millimoles of a thermally treated mixture (170°, 6 hr) which contained **3** and **14** in a ratio of 25:70 was distilled through a short Vigreux column to give 28.8 g (76%) of a distillate in two fractions. The first fraction, bp 74–78° (2 mm), weighed 25.4 g and the second, bp 79–86° (2 mm), 3.4 g. A glpc analysis indicated that no satisfactory separation was accomplished. Two fractions were combined and distilled through a spinning band column. Among four fractions thus obtained, the second fraction, (10.3 g) bp 64–65° (1 mm), and the fourth fraction (6.0 g), bp 76–78° (1 mm), were 98% pure **14** and 95% pure **3**, respectively, by glpc.

Oxidation of the Organoboranes from 1,3-Butadiene. In a typical run, 10 mmol of a 3:2 product from 1,3-butadiene dissolved in 30 ml of THF was oxidized with 10 ml (50% excess) of 3 *N* sodium hydroxide and 10 ml of 30% hydrogen peroxide. In order to minimize protonolysis, 30% hydrogen peroxide was added below 30° immediately after the addition of 3 *N* sodium hydroxide below 10°. The working-up procedure was as described previously.[8d]

Carbonylation of 1,4-Bis(1-boracyclopentyl)butane (3). 1,4-Bis(1-boracyclopentyl)butane (1.8 g, 10 mmol) was dissolved in 50 ml of THF and carbonylated in a 250-ml autoclave using carbon monoxide at 1000 psi and 100° for 15 hr. The autoclave was cooled, opened, and ethylene glycol (3.7 g, 60 mmol) was added to the reaction mixture. It was then heated to 150° for 3 hr in an atmosphere of carbon monoxide (1000 psi). After cooling, the reaction mixture was oxidized with 10 ml (60 mmol) of 6 *N* sodium hydroxide and 10 ml of 30% hydrogen peroxide after addition of 20 ml of ethanol. After heating the mixture at 50° for 1 hr, it was saturated with potassium carbonate and the organic layer extracted with THF, dried over magnesium sulfate, and examined by glpc before and after silylation. A small quantity of the product **8** eluted with benzene and diethyl ether on neutral alumina (Merck) was recrystallized from *n*-hexane, mp 99–100° (lit.[23] mp 98–99°); ir (Nujol) 3370 and 3300 cm^{-1}; pmr (DMSO-d_6) δ 3.7 (exchangeable with D_2O, 2 H), 1.54 and 1.44 (poorly resolved doublet, 24 H) ppm. No depression was observed in the mixture melting point measurement with an authentic sample.

Preparation of 1,1′-Tetramethylenedicyclopentanol. The compound was obtained from 1,4-dibromobutane and cyclopentanone according to the literature procedure,[23] mp 99–100°, (lit.[23] mp 98–99°).

Preparation of B-Methoxyboracyclopentane. The compound was prepared according to the method of Mikhailov and his coworkers,[15] yield 70%, bp 44–46° (90 mm) (lit.[15] bp 42–43° (87 mm)). Borane in THF was used instead of tetra-1-propyldiborane in the identical hydride concentration.

Preparation of 1,4-Bis(1-boracyclopentyl)butane (3) from B-Methoxyboracyclopentane and 1,3-Butadiene. To a 100-ml three-necked flask equipped with a mechanical stirrer, a Dry Ice trap, and a thermometer were added 12 ml of THF, 0.85 g (5 mmol) of *n*-dodecane, 0.54 g (10 mmol) of 1,3-butadiene, and 3.7 ml (5 mmol) of 1.35 *M* lithium aluminum hydride in THF. While stirring at room temperature, 1.96 g (20 mmol) of freshly distilled B-methoxyboracyclopentane was added slowly. An aliquot of the reaction mixture was withdrawn after 3 hr and examined by glpc. Two peaks (90:10) were observed in the 3:2 product region (33%).[16] A mixture of the reaction mixture and purified I gave the same two peaks with the major peak intensified. An unidentified peak which appeared earlier had a peak which is comparable in size to that of I.

Preparation of B-(1-Butyl)boracyclopentane (10) from B-Methoxyboracyclopentane and 1-Butene. The compound was prepared in a manner similar to the preparation of **3** described above, except that 1-butene (10 mmol) was used instead of 1,3-butadiene (70% by glpc).[16]

Attempted Preparation of 1,4-Bis(1-boracyclopentyl)butane (3) from B-Methoxyboracyclopentane and 1,4-Dibromobutane. The Grignard reagent from 1,4-dibromobutane was prepared from 2.16 g (10 mmol) of 1,4-dibromobutane and 0.72 g (30 mmol) of Mg in ether. To 2.5 g (25 mmol) of B-methoxyboracyclopentane in 10 ml of ether was added the above-obtained Grignard reagent. A white precipitate formed immediately. After 30 min an aliquot was treated with aqueous ammonium chloride. The major peak in the glpc analysis of the organic layer was identified as **10** by simultaneous injection with a sample of **10** obtained above. A minor peak (<5%) in the 3:2 product region had the identical retention time as a sample of **3** obtained above.

Hydrolysis of the Distilled 3:2 Hydroboration Product from 1,3-Butadiene. Fifty millimoles of the distilled product (containing the organoboranes I and II in an approximate ratio of 30:70) was treated with water (250 mmol) in 150 ml of THF at 25°. Aliquots were withdrawn at intervals and oxidized in the usual manner. After the standard work-up procedure, glpc analyses were performed. The results are presented in Table V.

Reaction of the 3:2 Hydroboration Product from 1,3-Butadiene with Water. The 3:2 hydroboration product (100 mmol) was refluxed with water (9 g, 0.5 mol) in THF (300 ml) for 24 hr. Evaporation of the solvent followed by distillation of the residue through a 4-in. Vigreux column gave 9.4 g (45%) of a pyrophoric liquid, bp 70° (1 mm). A redistillation through a Teflon spinning band column provided 7.2 g of **12**, bp 46° (0.1 mm); pure by glpc; ir (neat) 1330 cm^{-1}; nmr (neat, TMS) δ 0.73 (m, 16) and 1.21 ppm (m, 10); mass spectrum (75 eV) *m/e* (rel mol ion abundance) 208 (15.7), 207 (8.2), 206 (1).

Anal. Calcd for $C_{12}H_{26}B_2O$: C, 69.35; H, 12.51. Found: C, 69.00; H, 12.65.

Preparation of 1-Butanol-4-d_1. The 3:2 hydroboration product from 1,3-butadiene (50 mmol) in 150 ml of THF was refluxed with D_2O (9 g, 0.5 mol) for 2 hr. A glpc examination indicated the appearance of a new peak and the disappearance of the 3:2 organoborane peaks. The usual alkaline hydrogen peroxide oxidation and the product retrieval procedures gave 3 g (40%) of the title compound, bp 35° (10 mm); n^{20}D 1.3965; pmr (neat, TMS) δ 5.17 (broad, 1), 3.65 (poorly resolved triplet, 2), 1.58 (m, 2), and 1.05 ppm (m, 2); mass spectrum (75 eV) *m/e* (rel intensity), 75 (2), 74 (3), 57 (90), 56 (53), 44 (60), 43 (40), 42 (49), and 31 (100).

Reaction of B-(1-Butyl)boracyclopentane with Water. B-(1-Butyl)boracyclopentane (1.24 g, 10 mmol) was dissolved in 16 ml of THF, containing 0.565 g (2.5 mmol) of *n*-hexadecane as an internal standard, and refluxed. At this temperature, 1.8 g (100 mmol) of water was added. The reaction was followed by glpc. After 3 hr the original peak disappeared almost entirely. The reaction mixture was cooled and oxidized as described above.

Reaction of 1,1-Bis(1-boracyclopentyl)butane (14) with Absolute Methanol. 1,1-Bis(1-boracyclopentyl)butane (3.8 g, 20 mmol) dissolved in 20 ml of THF was treated with 0.8 ml (20 mmol) of methanol at 25° in the presence of 200 μl (1 mmol) of 5 *M* sodium methoxide in methanol. After 1 hr, an aliquot was examined by

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(23) A. S. Bailey, D. G. M. Diaper, and M. V. H. Schwemin, *Can. J. Chem.*, **39**, 1147 (1961).

glpc. The original peak for **14** disappeared almost completely and two new peaks were identified as B-methoxyboracyclopentane (98%) and B-(1-butyl)boracyclopentane (100%). The carbonylation–oxidation of the reaction mixture was carried out as described above for the carbonylation of **3**.

Preparation of 1-(1-Butyl)cyclopentanol from Cyclopentanone. Cyclopentanone (4.2 g, 50 mmol) was added to 50 ml (60 mmol) of 1.2 *N* *n*-butyllithium at room temperature. After working up with aqueous ammonium chloride, distillation afforded 4.6 g (65%) of **19**, bp 110–112° (43 mm), $n^{20}\text{D}$ 1.4537 (lit.[24] bp 193° (760 mm), $n^{25}\text{D}$ 1.4535).

Preparation of 1,1-Bis(1-boracyclopentyl)butane (14) from B-Methoxyboracyclopentane and 1-Butyne. The compound was prepared in a manner similar to the preparation of **3** described above, except that 1-butyne was used instead of 1,3-butadiene; yield by glpc 53%.[16] The peak size for the product increased when III was added to the reaction mixture without showing any sign of splitting.

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[24] C. R. McLellan and W. R. Edwards, Jr., *J. Amer. Chem. Soc.*, **66**, 409 (1944).

Organoboranes. X. A Fast Reaction of Organoboranes with Mercuric Acetate. A Convenient Procedure for the Conversion of Terminal Olefins into Alkylmercuric Salts *via* Hydroboration–Mercuration

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Contribution from Richard B. Wetherill Laboratory,
Purdue University, Lafayette, Indiana 47907. *Received September 20, 1969*

Abstract: Organoboranes derived from terminal olefins *via* hydroboration undergo a rapid quantitative reaction with mercuric acetate at room temperature to give the corresponding alkylmercuric acetate. The fact that secondary alkyl groups do not react under these mild reaction conditions makes possible the use of dicyclohexylborane for selective hydroboration–mercuration. Functional groups are readily accommodated in this reaction. The alkylmercuric acetates are easily converted into the corresponding alkylmercuric halides to give greater than 90% isolated yields. This development makes a whole range of alkylmercuric salts and dialkylmercurials readily available.

Mercury(II) salts have been shown to react with aryl and alkyl boronic acids,[2a,b] diaryl borinic acids,[2c] and triaryl- and trialkylboranes[2d,e] to yield a variety of organomercurials.

Until recently these reactions proved to be of no practical synthetic utility. Prior to 1956, these organoboron compounds were generally prepared by the reaction of the appropriate Grignard reagent with a boron halide or ester.[3] Since the organomercurials could be obtained directly through reaction of a Grignard reagent with a mercuric halide, there was no advantage to be gained by going through the organoboron intermediate[4,5] (eq 1).

$$\begin{aligned} \text{RMgX} + \text{HgX}_2 &\longrightarrow \text{RHgX} + \text{MgX}_2 \\ 2\text{RMgX} + \text{HgX}_2 &\longrightarrow \text{R}_2\text{Hg} + 2\text{MgX}_2 \end{aligned} \tag{1}$$

In 1956 a wide variety of trialkylboranes became readily available through the hydroboration of olefins.[6] Of particular significance is the fact that many functional groups are readily accommodated in this reaction.[7] Thus, through hydroboration–mercuration, the organic chemist has for the first time a convenient route to a variety of organomercurials not previously available.

Honeycutt and Riddle established that the trialkylboranes could be utilized for the synthesis of dialkylmercurials.[2e] However, it is not clear from their work whether only two or all three alkyl groups can be transferred from boron to mercury, nor was the scope of the reaction determined. We were interested in extending this reaction to the synthesis of alkylmercuric salts and undertook a detailed study of this possibility.

Results

Hydroboration–Mercuration of Representative Olefins. 1-Butene, 2-butene, and isobutylene were selected as typical representatives of terminal and internal olefins. These olefins were converted into the corresponding trialkylboranes (eq 2) and treated with 3 equiv of mercuric acetate (eq 3). Aliquots were removed at various

$$3\text{RCH}{=}\text{CH}_2 + \text{BH}_3 \xrightarrow{\text{THF}} (\text{RCH}_2\text{CH}_2)_3\text{B} \tag{2}$$

$$(\text{RCH}_2\text{CH}_2)_3\text{B} + 3\text{Hg(OAc)}_2 \xrightarrow{\text{THF}} 3\text{RCH}_2\text{CH}_2\text{HgOAc} + \text{B(OAc)}_3 \tag{3}$$

times and the alkylmercuric acetate reduced with alkaline sodium borohydride (eq 4). Oxidation of the

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