Table III. Product Compositions of Deuterio-2-*exo*-norbornenyl Acetate from Acetolysis of 3-*exo*-Deuterio-2-*exo*-norbornenyl *p*-Bromobenzenesulfonate (**1**-OBs)[a] under Various Conditions

[**1**-OBs], *M*	[NaOAc], *M*	[KOAc], *M*	Temp, °C	% D at C-7	Total % D	% rearrangement
0.48		0.52	24	44.0	88.4	49.8[b]
0.03	0.30		24	41.2	85.3	48.4[b]
0.48		0.52	45	44.9	85.7	52.4[b]
				43.4	85.2	50.9[c]
0.03	0.30		45	45.6	85.6	53.3[b]
				44.7	88.2	50.7[c]
0.03		0.52	45	40.6	85.5	47.5[b]
				44.5	87.6	50.8[c]
0.48		0.52	65	43.2	84.6	51.1[b]
				43.3	85.1	50.9[c]
0.03	0.30		65	44.1	88.7	49.7[b]
				45.1	88.5	51.0[c]

[a] Mass spectrometer analysis on starting material indicated starting material was 86.5 ± 1.0% **1**-OBs, 12.5% **8**-OBs, and 1.0% **2**-OBs, but each determination of % rearrangement was calculated using individual data points for total D content. [b] Analysis at 15 eV. [c] Analysis at 70 eV.

scans of data at 15 eV (inlet temperature 120°) were averaged to give the data in Table II.

Treatment of Mass Spectral Data. The starting nominal **1**-SCN was a mixture containing 2.4% **8**-SCN, 84.7% **1**-SCN, and 12.8% **16**-SCN, with less than 0.5% of **2**-SCN and **17**-SCN. Any reaction which proceeds through a symmetrical intermediate, *e.g.*, **4**, which is captured equally well at C-1 and C-2, would lead to a product mixture containing 2.4% of **8**-X, 42.3% of **1**-X, 42.3% of **2**-X, 6.4% of **16**-X, and 6.4% of **17**-X. Such a mixture would have the analysis *m/e* 66:67:68 (after isotope abundance correction) of 51.2:42.3:6.4. Therefore the nominal value for **2**-X, that is, the value which would have been obtained if the starting material had been pure **1**-X, is calculated as **1**-d_0/102.4, and an independent value for **2**-X is given by d_1/84.7 where d_0 and d_1 are observed percentages of undeuterated and monodeuterated species. (In principle, the amount of scrambled deuterium can also be calculated from the data for the d_2 species, but in practice, these data have larger per cent errors and have been ignored.) The results given in Table II are the averages of the **1**-X:**2**-X ratios calculated in each way.

Acknowledgment. The authors are indebted to the National Science Foundation for generous support of this work.

Hydroboration. XXXIV. The Cyclic Hydroboration of 1,5-Hexadiene with Borane in Tetrahydrofuran and 9-Borabicyclo[3.3.1]nonane. A New Convenient Route to the Borepane Ring System Utilizing 9-Borabicyclo[3.3.1]nonane

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Contribution from the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907. *Received December 11, 1972*

Abstract: Confirming evidence is presented for the formation of a mixture of 3:2 dumbbell-shaped compounds in the hydroboration of 1,5-hexadiene with borane in tetrahydrofuran in the molar ratio of 3:2. Oxidation of the products provides 1,6-, 1,5-, and 2,5-hexanediols in a ratio of 72:22:6. Evidence is presented for the facile conversion of the boracycloheptyl ring moiety to the 2-methylboracyclohexyl moiety in the distillation or thermal treatment of the 3:2 products. The reaction of the 3:2 products or thermally treated 3:2 products with an equimolar quantity of borane in tetrahydrofuran provides mixtures containing predictable ratios of borepane and 2-methylborinane. Alternative methods for the preparation of the *B*-methoxy derivatives of these compounds are described. Evidence is presented that the reaction of 1,5-hexadiene with borane in a 1:1 molar ratio proceeds through the initial formation of the 3:2 product, followed by the subsequent reaction of this product with borane. The thermal treatment at 70° of the initial 1:1 hydroboration products provides a 78% yield of borepane and 2-methylborinane in a ratio of 70:30. The boracycloheptane ring is relatively stable in THF in the absence of borane, but in its presence the ring system undergoes a slow reaction involving opening of the ring. Thus the stability of the boracycloheptane ring appears to lie between the stabilities of the boracyclopentane and boracyclohexane rings. The hydroboration of 1,5-hexadiene with 9-borabicyclo[3.3.1]nonane (9-BBN) followed by treatment with borane in tetrahydrofuran provides a new synthesis of the boracycloheptyl ring system uncontaminated by isomeric boracyclanes. The method holds promise for the ready synthesis of boracyclanes in high yield and purity.

The hydroboration of 1,5-hexadiene with borane (or diborane) in the stoichiometric ratio 3:2 has been investigated previously by several workers.[2] Although some confusion had persisted regarding the

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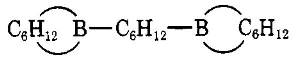
[1] (a) Graduate Assistant on a research grant (GM 10937) supported by the National Institutes of Health; (b) Postdoctoral Research Associate on a research grant (DA 31-134 ARO(D) 453), supported by the U. S. Army Research Office (Durham).

[2] (a) K. A. Saegebarth, *J. Amer. Chem. Soc.*, **82**, 2081 (1960); (b) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962); (c) B. M. Mikhailov, L. S. Vasil'ev, and E. Safonva, *Dokl. Akad. Nauk SSSR*, **147**, 630 (1962); (d) L. I. Zakharkin and A. I. Kovredov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 357 (1962); (e) L. I. Zakharkin and A. I. Kovredov, *ibid.*, 106 (1969).

structure of the product, Zakharkin and Kovredov[2e] recently corrected earlier conclusions and determined that the product consisted of a mixture of dumbbell-shaped compounds (**1**) on the basis of elemental analy-



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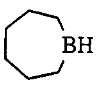
sis, molecular weight determination, and analysis of the oxidation products. However, until recently, no attempt had been made to synthesize the monocyclic organoborane, borepane (**2**), by hydroboration of 1,5-hexadiene. Our recent study[3] has shown that the hydroboration of 1,5-hexadiene with borane in the 1:1 molar ratio provides a 70:30 mixture of borepane and 2-methylborinane (**3**) in 78% yield using either the borane-to-diene or diene-to-borane mode of addition. It was suggested that the reaction to form borepane and 2-methylborinane occurs in essentially two distinct steps. Addition of borane to 1,5-hexadiene results in the rapid formation of dumbbell-shaped compounds (**1**) which subsequently undergo a slower exchange with the remaining borane to form a mixture of **2** and **3** (eq 1). The yield of monocyclic products (78%) suggests that the acyclic central chain moiety undergoes cyclization in the exchange reaction. However, this point has not been clearly established.



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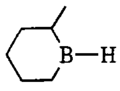

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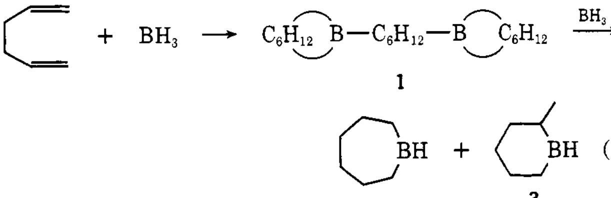


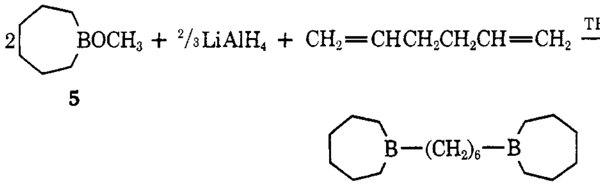
(1)

In the present study, results of the hydroboration of 1,5-hexadiene are reported with emphasis on the nature of the exchange reaction of dumbbell-shaped compounds containing the $-C_6H_{12}-$ chain moiety with borane.

Results and Discussion

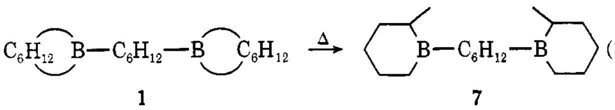
The hydroboration of 1,5-hexadiene with borane was first carried out in the molar ratio of 3:2 using the borane-to-diene mode of addition. Residual hydride analysis indicated the hydroboration was essentially over on completing the addition of borane. Oxidation of the hydroboration mixture with alkaline hydrogen peroxide provided 1,6-,1,5-, and 2,5-hexanediols in 93% yield in the ratio of 72:22:6, similar to the ratio of 69:22:9 observed earlier.[2b] Methanolysis of aliquots of the 3:2 hydroboration mixture and glpc analysis revealed only minor amounts of 2:1 hydroboration products and a broad, trailing peak in the expected 3:2 product region. Distillation of the hydroboration product gave a colorless liquid, bp 125–130° (0.1 mm), of elemental composition $(C_6H_{12})_3B_2$ and corresponding molecular weight 274 (mass spectrum). Oxidation of the distilled product gave 1,6-, 1,5-, and 2,5-hexanediols in 99% yield in the ratio of 49:50:1 indicating some positional isomerization of the boron atom during the distillation. Except for slight differences in the distribution of oxidation products, these results confirm the findings of Zakharkin and Kovredov.[2e] The conclusions of earlier studies[2a,c,d] apparently must be modified.[4]

An authentic sample of the 3:2 compound, 1,6-bis(boracycloheptyl)hexane (**6**), was prepared by the reduction of *B*-methoxyborepane (**5**) in the presence of 1,5-hexadiene (eq 2).[5] The pmr and mass spectra of the organoborane **6** were analogous to those of the initial or distilled 3:2 products formed in the hydroboration of 1,5-hexadiene with borane with the exception that no peak due to methyl groups was observed in the pmr spectrum.



(2)

Thermal Treatment of the 3:2 Hydroboration Products. Earlier, Saegebarth[2a] reported that thermal treatment of the 3:2 hydroboration products of 1,5-hexadiene at 170° (6 hr) converted the initially formed dumbbell compound **1** to 1,6-bis(2-methylboracyclohexyl)hexane (**7**) (eq 3). On the other hand, in our recent studies with the analogous 3:2 compounds derived from 1,3-butadiene[6] and 1,4-pentadiene,[7] we have observed in addition to ring isomerization, a novel thermal transformation of these compounds to form 1,1-bis(boracycloalkyl)alkanes. Formation of the latter compounds is reflected by the formation of monools on oxidation. Since the formation of *gem*-dibora compounds was not reported by Saegebarth[2a] we examined this point.



(3)

The solvent was evaporated from the 3:2 hydroboration mixture and the residual organoboranes were heated to 170–175°. At intervals, aliquots were oxidized

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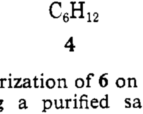
[3] H. C. Brown, E. Negishi, and P. L. Burke, *J. Amer. Chem. Soc.*, **94**, 3561 (1972).

[4] The available data do not strictly exclude 3:2 compounds possessing a "cage"-type structure (**4**). Evidence for such structures has not yet been encountered in our studies of the hydroboration of acyclic dienes.



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[5] The anticipated isomerization of **6** on heating and its air-sensitive nature precluded obtaining a purified sample by readily available methods. The product, however, is estimated to be approximately 90% pure from oxidation results. The preparation of *B*-methoxyborepane (**5**) is described later in this paper.

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

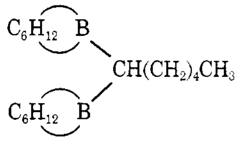
[7] E. Negishi, P. L. Burke, and H. C. Brown, *ibid.*, **94**, 3561 (1972).

and the oxidation products analyzed by glpc. The results are summarized in Table I. After the organoboranes were heated for 3 hr at 170–175°, the oxidation products consisted of an approximately 2:1 mixture of 1,5- and 1,6-hexanediol. Only minor amounts of 1-hexanol and isomeric diols were observed at this time. These results appear to confirm the conclusion by Saegebarth[2a] that the thermally treated products largely consist of **7**. On prolonged heating, however, the amount of 1-hexanol in the oxidation products increased with time. Although no attempt was made to determine the exact structures of the organoboranes, it is reasonable, based on our recent observations,[4,6] to correlate the presence of 1-hexanol in the oxidation products with that of the 1,1-dibora compound **8** in the isomerized organoboranes.

Table I. Thermal Treatment at 170° of the 3:2 Hydroboration Products Derived from 1,5-Hexadiene and Borane

Time of heating,[a] hr	Composition of oxidation products,[c] %					
	1-Hexanol[b]	Hexanediol 2,5-	1,5-	1,6-	Other[d]	Total yield[e]
0	0[f]	5	19	73	0	93
1	1	0	52	45	2	94
2	1	0	59	38	2	93
3	5	0	60	33	2	94
6	8	0	62	27	3	90
24	18	0	55	18	9	84
48	21	0	45	17	17	87

[a] At 170°. [b] Major product. Minor amounts of unidentified products of similar retention times were also present. [c] Analyses performed on a 6-ft SE-30 column after silylation. [d] Unidentified isomers (2). One has the same retention time as that of 2,5-hexanediol. Identification as diols made on basis of retention time. [e] Based on 1,5-hexadiene. [f] Small amounts of 5-hexen-1-ol observed (3%).



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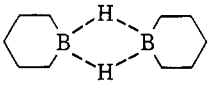
The slow decrease in the amount of 1,5-hexanediol after 6 hr at 170° suggests more complex changes also accompany the formation of **8**.

If the isomerization of the 3:2 compounds was terminated after 3 hr at 170°, distillation afforded a mobile liquid, bp 125–129° (0.1 mm), molecular weight 274 (mass spectrum), in 77% yield. Oxidation of the distilled material gave 1,5- and 1,6-hexanediols in 60 and 31% yields, respectively, and only minor amounts of monools and isomeric diols (*ca.* 5%). Apparently the isolated material consists largely of **7** and little additional isomerization of this material occurs during distillation. Additional evidence supporting this conclusion is presented in the next section.

Exchange Reaction of the 3:2 Products with Borane. Isomerization of the 3:2 products derived from 1,4-pentadiene followed by redistribution with an equimolar quantity of borane in THF provides a convenient synthesis of bisborinane (**9**) in 80% yield.[8] It was of interest to determine if a similar sequence of reactions with 1,5-hexadiene would provide a convenient route to either borepane (**2**) or 2-methylborinane (**3**). Furthermore, the investigation of the exchange reaction of the 3:2 compounds with borane would serve to clarify the suggested two-stage mechanism for the formation of a mixture of borepane and 2-methylborinane in the 1:1 hydroboration of 1,5-hexadiene with borane.[3]



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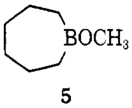
Accordingly, the initial 3:2 hydroboration product of 1,5-hexadiene, freed of solvent and characterized as previously described, was treated with an equimolar quantity of borane in THF (final composition, diene: boron = 1:1) at 0–5° for 1 hr, then allowed to warm to room temperature. Aliquots were periodically methanolyzed and analyzed for borepane (**2**) and 2-methylborinane (**3**) as the corresponding *B*-methoxy derivatives, **5** and **10**, by glpc. The results are tabulated in Table II. The formation of borepane (**2**) and 2-methylborinane (**3**) in the ratio of 75:25 and 73% yield after 48 hr parallels the results obtained in the direct 1:1 hydroboration of 1,5-hexadiene with borane.[3] (The formation of monocyclic products was accompanied by formation of a small amount of gelatinous solid, presumably polymer, as discussed later.) Clearly, these results support our earlier conclusion that the 3:2 products are formed as intermediates in the 1:1 hydroboration. Since the yield of monocyclic products increases similarly with time using either the borane-to-diene or diene-to-borane mode of addition in the 1:1 hydroboration, it may be tentatively concluded that both modes involve the prior formation of 3:2 products.



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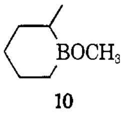

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Table II. Exchange Reaction of the Initial 3:2 Hydroboration Products with Borane in THF in the Molar Ratio of 1:1[a]

Time, hr	Active hydride,[b] %	Glpc yield of methanolysis product,[c] %			Glpc yield of hexanediol,[d] %			
		5	10	Total[e]	1,6-	1,5-	2,5-	Total
0	90	2	2	4	65	17	5	87
1[f]	91	3	3	6	65	17	4	86
24	94	52	20	72	65	16	4	85
48	95	54	19	73	65	16	5	86

[a] At 0–5° for 1 hr, then 25°. [b] By methanolysis. [c] Glpc analysis on 3-ft 10% Apiezon L column (Chromosorb W as solid support); injection block at 100°. [d] Glpc analysis of the trimethylsilyl derivatives on 6-ft 10% SE-30 column. [e] Minor amounts (1–2%) of *B*-methoxy-2,5-dimethylborolane (assumed structure) not included. [f] After *ca.* 2 hr, small amounts of gelatinous solid precipitates from solution; 24- and 48-hr aliquots are samples of supernatant solution.

The constant ratio of oxidation products found over the 48-hr reaction period (Table II) indicates that no

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

positional isomerization of the boron moiety occurs in the exchange reaction. The maximum possible yield of a monocyclic product of given structure is therefore predetermined by the position of boron attachment in the parent 3:2 compounds. Thus when the distilled 3:2 compounds of 1,5-hexadiene were treated with an equimolar amount of borane, borepane (**2**) and 2-methylborinane (**3**) were formed in 87% yield in the ratio of 48:52, essentially the ratio of 1,6- and 1,5-hexanediols formed on oxidation of the distilled 3:2 compounds (Table VI, Experimental Section).

On the basis of these experiments, it was anticipated that the reaction of 1,6-bis(boracycloheptyl)hexane (**6**) with borane would provide a source of borepane (**2**) of high purity. Unexpectedly, however, the reaction gave only a 54% yield of borepane accompanied by copious amounts of a gelatinous solid, apparently polymeric in nature (Table VII, Experimental Section). Reflux of the exchange products failed to increase the yield of borepane.

The results of the latter experiment suggest that the 3:2 compounds derived from 1,5-hexadiene containing the boracycloheptyl moiety may be largely responsible for the formation of polymeric side products produced in the exchange reactions. This point is discussed in more detail elsewhere.

Although the glpc yields of monocyclic organoboranes formed in these exchange reactions exceed 66%, the possibility of depolymerization on the injection block of the gas chromatograph to give monocyclic *B*-methoxyboracyclanes[9] does not permit us to conclude with confidence that the exchange reaction involves cyclization of the $-C_6H_{12}-$ chain moiety of the 3:2 compounds. The exchange reaction of the isomerized 3:2 product of 1,5-hexadiene, isolated after 3 hr at 170°, with borane appeared to offer a less ambiguous test of the latter point. Since the isomerized product should consist largely of **7**, formation of borepane (**2**) would be indicative of the cyclization of the central moiety.

Treatment of the isolated, isomerized 3:2 products with borane in the usual manner gave a 24:76 mixture of borepane (**2**) and 2-methylborinane (**3**) in 62% yield after 48 hr (Table III). Although only 40–50% of the theoretical quantity of borepane (**2**) (based on 1,6-hexanediol formed on oxidation) is formed, partial cyclization of the central chain moiety is indicated (eq 4).

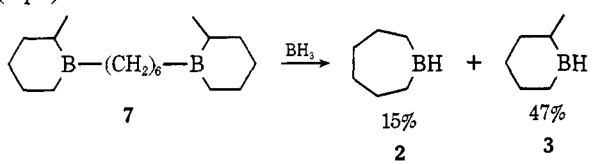

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Table III. Exchange Reaction of the Isomerized 3:2 Hydroboration Product with Borane in THF in the Molar Ratio of 1:1[a]

Time, hr	Active hydride,[b] %	Glpc yield of methanolysis products,[c] %		
		5	10	Total
0	73	0	9	9[e]
1	80[d]	1	12	13
3	87	9	35	44
6	80	15	44	59
24	84[d]	14	47	61
48	84	15	47	62[e]

[a–c] See corresponding footnotes, Table II. [d] By hydrolysis samples gave 93 and 92% hydrogen evolution, respectively. [e] Samples gave 1,6-, 1,5-, and isomeric hexanediols in the ratio of 36:64:trace and 38:60:2, respectively.

Exchange Reaction of the 3:2 Hydroboration Products with Trimethyl Borate. Mikhailov and coworkers[2c] have demonstrated that the exchange reaction of 3:2 compounds derived from the hydroboration of dienes with an equimolar quantity of trimethyl borate provides a convenient route to *B*-methoxyboracyclanes in good yields. Such compounds are readily employed for the synthesis of the corresponding *B*-alkylboracyclanes *via* reaction with alkyllithium reagents[10] or reduction with $LiAlH_4$ in the presence of olefins.[11] We examined this procedure as a potential route to *B*-methoxyborepane (**5**) or *B*-methoxy-2-methylborinane (**10**).[12]

The 3:2 hydroboration products (after removal of solvent) were treated with an equimolar quantity of trimethyl borate in the presence of a catalytic amount of borane in THF for 3 hr at 120–130° (bath temperature). Addition of a small amount of methanol and distillation afforded a 79% isolated yield of a mixture of 71% *B*-methoxyborepane (**5**), 28% *B*-methoxy-2-methylborinane (**10**), and 1% unidentified compound, presumably *B*-methoxy-2,5-dimethylborolane. The ratio of **5** to **10** approximates that of 1,6- and 1,5-hexanediols observed on oxidation of the 3:2 compounds (72:22) and indicates that little or no isomerization is induced during the formation and isolation of the *B*-methoxyboracyclanes. Apparently, as in the related exchange reaction with borane, the products resulting from the exchange reaction of the 3:2 products with trimethyl borate are predetermined by the position of boron in the 3:2 compound.

It proved possible to separate **5** and **10** in high purity (≥95%) by distillation through a Teflon spinning band column. As was pointed out earlier, thermal isomerization of the 3:2 product at 170° for 3 hr converts it into 1,6-bis(2-methylboracyclohexyl)heptane (**7**). Consequently, treatment of the thermally isomerized 3:2 product with methyl borate, followed by careful fractional distillation, provides **10** in good yield.

Thermal Treatment of the 1:1 Hydroboration Product. The foregoing discussion indicates that hydroboration of 1,5-hexadiene with borane in the molar ratio of 3:2 apparently is not a useful approach to the synthesis of either borepane (**2**) or 2-methylborinane (**3**) in a high state of purity.

In general, positional isomerization of the 1:1 hydroboration products derived from dienes and borane has not been observed below 100°.[7,8,13a–c] The ap-

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[9] Precautions to avoid this potential difficulty were exercised in this study. These have been discussed in some detail previously; see ref 7.

[10] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **93**, 3777 (1971).

[11] H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 6648 (1970).

[12] Mikhailov and coworkers[2c] have reported the isolation of *B*-methoxyborepane (**5**) by reaction of the *distilled* 3:2 products of 1,5-hexadiene with equimolar quantity of trimethyl borate. However, from our results it is probable that they actually isolated a mixture of **5** and **10**.

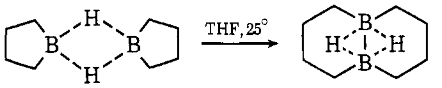
[13] (a) H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **28**, C1 (1971); (b) H. C. Brown, E. Negishi, and P. L. Burke, *J. Amer. Chem. Soc.*, **93**, 3400 (1971). (c) A notable exception is the facile conversion of 9-borabicyclo[4.2.1]nonane, formed in the 1:1 hydroboration of 1,5-cyclooctadiene, to 9-borabicyclo[3.3.1]nonane (9-BBN) at *ca.* 70°; see E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280 (1968).

Table IV. Thermal Treatment at 70° of the 1:1 Hydroboration Mixture Derived from 1,5-Hexadiene and Borane in THF

Time of refluxing,[a] hr	Active hydride,[b] %	Glpc yield of methanolysis product,[c] %			Glpc yield of hexanediol,[d] %				
		5	10	Total[e]	2,5-	1,5-	1,6-	Other	Total
0 (at 0°)	80	11	10	21	5	24	70	Traces	99
1	88	59	24	83	4	19	63	Traces	86
2	88	55	24	79	4	21	66	Traces	91
6	84	56	24	80	4	22	66	Traces	92
24	86	52	25	77	5	21	65	Traces	91
48	82	56	21	77	4	23	68	1	96

[a] At *ca.* 70°. [b–e] See corresponding footnotes, Table II.

parent increased stability of the 2-methylborinyl ring system reflected in the isomerization of **1** to **7**, however, suggested the possible thermal conversion of the 70:30 mixture of borepane (**2**) and 2-methylborinane (**3**) formed in the 1:1 hydroboration reaction to **3**. Heating the initial 1:1 hydroboration mixture in THF under reflux (*ca.* 70°) merely accelerated the formation of **2** and **3** in essentially the same ratio (71:29). The results of glpc analyses of methanolyzed aliquots are shown in Table IV. The combined yield of **2** and **3** reaches a maximum in 1 hr, and prolonged heating for 48 hr provides no evidence for the interconversion of the products. The stability of **2** and **3** toward further changes is in sharp contrast to that of bisborolane (**11**) which rapidly converts largely to the unusually stable, 1,6-diboracyclodecane (**12**) in THF at 25° (eq 5).[14]



11 **12** (5)

Hydroboration of 1,5-hexadiene with borane in the molar ratio of 1:1, heating the reaction under reflux for 1 hr, followed by methanolysis and distillation, provides a convenient alternate route to a mixture of *B*-methoxyborepane (**5**) and *B*-methoxy-2-methylborinane (**10**). Thus a 79% isolated yield of 68% of **5**, 27% of **10**, and 5% of *B*-methoxy-2,5-dimethylborolane (assumed structure) was obtained. Subsequent distillation through a Teflon spinning-band column provided **5** and **10** in high purity (97 and 94%, respectively).

This procedure, or that involving the exchange reaction with trimethyl borate, provides an entirely acceptable route for the synthesis of the boracycloheptyl and 2-methylborinyl ring systems.

However, the necessity of separating the isomeric *B*-methoxy derivatives by an efficient fractional distillation reduces its convenience. Fortunately, we were able to partially overcome this inconvenience by means of a highly promising new route to isomerically pure boracyclanes employing 9-borabicyclo[3.3.1]nonane (9-BBN) as the hydroborating agent.

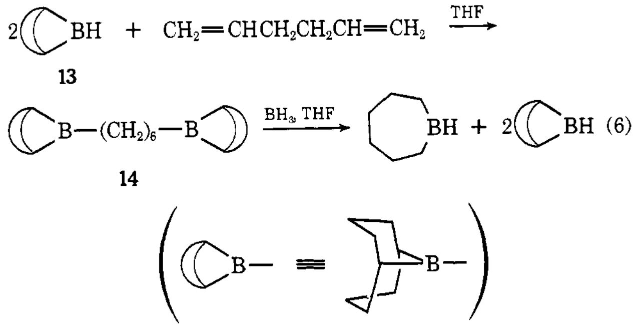
Synthesis of Borepane and *B*-Methoxyborepane *via* Hydroboration of 1,5-Hexadiene with 9-Borabicyclo[3.3.1]nonane. One of the major difficulties with the synthesis of pure boracyclanes *via* hydroboration of unsubstituted, acyclic dienes arises from the attack of borane at internal positions of the diene. This difficulty can be overcome in the case of 1,4-pentadiene by isomerization of the 3:2 product prior to the exchange reaction with borane.[8] The present study has demonstrated that thermal isomerization of either the 3:2 products or the 1:1 products from 1,5-hexadiene does not offer any major advantages for the direct synthesis of pure borepane (**2**) or 2-methylborinane (**3**).

Table V. Exchange Reaction of 1,6-Bis(9-borabicyclo[3.3.1]nonyl)hexane with Borane in THF in 1:1 Molar Ratio[a]

Time, hr	Active hydride,[b] %	Glpc yield of methanolysis products,[c] %		
		8	*B*-CH_3O-9-BBN	Total
		At 25°		
0	96	5	29	34
1	101	12	56	68
3	101	20	60	80
6	99	27	66	93
24	100	33	73	106
		At Reflux (*ca.* 70°)		
1	96	29	67	96
2	98	31	71	102

[a] 100-mmol (1,5-hexadiene) scale. [b] By methanolysis. [c] Analyzed on 3-ft 10% Apiezon L column; injection block 100°.

It appeared possible that the problem of isomer formation might be simply avoided by use of the readily available and highly selective hydroborating agent, 9-borabicyclo[3.3.1]nonane (9-BBN, **13**).[13c,15] Hydroboration of a simple acyclic diene with 9-BBN is expected to give essentially one product with terminal attachment of the two 9-BBN moieties. Subsequent treatment with an equimolar quantity of borane should result in cleavage and cyclization of the central chain moiety to yield isomerically pure boracyclane as an admixture with 9-BBN. Indeed, this procedure, when applied to 1,5-hexadiene, gave an essentially quantitative yield (Table V) of borepane (**2**) with a quantitative recovery of 9-BBN, as indicated by glpc analysis of the methanolysis products (eq 6).



13 **14** (6)

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(14) H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **93**, 6682 (1971).

(15) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281 (1968).

This conclusively establishes that the cyclization of the central $-C_6H_{12}-$ moiety of the dumbbell-shaped compounds is potentially quantitative. The exchange reaction is complete in 24 hr at 25° or 2 hr at reflux. The experimental procedure is exceedingly simple. 1,5-Hexadiene (1 mol) is added neat, all at once to a THF solution of 2 mol of 9-BBN at 25° (with cooling if on a large scale). The hydroboration is allowed to proceed for 2–3 hr at 25°, then 1 mol of BH_3 in THF is added all at once to the solution of the hydroboration product, and the reaction is heated to reflux for 2 hr. Although we have not yet achieved a simple separation of 9-BBN from borepane, methanolysis of the exchange products followed by simple distillation provided at least 95% pure *B*-methoxyborepane (**5**) in 84% yield, contaminated by only a small amount (*ca.* 5%) of *B*-OCH_3-9-BBN. No formation of *B*-methoxy-2-methylborinane (**10**) was observed.

Alternatively, the hydroboration product, **14**, may be redistributed with an equimolar amount of trimethyl borate in the presence of added borane in THF at 120–130° (bath temperature) for 3 hr. Distillation of the resultant products gave a 74% isolated yield of **5** in *ca.* 95% purity. Thus this procedure at present offers the most convenient synthesis of *B*-methoxyborepane.

We are pursuing this promising new approach to the synthesis of boracyclanes.

Relative Reactivity of Boracycloalkyl Groups toward Borane in THF. Our earlier studies on the hydroboration of 1,3-butadiene[13b] and 1,4-pentadiene[7] have revealed an interesting contrast between the relative reactivities of the boracyclopentyl and boracyclohexyl groups toward ring cleavage by borane in THF. The boracyclopentyl group, formed in hydroboration of 1,3-butadiene, is rapidly and preferentially opened in the presence of borane. In contrast, redistribution of the isomerized 3:2 products of 1,4-pentadiene with borane results in the formation of bisborinane (**9**) in high yield indicating little or no ring opening of the boracyclohexyl group. Presumably the 2-methylboracyclohexyl ring encountered in the present study possesses a similar stability.

The reactivity of the boracycloheptyl group toward borane appears to lie between those of the boracyclopentyl and boracyclohexyl groups. In the exchange reaction of the dumbbell-shaped molecules derived from 1,5-hexadiene with borane in THF, we have observed varying yields of monomeric boracyclanes. Moreover, in some cases the formation of monomeric products was accompanied by the formation of varying amounts of a gelatinous solid, presumably a polymer. The results summarized in Tables II, V, VI, and VII indicate that the greater the initial content of the boracycloheptyl group in a dumbbell-shaped compound, the lower the yield of borepane, based on the amount of the $-C_6H_{12}-$ moiety, and the lower the yield of the total monomeric boracyclanes. This seemingly contradictory tendency could be rationalized on the basis of an assumption that the boracycloheptyl group is slowly opened by borane in THF, but not by itself or by other dialkylboranes, such as 9-BBN. Thus the yield of borepane or total boracyclanes realized with **14**, which does not contain the boracycloheptyl group, is nearly 100%. No gel formation is observed. As shown in Table V, little loss of borepane is observed even at the refluxing temperature of THF. On the other hand, the reaction of the dumbbell-shaped compound **6**[16] with borane produced only a 54% yield of borepane accompanied by a considerable amount of a gelatinous solid (Table VII, Experimental Section).

In order to test this proposal of a slow opening of the boracycloheptyl group by borane, borane in THF was added to a solution containing borepane and 9-BBN such that the molar ratio of borane to borepane was 1:1. Loss of 14% of the borepane was observed in 49 hr at 25°, whereas the 9-BBN was unaffected. When the ratio was raised to 2:1, the loss of borepane increased to *ca.* 35% in 48 hr. Glpc analysis of the methanolysis products revealed the presence of only a small amount of tetramethyl 1,6-hexanediboronate (**15**), an anticipated product of ring opening. Thus,

$$(CH_3O)_2B(CH_2)_6B(OCH_3)_2$$
15

it has been established that, although borepane is stable in the absence of borane even at the refluxing temperature of THF, it is slowly opened by borane. The structure of the ring opening product has not been established, but appears to be largely polymeric based on the glpc examination of the methanolysis products.

Conclusions

The nature of the 3:2 products derived from 1,5-hexadiene and the thermally treated 3:2 products has been clarified. The hydroboration of 1,5-hexadiene with borane in the molar ratio of 1:1 proceeds initially to form 3:2 products which subsequently undergo an exchange reaction with the unreacted borane to produce a mixture of borepane and 2-methylborinane in high yield. The boracycloheptane ring is relatively stable in THF in the absence of borane, but in its presence the ring system undergoes a slow reaction involving opening of the ring. Thus the stability of the boracycloheptane ring appears to lie between the stabilities of the boracyclopentane and boracyclohexane rings. Methods for the synthesis and separation of *B*-methoxyborepane and *B*-methoxy-2-methylborinane have been described. A new, convenient synthesis of *B*-methoxyborepane in high purity has been accomplished through the selective hydroboration of 1,5-hexadiene with 9-BBN, followed by redistribution of the product with borane (and methanolysis) or with methyl borate.

Experimental Section

The organoboranes were always handled under nitrogen with careful exclusion of oxygen and moisture. Pmr, ir, and mass spectra were obtained with a Varian T-60, a Perkin-Elmer 137B, and a Hitachi RMU-6A or a Consolidated Electrodynamic 110 spectrometer, respectively.

Materials. The preparation of borane solutions in THF was carried out as previously described.[17] 9-BBN in THF was prepared by methods previously described.[13c] Commercially available 1,5-hexadiene (Chemical Samples Co.) and anhydrous methanol (Baker) were used as supplied after checking the refractive indices. Commercially available trimethyl borate was distilled

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(16) As was pointed out earlier, the compound **6** can be synthesized by the reaction of 2 equiv of *B*-methoxyborepane with lithium aluminum hydride in the presence of 1 equiv of 1,5-hexadiene.

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

from excess sodium and stored in serum stoppled containers under nitrogen.

Hydroboration of 1,5-Hexadiene with Borane in THF in the Molar Ratio of 3:2. A 300-ml, three-necked flask fitted with a septum inlet, a magnetic stirring bar, a connecting tube for nitrogen inlet, and a septum-capped dropping funnel was flame-dried and flushed with nitrogen. The flask was cooled to 0–5° and charged with 88.1 ml of dry THF and 8.21 g (100 mmol) of 1,5-hexadiene. To this was added at 0–5° 27.6 ml (66.6 mmol) of a 2.42 *M* solution of borane in THF diluted to *ca.* 1 *M* with 39.1 ml of dry THF. The reaction was kept at 0–5° for 3 hr and then allowed to warm to 25°. At periodic intervals beginning with the completion of the addiion, 10-ml aliquots were removed at 0, 1, 3, 6, 24, and 48 hr and treated with 0.4 ml (9 mmol, ~50% excess) of anhydrous methanol; the hydrogen evolved was measured by water displacement. The 0-hr sample gave 5.5 cc of H_2 (23.5°, 749 mm) corresponding to 3.5 mmol (1.7%) of unreacted hydride in the total reaction mixture. After 48 hr the residual hydride had decreased to 2.2 mmol (1.1%). Analysis of the 0-hr methanolyzed sample[18] revealed only a broad single peak in the expected 3:2 compound region[19] and small amounts of three compounds in the 2:1 compound region. No *B*-methoxyboracyclanes (**5** or **10**) were observed. No changes were observed in the glpc analysis over 48 hr. Infrared spectral analysis of the hydroboration mixture at 0 hr showed only very weak bands at 2500 cm^{-1} (terminal B–H), 2400 cm^{-1} (borane in THF), and 1560 cm^{-1} (BH_2B), and no significant changes were observed in these regions in 48 hr. Oxidation of the 0-, 6-, and 48-hr methanolyzed samples with alkaline hydrogen peroxide in the usual manner[17] gave 1,6-, 1,5-, and 2,5-hexanediols in the approximate ratio of 72:22:6 in each case in $\geq 85\%$ yield. A small amount of 5-hexen-1-ol (4–7%) was also observed in each case.[20]

After removal of the 48-hr aliquot, the solvent was evaporated at reduced pressure to leave a colorless liquid. Glpc analysis[18] of the liquid revealed only a trace of residual solvent and a broad, trailing peak in the expected 3:2 compound region and three peaks in the expected 2:1 compound region: mass spectrum (70 eV) *m/e* (rel intensity) 274 (12), 273 (4.5), 272 (1); pmr (CCl_4, TMS) δ 0.4–2.1 (broad multiplet with peaks at 0.99, 1.30, and 1.53) ppm.

In a separate experiment 37.6 g (459 mmol) of 1,5-hexadiene in 100 ml of THF was hydroborated with 120.8 ml of 2.48 *M* borane in THF in the manner described above. Evaporation of the solvent at reduced pressure and distillation provided 36.3 g (85%) of a mixture of 3:2 compounds: bp 125–130° (0.1 mm) (lit.[2a] 131–132° (1 mm)); mass spectrum (70 eV) *m/e* (rel intensity) 274 (10.9), 273 (5), 272 (1); pmr (CCl_4, TMS) δ 0.3–2.1 (broad multiplet with peaks at 1.02, 1.32, and 1.55) ppm.

Anal. Calcd for $C_{18}H_{36}B_2$: C, 78.87; H, 13.24; B, 7.89. Found: C, 78.57; H, 13.52; B, 8.01.

Oxidation with alkaline hydrogen peroxide[17] of a 0.92-g (3.4 mmol) sample of the distillate gave 9.7 mmol (95%) of 1,6-, 1,5-, and 2,5-hexanediols in the ratio of 48:51:1.

Synthesis of 1,6-Bis(borabicycloheptyl)hexane (6). The general procedure used, with some modifications, has been described previously.[11] To 50 ml of dry THF were added 4.15 g (50.5 mmol) of 1,5-hexadiene and 20 ml (33.3 mmol) of 1.66 *M* $LiAlH_4$ in THF (prefiltered through Celite) followed by a dropwise addition of 12.8 g of *B*-methoxyborepane (**5**) containing 5 mol % of *B*-OCH_3-9-BBN.[21] Slight cooling was required to maintain the temperature at *ca.* 25°. The addition is accompanied by precipitation of white solid. After the mixture was stirred for 2–3 hr at *ca.* 25°, the reaction was cooled to 0–5° and 6.9 g (67 mmol) of 96% H_2SO_4 was added slowly followed by *ca.* 5 ml of water. Hydrogen (1115 cc) was evolved at 22.5° (746 mm), corresponding to 44 mmol of residual hydride. After addition of 25 ml of purified pentane, the supernatant solution was withdrawn and the solids were washed with four 10-ml portions of pentane. The organic solution was evaporated to leave a colorless liquid. On standing, solid material appeared in the liquid and addition of pentane (50 ml) caused additional precipitation. The pentane solution was therefore washed, by stirring vigorously with 4-ml portions of deoxygenated water and brine, and dried over anhydrous $CaSO_4$ overnight. Evaporation of the dry pentane solution at reduced pressure left 11.1 g (*ca.* 80%) of a clear, colorless, mobile liquid: pmr (CCl_4, TMS) δ 0.4–2.1 (broad multiplet with peaks at 1.30, 1.55, and 1.78), 5–6 (minor peaks) ppm; mass spectrum (70 eV) *m/e* (rel intensity) 274 (14.5), 273 (7.0), 272 (1); also 300 (16.4), 299 (7.2), 298 (1) due to anticipated impurity resulting from presence of *B*-OCH_3-9-BBN in starting material. No further purification of this material was attempted.[5]

Oxidation of a 0.45-g sample of the organoborane gave 3.8 mmol of 1,6-hexanediol, a trace of 1,5-hexanediol, 0.3 mmol of 1,5-cyclooctanediol, and 0.4 mmol of monools (3 peaks) (total *ca.* 92%).

Thermal Treatment of the 3:2 Hydroboration Product at 170°. 1,5-Hexadiene (8.2 g, 100 mmol) was hydroborated with 66.6 ml (66.6 mmol) of 1.00 *M* borane in THF in the usual manner. After the addition (0–5°) the reaction was allowed to stand overnight at 25°. The solvent was evaporated at reduced pressure and the remaining crude products (9.1 g), after sampling for oxidation, were heated to *ca.* 170° (bath temperature, preheated) under nitrogen in a 50-ml flask fitted with a condenser and connecting tube attached to a mercury bubbler. At scheduled intervals 1.0 ml of the organoborane was removed, weighed, dissolved in 10 ml of THF, and oxidized in the usual manner.[17] Analysis of the oxidation products[20] gave the results summarized in Table I.

In an analogous experiment (450 mmol 1,5-hexadiene scale), isomerization of the 3:2 hydroboration products was terminated after 3 hr and the organoboranes were distilled. After a forerun (6.07 g), 31.5 g (77%) of a mobile, colorless liquid was obtained: bp 125–129° (0.1 mm); pmr (CCl_4, TMS) δ 0.6–2.4 (broad multiplet with peaks at 1.01, 1.33, and 1.55) ppm; mass spectrum (70 eV) *m/e* (rel intensity) 274 (17.3), 273 (8.3), 272 (1). Oxidation of a 0.85-g (3.1 mmol) sample of the distillate with alkaline hydrogen peroxide[14] gave 5.6 mmol of 1,5-hexanediol and 2.9 mmol of 1,6-hexanediol as well as smaller amounts of monools (0.31 mmol) and isomeric diols (0.2 mmol, unidentified) by glpc analysis[20] (total 97%).

Exchange Reaction of the 3:2 Hydroboration Products with Borane in THF in the Molar Ratio of 1:1. (a) Initial 3:2 Hydroboration Products. The initial 3:2 hydroboration products, 2.83 g (10.3 mmol), formed by hydroboration of 1,5-hexadiene with borane in the 3:2 molar ratio and freed of tetrahydrofuran solvent were redissolved in 50 ml of dry THF and 2.46 ml (15 mmol) of *n*-octane (internal standard). The solution was cooled to 0–5° and 4.3 ml (10.3 mmol) of 2.40 *M* borane in THF was added all at once. After 1 hr at 0–5°, the reaction was allowed to warm to 25°.[22] At periodic intervals, 10-ml aliquots (5.1 mmol of $-C_6H_{12}-$ moiety) were treated with 0.3 ml (7.5 mmol, 50% excess) of anhydrous methanol and analyzed by glpc.[18] The results are summarized in Table II. Approximately 2 hr after the addition of the borane, the exchange reaction became somewhat cloudy thus precluding homogeneous sampling. After the mixture was stirred overnight, the small quantity of solid material coagulated and samples of the supernatant liquid were withdrawn at 24 and 48 hr. Infrared spectral analysis of the exchange reaction at 0 hr indicated bands at 2400 (m) and 1560 cm^{-1} (m). After 48 hr the band at 2400 cm^{-1} was absent and that at 1560 cm^{-1} had increased to one of strong intensity.

(b) Distilled 3:2 Hydroboration Products. In a similar experiment 2.73 g (10 mmol) of the distilled 3:2 hydroboration products, dissolved in 51.7 ml of dry THF and 0.68 g (6.0 mmol) of *n*-octane (internal standard) at 0–5°, was treated with 4.17 ml (10 mmol) of 2.39 *M* borane in THF. Glpc analysis of methanolyzed aliquots[18] gave the results summarized in Table VI. Infrared analysis of the exchange reaction at 0 hr indicated a band at 2400 (m) and 1560 cm^{-1} (w). After 3 hr the band at 2400 cm^{-1} was absent and that at 1560 cm^{-1} was of moderate intensity and increased in intensity over 48 hr. Oxidation of the 0-, 6-, and 48-hr samples with alkaline hydrogen peroxide[17] gave 1,6-, 1,5-, and 2,5-hexanediols in the approximate ratio of 49:50:1 in each case in $\geq 92\%$ yield by glpc.[20]

(c) 1,6-Bis(boracycloheptyl)hexane (6). In an analogous manner, 2.78 g (10 mmol) of 1,6-bis(boracycloheptyl)hexane (**6**), prepared as described previously, was dissolved in 50 ml of dry THF and 2.46 ml (15 mmol) of *n*-octane and treated with 4.3 ml (10.3 mmol)

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[18] 3 ft × 0.25 in., 10% Apiezon L on Chromosorb W, 60–80, AW, DMCS column programmed from 60 to 250° at 10°/min with 4-min post-injection delay; injection block of instrument kept at *ca.* 100°.

[19] Attempts to qualitatively or quantitatively analyze the initial 3:2 hydroboration products or those isolated by distillation on columns of 10% Apiezon L as short as 15 in. were unsuccessful. Apparently temperatures required for elution of the high molecular weight compounds also induced isomerization during analysis.

[20] Oxidation products analyzed as trimethyl silyl ether using *n*-undecane as standard on a 6 ft × 0.25 in. 10% SE-30 on Chromosorb W column programmed from 60 to 250° at 8°/min with 4-min post-injection delay.

[21] Preparation of this material is described elsewhere in this section.

[22] Approximately simulates the conditions employed in the hydroboration of 1,5-hexadiene in the 1:1 molar ratio.[3]

Table VI. Exchange Reaction of the Distilled 3:2 Hydroboration Products with Borane in THF in the 1:1 Molar Ratio[a]

Time, hr	Active hydride,[b] %	Glpc yield of methanolysis product,[c] %		
		5	**10**	Total
0	70	Trace	Trace	Trace
1	80	3	13	16
3	90	22	35	57
6	80	20	42	62
24	87	42	44	86
48	93	42	45	87

[a–c] See corresponding footnotes, Table II.

of 2.40 *M* borane in THF. After 3 hr large amounts of gelatinous solid formed precluding homogeneous sampling of the reaction. The remainder of the reaction was methanolyzed at 48 hr. The results of the glpc analysis of the methanolyzed aliquots[18] are summarized in Table VII.

Table VII. Exchange Reaction of 1,6-Bis(boracycloheptyl)hexane with Borane in the 1:1 Molar Ratio[a]

Time, hr	Active hydride,[b] %	Glpc yield of methanolysis products,[c] % **5**
0	85	13
1	92	36
3[d]	90	54
48	81	48

[a–c] See corresponding footnotes, Table II. [d] After 3 hr, copious amounts of gelatinous solid precipitates precluding further sampling; remainder of reaction methanolyzed at 48 hr.

Oxidation of the 48-hr sample gave 1,6- and 1,5-hexanediols in the ratio of 12.2 mmol:trace, 0.5 mmol of 1,5-cyclooctanediol, and *ca.* 0.7 mmol of unidentified products (total *ca.* 89%) indicating no positional isomerization of the boron atoms had occurred.

In a similar experiment, the reaction was heated to reflux (*ca.* 70°) after addition of borane. After 2 hr at reflux, glpc analysis of a methanolyzed sample indicated only a 56% yield of *B*-methoxyborepane (**5**). On cooling the exchange reaction copious amounts of gelatinous solid precipitated.

(d) Isomerized, Distilled 3:2 Hydroboration Products. In a similar experiment, 4.59 g (16.8 mmol) of the 3-hr isomerized product, isolated by distillation, was dissolved in 77 ml of dry THF and treated with 16.8 ml (16.9 mmol) of 1.01 *M* borane in THF. The results of the glpc analysis of methanolyzed aliquots are summarized in Table III.[18] Oxidation of the 0- and 48-hr methanolyzed samples gave 1,6-, 1,5-, and isomeric hexanediols in the ratio of 36:64:trace and 38:60:2 in 95 and 79% yields, respectively. Small amounts (∼5%) of monools were also observed.

Exchange Reaction of the 3:2 Hydroboration Products with Trimethyl Borate in the 1:1 Molar Ratio. 1,5-Hexadiene (24.6 g, 300 mmol) in 100 ml of dry THF was hydroborated with 82.6 ml (200 mmol) of 2.42 *M* borane in THF at 0–5°. After warming to 25° the solvent was evaporated at reduced pressure and 1 ml of 2.42 *M* borane in THF (catalyst) and 10.4 g (100 mmol) of trimethyl borate were added to the crude organoboranes. The mixture was heated under nitrogen for 3 hr at 120–130° (bath temperature). At this time glpc analysis[18] indicated the presence of **5** and **10** in the ratio of *ca.* 70:30 in addition to small amounts of presumably isomeric *B*-methoxyborolane derivatives, trimethyl borate, and THF. Distillation afforded a small forerun (2 g) followed by a mixture of **5** and **10** (29.9 g, 79%) in the ratio of 71:29, bp 56–62° (25 mm). The pmr spectrum was consistent with a mixture of these compounds in the indicated ratio. Oxidation of a 0.93-g (7.4 mmol) sample of the mixture gave 7.0 mmol (94%) of 1,6-, 1,5-, and 2,5-hexanediols in the ratio of 73:27:trace.

Thermal Treatment of the 1:1 Hydroboration Product of 1,5-Hexadiene at 70°. 1,5-Hexadiene, 50 mmol (1.0 *M* solution in THF; 0.2 *M* in *n*-octane), was hydroborated with 50 ml (50 mmol) of 1.01 *M* borane in THF at 0–5° employing the diene-to-borane mode of addition. After 1 hr at 0–5° the reaction was heated to reflux (*ca.* 70°). At periodic intervals 10-ml samples of the reaction were removed, and methanolyzed (0.3 ml, 7.5 mmol, 50% excess); the hydrogen evolved was measured, analyzed by glpc[18] for *B*-methoxyboracyclanes, and oxidized. The results are tabulated in Table IV.

Preparation of *B*-Methoxyborepane (5) and *B*-Methoxy-2-methylborinane (10) *via* Methanolysis of the Thermal Treated 1:1 Hydroboration Product. 1,5-Hexadiene (100 mmol, 1 *M* in THF) was hydroborated at 0–5° with 100 ml (101 mmol) of 1.01 *M* borane in THF in the usual manner (diene-to-borane mode of addition). After 1 hr at 0–5°, the reaction was brought to reflux (*ca.* 70%) for 1 hr and cooled and 6 ml (150 mmol) of anhydrous methanol was added dropwise. Hydrogen (2538 cc at 25.5°, 747 mm; 98.5%) was evolved. The solvent and excess methanol were removed at reduced pressure (*ca.* 100 mm) and the remaining material was distilled to give, after a small amount of forerun, 10.0 g (79%)[23] of a mixture of 68% *B*-methoxyborepane (**5**), 27% *B*-methoxy-2-methylborinane (**10**), and 5% unidentified isomers, bp 78–88° (58 mm); mass spectrum (70 eV) *m/e* (rel intensity) 126 (4), 125 (1).

Anal. Calcd for $C_7H_{15}BO$: C, 66.72; H, 12.00; B, 8.58. Found: C, 66.43; H, 12.23; B, 8.71.

The isomeric *B*-methoxyboracyclanes isolated were redistilled on an auto-annular Teflon spinning band column at reduced pressure with nitrogen bleed. The first fraction was collected (100:1 reflux ratio) at 61–62° (25 mm); pmr (CCl_4, TMS) δ 0.2–2.0 (broad multiplet with sharp peak at 0.88, *ca.* 12 H), 3.67 (singlet, 3 H) ppm. After an intermediate fraction, bp 62–67° (25 mm), a third fraction was collected, bp 67–68° (25 mm); pmr (CCl_4, TMS) δ 1.0 (broad singlet, *ca.* 4 H), 1.57 (broad singlet, *ca.* 8 H), 3.58 (singlet, 3 H) ppm. A 0.48-g (3.8 mmol) sample of the first fraction was oxidized in the usual manner to give 3.6 mmol (95%, glpc)[20] of 1,5- and 1,6-hexanediol in the ratio of 94:6. A 0.49-g (3.8 mmol) sample of the third fraction gave 3.5 mmol (96%) of 1,5- and 1,6-hexanediol in the ratio of 4:96.

Exchange Reaction of 1,6-Bis(9-borabicyclo[3.3.1]nonyl)hexane (14) with Borane in THF in the Ratio of 1:1. (a) At 25°. A dry, nitrogen flushed 200-ml, one-necked flask, fitted with a septum-inlet, a magnetic stirring bar, connecting tube, and mercury bubbler, was charged with 101 ml (50 mmol) of 0.492 *M* solution of 9-BBN in THF at 25°. To this were added 10 mmol of *n*-octane as a standard and 2.04 g (24.8 mmol) of 1,5-hexadiene all at once. The reaction was allowed to proceed for 2 hr and 10.6 ml (25.6 mmol) of 2.42 *M* solution of borane in THF was added all at once. At periodic intervals 10-ml aliquots of the reaction mixture were treated with 0.4 ml of anhydrous methanol and the hydrogen evolved was measured. The methanolyzed samples were analyzed by glpc for *B*-methoxyborepane (**5**) and *B*-OCH_3-9-BBN.[18] The results are summarized in Table V. Oxidation in the usual manner of a 1-week old reaction sample (20 ml), after methanolysis, gave 4.27 mmol of 1,6-hexanediol (99.5%, based on 1,5-hexadiene), 1,5-hexanediol (<1%), and 8.37 mmol of cyclooctanediol (97.5%, based on 9-BBN).

(b) At Reflux. The experiment was conducted as in (a) except the reaction was brought to reflux 15 min after the addition of the borane in THF. Reaction samples were methanolyzed and analyzed by glpc as in (a). The results are summarized in Table V.

Preparation of *B*-Methoxyborepane (5) *via* Hydroboration of1,5-Hexadiene with 9-BBN. 1,5-Hexadiene (207 mmol) was treated with 9-BBN (456 mmol, 10% excess) and borane (207 mmol) in THF as in (b) above. After the reaction was refluxed, the reaction was cooled and 40 ml (994 mmol) of anhydrous methanol was added dropwise. Hydrogen (16.4 l.) was evolved at 25° (746 mm), corresponding to 638 mmol of active hydride (96%). The methanolyzed reaction was allowed to stand for 2 hr and then THF and methanol were removed at reduced pressure (*ca.* 100 mm). Distillation of the remaining crude products through a 10-in. concentric tube column gave, after a forerun of primarily residual THF, 21.9 g (84%, based on 1,5-hexadiene) of *B*-methoxyborepane (**5**) in 95% purity, bp 74–76° (32 mm). The product was identified by simultaneous elution (glpc) with an authentic sample and comparison of the pmr spectrum. The only observed contaminant by glpc was *B*-OCH_3-9-BBN (5%).

Preparation of *B*-Methoxyborepane (5) *via* Exchange of 1,6-Bis(9-borabicyclo[3.3.1]nonyl)hexane (14) with Trimethyl Borate. To 9-BBN, 27.4 g (224.6 mm), partially dissolved in 100 ml of dry THF was added 9.23 g (112 mmol) of 1,5-hexadiene all at once. Cooling was required to maintain the reaction at *ca.* 25°. The reaction was permitted to stand overnight (2–3 hr is sufficient) at 25° and the

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(23) Attempts to scale up this preparation using *ca.* 4 *M* 1,5-hexadiene in THF and 2.48 *M* borane in THF gave lower isolated yields (∼40%).

solvent evaporated at reduced pressure. Trimethyl borate, 12.8 ml (11.8 g, 113 mmol), and 2.5 ml of 2.42 *M* borane in THF (catalyst) were added to the crude organoborane and the mixture was heated to 120–130° (bath temperature) for 3 hr. Distillation of the resultant products (10-in. concentric tube column) gave, after a forerun (3.05 g), 10.4 g (74%) of *B*-methoxyborepane (**5**), bp 74–78° (32 mm), in *ca.* 95% purity. The only contaminant was *B*-OCH_3-9-BN (*ca.* 5%) as determined by glpc.[18] No *B*-methoxy-2-methylborinane (**10**) was detected.

Reactivity of 9-BBN (13) and Borepane (2) toward Ring Opening by Borane. (a) 9-BBN. To 32.8 ml (20 mmol) of 0.611 *M* 9-BBN in THF at *ca.* 25° was added 1.64 ml (10 mmol) of *n*-octane (glpc standard) followed by 8.3 ml (20 mmol) of 2.40 *M* borane in THF. At periodic intervals 10-ml samples of the solution were treated with 1.1 ml (28 mmol) of methanol and analyzed by glpc for *B*-OCH_3-9-BBN.[18] After 48 hr only a 0.7-mmol (3.5%) loss of 9-BBN was observed. Infrared spectral analysis after addition of borane revealed bands at 2400 cm^{-1} (s) (BH_3 in THF), 1550 cm^{-1} (s) (BH_2B bridge), and weak bands in the 2500–2600 cm^{-1} region (terminal B–H of $R_3BH \cdot BH_3$ complex). No change in the spectrum was observed in 48 hr.

(b) Borepane (2). A THF solution of borepane (theory 25 mmol), 9-BBN (theory 50 mmol), and *n*-octane (15 mmol) was prepared in the manner previously described for the exchange reaction of **14** at reflux. The final volume of the solution was adjusted to 110 ml with dry THF. Glpc analysis[18] of a 10-ml methanolyzed sample indicated a 22.2 mmol (89%) yield of borepane and 45.7-mmol (91%) yield of 9-BBN. The remaining reaction mixture was divided into two 50-ml portions. To one was added 4.7 ml (11.3 mmol, equal to theoretical quantity of borepane) and the other 9.4 ml (22.6 mmol, twice the theoretical quantity of borepane) of 2.4 *M* borane in THF at *ca.* 25°. At scheduled intervals 5-ml samples were methanolyzed and analyzed by glpc for *B*-methoxyborepane (**5**) and *B*-OCH_3-9-BBN.[18] The quantity of **5** present after 48 hr was 19.1 mmol in the former experiment and 14.2 mmol in the latter experiment. This represents a 14 and 36% loss of borepane, respectively, based on the experimentally determined initial quantity. Small amounts of tetramethyl 1,6-hexanediboronate (**15**) were observed in the 48-hr glpc analysis in the latter experiment (identified by comparison of retention time with authentic sample). No significant changes in the amount of 9-BBN present were observed in either experiment.

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Selective Deoxygenation of Ketones and Aldehydes Including Hindered Systems with Sodium Cyanoborohydride[1]

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Abstract: The reduction of aliphatic ketone and aldehyde tosylhydrazones with sodium cyanoborohydride in acidic 1:1 DMF–sulfolane provides a mild, convenient, and high-yield method for deoxygenation without the production of side products. Noteworthy features and advantages of the procedure include: (a) superior selectivity in that most other functional groups (*i.e.*, ester, amide, cyano, nitro, chloro) are not affected under the reaction conditions allowing carbonyls to be removed in their presence; (b) most hindered carbonyls are reliably reduced to hydrocarbons without side reactions; (c) α,β-unsaturated carbonyls are reduced in good yields specifically to alkenes with migration of the double bond; (d) a limitation of the method involves aryl carbonyls which are resistant to reduction unless the ring is substituted with an electron donating group.

A key functional group transformation which often presents itself in organic synthesis is the conversion of carbonyl derivatives to methyl or methylene groups after such intermediates have served their synthetic purpose of activating molecules for the host of reactions essential for building complex structures. Consequently, a voluminous amount of literature exists concerning direct[3] or indirect[3,4] deoxygenation methods, but the standard procedures are often afflicted with problems. In particular, the rather vigorous conditions and harsh reagents required for most methods preclude the presence of many other susceptible

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(1) A preliminary account of portions of this work has been previously reported: R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, *J. Amer. Chem. Soc.*, **93**, 1793 (1971).

(2) National Science Foundation undergraduate research participant, 1971.

(3) Excellent recent critical reviews of deoxygenation methods are available; see W. Reusch in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, pp 171–211; (b) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 4.

(4) A common and often effective indirect method involves the reduction of carbonyl derivatives to alcohols, which are converted to a suitable leaving group and subsequently displaced by a hydride source, usually lithium aluminum hydride (ref 3a and 3b, Chapter 2; and C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Amer. Chem. Soc.*, **94**, 8905 (1972)) or a trialkyltin hydride (ref 5). (b) Sodium borohydride or cyanoborohydride in polar aprotic solvents also serve as effective displacing agents for aliphatic halides and tosylates; see R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Lett.*, 3495 (1969); H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969); M. Vol'pin, M. Dvolaitzky, and H. Levitin, *Bull. Soc. Chim. Fr.*, 1526 (1970); E. J. Corey, H. A. Kirst, and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **92**, 6314 (1970); R. O. Hutchins, R. Bertsch, and D. Hoke, *J. Org. Chem.*, **36**, 1568 (1971); J. Jacobus, *Chem. Commun.*, 338 (1970). (c) For use of cyanoborohydride, see R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, *ibid.*, 1097 (1971). (d) Aromatic acids may be converted directly to hydrocarbons with trichlorosilane and a trialkylamine, see R. A. Benkeser, K. M. Foley, J. M. Gaul, and G. S. Li, *J. Amer. Chem. Soc.*, **92**, 3232 (1970); other methods for the conversion of carbonyls to hydrocarbons are also available; see for examples, ref 6 and 7.

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