consequent to our earlier report on the kinetics of hydroboration of alkenes with (Sia$_2$BH)$_2$, McKenna et al. proposed a model based on the dimer for asymmetric hydroborations involving (Ipc$_2$BH)$_2$.[5] Our present results on (Sia$_2$BH)$_2$, (9-BBN)$_2$, and borinane dimer settle this ambiguity. Any good model for asymmetric hydroboration by (Ipc$_2$BH)$_2$ must utilize the monomer rather than the dimer.[11]

Experimental Section

General Methods. Detailed procedures for the manipulation of boron reagents have been outlined in Chapter 9 of ref 12. Glassware, syringes, and needles were dried for several hours in an oven at 140 °C and cooled in a stream of dry nitrogen before use. Syringes were assembled while hot and cooled as assembled units in a nitrogen atmosphere. For kinetic studies, a Miran-1A variable-filter infrared spectrometer from Wilks Scientific Corporation was used. The calculations of the kinetic data were carried out on a Hewlett-Packard 9820 calculator.

Materials. Tetrahydrofuran was purified as described elsewhere.[12] All of the alkenes used were obtained commercially and were distilled over LAH in a nitrogen atmosphere before use. BH$_3$·THF, obtained from Aldrich, was used as such for the preparation of disiamylborane.[13] Disiamylborane was prepared freshly before each kinetic run.[14]

Kinetic Studies. The following procedure is typical. To BH$_3$·THF (4.90 mL of 1.02 M solution in THF), well-cooled with ice–salt bath, was added 2-methyl-2-butene in THF (5 mL of a 2.0 M solution) dropwise over a period of 15 min. The mixture was kept at 0 °C for 8 h for the complete formation of disiamylborane. Precooled THF (14.66 mL) was then added and the solution was allowed to equilibrate at 0.0 ± 0.1 °C for 0.5 h. It was then pumped[15] through a 0.20-mm NaCl IR cell at a rate of 4 mL/min to determine the absorbance of boron–hydrogen bridge bonds at 1570 cm^{-1}. The reaction was started by adding cyclopentene (0.44 mL) by using a syringe. The initial concentrations of cyclopentene and (Sia$_2$BH)$_2$ are 0.200 and 0.100 M, respectively. The reaction mixture was pumped through the IR cell continuously and the absorbance was recorded on chart paper. After the reaction was over, pure THF was pumped through the cell to determine the background absorbance. The three-halves-order rate constant was obtained graphically[6c] (Figure 1).

Acknowledgment. We thank the National Science Foundation for financial support (Grant CHE 79-18881).

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[11] Brown, H. C.; Ayyangar, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1964**, *86*, 1071.

[12] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

[13] Commercial BH$_3$·THF contains a small amount of NaBH$_4$ (< 5 mol %) as a stabilizer. It does not affect the hydroboration kinetics; BH$_3$·THF free from BH$_4^-$ behaved exactly like the commercial sample in trial experiments. Hence, the commercial sample was used for all kinetic runs.

[14] Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 3222.

[15] The IR cell holder was surrounded by a metal jacket through which a coolant at −2 °C was circulated in order to maintain the temperature of the reaction mixture at the reaction temperature.

Hydroboration. 70. The Polycyclic Hydroboration of Acyclic and Cyclic Trienes with Borane in Tetrahydrofuran and Triethylamine–Borane. Reexamination of the Stereochemistry of Isomeric Perhydro-9b-boraphenalenes[1,2]

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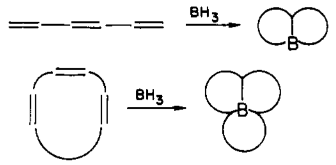
Received May 22, 1984

The hydroboration of 1,4,8-nonatriene (**1**), 5-methyl-1,4,8-nonatriene (**2**), 1,3,7-octatriene (**3**), and *trans,-trans,trans*-1,5,9-cyclododecatriene (**4**) with borane in tetrahydrofuran (THF) and triethylamine–borane was studied. The hydroboration of the acyclic trienes with borane in THF at 0 °C produced monomeric bicyclic boranes in low yields. Moreover, thermodynamically stable organoboranes with fused six-membered rings, such as 9-boradecalin (**15**) and 10-methyl-9-boradecalin (**20**), were not formed as the major monomeric cyclic products. However, thermal treatment of the hydroboration product from **1** produced **15** as the only monomeric bicyclic organoborane in high yield. The thermodynamically favored major product from **2** was **20** which amounted to 62% of the monomeric boranes formed in 74% yield. With **1** and **2**, both borane in THF and triethylamine–borane gave comparable results after thermal treatment. However, in the hydroboration of **3**, use of triethylamine–borane resulted in a considerably higher yield of perhydro-8-boraindan. The carbonylation–oxidation of **15** provided an 80:20 mixture of *cis*- and *trans*-9-decalols. The ratio of *cis*-10-methyl-9-decalol to its trans isomer obtained by the carbonylation–oxidation of **20** was at least 62:1. The carbonylation–oxidation of **3** produced only *cis*-8-hydrindanol. The hydroboration of the cyclic triene **4** followed by thermal treatment at 160 °C for 6 h produced a mixture consisting largely of *cis,trans*-perhydro-9b-boraphenalene (**6**) and a constitutional isomer in 83% yield. However, thermal treatment at 200 °C for 6 h provided a 92:8 mixture of **6** and its all-cis isomer **5**, uncontaminated with the constitutional isomer. The hydroisomerization of **5** or **6** at 220 °C in the presence of triethylamine under 140 atm of hydrogen gave an equilibrium mixture of 88 ± 1% **5** and 12 ± 1% **6**. The difference between the free energies of **5** and **6** was estimated to be 1.9 ± 0.1 kcal/mol. The stereochemistry of **5** and **6** was established by ^{1}H NMR examination of the pyridine adducts of **5** and **6** as well as of free **5** and **6**. The original structural assignments by Rotermund and Köster must therefore be reversed.

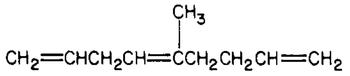
We have previously established that the hydroboration of dienes that are capable of forming common rings (five- to seven-membered) with borane in tetrahydrofuran (THF)[4] or thexylborane[5] is generally highly cyclic.[6] On the basis of these results, it appeared reasonable that appropriately constructed acyclic and cyclic trienes could also be converted into the corresponding bicyclic and tricyclic organoboranes. Accordingly, we selected 1,4,8-nonatriene



(1), 5-methyl-1,4,8-nonatriene (2), 1,3,7-octatriene[7] (3), and *trans,trans,trans*-1,5,9-cyclododecatriene (4) and undertook to study their reactions with borane in THF and triethylamine–borane.

$CH_2{=}CHCH_2CH{=}CHCH_2CH_2CH{=}CH_2$

1

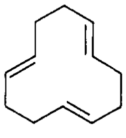


$CH_2{=}CHCH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_2CH{=}CH_2$

2

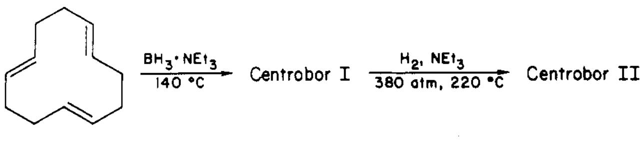
$CH_2{=}CHCH{=}CHCH_2CH_2CH{=}CH_2$

3

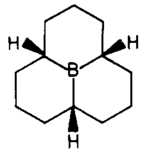


4

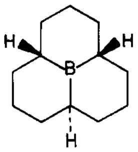
Earlier, Köster[8,9] investigated the reaction of 4 with triethylamine–borane at 140 °C and assigned the *all-cis*-perhydro-9b-boraphenalene structure 5 to the product (Centrobor I). The other stereoisomer (Centrobor II) was obtained by treating Centrobor I with hydrogen and triethylamine at 220 °C and 380 atm, and the cis,trans structure 6 was assigned to this compound.[8]



4

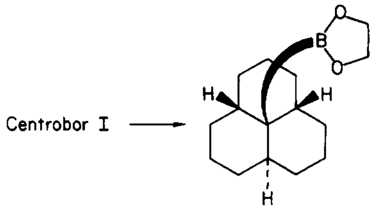


5



6

We have carbonylated both Centrobor I and Centrobor II in the presence of ethylene glycol and obtained the boronates 7 and 8, respectively.[1,10] If Köster's assignments were correct, it must be concluded that the all-cis isomer 5 is converted into the cis,cis,trans boronate 7 and the cis,trans isomer 6 into the cis,cis,cis boronate 8. Such transformations would require inversion of the stereochemistry at one of the three carbon atoms adjacent to the boron atom.[11] These seemingly inconsistent results, coupled with the at best tenuous structural assignments by Köster,[8] led us to question the original structural assignments and reexamine the stereochemistry of the two isomeric organoboranes by a detailed NMR investigation of the free organoboranes and their pyridine addition compounds.



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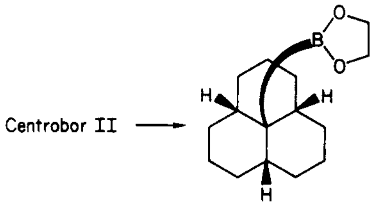

8

Results and Discussion

Hydroboration of Acyclic Trienes. Prior to our investigation, relatively little work had been reported on the

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(1) Reported in part as preliminary communications. (a) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1969**, *91*, 1224. (b) Brown H, C.; Dickason, W. C. *Ibid.* **1969**, *91*, 1226.

(2) Based in part on a thesis submitted by W. C. Dickason in partial fulfillment of the requirements for the degree of Doctor of Philosophy: Dickason, W. C., Ph.D. Thesis, Purdue University, 1970.

(3) (a) Postdoctoral Research Associate on a grant (GM 10937) supported by the National Institutes of Health. (b) Graduate Research Assistant on grants (G 19875 and GP 6492X) supported by the National Science Foundation.

(4) (a) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5280. (b) Brown, H. C.; Negishi, E.; Gupta, S. K. *Ibid.* **1970**, *92*, 2460. (c) Brown, H. C.; Negishi, E. *J. Organomet. Chem.* **1971**, *26*, C67, C1. (d) Brown, H. C.; Negishi, E.; Burke, P. L. *J. Am. Chem. Soc.* **1971**, *93*, 3400. (e) Brown, H. C.; Negishi, E. *Ibid.* **1971**, *93*, 6682. (f) Brown, H. C.; Negishi, E.; Burke, P. L. *Ibid.* **1972**, *94*, 3561. (g) Negishi, E.; Burke, P. L.; Brown, H. C. *Ibid.* **1972**, *94*, 7431. (h) Burke, P. L.; Negishi, E.; Brown, H. C. *Ibid.* **1973**, *95*, 3654.

(5) (a) Brown, H. C.; Pfaffenberger, C. D. *J. Am. Chem. Soc.* **1967**, *89*, 5475. (b) Brown, H. C.; Negishi, E. *Ibid.* **1967**, *89*, 5477. (c) Brown, H. C.; Negishi, E. *Chem. Commun.* **1968**, 594. (d) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1972**, *94*, 3567.

(6) For a review with other pertinent references, see: Brown, H. C., Negishi, E. *Pure Appl. Chem.* **1972**, *29*, 527.

(7) Smutny, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 6793. We are indebted to Dr. Smutny for a generous gift of the triene.

(8) Rotermund, G. W.; Köster, R. *Liebigs Ann. Chem.* **1965**, *686*, 153.

(9) For other related references, see: (a) Köster, R. *Angew. Chem.* **1957**, *69*, 684. (b) Köster, R.; Griaznov, G. *Ibid.* **1961**, *73*, 171. (c) Köster, R.; Bruno, G.; Binger, P. *Liebigs Ann. Chem.* **1961**, *644*, 1. (d) Köster, R.; Rotermund, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 217. (e) Rotermund, G.; Köster, R. *Ibid.* **1962**, *1*, 269. (f) Köster, R. *Ibid.* **1964**, *3*, 174. (g) Köster, R. *Prog. Boron Chem.* **1964**, 1, 289. (h) Köster, R. *Adv. Organomet. Chem.* **1964**, *2*, 257. (i) Köster, R.; Larbig, W.; Rotermund, G. W. *Liebigs Ann. Chem.* **1965**, *682*, 21. (j) Greenwood, N. N.; Morris, J. H. *J. Chem. Soc.* **1960**, 2922. (k) Köster, R.; Griaznov, G.; Larbig, W.; Binger, P. *Liebigs Ann. Chem.* **1964**, *672*, 1.

(10) For the use of 5 and 6 as intermediates, see: Boron-containing derivatives: (a) Brown, H. C.; Dickason, W. C. *J. Am. Chem. Soc.* **1970**, *92*, 709. (b) Corey, E. J.; Varma, R. K. *Ibid.* **1971**, *93*, 7319. (c) Grudzinskas, C. V.; Weiss, M. J. *Tetrahedron Lett.* **1973**, 141. (d) Köster, R.; Bellut, H.; Fenzyl, W. *Liebigs Ann. Chem.* **1974**, 54. (e) Brown, H. C.; Krishnamurthy, S.; Hubbard, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3343. (f) Brown, C. A.; Krishnamurthy, S. *J. Organomet. Chem.* **1978**, *156*, 111. (g) Brown, H. C.; Hubbard, J. L.; Singaram, B. *J. Org. Chem.* **1979**, *44*, 5004. (h) Brown, H. C.; Kramer, G. W.; Hubbard, J. L.; Krishnamurthy, S. *J. Organomet. Chem.* **1980**, *188*, 1. Alcohols: (i) Fujita, S.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2995. (j) Yamamoto, Y.; Brown, H. C. *J. Am. Chem. Soc.* **1974**, *39*, 861. (k) Collins, D. J.; Lewis, C.; Swan, J. M. *Aust. J. Chem.* **1974**, *27*, 2593. (l) Corey, E. J.; Hurt, S. D. *Tetrahedron Lett.* **1977**, 3923. (m) Pelter, A.; Maddocks, P. J.; Smith, K. *J. Chem. Soc., Chem. Commun.* **1978**, 805. Amines: (n) Fujita, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2827. (o) Mueller, R. H.; DiPardo, R. M. *J. Chem. Soc., Chem. Commun.* **1975**, 565. (p) Mueller, R. H. *Tetrahedron Lett.* **1976**, 2925. (q) Mueller, R. H.; Thompson, M. E. *Ibid.* **1979**, 1991; **1980**, *21*, 1093.

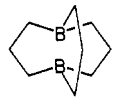
(11) In no case has the carbonylation of organoboranes been shown to involve inversion of the stereochemistry at the carbon atoms adjacent to the boron atom.[5b,c,12,13]

Table I. Reaction of 1,4,8-Nonatriene with Borane in Tetrahydrofuran or Triethylamine–Borane and the Thermal Treatment of the Hydroboration Products

hydroboration[a]			thermal treatment		alcohol products[c]					
						distribution,[e] %				
agent	solvent[b]	temp, °C	temp, °C	time, h	total yield,[d] %	I	II (13)	III	IV	V (14)
BH_3·THF	THF-DG	0		0	31	40	5	15	20	20
BH_3·THF	THF-DG	0	160	6	73		20[f]		~0	80
BH_3·NEt_3	DG	130–140		0	66	14	16	5	5	60
BH_3·NEt_3	DG	130–140	160	6	77		21[f]		~0	79

[a] By simultaneous addition of a hydroborating agent and 1,4,8-nonatriene. [b] THF = tetrahydrofuran; DG = diglyme. [c] Obtained after carbonylation–oxidation. [d] By GC (Carbowax 20M). [e] In the order of appearance in the GC analysis. [f] Including minor amounts of I and III.

hydroboration of acyclic trienes. The synthesis of two cyclic organoboranes, **9** and **10**, by the hydroboration of triallylborane and triallylamine–hydrochloride by Greenwood and co-workers[14] appeared to represent the only study in this area.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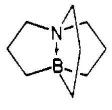
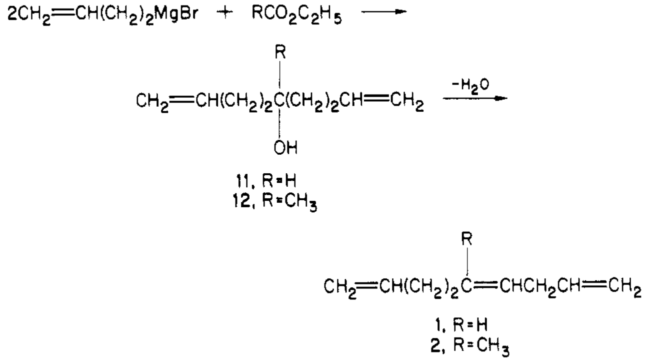

10

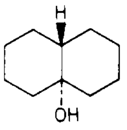
In the present study, we chose 1,4,8-nonatriene (**1**) as a model system and studied its reaction with borane in THF as well as with triethylamine–borane. A few satisfactory procedures were then applied to the cyclic hydroboration of 5-methyl-1,4,8-nonatriene (**2**) and 1,3,7-octatriene (**3**). The triene **1** was prepared in 80% yield by the dehydration of 1,8-nonadien-5-ol (**11**) by using an equimolar amount of boric acid as the dehydrating agent.[15] The dienol **11**, in turn, was synthesized in 90% yield from 4-bromo-1-butene and ethyl formate via the Grignard reaction. Similarly, the triene **2**[16] was prepared in 60% overall yield (based on 4-bromo-1-butene) by the dehydration of the intermediate tertiary alcohol **12** with 50% sulfuric acid. 1,3,7-Octatriene (**3**), prepared by the dimerization of 1,3-butadiene in the presence of phenol and (π-allyl)palladium chloride, was supplied by Dr. Smutny of Shell Development Co.[7]

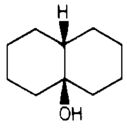

$$2CH_2{=}CH(CH_2)_2MgBr + RCO_2C_2H_5 \longrightarrow CH_2{=}CH(CH_2)_2\underset{OH}{\overset{R}{C}}(CH_2)_2CH{=}CH_2 \xrightarrow{-H_2O} CH_2{=}CH(CH_2)_2\overset{R}{C}{=}CHCH_2CH{=}CH_2$$

11, R=H
12, R=CH_3

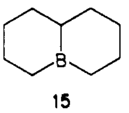
1, R=H
2, R=CH_3

Hydroboration of **1** with borane in THF in the molar ratio of 1:1 at 0 °C gave largely insoluble products, apparently polymeric organoboranes. The heterogeneous hydroboration mixture was not examined by GC or NMR. Instead, it was transferred into an autoclave under nitrogen and carbonylated with carbon monoxide at 70 atm, first at 50 °C (1 h) and then at 150 °C, in the presence of ethylene glycol (300 mol %).[12] After oxidation with alkaline hydrogen peroxide, the products were examined by GC (Carbowax 20M). There were present five peaks (I–V) in the ratio of 40:5:15:20:20 along with a few other very minor ones in the region expected for tertiary C_{10} alcohols. Since the results of elemental analyses of the crude distilled product correspond to the values for decalol, it appears safe to assume that all of these compounds are isomeric to each other. The combined yield of the five compounds was 31% using the GC response factor for *cis*-9-decalol. The peaks II and V were identified as *trans*- and *cis*-9-decalols (**13** and **14**). The experimental results are summarized in Table I, together with the results of thermal treatments.


13


14

The results described above indicate the following. First, unlike the cases of various dienes we have studied,[4-6] the hydroboration of 1,4,8-nonatriene (**1**) with borane in THF at 0 °C produces largely polymeric products. The relatively low yield of the monomeric bicyclic boranes may partly be attributable to the trifunctional nature of the triene.[17] Second, 9-boradecalin[9i,18] (**15**) is not the major monomeric bicyclic borane obtained by the hydroboration of 1,4,8-nonatriene at 0 °C. Although no effort was made to identify the other borane products, it is likely that the other major bicyclic boranes are perhydro-9-borazulene (**16**) and 1-methyl-8-borahydrindan (**17**) based on the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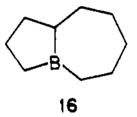
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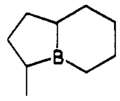
17

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(12) Brown, H. C. *Acc. Chem. Res.* **1969**, *2*, 65.

(13) Brown, H. C.; Rogić, M. M.; Rathke, M. W.; Kabalka, G. W. *J. Am. chem. Soc.* **1969**, *91*, 2150.

(14) Greenwood, N. N.; Morris, J. H.; Wright, J. C. *J. Chem. Soc.* **1964**, 4753.

(15) Presumably, a mixture of the cis and trans isomers was obtained. However, only a single peak was observed by GC (SE-30 or Carbowax 20M).

(16) A mixture of the cis and trans isomers. Two partially resolved peaks were observed by GC (SE-30).

(17) In order to observe comparable yields of monomeric cyclic products from a diene and a triene, the triene must possess a greater tendency to undergo cyclic hydroboration than the diene merely based on probability considerations.

(18) Köster and co-workers[9i] reported the synthesis of 9-boradecalin (**15**) and 8-boraindan from 1-nonene and 1-octene, respectively, via hydroboration–pyrolysis. Unfortunately, the pyrolytic preparation of bicyclic boranes from monoolefins usually requires a very high temperature, ≳300 °C, and the borane products are usually obtained only as impure mixtures in low yields, unless a specially designed circulating apparatus[9i] is used for pyrolysis. For example, the yield of 8-boraindan from 1-octene was reported to be only ca. 5%[9i] (based on borane used). Similarly, in our hand, the yield of **13** and **14** (24:76) obtained from 1-nonene was a mere 13%. Moreover, the products were contaminated by at least two other closely appearing byproducts.

Table II. Thermal Treatment of the Product Obtained by the Reaction of 5-Methyl-1,4,8-nonatriene with Triethylamine–Borane[a]

		alcohol products[b]								
thermal treatment			distribution,[d] %							
time, h	temp, °C	total yield,[c] %	I	II	III	IV	V	VI (18)	VII	VIII (19)
0		36	1	6	25	12	2	trace	32	22
6	160	74	7	trace	11	5	15	trace	trace	62
24	160	64	11	trace	10	5	19	trace	trace	55

[a] Hydroboration was carried out by the simultaneous addition of 5-methyl-1,4,8-nonatriene and triethylamine–borane to diglyme at 130–140 °C. [b] Obtained after carbonylation–oxidation. [c] By GC (Carbowax 20M). The products I–VIII were assumed to be isomeric to each other. [d] In the order of appearance in the GC analysis.

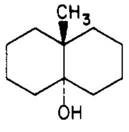
following general observations we have made with dienes.[6] First, in the competitive formation of five- and six-membered boranes via hydroboration, the former is kinetically favored. Second, in the competitive formation of six- and seven-membered boranes, neither is strongly favored, and the results are largely governed by the usual steric and electronic factors involved in the hydroboration of monoolefins.[19] Third, formation of four-membered boranes has not been observed. Fourth, little indication has been obtained for direct formation of nine- through thirteen-membered boranes by the hydroboration of dienes.[20] In the above discussion, we assume that the organoborane species present in the hydroboration mixture are converted into the corresponding alcohols having the same skeletal arrangements. This assumption is supported by the fact that, except with a few highly crowded organoboranes, such as *B*-thexyl-9-borabicyclo[3.3.1]nonane,[21] no noticeable isomerization or skeletal rearrangement accompanies the reaction of organoboranes with carbon monoxide.[10,12]

We then turned our attention to the thermal treatment of the hydroboration product derived from **1** and borane. The experimental results are also summarized in Table I. When the hydroboration mixture was refluxed in diglyme at ca. 160 °C for 6 h, a major change took place. The total yield of bicyclic alcohols obtained after carbonylation–oxidation was increased to 73% and the peaks, I, III, and IV, disappeared almost entirely. The only major products were **13** and **14** (20:80). Clearly, the thermal treatment converted essentially all monomeric bicyclic boranes as well as a major portion of polymeric species into **15**. When a distilled pure sample of **15** was carbonylated, even a higher yield (89%) of **13** and **14** was observed. These results, coupled with those discussed earlier which showed a markedly different product distribution, render further strong support for the assumption that no significant isomerization takes place during the carbonylation and that GC examination of the carbonylation product provides a convenient and reliable means of analyzing the hydroboration product.

The hydroboration of 1,4,8-nonatriene with triethylamine–borane was carried out at 130–140 °C by the simultaneous addition of the reactants to diglyme over 2–3 h. At no time was the formation of insoluble polymers observed. GC examination after carbonylation–oxidation revealed the presence of peaks I–V in 66% yield. However, thermal treatment of the hydroboration product for 6 h at 160 °C produced isomerically pure 9-boradecalin (**15**) in 77% yield. These experimental results are summarized in Table I. As shown in Table I, the use of triethylamine–borane does not increase the yield of 9-boradecalin significantly. However, if it is desirable to avoid the formation of insoluble polymers during hydroboration, this reagent may be used to advantage.

From the synthetic point of view, it was felt desirable to be able to accommodate an angular substituent in the C(10) position of 9-decalols. Accordingly, we synthesized 5-methyl-1,4,8-nonatriene (**2**) as described earlier and studied its hydroboration. It should be noted that the method for the preparation of the triene can accommodate various other groups in the C(10) position.

Hydroboration of **2** was carried out at 130–140 °C by the simultaneous addition of **2** and triethylamine–borane. After carbonylation–oxidation, GC examination (Carbowax 20M) revealed the presence of eight peaks (I–VIII) in the ratio of 1:6:25:12:2:trace:32:22 (in the order of appearance). Using authentic samples, peaks VI (present in a trace amount) and VIII were identified as *trans*- and *cis*-10-methyl-9-decalols[22] (**18** and **19**), respectively. The other products were not identified. However, judging from their GC retention times, it appears that they are isomeric to 10-methyl-9-decalol. The four most likely products would be alcohols produced in the carbonylation–oxidation of isomeric organoboranes analogous to **16** and **17**. Based on this assumption, the total yield was 36%. Here again, it is noteworthy that the largest two peaks do not correspond to **18** and **19**.



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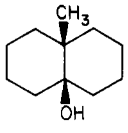
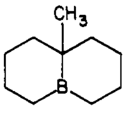


19

The hydroboration product was then subjected to thermal treatment for 6 h at 160 °C. After carbonylation–oxidation, GC examination indicated that peak VII, the largest peak in the previous experiment, and peak II disappeared almost completely. The total yield increased to 74% and **19** amounted to 62% of the total. These results are summarized in Table II. The major product **19**, which eluted last on a Carbowax 20M column, was isolated by preparative GC. Two especially interesting features of this synthesis should be pointed out. First, synthesis of the intermediate borane **20** involves placing the boron atom in the tertiary position of the carbon chain, rather than in the competing secondary or primary positions. It is likely that the strong tendency to form two fused six-membered rings is responsible. Second, this is the first observation of a successful migration of a tertiary



20

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(19) Brown, H. C. "Hydroboration"; W. A. Benjamin: New York, 1962.

(20) Unpublished observations by E. Negishi.

(21) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5283.

(22) We thank Professor J. A. Marshall of Northwestern University for these authentic samples.

Table III. Hydroboration of 1,3,7-Octatriene with Borane in Tetrahydrofuran or Triethylamine-Borane and the Thermal Treatment of the Hydroboration Products

hydroboration[a]			thermal treatment		yield of *cis*-8-hydrindanol,[c]
agent	solvent[b]	temp, °C	time, h	temp, °C	%
$BH_3 \cdot THF$	THF-DG	0	0		*d*
$BH_3 \cdot THF$	THF-DG	0	6	160	14
$BH_3 \cdot NEt_3$	DG	130–140	0		25
$BH_3 \cdot NEt_3$	DG	130–140	6	160	33
$BH_3 \cdot NEt_3$	TG	130–140	3	210	26
$BH_3 \cdot NEt_3$	TG	130–140	6	210	18

[a] By the simultaneous addition of 1,3,7-octatriene and a hydroborating agent. [b] DG = diglyme; TG = triglyme. [c] Obtained after carbonylation–oxidation. By GC (Carbowax 20M). [d] The hydroboration mixture was heterogeneous and its carbonylation was not attempted.

Table IV. Hydroboration of *trans,trans,trans*-1,5,9-Cyclododecatriene with Borane in Tetrahydrofuran or Triethylamine-Borane and the Thermal Treatment of the Hydroboration Products

hydroboration			thermal treatment		alcohol products[b]				
						distribution,[c] %			
agent	solvent[a]	temp, °C	time, h	temp, °C	total yield,[c] %	I	II (**23**)	III	IV (**24**)
$BH_3 \cdot THF$	THF-DG	0	6	160[d]	83	4.5	56	35	4.5
$BH_3 \cdot THF$	THF-TG	0	3	200[d]	68	1	84	10	5
$BH_3 \cdot THF$	THF-TG	0	6	200[d]	71	~0	92	~0	8
$BH_3 \cdot NEt_3$	DG	130–140	3	200[e]	75	~0	85	9	6
$BH_3 \cdot NEt_3$	DG	130–140	6	200[e]	73	~0	92	~0	8

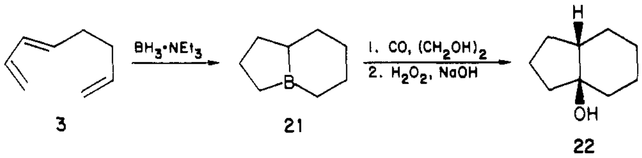
[a] DG = diglyme; TG = triglyme. [b] Obtained after carbonylation–oxidation. [c] By GC (Carbowax 20M). [d] THF was distilled. [e] Diglyme was removed.

Table V. Original and Revised Structural Assignments of Centrobors I and II

organoborane	original assignment[8]	revised assignment
Centrobor I	all-cis (**5**)	cis,trans (**6**)
Centrobor II	cis,trans (**6**)	all-cis (**5**)

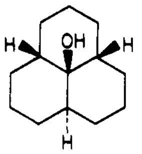
alkyl group from boron to carbon in the carbonylation reaction.[23]

Hydroboration of 1,3,7-octatriene with triethylamine–borane, followed by carbonylation–oxidation, produced a single monomeric bicyclic alcohol, identified as *cis*-8-hydrindanol (**22**) in 25% yield. Therefore, **21** must be the sole monomeric bicyclic borane product. A modest increase in yield (33%) was observed by subjecting the hydroboration mixture to thermal treatment for 6 h at 160 °C before carbonylation–oxidation. Thermal treatment at higher temperatures seems to have adverse effects on the yield of the product. The experimental results are summarized in Table III. As indicated in the table, at least in this case triethylamine–borane appears to be a superior hydroborating agent to borane in THF.

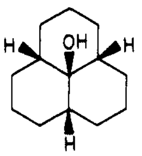


3 **21** **22**

Hydroboration of 1,5,9-Cyclododecatriene. The hydroboration of *trans,trans,trans*-1,5,9-cyclododecatriene (**4**) with an equimolar amount of borane in THF at 0 °C produced a white, apparently polymeric material. This product was not subjected to carbonylation. After the mixture was refluxed in diglyme for 6 h at ca. 160 °C, carbonylation–oxidation produced an 83% total yield of four apparently isomeric alcohols (I–IV) in the ratio of 4.5:56:35:4.5 (in the order of appearance in GC examination on a Carbowax 20M column). Alcohols II and IV were identified as **23** and **24**, respectively.[1] No detectable amounts of the other two stereoisomers **25** and **26**[2] were present. It is therefore probable that alcohols I and III correspond to two stereoisomers of a likely constitutional isomer **31**. Indeed, alcohol III was isolated and shown to be an isomeric tertiary C_{13} alcohol by elemental analyses and IR, NMR, and MS. No definitive conclusions, however, have been reached as to the exact skeletal arrangement and stereochemistry. When thermal treatment of the hydroboration mixture was carried out at ca. 200 °C for 6 h, the product obtained after carbonylation–oxidation consisted of a 92:8 mixture of **23** and **24**. No more than trace quantities of other products were observed. Quite similar results were obtained by using triethylamine–borane as a hydroborating agent. The experimental results are summarized in Table IV.



23



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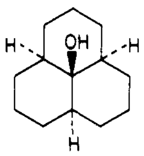

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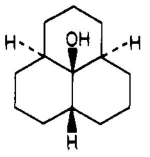

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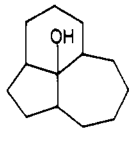

27

We have subsequently prepared and identified the other two stereoisomers **25** and **26** of perhydro-9b-phenalenol. The predominant formation of *cis,cis,trans*-perhydro-9b-phenalenol (**23**) from the hydroboration product strongly suggested that Centrobor I was *cis,trans*-perhydro-9b-boraphenalene (**6**) rather than the all-cis isomer **5**. In order to establish this point, we undertook to examine the free organoboranes (Centrobors I and II) as well as their pyridine adducts by NMR. A pure sample of Centrobor II was prepared by the isomerization of Centrobor I at 220 °C in the presence of triethylamine under 140 atm of hydrogen, followed by selective removal of the remaining

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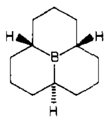
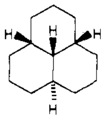
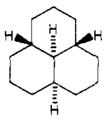
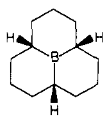
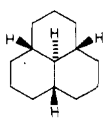
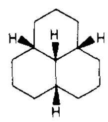
(23) For results obtained more recently, see: Negishi, E.; Brown, H. C. *Synthesis* **1972**, 197.

Table VI. NMR Data for Perhydro-9b-boraphenalenes and Perhydrophenalenes

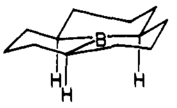
compound	NMR data, δ
 6	1.53
 28	1.46
 30	1.42 with a minor peak at 1.12
 5	1.85 and 1.32
 29	1.65 and 1.03
 31	1.47

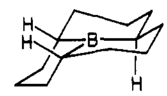
Centrobor I as the acetylacetonate.[8]

The NMR spectrum of the pyridine adduct of Centrobor I exhibited two distinct, but not entirely separated, peaks at δ 1.45 and 0.55 in the ratio of 19:2. On the other hand, the NMR spectrum of Centrobor II exhibited two completely separated peaks at δ 1.50 and 0.67 in the ratio of 18:3. Coordination of these boranes with pyridine could conceivably take place from either side, producing two possible adducts for each borane. Irrespective of the side of attack, however, the NMR data presented above are consistent only with our revised structural assignment (Table V).

Comparison of the NMR spectra of the free boranes with those of the hydrocarbon analogues was also made. The NMR spectrum of Centrobor I showed a broad peak with a maximum at δ 1.53 and strongly resembled that of *cis,cis,trans*-perhydrophenalene (28), which exhibited an essentially single peak centered at δ 1.85 and 1.32. This spectrum strongly resembled that of *trans,trans,trans*-perhydrophenalene[24] (29) with two peaks centered at δ 1.65 and 1.03. These results summarized in Table VI render a further strong support for the revised structural assignment.

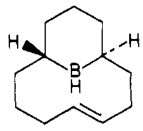
On the basis of the NMR data summarized in Table VI, it may be concluded that the conformation of 6 resembles that of 28 more closely than that of 30. Similarly, 29, but not 30, provides an excellent conformational model of 5. Thus, taking the trigonal planar nature of the trivalent boron atom into account, the approximate conformations of 5 and 6 may be represented as shown by 5a and 6a.


5a


6a

In the original study of Rotermund and Köster,[8] no effort was made to determine the equilibrium composition of the two isomeric perhydro-9b-boraphenalenes (5 and 6). So, we treated a pure sample of the cis,trans isomer 6 under the established equilibration conditions.[8] Periodic analysis of the organoboranes by GC (SF-96) indicated that the equilibrium mixture consisted of 87% 5 and 13% 6. Similarly, a pure sample of the all-cis isomer 5 was subjected to the hydroisomerization conditions. An equilibrium mixture of 89% 5 and 11% 6 was obtained. From these data, the difference between the free energies of 5 and 6 is estimated to be 1.9 ± 0.1 kcal/mol.

One puzzling result of the hydroboration of *trans,-trans,trans*-1,5,9-cyclododecatriene is the predominant formation of the less stable cis,trans isomer 6 as the initial thermal product. Simple model considerations do not seem to provide any clear-cut explanations. It may well be that the reaction involves the intermediacy of a trans bicyclic species, such as 32. Such a possibility may be tested by examining the reaction of the triene 4 with difunctional hydroborating agents, such as chloroborane and thexylborane.


32

Conclusions

First, the hydroboration of acyclic and cyclic trienes with borane in THF at 0 °C produces largely polymeric products, even when the trienes can, in principle, form bicyclic or polycyclic boranes consisting of common rings. The largely polymeric nature contrasts with the highly cyclic nature of the corresponding hydroboration of appropriate dienes.

Second, thermodynamically stable organoboranes with fused six-membered rings have not formed as the major kinetically favored monomeric cyclic products in the hydroboration of acyclic trienes[25] with borane in THF at 0 °C. These results are in accordance with the generalization made with dienes.[6]

Third, when possible, however, thermal treatment of the hydroboration products derived from acyclic and cyclic trienes results in the predominant formation of organoboranes with fused six-membered rings in high yields.

Fourth, the carbonylation–oxidation of organoboranes with fused six-membered rings provides predominantly one of the two possible stereoisomers. The preferred isomers are those which contain the maximum number of bridgehead hydrogen and/or carbon substituents that are α and cis to the hydroxy group, irrespective of the relative thermodynamic stability.

Fifth, NMR examination of the pyridine adducts of polycyclic organoboranes appears to provide a convenient means of establishing their stereochemistry. Using this technique, the original structural assignment of two isomeric perhydro-9b-boraphenalenes (5 and 6) was reversed. NMR examination of 5 and 6 themselves as well as the

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(24) An authentic sample of 29 was kindly supplied by Dr. A. Schneider.

(25) Although highly likely, this point has not been established with the cyclic triene 4.

results of carbonylation of **5** and **6**[1,2] are also consistent with the revised assignment.

Experimental Section

Boiling points and melting points were uncorrected. NMR and IR spectra were taken on a Varian A-60A spectrometer and a Perkin-Elmer 137B spectrometer, respectively.

Materials. Tetrahydrofuran (THF), diglyme, and triglyme were purified by distillation from lithium aluminum hydride and stored under nitrogen. The preparation of borane in THF was carried out as described previously.[26]

Preparation of 1,8-Nonadien-5-ol (11). To 3-butenylmagnesium bromide prepared from 100 g (740 mmol) of 4-bromo-1-butene and 16.8 g (700 mmol) of magnesium in diethyl ether was added dropwise under nitrogen 22.2 g (300 mmol) of ethyl formate purified by the reported procedure.[27] After treatment of the reaction mixture with saturated aqueous ammonium chloride (120 mL), extraction with diethyl ether, drying over magnesium sulfate, and distillation provided 38 g (90% based on ethyl formate) of **11**: bp 73–76 °C (5 mm); n^{20}_{D} 1.4541; NMR (CCl_4, Me_4Si) δ 1.30–1.75 (m, 4 H), 1.95–2.40 (m, 4 H), 3.57 (t of d, J = 6 and 6 Hz, 1 H), 4.10 (d, J = 6 Hz, 1 H), 4.93 (d, J = 9.5 Hz, 2 H), 4.97 (d, J = 17.5 Hz, 2 H), 5.50–6.20 (d of d of t, J = 17.5, 9.5 and 6 Hz, 2 H); IR (neat) 3300 (s), 1800 (w), 1700 (w), 1620 (s), 985 (s), 905 (s) cm^{-1}.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.95; H, 11.66.

Preparation of 1,4,8-Nonatriene (1). In a flask connected to a simple distillation apparatus were placed 6.2 g (100 mmol) of boric acid, 14.0 g (100 mmol) of 1,8-nonatrien-5-ol, and a trace amount of hydroquinone. The mixture was heated at 200 °C for 1 h without distillation. The temperature was then raised to ca. 300 °C, and the product was azeotropically distilled. The first minor fraction was mostly the starting dienol **11**. The major fraction was ca. 90% pure 1,4,8-nonatriene contaminated with **11**. Redistillation of this fraction provided 9.6 g (80%) of **1**: bp 86–88 °C (120 mm); n^{20}_{D} 1.4454; NMR (CCl_4, Me_4Si) δ 1.95–2.2 (m, 4 H), 2.55–2.85 (m, 2 H), 4.90 (d, J = 9.5 Hz, 2 H), 4.92 (d, J = 17.5 Hz, 2 H), 5.25–6.10 (m, 4 H); IR (neat) 1820 (w) 1640 (s), 995 (s), 975 (s), 915 (s) cm^{-1}.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.63; H, 11.85.

Preparation of 5-Methyl-1,8-nonadien-5-ol (12). The compound was prepared in a manner similar to that for the preparation of **11** described above, except that ethyl acetate was used instead of ethyl formate. Distillation provided the title substance in 77% yield: bp 83–84 °C (7 mm); n^{20}_{D} 1.4580; NMR (CCl_4, Me_4Si) δ 1.06 (s, 3 H), 1.25–1.75 (m, 4 H), 1.80–2.50 (m, 4 H), 4.80–5.10 (m, 4 H) and 5.40–6.10 (m, 2 H); IR (neat) 3460 (s), 1630 (s), 900 (s) cm^{-1}.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.05; H, 12.02.

Preparation of 5-Methyl-1,4,8-nonatriene (2). This compound was prepared by the dehydration of 5-methyl-1,8-nonadien-5-ol (**12**) with 50% sulfuric acid in 76% yield: bp 63–64 °C (25 mm); n^{20}_{D} 1.4500; NMR (CCl_4, Me_4Si) δ 1.40–1.70 (doublet-like m, 3 H), 1.90–2.20 (doublet-like m, 4 H), 2.40–2.80 (triplet-like m, 2 H), 4.60–5.20 (m, 5 H), 5.20–6.00 (m, 2 H); IR (neat) 1630 (s), 900 (s).

Hydroboration of 1,4,8-Nonatriene with Borane in Tetrahydrofuran in the Molar Ratio of 1:1. In a 200-mL flask equipped with a magnetic stirrer, a thermometer, a septum inlet, and a condenser connected to a mercury bubbler were placed 50 mL of diglyme. To this were added simultaneously at 0 °C over 2.5 h 18.4 mL (50 mmol) of 2.73 M borane in THF and 6.1 g (50 mmol) of 1,4,8-nonatriene dissolved in 11 mL of diglyme by using a Sage constant-speed, double-track spyringe pump. A largely insoluble, apparently polymeric product was formed. The heterogeneous hydroboration mixture was not examined directly, but carbonylated, as described below.

Carbonylation–Oxidation of the Product Obtained by the Hydroboration of 1,4,8-Nonatriene with Borane in THF. The hydroboration mixture obtained above was transferred into a 250-mL autoclave in a drybox. The carbonylation with carbon monoxide was carried out at 70 atm first at 50 °C (1 h) and at 150 °C (1 h, then cooled overnight) in the presence of 9.3 g (150 mmol) of ethylene glycol. The carbonylated mixture was oxidized with 20 mL (120 mmol) of 6 N sodium hydroxide and 20 mL of 30% hydrogen peroxide after addition of 20 mL of 95% ethanol as a cosolvent. The oxidation product was extracted with hexane, washed with water to remove diglyme, and dried over magnesium sulfate. One-half of the product was examined by GC (Carbowax 20M) using *n*-decane as internal standard. There were present five peaks (I–V) in the ratio 40:5:15:20:20 along with a few other very minor ones in the region expected for tertiary C_{10} alcohols. The combined yield of the five compounds was 31% by using the GC response factor for *cis*-9-decalol. Peaks II and V were identified as *trans*- and *cis*-9-decalols by coinjection of the authentic samples available in our laboratories. The results are summarized in Table I. The remainder of the oxidation product was evaporated and distilled. No attempt was made to record the distillation temperatures. GC examination showed all five peaks present before distillation. This crude distilled mixture was subjected to elemental analyses.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.69; H, 11.80.

Hydroboration of 1,4,8-Nonatriene with Triethylamine–Borane. Triethylamine–borane was prepared by the addition of 20.2 g (200 mmol) of triethylamine to borane in THF (75 mL, 2.67 M, 200 mmol) at 0–10 °C. Distillation at reduced pressure provided 20.9 g (91%) of triethylamine–borane. A flask equipped with a magnetic stirring bar, a thermometer, and a septum-inlet was connected to a distillation setup, and flushed with nitrogen. Diglyme (50 mL) was placed in the flask. To this were added simultaneously at ca. 130–140 °C over 2 h 6.1 g (50 mmol) of 1,4,8-nonatriene in 25 mL of diglyme and 5.75 g (50 mmol) of triethylamine–borane in 25 mL of diglyme.

Thermal Treatment of the Hydroboration Product Derived from 1,4,8-Nonatriene. The hydroboration of 1,4,8-nonatriene with either borane in THF or triethylamine–borane was carried out in a manner similar to those described earlier in this section except that the reaction flask in this case was connected to a short upright condenser which in turn was connected to a distillation setup. After completion of the hydroboration, the volatile substances were removed by distillation at atmospheric pressure and the residual mixture in diglyme was refluxed at ca. 160 °C. The thermally treated products were subjected to the carbonylation–oxidation, as described earlier in this section. The results are summarized in Table I.

Isolation and Identification of 9-Boradecalin (15). A sample of thermally treated product derived from 50 mmol of 1,4,8-nonatriene was distilled in vacuo to provide 4.55 g (67%) of **15**, which exhibited an IR spectrum superimposable to that reported previously:[9i] bp 104–106 °C (90 mm) [lit.[9i] bp 102–103 °C (100 mm)]; NMR (CCl_4, Me_4Si) δ multiplet at 0.5–2.3 with peaks at 0.89, 0.99, 1.05, 1.33 and 1.58.

Preparation of 2-(9-Decalyl)-1,3,2-dioxaborole. 9-Boradecalin (30 mmol) was carbonylated in a manner similar to that described earlier. After extraction with hexane and drying over magnesium sulfate, a 5-mmol aliquot was oxidized and analyzed by GC. The combined yield of *cis*- and *trans*-decalols (4:1) was 89%. The remaining 25-mmol aliquot was used to obtain *cis*-2-(9-decalyl)-1,3,2-dioxaborole by preparative GC (SE-30): NMR (CCl_4, Me_4Si) δ 1.43 (a relatively sharp peak with a broad background peak ranging from 0.7 to 2.1, 17 H), 4.10 (s, 4 H); IR (neat) 1375 (s), 1310 (s), 1240 (s), 1190 (s), 1130 (s), 1020 (s), 940 (m), 870 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{21}BO_2$: C, 69.26; H, 10.17. Found: C, 69.38; H, 10.32.

Preparation of *cis*-9-Decalol. An analytically pure sample of *cis*-2-(9-decalyl)-1,3,2-dioxaborole was oxidized in the usual manner with 6 N sodium hydroxide and 30% hydrogen peroxide. *cis*-9-Decalol thus obtained was >99% pure by GC, mp 64–65 °C [lit.[28] mp 64–65 °C], and exhibited IR and NMR spectra identical with those of an authentic specimen. An authentic sample of

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Table VII. Equilibration of *cis,trans*- and *all-cis*-Perhydro-9b-boraphenalenes

time, days	product composition, %	
	5	6
0 (using 6 as the starting material)	0	100
3	84	16
20	87	13
40	87	13
0 (using 5 as the starting material)	100	0
10	93	7
20	89	11

trans-decalol was also available in our laboratories.

Hydroboration of 5-Methyl-1,4,8-nonatriene (12) and 1,3,7-Octatriene (3). These experiments were carried out in a manner similar to those described above for the hydroboration of 1,4,8-nonatriene.

Carbonylation–Oxidation of the Products Obtained by the Hydroboration of 5-Methyl-1,4,8-nonatriene (2) and 1,3,7-Octatriene (3). These experiments were carried out in a manner similar to that described for the carbonylation–oxidation of the product derived from 1,4,8-nonatriene.

Identification of *trans*- and *cis*-10-Methyl-9-decalols (18 and 19). The cis isomer 19 was isolated from the reaction mixture obtained above by preparative GC (Carbowax 20M) and identified by comparing the GC retention time and spectral data with those of an authentic sample.[22] The trans isomer was identified by comparing the GC retention time with that of an authentic sample.[22]

Identification of *cis*-8-Perhydrindanol (21). The stereochemistry of 21 was initially established by its transformation into $\Delta^{8(9)}$-hexahydrindene by treatment with 50% sulfuric acid, followed by hydroboration–oxidation, to yield the original alcohol. Its identity was later confirmed by comparing the GC retention time with a sample prepared by a method developed recently.[29]

Hydroboration of *trans,trans,trans*-1,5,9-Cyclododecatriene. (a) With Borane in THF. This experiment was carried out in a manner similar to that described above for the hydroboration of 1,4,8-nonatriene with borane in THF. A white, apparently polymeric product was obtained and was subjected to thermal treatment, as described later.

(b) With Triethylamine–Borane. This experiment was carried out in a manner similar to that described above for the hydroboration of 1,4,8-nonatriene with triethylamine–borane. One representative procedure for the preparation of *cis,trans*-perhydro-9b-boraphenalene (6) is described later in this section.

Thermal Treatment of the Reaction Mixture Obtained by the Hydroboration of *trans,trans,trans*-1,5,9-Cyclododecatriene. Three different sets of conditions were employed. When THF and diglyme were used as solvents, THF evaporated, and the hydroboration mixture in diglyme was refluxed at ca. 160 °C. When THF and triglyme were used as solvents, THF was evaporated, and the residual mixture in triglyme was heated to 200 °C. When diglyme was used as a solvent, diglyme was distilled, and the residue was heated to 200 °C. The experimental results of thermal treatment are summarized in Table IV.

Preparation of *cis,trans*-Perhydro-9b-boraphenalene[30] (6). Triethylamine (54.6 g, 76 mL, 540 mmol) was slowly added to 540 mL (540 mmol) of 1.0 M borane in THF in a 1-L flask fitted with a thermometer and a Vigreux column connected to a distillation setup. Most of the THF was removed by distillation and 300 mL of diglyme was added. While maintaining the temperature of the reaction mixture at 130–140 °C, a solution of 87 g (536 mmol) of *trans,trans,trans*-1,5,9-cyclododecatriene in 100 mL of diglyme was added over 2.5 h by means of a syringe pump. Most of the diglyme was removed by distillation at atmospheric pressure under nitrogen. Thermal treatment of the hydroboration product was carried out at the pot temperature of 200 °C for 6 h. Simple distillation provided 80.0 g (85% yield) of a 92:8 mixture of *cis,trans*- and *all-cis*-perhydro-9b-boraphenalenes, bp 115–117 °C (10 mm). Spinning band distillation provided 98% pure *cis,trans*-perhydro-9b-boraphenalene, which exhibited an IR spectrum superimposable to that reported for Centrobor I.[8] GC examination of perhydro-9b-boraphenalenes was carried out on a Perkin-Elmer 226 capillary gas chromatograph with a 150 ft × 0.01 in. SF-96 column.

Preparation of *all-cis*-Perhydro-9b-boraphenalene (5). The following procedure is largely based on that reported by Rotermund and Köster[8] for the preparation of Centrobor I. *cis,trans*-Perhydro-9b-boraphenalene (50.0 g, 284 mmol) was mixed with 50 mL (357 mmol) of triethylamine in a 250-mL autoclave flushed with nitrogen. The vessel was charged with 100 atm of hydrogen and heated at 220 °C for 72 h. The volatile substances were removed at reduced pressure. The residue which consisted of an 85:15 mixture of 5 and 6 was heated with 7.0 g (70 mmol) of acetylacetone at 130 °C for 18 h.[8] Distillation provided a 70–75% yield of >99% pure *all-cis*-perhydro-9b-boraphenalene, bp 97 °C (5 mm), which exhibited an IR spectrum superimposable to that reported for Centrobor II.[8]

Equilibration of *cis,trans*-Perhydro-9b-boraphenalene (6). In an autoclave flushed with nitrogen was placed 15.0 g (85.0 mmol) of *cis,trans*-perhydro-9b-boraphenalene (6) and 15 mL (10.9 g, 107 mmol) of triethylamine. The vessel was charged with 100 atm of hydrogen at 25 °C and heated at 220 °C. Periodically, the reaction mixture was cooled and analyzed by GC. The results are summarized in Table VII.

Equilibration of *all-cis*-Perhydro-9b-boraphenalene (5). A 15-g sample of pure 5 was subjected to the same equilibration conditions as described above. The experimental results are summarized in Table VII.

Carbonylation of Perhydro-9b-boraphenalenes. This experiment was carried out as described in detail elsewhere.[30]

Oxidation of 2-(Perhydro-9b-boraphenalyl)-1,3,2-dioxaboroles. This experiment was carried out as described in detail elsewhere.[30]

Isolation and Characterization of Alcohol III Obtained by the Hydroboration–Carbonylation–Oxidation of *trans,trans,trans*-1,5,9-Cyclododecatriene. A mixture of alcohols consisting mostly of **23** and alcohol III in the ratio of approximately 60:40 was obtained by the hydroboration of *trans,trans,trans*-1,5,9-cyclododecatriene (4) with borane in THF followed by thermal treatment at 160 °C for 6 h and carbonylation–oxidation. A 3.8-g portion of the crude evaporated product was purified by column chromatography (neutral alumina, Merck) using hexane and benzene as solvents. The first fraction (1.2 g) was >95% pure **23**. After collecting 1.7 g of intermediate fractions, 0.6 g of at least 95% pure alcohol III was obtained. Fractional recrystallization from pentane or acetone did not improve the purity significantly: mp 43.5–45.0 °C; NMR (CCl_4, Me_4Si) δ broad peaks at 1.32 (exchangeable with D_2O), 1.42, and 1.83 with shoulders at 1.13 and 1.58; IR (KBr) 3450 (s), 2900 (s), 2860 (s), 1470 (s), 1460 (s), 1200 (m), 1068 (m), 1030 (m), 955 (m).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.22; H, 11.63. Found: C, 80.35; H, 11.41.

NMR Examination of the Pyridine Adducts of Perhydro-9b-boraphenalenes. The pyridine adducts were prepared by mixing perhydro-9b-boraphenalene with a 10% excess of pyridine in an NMR tube under nitrogen. The results are described in detail in the main text.

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