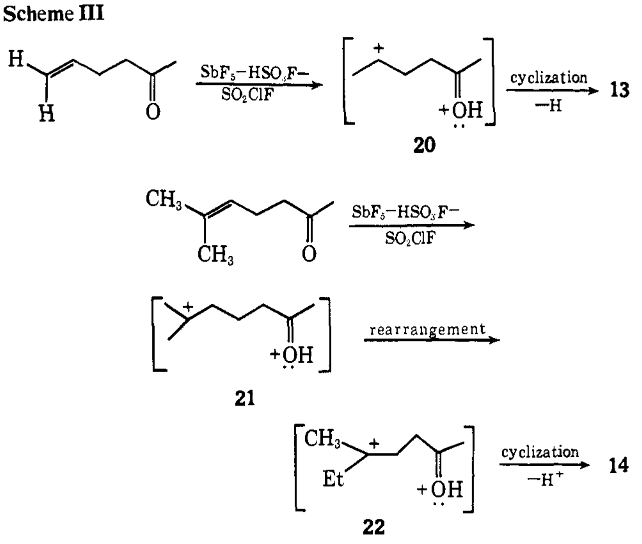
Scheme III



expected to give ion **21**. Dications are generally stable when two or more methylene carbons separate the charged carbons.[20] Dication **21** did not cyclize to form the cyclic six-membered oxonium ion, but rearranged to dication **22**. Ion **22** is considerably more stable than ion **21** and cyclized to form the five-membered ring oxonium ion **14**. Similar behaviors are found in the preparation of cyclic halonium ions.[21] To our knowledge, no six-membered ring halonium ions have been observed.

Experimental Section

Materials. All unsaturated aldehydes and ketones used were commercially available except for Δ^3-cyclopentenone, which was prepared according to Hess and Brown.[22]

Nmr Spectra. A Varian Model A56/60A nmr spectrometer was used to obtain pmr and fmr spectra. A Varian Model HA-100 nmr spectrometer was used to obtain the indor carbon-13 nmr spectra[23] and for the proton–proton decoupling experiments. Both instruments were equipped with variable-temperature probes.

Protonation of α,β-Unsaturated Aldehydes and Ketones. Samples were prepared by dissolving ~1.5 ml of 1:1 (mol/mol) FSO$_3$H–SbF$_5$ in an equal volume of SO$_2$ClF at $-80°$. The α,β-unsaturated aldehyde or ketone (approximately 0.3 ml) was dissolved in about 1 ml of SO$_2$ClF at $-80°$ and slowly added to the acid solution with vigorous stirring.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(20) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

(21) G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. Brinich, *ibid.*, **94**, 1164 (1972).

(22) H. M. Hess and J. C. Brown, *J. Org. Chem.*, **32**, 4138 (1967).

(23) For details, see G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

Hydroboration. XXXI. The Cyclic Hydroboration of Dienes with Borane in Tetrahydrofuran in the Molar Ratio of 1:1

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Contribution from the Richard B. Wetherill Laboratory,
Purdue University, Lafayette, Indiana 47907. *Received July 6, 1971*

Abstract: Glpc conditions for determining the exact quantities of *B*-methoxyboracyclanes are established. The hydroboration of a representative series of dienes with borane in the molar ratio of 1:1 with the diene-to-borane mode of addition is examined by (1) active hydride analyses, (2) ir, (3) glpc analyses of the methanolysis products, and (4) glpc analyses of the oxidation products. The total amount and product distribution of monomeric cyclic boranes formed under the ordinary hydroboration conditions are determined. The methoxy derivatives of the monomeric cyclic boranes are isolated and identified whenever possible. A tentative generalization which would permit one to understand and predict the course of hydroboration of acyclic dienes is made.

In spite of the fact that a number of publications dealing with the hydroboration of dienes and polyenes have appeared, little effort had been made until recently to control the hydroboration of dienes with borane in the molar ratio of 1:1 in order to produce the corresponding boracyclanes.[2,3] In our recent study[4] we described a simple diagnostic test for the formation of cyclic organoboranes *via* intramolecular cyclic hydroboration. Unfortunately, the test does not appear valid when borane itself (or diborane) is used.

In our earlier study[5] on the hydroboration of monoolefins with excess borane, the hydride-containing species formed were first converted to the corresponding *B*-methoxyboranes by methanolysis, and the *B*-methoxyboranes were distilled for quantitative determination. Although the method appeared reliable, the distillation step was quite tedious.

We have recently demonstrated the feasibility of a much more convenient glpc analysis of *B*-dimethoxy-

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

(3) (a) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968); (b) H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971); (c) *ibid.*, **28**, C1 (1971).

(4) H. C. Brown and C. D. Pfaffenberger, *J. Amer. Chem. Soc.*, **89**, 5475 (1967); for experimental detail, see C. D. Pfaffenberger, Ph.D. Thesis, Purdue University, 1967.

(5) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Amer. Chem. Soc.*, **82**, 4703 (1960).

alkylboranes and *B*-methoxydialkylboranes[6] (but not mono- and dialkylboranes) and have accordingly decided to apply this analytical method to the products of hydroboration of selected dienes after methanolysis.

Results and Discussion

Methanolysis–Glpc Technique for the Determination of Boracyclanes. Methanolysis of hydride-containing boranes, in most cases, is a rapid, quantitative reaction,[5,7] and the reaction itself involves little or no disproportionation or isomerization of borane species.[8]

Glpc examination of trialkylboranes has been successfully utilized as a powerful analytical tool.[9–11] We have learned that *B*-methoxyboranes can also be analyzed on a normal glpc instrument. The precautions necessary for the glpc analysis of trialkylboranes[11] must also be taken in the glpc analysis of *B*-methoxyboranes. Such precautions include (1) selection of inert liquid-phase materials, such as SE-30, and solid support materials, such as Chromosorb W; (2) rigorous exclusion of oxygen and any species containing active B–H bonds; and (3) use of low block temperatures (~50–100°). Unlike most trialkylboranes, *B*-methoxyboranes are generally highly susceptible to hydrolysis and solvolysis. Therefore, moisture and protic substances must also be rigorously excluded. By taking these precautions, reproducible results are obtainable in the analyses of various *B*-methoxyboranes. Moreover, we have been able to suppress almost entirely the undesirable conversion of the polymeric *B*-methoxyborane derived from 1,3-butadiene and borane to *B*-methoxyborolane.[11] We have not so far observed any sign of extensive isomerization of *B*-methoxyboranes under these glpc conditions. It thus appears that under these conditions the exact quantities of *B*-methoxyboracyclanes present in the methanolyzed hydroboration mixtures derived from dienes and borane can be determined without the complication of extensive disproportionation or isomerization.

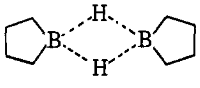
General Method of Hydroboration of Dienes with Borane in Tetrahydrofuran. In the present study each diene was hydroborated by its addition to an equimolar quantity of borane in tetrahydrofuran (THF) at 0°. At appropriate times, the reaction mixture was examined by (1) active hydride analysis, (2) ir, (3) glpc analyses of the methanolysis products, and (4) glpc analyses of the oxidation products. The experimental results of glpc examination of the methanolyzed hydroboration mixtures are summarized in Table I. In the following discussion we attempt to clarify the course of the hydroboration of each diene in more detail.

Table I. Glpc Examination of the Methanolyzed Hydroboration Mixtures Obtained by the Hydroboration of Dienes with Borane in THF in the Molar Ratio of 1:1[a]

Diene	Total quantity of *B*-methoxy-bora-cyclanes,[b] %	Product distribution,[b] %	
1,3-Butadiene	Trace[c]		
1,4-Pentadiene	30[c]	*B*-Methoxyborinane	83
		B-Methoxy-2-methylborolane	17
1,5-Hexadiene	78[c]	*B*-Methoxyborepane	70
		B-Methoxy-2-methylborinane	30
1,7-Octadiene	0[d]		
1,4-Cyclohexadiene	0[d]		
1,5-Cyclooctadiene	91[c]	*B*-Methoxy-9-bora-bicyclo[3.3.1]nonane	72[e]
		B-Methoxy-9-borabicyclo-[4.2.1]nonane	28[e]
4-Vinylcyclohexene	18[d]	Three poorly resolved peaks[f]	
D-(+)-Limonene	31[d]	*B*-Methoxy-4,8-dimethyl-2-borabicyclo[3.3.1]nonane[g]	90
		Unidentified compounds	10

[a] Hydroboration was carried out at 0° by the addition of a diene to borane in THF. After stirring for ~1 hr at 0°, the temperature of the hydroboration mixture was allowed to rise to 25°. [b] By glpc. See the appropriate footnotes in Tables II–IV for detailed glpc conditions. [c] Value at 24 hr. [d] Value at 48 hr. [e] By glpc analysis of the diacetoxy derivatives of the diols obtained by oxidation of the methanolyzed hydroboration mixture. [f] Products not fully identified. However, the major component appears to be *B*-methoxy-2-borabicyclo[3.2.2]nonane based on the glpc analysis of the oxidation products. [g] An approximately 1:1 mixture of cis and trans isomers.

Cyclic Hydroboration of Straight-Chain Dienes. (a) 1,3-Butadiene and 1,4-Pentadiene. The hydroboration of 1,3-butadiene under various conditions does not produce bisborolane (1). This was interpreted in terms of a high reactivity of the borolane ring toward the action of borane (eq 1). The borolane ring proved to be susceptible even to the action of 2 with the terminal B–H bond. This reaction leads to the formation of a polymer, 3.[6b] This polymer, in turn, could be transformed into a more stable compound, 1,6-diboracyclodecane (4) by heating.[12]



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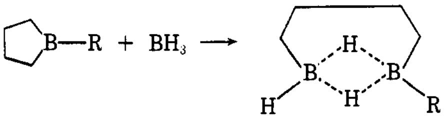
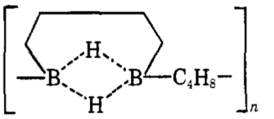


2

R= H or $-C_4H_8-$



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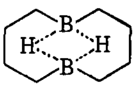

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Little has been reported on the hydroboration of 1,4-pentadiene with borane (or diborane).[1,13] Our earlier study[13] established that the hydroboration of 1,4-pentadiene with borane in the 3:2 molar ratio yields, after oxidation, 1,5- and 1,4-pentanediols in the ratio of 38:62. A similar ratio of 45:55 has been observed in the hydroboration in the 1:1 molar ratio.

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(6) (a) H. C. Brown, E. Negishi, and P. L. Burke, *J. Amer. Chem. Soc.*, **92**, 6649 (1970); (b) *ibid.*, **93**, 3400 (1971). See also ref 3b and 3c.

(7) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, p 175.

(8) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 206 (1962).

(9) G. Schomburg, R. Köster, and D. Henneberg, *Z. Anal. Chem.*, **170**, 285 (1959).

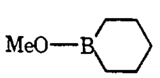
(10) H. C. Brown, E. Negishi, and S. K. Gupta, *J. Amer. Chem. Soc.*, **92**, 2460 (1970).

(11) H. C. Brown and E. Negishi, *ibid.*, **94**, 3567 (1972).

(12) E. Breuer and H. C. Brown, *ibid.*, **91**, 4164 (1969).

(13) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

As shown in Table I, glpc examination of the methanolyzed hydroboration mixture obtained by the hydroboration of 1,4-pentadiene with borane in the ratio of 1:1 at 24 hr revealed the formation of *B*-methoxyborinane (**5**) and *B*-methoxy-2-methylborolane (**6**) in 25 and 5% yields, respectively. Since the corresponding values at 0 hr were 20 and 5%, only a minor change was observed during this period. It is clear that the 1-methyltetramethylene moiety which amounts to ~55% of the total is largely incorporated in some species other than **7a**. Therefore, it is not unreasonable to account for the result in terms of opening of the borolane ring analogous to that observed in the case of 1,3-butadiene (eq 2).



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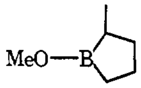

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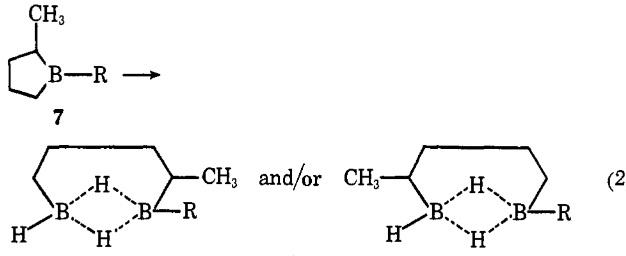

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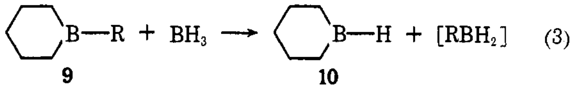
a; R = H; **b**; R = $-C_5H_{10}-$

In contrast to the borolane ring, the borinane ring is not opened by borane[6a] (eq 3). The 25% yield of *B*-methoxyborinane (**5**) (Table I) corresponds to a yield of 56% based on the pentamethylene moiety. Therefore, the result is in good agreement with the finding mentioned above.



9 **10**

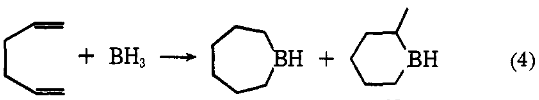
(b) 1,5-Hexadiene. The hydroboration of 1,5-hexadiene with borane (or diborane) has been investigated by several workers.[13,14] However, there has not been any attempt to synthesize borepane (**11**) by the hydroboration of 1,5-hexadiene with borane in the molar ratio of 1:1.

Table II. Cyclic Hydroboration of 1,5-Hexadiene with Borane in THF in the 1:1 Molar Ratio with the Diene-to-Borane Mode of Addition (100-mmol Scale)

Time of stirring,[a] hr	Residual hydride,[b] mmol	*B*-Methoxy-boracyclane,[c] mmol **11** + **12** (**11**/**12**)[d]	Hexanediol,[e] mmol 1,6-	1,5-	2,5-	Total
0 (0°)	104	15 (~40/60)	69	20	4	93
1 (0°)	102	29 (~40/60)				
3	98	70 (~70/30)	69	19	6	94
6	100	78 (~70/30)				
24[f]	95	75 (~70/30)	71	20	6	97
0 (−25°)	105	7 (~50/50)	70	20	4	94

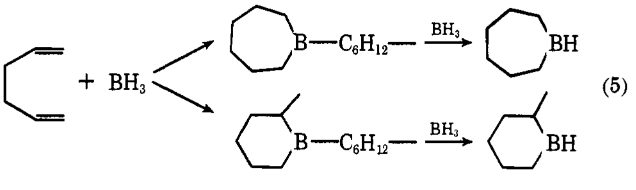
[a] At 25° unless otherwise stated. [b] By hydrolysis. [c] By glpc on a 2-ft SE-30 column using a block temperature of ~100°. [d] Due to poor resolution only approximate figures were obtainable. [e] By glpc examination of the oxidized products on a 6-ft SE-30 column after silylation. [f] A slight precipitate formation was observed.

As shown in Table I, the cyclic hydroboration of 1,5-hexadiene provided a mixture of borepane[15] (**11**) and 2-methylborinane[15] (**12**) in high yield (eq 4).

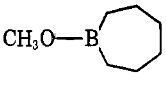


11 (70:30) **12**

However, as is clear from Table II, a high yield of the mixture of **11** and **12** was realized only after the hydroboration mixture had been stirred for at least 3 hr. Thus, the combined yield of **11** and **12** immediately after the addition of 1,5-hexadiene was only 15% (or 7% at −25°) in spite of the fact that the hydroboration of 1,5-hexadiene was essentially complete as shown by the active hydride and diol analyses. The ir spectrum of the hydroboration mixture at this time revealed the presence of a band of considerable intensity at 2400 cm^{-1} for borane in THF. This band diminished with time and became almost negligible after 24 hr. On the other hand, a band at 1560 cm^{-1} grew to one of strong intensity. These results suggested that, even when 1,5-hexadiene was added to borane, the hydroboration did not stop at the dialkylborane stage but proceeded largely to the trialkylborane stage with the excess of borane unreacted. The trialkylborane intermediate then slowly reacted with the remaining borane to form borepane (**11**) and 2-methylborinane (**12**) as shown by eq 5.



By distillation of the methanolysis product at 6 hr, a mixture of *B*-methoxyboracyclanes (**13**:**14**:**15** = 73:20:7), bp 57–64° (17 mm), was obtained in 85% yield. Undoubtedly, the distillation must have caused the breakdown of some polymeric species which is reflected by the formation of **15** as well as by the increase in the ratio of **13** to **14**.



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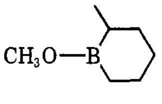

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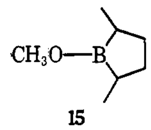

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(c) 1,7-Octadiene. Glpc examination of the methanolyzed hydroboration mixture derived from 1,7-octadiene revealed the essential absence of any volatile compounds. This suggests that the hydroboration of 1,7-octadiene under the hydroboration conditions employed must be polymeric. Unlike the hydroboration of 1,3-butadiene with borane in the molar ratio of 1:1, which resulted in the formation of a clear solution, the hydroboration of 1,7-octadiene resulted in an

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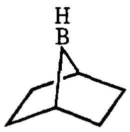
(14) (a) K. A. Saegebarth, *ibid.*, **82**, 2081 (1960); (b) B. M. Mikhailov, L. S. Vasil'ev, and E. Safonova, *Dokl. Acad. Nauk SSSR*, **147**, 630 (1962); (c) L. I. Zakharkin and A. I. Kovredov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 357 (1962); (d) L. I. Zakharkin and A. I. Kovredov, *ibid.*, 106 (1969).

(15) it is certain that 11 and 12 exist as dimers (presence of a strong band at 1560 cm^{-1} in the ir spectrum). However, since there are three possible combinations for the bisboracyclanes consisting of 11 and/or 12, it is more convenient to discuss them in terms of the monomeric structures.

extensive formation of a gelatinous substance, suggesting the formation of a polymer with a three-dimensional network.

Hydroboration of Cyclic Dienes. (a) 1,4-Cyclohexadiene. The hydroboration mixture derived from 1,4-cyclohexadiene with borane in THF in the molar ratio of 1:1 was entirely gelatinous. This gelatinous feature remained unchanged for at least 48 hr at 25°. On methanolysis, a nongelatinous layer was partially formed. Glpc examination of the nongelatinous layer revealed the absence of any peaks in the general region expected for the methoxy derivatives of **16** and **17**.



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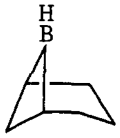
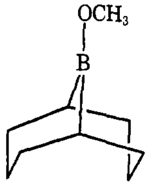


17

Clearly, the hydroboration product must be highly polymeric. At present, it is not clear whether **16** and/or **17** are at all formed as unstable intermediates and subsequently cleaved by borane. However, oxidation of the hydroboration mixture derived from 1,4-cyclohexadiene and borane in the molar ratio of 1:1 provided a mixture of *cis*-1,3-, *cis*-1,4-, *trans*-1,3-, and *trans*-1,4-cyclohexanediols in the ratio of 20:28:22:30. Therefore, the extent of intramolecular cyclization cannot exceed 48%.

(b) 1,5-Cyclooctadiene. In marked contrast to the case of 1,4-cyclohexadiene, glpc examination of the hydroboration mixture derived from 1,5-cyclooctadiene and borane in the ratio of 1:1 with the diene-to-borane mode of addition revealed the presence of *B*-methoxy-9-borabicyclo[3.3.1]nonane (**18**) and *B*-methoxy-9-borabicyclo[4.2.1]nonane (**19**) in an overall yield of 91%. Although the glpc analysis did not permit us to determine the exact ratio of the two products, the oxidation products consisted of a mixture of *cis*-1,5- and *cis*-1,4-cyclooctanediols in the ratio of 70:30.



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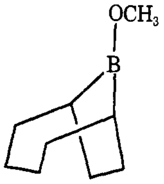

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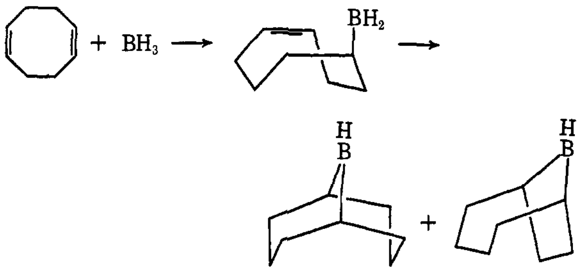
The experimental results are summarized in Table III.

Table III. Cyclic Hydroboration of 1,5-Cyclooctadiene with Borane in THF in the Molar Ratio of 1:1 with the Diene-to-Borane Mode of Addition (100-mmol Scale)

Time of stirring,[a] hr	Residual hydride,[b] mmol	*B*-Methoxy-bora-cyclane[c] **18** + **19**, mmol	Cyclooctanediol,[d] mmol *cis*-1,5-	*cis*-1,4-	Total
0 at 0°	95	90	64	28	92
3	86	91	67	29	96
24	98	91	68	26	94

[a] At 25° unless otherwise stated. [b] By methanolysis. [c] By glpc on a 3-ft column packed with Apiezon L on Chromosorb W using a block temperature of 70–90°. [d] The total yield of diols was determined by glpc examination of the oxidation products on an SE-30 column after silylation. The ratio of diol products was determined by glpc examination of the corresponding diacetates.

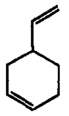
Unlike the case of 1,5-hexadiene (*vide supra*), a very high yield of *B*-methoxyboracyclanes (90%) was realized immediately after completing the addition of 1,5-cyclooctadiene, suggesting that the hydroboration was highly cyclic and that the boracyclane products did not compete favorably with borane for 1,5-cyclooctadiene. This conclusion was also supported by the results of glpc analysis of the oxidation products. The oxidation of the hydroboration mixture produced a mixture of *cis*-1,5- and *cis*-1,4-cyclooctanediols in 92% yield. No more than trace quantities of other diol products were observed. This result is most readily explained in terms of a simple cyclic hydroboration (eq 6).



20 **21**

(6)

Cyclic Hydroboration of "Mixed" Dienes. (a) 4-Vinylcyclohexene. It is not unreasonable to anticipate that the cyclic hydroboration of 4-vinylcyclohexene (**22**) would produce 2-borabicyclo[3.3.1]nonane (**23**) in high yield. Contrary to our expectation, however, the yield of bicyclic boranes realized under ordinary hydroboration conditions turned out to be rather low. Thus, the combined yield of monomeric *B*-methoxyboracyclanes immediately after completing the addition of 4-vinylcyclohexene was merely 12%. Even after stirring for 48 hr at 25° only a slight increase in the overall yield, 18%, was observed (Table IV). There were present at 3 hr at least three peaks in the general region expected for the monomeric *B*-methoxyboracy-



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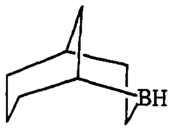

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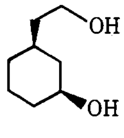
Table IV. Cyclic Hydroboration of 4-Vinylcyclohexene and D-(+)-Limonene with Borane in THF in the Molar Ratio of 1:1 with the Diene-to-Borane Mode of Addition (100-mmol Scale)

Time of stirring,[a] hr	4-Vinylcyclohexene Residual hydride,[b] mmol	*B*-Methoxy-boracy-clanes,[c,d] mmol	D-(+)-Limonene Residual hydride,[b] mmol	*B*-Methoxy-boracy-clanes,[c,e] mmol
0 (0°)	83	12	85	25
1 (0°)	87	12	85	26
3	87	13	89	25
24	85	15	87	28
48	82	18		31

[a] At 25° unless otherwise stated. [b] By methanolysis. [c] By glpc on a 3-ft column packed with Apiezon L on Chromosorb W using block temperature of 70–90°. [d] At least three poorly resolved peaks were present in the general region expected for the monomeric *B*-methoxyboracyclanes. [e] At least four poorly resolved peaks were present in the general region expected for the monomeric *B*-methoxyboracyclanes.

clanes. However, determination of the amount of each isomer was not possible because of the poor resolution of the peaks. Oxidation of the hydroboration mixture at 3 hr produced a mixture of several diols. Four identified diols, **24**, **25**, **26**, and **27**, amounted to 10, 38, 13, and 16%, respectively, of the total and a few other diols possessing two secondary hydroxyl groups accounted for the balance (23%). Therefore, it appears that the major component of the kinetically controlled cyclic product is 2-borabicyclo[3.2.2]nonane (**28**) rather than **23**.



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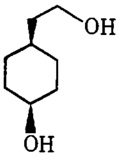

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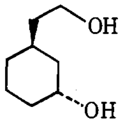

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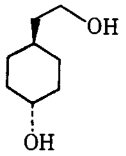

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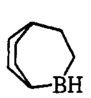

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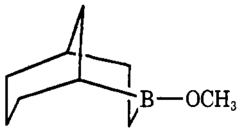

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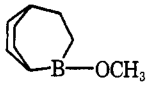

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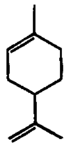
On distillation of the methanolyzed hydroboration product (at 48 hr), a mixture of *B*-methoxyboracyclanes, bp 30–32° (0.2 mm), was obtained in 56% overall yield. Glpc examination of the oxidation products derived from the distillate indicated that **24** accounted for 64% of the total quantity of diols. Only a trace quantity of **25** was present, indicating that an extensive isomerization had taken place during the distillation.[16] Clearly, *B*-methoxy-2-borabicyclo[3.3.1]nonane (**29**) is thermodynamically more stable than **30**.

(b) D-(+)-Limonene. The cyclic hydroboration of D-(+)-limonene (**35**) did not produce monomeric bicyclic boranes in high yield either. The experimental results are summarized in Table IV. At 48 hr glpc examination of the methanolyzed hydroboration mixture revealed the presence of two partially resolved major peaks of comparable sizes (~90%) along with a few rather minor peaks (~10%) with shorter retention times. The overall yield of these *B*-methoxyboracyclanes was 31%. Since the oxidation product of the 48-hr old hydroboration mixture consisted largely (~85%) of **36**, the two partially resolved peaks must correspond to the methoxy derivatives of *cis*- and *trans*-4,8-dimethyl-2-borabicyclo[3.3.1]nonanes (**38** and **39**).



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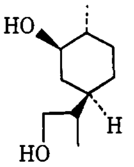

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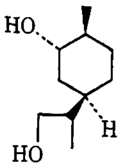

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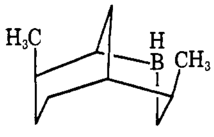

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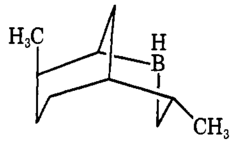
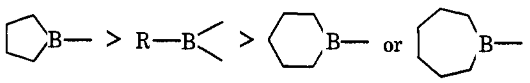


39

On distillation of the methonolyzed hydroboration mixture (at 48 hr), an approximately 1:1 mixture of the methoxy derivatives of **38** and **39**, bp 39–44° (0.15–0.2 mm), contaminated with minor amounts of isomeric compounds was obtained in 74% yield. On oxidation of the distillate 94% pure **36** was obtained in 85% yield. Several other peaks were present in trace quantities.

Conclusions

The hydroboration of acyclic dienes with borane in the molar ratio of 1:1 proceeds in many cases through an extensive formation of fully substituted trialkylboranes even when the dienes are added to borane in THF. The fully substituted boranes derived from 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene appear to be largely mixtures of dumbbell compounds with five-, six-, and/or seven-membered ring moieties. These dumbbell compounds are susceptible to the action of the unreacted borane. The fate of a dumbbell compound is predicted by the following generalization. The order of reactivity toward borane is



R = alkyl or alkylene

Thus, a five-membered ring does not in general survive the reaction with borane and is opened to form a 1,2-tetramethylenediborane derivative (eq 1). On the other hand, a six- or seven-membered ring appears stable toward the action of borane, and the corresponding boracyclane is obtainable in high yield. Moreover, a chain moiety capable of forming a six- or seven-membered ring evidently has a tendency to cyclize during the exchange reaction with borane.

We have not so far obtained any evidence for the formation of a four-, eight-, or nine-membered ring. This suggests that the formation of such a ring under ordinary hydroboration conditions may be unfavorable.

The generalization above for the hydroboration of simple acyclic dienes does not appear applicable to predict the course of hydroboration of dienes containing cycloolefin moieties. Thus, the hydroboration of 1,5-cyclooctadiene appears to be essentially a simple cyclization, at least when the diene is added to an equimolar quantity of borane. The exchange reaction of trialkylboranes and borane does not appear to come into play to any significant extent. The extent of intramolecular cyclization in the hydroboration of 1,4-cyclohexadiene appears rather low. The yield of monomeric bicyclic boranes obtained by the hydroboration of 4-vinylcyclohexene or D-(+)-limonene is rather low. However, the corresponding bicyclic *B*-methoxyboranes

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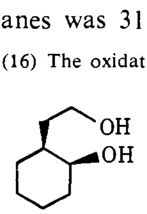
[16] The oxidation product also contained 5 and 1% of 31 and 32,



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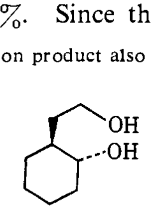

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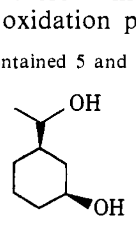

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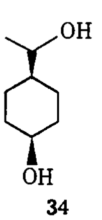

34

respectively. Two other diols possessing two secondary hydroxyl groups accounted for 11 and 17% of the total. They presumably correspond to 33 and 34, since these two are products from the oxidation of the distillate.

can be obtained by the distillation of the methanolyzed hydroboration mixture.

Experimental Section

Materials. The preparation of borane solutions in tetrahydrofuran was carried out as described previously.[17] The dienes were obtained from commercial sources. In some cases they were distilled from lithium aluminum hydride. *n*-Alkanes (Phillips) employed as internal standards were used as supplied. The organoboranes were always handled under nitrogen.

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

General Procedures for the Hydroboration of Dienes and for the Examinations of the Hydroboration Mixtures. (a) Hydroboration of Dienes. A one-necked, 300-ml, round-bottomed flask equipped with a magnetic stirring bar, a condenser (the tip of which is connected to a mercury bubbler), and a septum inlet was flushed with nitrogen. The flask was cooled to 0° and charged with 100 ml (100 mmol) of 1.0 *M* borane in tetrahydrofuran. A diene solution (100 ml, 100 mmol of diene) was added by means of a syringe pump. After stirring for 1 hr at 0° following the completion of the addition, the reaction mixture was allowed to warm to 25°.

(b) Methanolysis and Glpc Examination of the Methanolysis Products. At appropriate time intervals, 10-ml (5 mmol) samples of the reaction mixture were withdrawn and placed in a 25-ml flask equipped with a septum inlet and a magnetic stirring bar and connected to a gas meter. Absolute methanol (0.3 ml, 7.5 mmol) was added to the sample and the hydrogen evolved measured.

The methanolyzed samples were analyzed by glpc for monomeric cyclic *B*-methoxyboranes on 2- or 3-ft columns of 10% SE-30 or Apiezon L on Chromosorb W, AW-DMCS solid support taking the precautions mentioned in the previous section. The glpc response ratios of the *B*-methoxyboracyclanes were determined using the distilled products. The same response ratio was assumed for the isomeric products. The injection block temperature was maintained at 50–100° to minimize possible disproportionation and isomerization.

(c) Oxidation of Organoboranes. Oxidation of organoboranes was carried out as described previously.[17]

(d) Glpc Examination of the Oxidation Products. A sample of the oxidation products were treated with Tri-Sil (Pierce Chemical Co.) to convert the alcohols to the corresponding trimethylsilyl ethers and analyzed on a 6-ft column of 10% SE-30 on Chromosorb W. In the cases of the cyclic and "mixed" dienes, determination of the distribution of diol isomers required conversion of the diols to the corresponding diacetates. Glpc examination of the diacetates was carried out on a 150 ft × 0.01 in. capillary column of polyphenyl ether (PPE). The diacetates were prepared by heating the crude alcohol products (5 mmol), freed of the solvent, with 5 ml (~50 mmol) of acetic anhydride and a catalytic amount of pyridine (50 μl) at ~100° for 3–4 hr. The reaction mixture was worked up by treating with ice-cold water, pentane, dilute aqueous hydrochloric acid, water, and aqueous solution of sodium bicarbonate in this order followed by drying over magnesium sulfate.

The results of glpc examination of the oxidation products were discussed in the main text. The diol distributions derived from the hydroboration of 4-vinylcyclohexene are summarized in Table V

Preparation of *B*-Methoxyboracyclanes. (a) Methoxyborinane (5). The compound was prepared by methanolysis of bisborinane[3b] in 76% yield: bp 42–44° (22 mm); pmr (CCl_4, TMS) δ 0.83 (t, 4 H), 1.53 (broad peak, 6 H), and 3.60 (s, 3 H); mass spectrum (75 eV) *m*/*e* (rel intensity) 112 (4), 111 (1). Bisborinane was prepared as described previously.[3b] Oxidation of the product afforded 97% pure 1,5-pentanediol.

(b) A Mixture of *B*-Methoxyborepane, *B*-Methoxy-2-methylborinane, and *B*-Methoxy-2,5-dimethylborolane. The mixture was obtained by distillation of the methanolysis product of the 6-hr old 1,5-hexadiene-borane reaction mixture, yield 85%, bp 57–64° (17 mm). Oxidation of the product provided 1,6-, 1,5-, and 2,5-hexanediols in the ratio of 73:20:7.

(c) *B*-Methoxy-9-borabicyclo[3.3.1]nonane (18). The compound was prepared by methanolysis of 9-borabicyclo[3.3.1]nonane as described previously:[18] yield 92%; bp 48–50° (2 mm); $n^{20}\text{D}$ 1.4798; pmr (CCl_4, TMS) δ 1.0–2.0 (2 broad peaks centered at 1.25 and 1.75 ppm, 14 H) and 3.68 (s, 3 H). Oxidation of the compound afforded 99% pure *cis*-1,5-cyclooctanediol in quantitative yield.

Table V. Diol Distribution from the Hydroboration of 4-Vinylcyclohexene

Diol[a]	Relative distributions, %: Hydroboration mixture[b]	Distillate[c]	Residue[c]
Hydroxycyclohexaneethanol			
cis-2-(**31**)	0	5	1
cis-3-(**24**)	10	64	15
cis-4-(**25**)	38	0	17
trans-2-(**32**)	0	Trace	Trace
trans-(**26** or **27**)[d]	13	2	21
trans-(**26** or **27**)[d]	16	Trace	35
Hydroxy-α-methylcyclohexanemethanol[e]			
cis-(**33** or **34**)	5	11	2
cis-(**33** or **34**)	16	17	7
trans-[d]	1	0	0
trans-[d]	1	0	1

[a] Analyzed as diacetate on 150-ft capillary column of polyphenyl ether. [b] Formed by hydroboration at 0°, then 25° for 3 hr. [c] From the distillation of a 48-hr old methanolyzed 1:1 hydroboration product. [d] Identified only as *trans*-3- or *trans*-4 isomer; specific structures not determined. [e] Identified only as hydroxy-α-cyclohexanemethanols; specific structure not determined.

(d) *B*-Methoxy-2-borabicyclo[3.3.1]nonane (29). The compound was prepared by distillation of the methanolysis product of 48-hr old 4-vinylcyclohexene–borane reaction mixture: yield 56%; bp 30–32° (0.2 mm); mass spectrum (75 eV) *m*/*e* (rel intensity) 152 (4), 151 (1).

Anal. Calcd for $C_9H_{17}BO$: C, 71.10; H, 11.27; B, 7.11. Found: C, 71.00; H, 11.41; B, 7.02.

The results of glpc examination of the oxidation products are summarized in Table V.

(e) *B*-Methoxy-4,8-dimethyl-2-borabicyclo[3.3.1]nonane. The compound was prepared by distillation of the methanolysis product of the 48-hr old D-(+)-limonene–borane reaction mixture as described previously:[4] yield 74%; bp 39–44° (0.15–0.2 mm); ir (neat) 1350 (s), 1320 cm^{-1} (s); pmr (CCl_4, TMS) δ 0.5–2.5 (multiplet with major peaks at 0.95, 1.07, 1.16 and 1.64, 18 H) and 3.67 (s, 3 H); mass spectrum (75 eV) *m*/*e* (rel intensity) 180 (4), 179 (1).

Anal. Calcd for $C_{11}H_{21}BO$: C, 73.34; H, 11.76; B, 6.00. Found: C, 73.13; H, 11.58; B, 6.24.

Oxidation of the compound provided 94% pure D-(−)-(1*S*,2*R*,4*R*)-limonene-2,9-diol (**36**)[4] in 85% yield.

Authentic Samples of Diols. Pentanediols, hexanediols, octanediols, cyclohexanediols,[19] and cyclooctanediols[18] were either obtained from commercial sources or available in our laboratories. Hydroxy-α-methylcyclohexanemethanols, hydroxycyclohexaneethanols, and limonene-2,9-diols were prepared as described below.

Preparation of Hydroxycyclohexaneethanols. Mixtures containing *cis*-3- and *cis*-4-hydroxycyclohexaneethanols (**24** and **25**) as the major components were obtained by the hydroboration–oxidation of 4-vinylcyclohexene. The mixtures were then converted to mixtures containing known *cis*-3- and *cis*-4-ethylcyclohexanols through the following sequence

$$\text{ROH} \xrightarrow{\text{TsCl}} \text{ROTs} \xrightarrow{\text{LiAlH}_4} \text{RH}$$

In this manner, the major product derived from a distilled methanolysis product of the hydroboration of 4-vinylcyclohexene was identified as *cis*-3-hydroxycyclohexaneethanol (**24**). Similarly, the major product from the hydroboration mixture was identified as **25**.

A mixture of four products was obtained by the hydroboration of 3-cyclohexeneethanol.[20] Two of the products were **24** and **25**. Thus the remaining two were assumed to be *trans*-3- and *trans*-4-hydroxycyclohexaneethanols (**26** and **27**). *trans*-2-Hydroxycyclohexaneethanol was obtained *via* hydroboration–oxidation of 1-

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

(18) E. F. Knights, Ph.D. Thesis, Purdue University, 1968.

(19) H. C. Brown and G. Zweifel, *J. Org. Chem.*, 27, 4708 (1962).

(20) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 83, 1241 (1961).

vinylcyclohexene.[21] A mixture of *cis*- and *trans*-2-hydroxycyclohexaneethanol (**31** and **32**) was obtained by the reduction of commercially available ethyl 2-ketocyclohexaneacetate.

Preparation of Hydroxy-α-methylcyclohexanemethanols. A mixture of *cis*- and *trans*-3- and *cis*- and *trans*-4-hydroxy-α-methylcyclohexanemethanols was prepared by the hydroboration of α-methyl-3-cyclohexenemethanol. The presence of two of these isomers in the diol products derived from a distilled methanolysis product of the hydroboration of 4-vinylcyclohexene led to the assignment of the *cis*-3- and *cis*-4- structures to these compounds. The *trans*-3- and *trans*-4- structures were, therefore, tentatively assigned to the remaining two products.

Preparation of Limonene-2,9-diols. An authentic sample of D-(−)-(1*S*,2*R*,4*R*)-limonene-2,9-diol (**36**) was prepared as described previously,[4] mp 92–92.5°. Its identification was carried out by C. D. Pfaffenberger by converting the diol to the known D-(−)-carvomenthol[22] by the following sequence[4]

$$\mathrm{ROH} \xrightarrow{\mathrm{TsCl}} \mathrm{ROTs} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{RH}$$

The isomeric diol (**37**) was not prepared as a pure substance. A mixture of **36** and **37** was prepared by the hydroboration of D-(+)-limonene with borane. Two major diol products were obtained in the ratio of 84:16, the major component of which was **36**. The structure **37** was, therefore, tentatively assigned to the minor component.[4]

Acknowledgment. The authors are indebted to Drs. E. F. Knight and C. D. Pfaffenberger for the information provided by them in certain phases of the present study. Support of this research by the U. S. Army Research Office (Durham) and the National Institutes of Health is gratefully acknowledged.

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[21] Kindly supplied by Professor C. A. Brown of Cornell University.

[22] D. K. Shumway and J. D. Barnhurst, *J. Org. Chem.*, **29**, 2320 (1964).

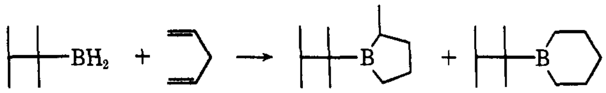
Hydroboration. XXXII. The Cyclic Hydroboration of Dienes with Thexylborane

Herbert C. Brown* and Ei-ichi Negishi[1]

Contribution from the Richard B. Wetherill Laboratory,
Purdue University, Lafayette, Indiana 47907. Received July 6, 1971

Abstract: Glpc conditions for determining the exact quantities of *B*-thexylboracyclanes present in the diene–thexylborane reaction mixtures are established. Glpc examination using the established conditions reveals that the hydroboration of 2,3-dimethyl-1,3-butadiene with thexylborane is 93% cyclic, whereas that of 1,3-butadiene is only 17% cyclic. An explanation for the marked difference in the extent of cyclic hydroboration is given. The extent of cyclic hydroboration with 1,4-pentadiene and 1,5-hexadiene is at least 80% in each case. In the competitive formation of five- and six-membered boracyclanes, there exists a strong preference for the formation of the five-membered ring. On the other hand, in the competitive formation of six- and seven-membered boracyclanes, neither is strongly favored over the other, and the usual directive effect appears to control the product distribution. These findings appear to provide a simple explanation for the initial 78:22 distribution of *B*-thexyl-9-borabicyclo[4.2.1]nonane and its [3.3.1] isomer in the highly cyclic hydroboration of 1,5-cyclooctadiene. In most cases examined, the *B*-thexylboracyclanes are isolated in excellent yields by distillation without noticeable isomerization of either the thexyl group or the ring moiety. Even from the largely polymeric 1,3-butadiene–thexylborane reaction mixture is isolated a 71% yield of *B*-thexylborolane. The distilled *B*-thexylboracyclanes are identified and characterized.

In our earlier study on the hydroboration of dienes with thexylborane, 2,3-dimethyl-2-butylborane,[2] it was found that the hydroboration of 1,4-pentadiene with an equimolar quantity of thexylborane yielded, after oxidation, 70% of 1,4- and 30% of 1,5-pentanediols, whereas the monofunctional disiamylborane, bis(3-methyl-2-butyl)borane, afforded mainly the 1,5-diol (85%).[3] This notable difference was rationalized in terms of a cyclization reaction, favoring the formation of a five-membered ring, in the case of hydroboration with thexylborane (eq 1). However, the hydroboration of 1,3-cyclopentadiene with thexylborane yielded, after oxidation, mainly *trans*-1,3-cyclopentanediol (trans:cis = 87:13).[2] Clearly, cyclization cannot be the major path in this case. Similarly, 1,4-cyclohexadiene did not appear to yield the corresponding cyclic organoborane by the hydroboration with thexylborane.[2] Consequently, these earlier observations did not encourage us to utilize thexylborane as a cyclic hydroborating agent to form *B*-thexylboracyclanes.



1 major

2 minor

(1)

On the other hand, our recent stoichiometry study[4] indicated that the hydroboration of dienes with thexylborane in many cases must be highly cyclic and that the results with 1,3-cyclopentadiene and 1,4-hexadiene did not reflect the entire picture.

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[1] Postdoctoral research associate on a research grant, DA 31-134 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

[2] G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 2066 (1963).

[3] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 190 (1962).

[4] H. C. Brown and C. D. Pfaffenberger, *ibid.*, **89**, 5475 (1967); for the experimental detail, see C. D. Pfaffenberger, Ph.D. Thesis, Purdue University, 1967.