ether as eluent to give **12c** in 61% yield: mp 78–79 °C (*n*-hexane); NMR ($CDCl_3$) δ 1.40 (3 H, t, $CH_2C\mathbf{H}_3$), 3.06 (2 H, t, $C\mathbf{H}_2CH_2O$), 4.2–4.7 (4 H, m, $C\mathbf{H}_2CH_3$ and $CH_2C\mathbf{H}_2O$), 6.77 (1 H, s, CH=), 7.1–7.4 (3 H, m, Ar), 7.75–8.05 (1 H, m, Ar). Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.19; H, 5.50; N, 10.68.

Rearrangement of 9b. A solution of **9b** (1.3 g) in dry toluene (250 mL) was heated under reflux for 60 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column. Elution with benzene–ethyl acetate (85:15) gave unchanged **9b** (0.40 g) followed by **13a** (0.49 g); mp 107–109 °C (*n*-hexane); IR (Nujol) 3250–3350 (NH and OH) and 1700 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.32 (3 H, t, $CH_2C\mathbf{H}_3$), 3.40 (2 H, d, $J = 6$ Hz, $C\mathbf{H}_2CH=$), 4.29 (2 H, q, $C\mathbf{H}_2CH_3$), 6.1–7.3 (10 H, overlapping signals, Ar and CH=CH), 7.6 (1 H, broad s, OH), 8.4 (1 H, broad s, NH). Anal. Calcd for $C_{19}H_{19}ClN_2O_3$: C, 63.59; H, 5.34; N, 7.81. Found: C, 63.29; H, 5.55; N, 7.57.

Treatment of 13a with Triethylamine. A solution of **13a** (0.26 g) and triethylamine (0.50 g) in dry toluene (70 mL) was heated under reflux for 30 min. The mixture was washed with aqueous HCl, dried over $MgSO_4$, and evaporated. The residue was taken up with diisopropyl ether and filtered to afford practically pure **14a** (0.18 g) (NMR analysis).

Registry No.—**1a,** 1118-84-9; **1b,** 61363-91-5; **1c,** 61363-92-6; **1d,** 61363-93-7; **1e,** 61363-94-8; **2a,** 21045-82-9; **2b,** 61363-95-9; **2c,** 61394-29-4; **2d,** 61363-96-0; **2e,** 61363-97-1; **3a,** 61363-98-2; **3b,** 61363-99-3; **3c,** 61364-00-9; **3d,** 61364-01-0; **3e,** 61364-02-1; **5a,** 61364-03-2; **5b,** 61364-04-3; **5c,** 61364-05-4; **6a,** 61364-06-5; **6b,** 61364-07-6; **6c,** 61364-08-7; **8a,** 27096-64-6; **8b,** 61364-09-8; **8c,** 56182-23-1; **9a,** 61364-10-1; **9b,** 61364-11-2; **9c,** 61364-12-3; **11a,** 61364-13-4; **11b,** 61364-14-5; **11c,** 61364-15-6; **12c,** 61364-16-7; **13a,** 61364-17-8; **14a,** 61364-18-9; **14b,** 61364-19-0; sulfuryl chloride, 7791-25-5; 4-chlorobenzenediazonium chloride, 2028-74-2; ethyl 2-chloroacetoacetate, 609-15-4; triethylamine, 121-44-8.

Supplementary Material Available. Full NMR data for compounds **1, 2, 3,** and **9** (2 pages). Ordering information is given on any current masthead page.

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Hydroboration. 45. New, Convenient Preparations of Representative Borane Reagents Utilizing Borane–Methyl Sulfide

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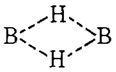
Convenient preparations for several highly useful borane reagents, such as thexyl-, disiamyl-, dicyclohexyl-, catechol-, diisopinocampheylborane, 9-borabicyclo[3.3.1]nonane, and 1,6-diboracyclodecane, utilizing the readily available, relatively stable reagent, borane–methyl sulfide (BMS), are described. The reactions of BMS with the respective olefins or with catechol proceed smoothly at room temperature in various solvents, such as tetrahydrofuran (THF), ethyl ether (EE), dichloromethane, and pentane. In some cases, the reaction involving the neat reagents at 0 °C can also be utilized. Methyl sulfide can be readily removed from the products. However, the presence of methyl sulfide does not interfere with typical applications of borane reagents, such as thexyl-, disiamyl-, dicyclohexyl-, and diisopinocampheylborane, normally utilized in situ, without isolation. This feature was examined by carrying out representative hydroborations with these reagents prepared from BMS and then subjecting the resulting organoboranes to subsequent representative transformations. In the case of stable and isolable reagents, such as 9-BBN, catecholborane, and 1,6-diboracyclodecane, methyl sulfide can be readily removed, along with the solvents, by distillation. A detailed study was made of the preparation of pure diisopinocampheylborane from (+)-α-pinene and BMS in various solvents, both at room temperature and at 0 °C. The applicability of this reagent thus produced in asymmetric synthesis was established by the hydroboration of *cis*-2-butene, followed by oxidation, to yield (*R*)-(−)-2-butanol in optical purities of 88–97%.

Both hydroboration and selective reduction based on organoborane derivatives are proving highly useful in organic synthesis.[2] Partially substituted borane reagents,[3] such as thexylborane, disiamylborane, dicyclohexylborane, diisopinocampheylborane (IPC_2BH), 9-borabicyclo[3.3.1]nonane (9-BBN), 1,3,2-benzodioxaborole (catecholborane), and 1,6-diboracyclodecane, are finding an increasing role in these applications.

Thexylborane is a highly versatile reagent,[4] especially valuable for the synthesis of unsymmetrical ketones and in the new annelation reactions leading to pure (100%) trans-fused bicyclic ketones. Disiamylborane and dicyclohexylborane are highly hindered dialkylboranes possessing better regioselectivity than borane itself.[2,5,6] These hindered reagents are used especially for the monohydroboration of alkynes to the vinylborane stage.[7] Catecholborane is a mild hydroborating[8] and reducing[9] agent, whose chemistry has recently been reviewed.[10] Unlike other dialkylboranes, 9-BBN is exceptionally stable toward disproportionation. Under nitrogen, it is indefinitely stable at room temperature. Its favorable physical properties and unusual stability have made 9-BBN the only commercially available dialkylborane.[11] It is both an exceptionally regioselective hydroborating agent[2,12] and a useful agent for the selective reductions of organic functional groups.[13] Diisopinocampheylborane (IPC_2BH) is both a chiral hydroborating and reducing agent,[14] extensively used for the asymmetric synthesis of optically active alcohols,[15-17] iodides,[18] and amines[19] from achiral olefins, and amino acids[20] from achiral nitriles. The cyanoborohydride obtained from IPC_2BH has been used for stereoselective reductions in the prostaglandin synthesis.[21] However, 1,6-diboracyclodecane is unique[22] in that it does not hydroborate olefins; it is stable to air, water, and alcohols at room temperature, and is apparently the first molecule containing a transannular hydrogen bridge:



A large number of interesting derivatives can be prepared by the symmetrical and unsymmetrical cleavage of the BH_2B bridge.[23,24]

Until recently, all of these mono- and disubstituted boranes were prepared from borane–tetrahydrofuran (BH_3·THF)[2] or sodium borohydride–boron trifluoride in diglyme (BH_3·DG).[2] However, borane–methyl sulfide[11,25] is a more convenient reagent for the following reasons: (1) BH_3·THF must be stored at 0 °C. Even then, THF is gradually cleaved and the cleavage can become significant upon long storage. But BMS is indefinitely stable at 0 °C and can even be kept at room temperature without detectable change. (2) Reactions with BH_3·THF or BH_3·DG limit the choice of solvents to THF and DG, respectively. Both of these solvents are relatively expensive, and require both careful purification and storage in the absence of oxygen. They are readily miscible with both polar and nonpolar solvents; consequently, they can offer difficulty in their separation from the desired products. On the other hand, BMS permits the use of a wide variety of solvents, such as ethyl ether, dichloromethane, benzene, pentane, hexane, etc. (3) While BH_3·THF is available only as a 1 M solution, BMS is available in highly concentrated form. The commercially available neat liquid is nearly 10 M in BH_3, and considerably more stable than BH_3·THF, offering special advantages in shipping, handling, and storing. (4) The odor of dimethyl sulfide, which might be considered to be a disadvantage, actually proves to be an advantage. The odor serves as a sensitive warning of poor techniques, which should be avoided in working with boranes.

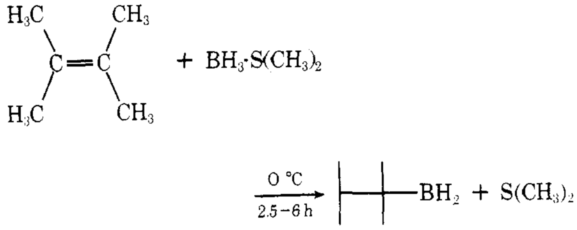
Because of these advantages, BMS is finding increasing application in hydroboration[25-27] and in selective reductions.[25,28,29] Unfortunately, thus far there have been no attempts to develop procedures for the preparation of the frequently applied borane reagents from BMS. We describe here both kinetic studies and convenient preparative methods for thexyl-, dicyclohexyl-, disiamyl-, catecholborane, IPC_2BH, 9-BBN, and 1,6-diboracyclodecane from BMS and the corresponding olefins or catechol in representative aprotic solvents of varied polarity, e.g., THF, ether, dichloromethane, and pentane, at both room temperature and at 0 °C. In addition, in some cases, the desired reagent can be synthesized easily merely by mixing the neat reactants in the stoichiometric quantity.

Methyl sulfide coordinates quite weakly with the monoalkyl-, dialkyl-, and dialkoxyboranes prepared in this study. Consequently, its presence in the reaction mixture does not interfere with the utilization of these reagents for subsequent applications.[29a] This was demonstrated for dicyclohexyl-, disiamyl-, thexyl-, and diisopinocampheylborane, which were used for representative application in situ. In the procedures involving the isolation of 9-BBN, catecholborane, and 1,6-diboracyclodecane, methyl sulfide (bp 38 °C) readily distills off with the solvent, leaving the pure reagent.

Results and Discussion

In the present study, particular importance was given to exploring the preparation of commonly used, substituted borane reagents from BMS in different solvents at two different temperatures. THF, EE, dichloromethane, and pentane were chosen as representative solvents for hydroboration at both room temperature and 0 °C. In the past, preparations and applications of these reagents were mainly studied at 0 °C, in THF or DG. In accordance with the previous reports,[29] we also observed that BMS reacts moderately slower than BH_3·THF. However, the difference in rates offered no major difficulty. Individual reagents are discussed below.

Thexylborane. The hydroboration of 2,3-dimethyl-2-butene with BMS in 1:1 ratio proceeds cleanly to the monoalkylborane stage. At 0 °C, the conversion of the olefin to thexylborane in THF, EE, CH_2Cl_2, and pentane is almost complete in 2.5–6 h (eq 1). Aliquots of the reaction mixture



(1)

were withdrawn at definite intervals of time and estimated for residual hydride by hydrolysis. The hydride utilized for hydroboration was calculated by difference and thus the rate of the reaction established.

The reaction with neat reagent is fast, complete in about 2 h at 0 °C. The rate of the reaction was determined by oxidizing individual reaction mixtures at appropriate intervals of time. The yields of 2,3-dimethyl-2-butanol, analyzed by GC at these intervals, correspond to the percentage of hydroboration at the specified intervals and hence to the rate of reaction.

The reaction of 2,3-dimethyl-2-butene with borane in diglyme[30] or borane—THF[31] is virtually complete in 1–2 h at 0 °C. From the results of the BMS study, it is evident that the reaction of olefin with neat BMS is comparable in rate with that realized with 1 M BH_3·THF or BH_3·DG. The results of hydroboration with BMS in various solvents (e.g., THF, EE, CH_2Cl_2, and pentane) indicated that the reaction is slightly faster in THF. In the case of EE, CH_2Cl_2, and pentane, the hydroboration is about 90% complete within 3 h, with further reaction being slow. As revealed in Figure 1, only minor variations in the rates of hydroboration in the different solvents are observed.

In the case of the reaction under neat conditions, methyl sulfide can be easily pumped off and the resulting neat thexylborane (liquid at room temperature) can be used as such, or converted to its amine complexes by addition of the appropriate amine or to the dimethyl thexylboronate by methanolysis.

Application of Thexylborane in the Ketone Synthesis. The presence of methyl sulfide in solution with the reagent thexylborane does not interfere in its application for further hydroboration and subsequent reaction. This was demonstrated in the ketone synthesis via the cyanidation reaction[32] (eq 2). Thexylborane in THF, thus produced from BMS, reacted smoothly with 1 mol of cyclopentene at −25 °C to form thexylcyclopentylborane in 1 h (comparable with the reaction of thexylborane from BH_3·THF[33]). This dialkylborane was readily converted with 1-pentene to thexylcyclopentyl-*n*-pentylborane (1 h, 0 °C). Treatment with NaCN produced the trialkylcyanoborate. Acylation with trifluoroacetic anhydride

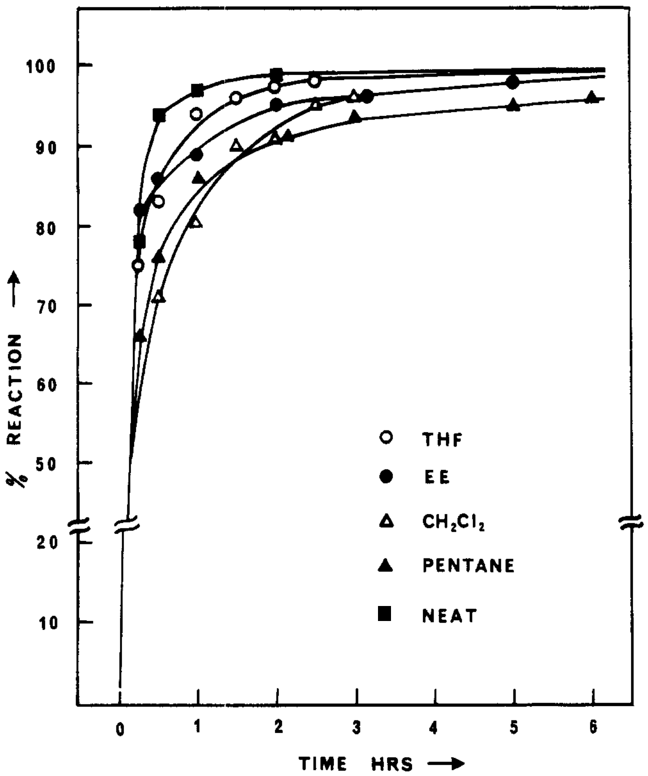
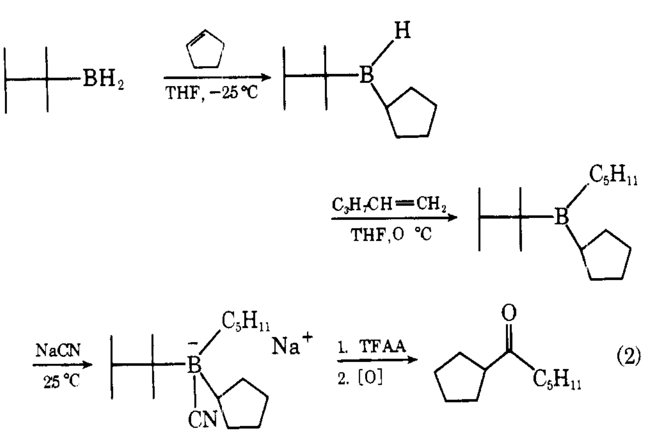


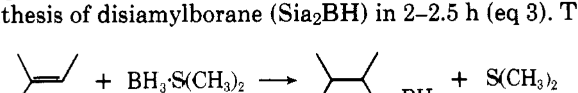
Figure 1. Reaction in a molar ratio of 1:1 of 2,3-dimethyl-2-butene with borane–methyl sulfide in various solvents at 0 °C.

(−78 to 25 °C), followed by oxidation, afforded cyclopentyl *n*-pentyl ketone in 95% yield by GC.



(2)

Disiamylborane. The reaction between 2-methyl-2-butene and BMS in 1 M THF,[34] EE, CH_2Cl_2, and pentane at room temperature, in the ratio of 2:1, proceeded smoothly to the synthesis of disiamylborane (Sia_2BH) in 2–2.5 h (eq 3). The



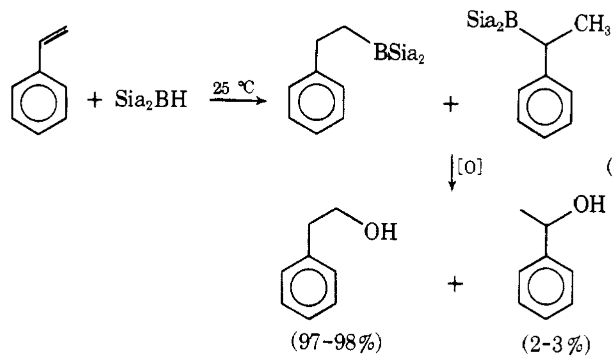
(3)

course of the reaction was followed by estimation of residual hydride in solution at different intervals of time. Following completion of the reaction, the mixtures were oxidized and 3-methyl-2-butanol was obtained in quantitative yield (GC).

For the reaction utilizing neat reagents, the reaction mixture was kept at −10 °C initially and then stirred at room temperature for 2 h. The rate of hydroboration was established as in the case of the neat thexylborane reaction.

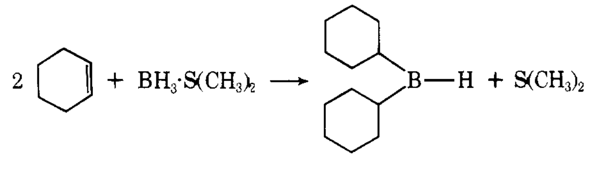
Disiamylborane thus prepared can be used as such for organic synthesis as described below or can be converted to the methyl disiamylborinate in good yield by methanolysis. This is a valuable intermediate for the synthesis of unsymmetrical diynes.[34]

Application of Disiamylborane for the Regiospecific Hydroboration of Styrene. Disiamylborane, prepared as described above, in THF, EE, CH_2Cl_2, and pentane was utilized for the hydroboration of styrene[35] at room temperature. The reaction was complete within 2 h in all of these solvents (eq 4). The reaction mixtures were then oxidized and the composition of the products determined by GC is shown in eq 4.



(4)

Dicyclohexylborane. The hydroboration of cyclohexene (2 M) with BMS (1 M in borane equivalent) was carried out at 0 °C in THF, EE,[36] CH_2Cl_2, and pentane. The hydroboration is also effected by mixing the neat reagents at 0 °C (eq 5).



(5)

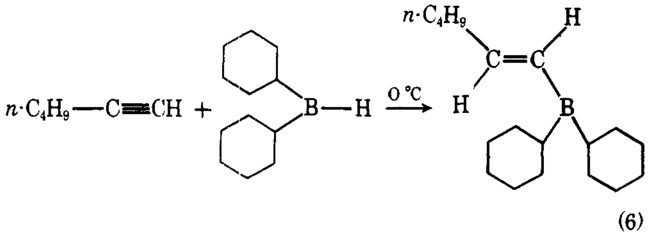
The procedure consists in adding cyclohexene to a well-stirred solution of BMS in the different solvents. At appropriate intervals of time, samples were removed and analyzed for residual olefin by GC for the reactions in EE, CH_2Cl_2, and pentane. The rate of the reaction was thus established. These reactions are essentially complete in 3 h. The rate of hydroboration in THF was followed by methanolyzing individual reaction mixtures at different time intervals. The amount of methyl dicyclohexylborinate was calculated from the NMR spectra using a known amount of benzene as internal standard.

Hydroboration under neat conditions is extremely fast, complete in 15 min at 0 °C. The rate of hydroboration was followed as previously described for neat conditions.

Solutions of dicyclohexylborane undergo disproportionation with time. Consequently, such solutions should be freshly prepared and utilized shortly after their preparation. The presence of dimethyl sulfide appears to stabilize such solutions somewhat, but not sufficiently so as to avoid such disproportionation over several hours.

Application of Dicyclohexylborane in the Zweifel Cis Olefin Synthesis.[37] Dicyclohexylborane in THF, EE, CH_2Cl_2, and pentane was prepared and 1-hexyne added to it at 0 °C. The vinylborane thus formed was treated with NaOH and iodine to yield *cis*-1-cyclohexyl-1-hexene (GC yield: THF, 89%; EE, 84%; CH_2Cl_2, 75%; pentane, 83%) (eq 6). Hence the presence of methyl sulfide does not interfere with this synthesis.

Catecholborane. Until recently, catecholborane was prepared by the reaction of catechol with BH_3-THF at 0 °C.[8] The difficulty in the reaction appears to be the complete removal of THF from the catecholborane during distillation at reduced pressure. The procedure is relatively tedious and time consuming. Hence, the synthesis of catecholborane by the reac-



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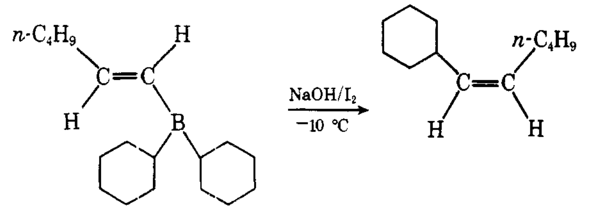
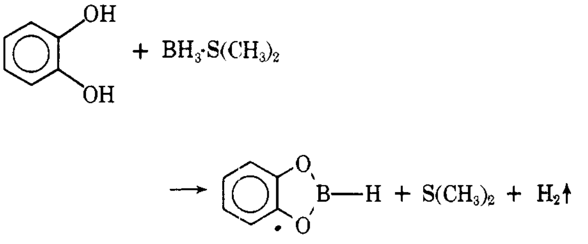


tion of catechol with BMS in a volatile solvent, such as EE, was explored (eq 7). The reaction of catechol (1 M) and BMS (1.1 M) in EE at 0 °C is slow and takes about 10 h (as monitored by gas meter) to go to approximate completion.[38] Distillation afforded about 75% catecholborane.



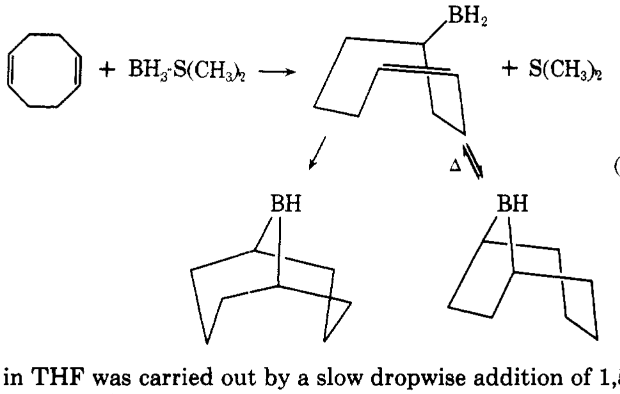
(7)

In one experiment, solid catechol (1 M) was added to neat BMS (1.1 M) at 0 °C. Catecholborane was obtained in poor yield (~46%), presumably due to the slow two-phase reaction.

To minimize the reaction time, it was decided to carry the reaction out at room temperature. The reaction of catechol with BMS at room temperature was carried out in both 1 M, as well as 2 M, ether solution and pure catecholborane was obtained by distillation in 72–73% yield. The rate of the reaction in 1 M ether solution was followed by the evolution of hydrogen (as monitored by a gas meter) at different intervals of time. The reaction is essentially complete in 3–4 h.

Catechol proved to be only sparingly soluble in CH_2Cl_2 and pentane. Hence, study of the synthesis in these solvents was not pursued.

9-BBN. Hydroboration of 1,5-cyclooctadiene with BMS, followed by thermal isomerization, yields 9-BBN in high yield (eq 8). Reactions in 2 M THF solution at room temperature and in neat reagents at 0 °C were studied (eq 8). The reaction in THF was carried out by a slow dropwise addition of 1,5-cyclooctadiene to a solution of BMS in THF at room temperature. Hydroboration was complete in 1 h at room temperature, as realized by residual hydride estimation. Oxidation of a small portion of the aliquot with alkaline hydrogen peroxide and GC analysis of the 1,4- and 1,5-cyclooctanediols revealed that the initial hydroboration product is a 30:70 mixture of borabicyclo[4.2.1]- and [3.3.1]nonanes. Thermal isomerization was effected by refluxing in THF. The rate of isomerization was followed by oxidation and GC analysis of a portion of aliquot at definite intervals. In a period of 2 h, isomerization was complete.

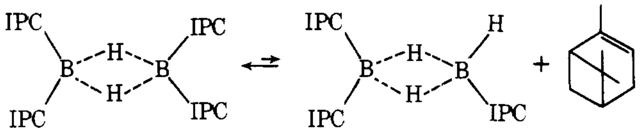


(8)

In the reaction under neat conditions, BMS was cooled to 0 °C and the diene was added very slowly with vigorous stirring. Several individual 5-mmol scale reactions were carried out. After appropriate time intervals, the contents of an individual reaction mixture were hydrolyzed to determine residual hydride. Hydroboration was complete after 0.5 h at room temperature. The product was approximately a 30:70 mixture of 1,4 and 1,5 isomers, respectively. Isomerization was effected by heating at 160 °C (above the melting point of 9-BBN) for 1 h, when methyl sulfide distilled off quantitatively.

Since 9-BBN can be isolated as a pure, stable crystalline solid, mp 153 °C, it did not appear desirable to examine its preparation in the various solvents. Also, the isomerization of the 1,4 to 1,5 isomer is very slow and incomplete in low-boiling solvents, such as dichloromethane.

Diisopinocampheylborane. The reaction of α-pinene with diborane to form diisopinocampheylborane (IPC_2BH) was previously studied in diglyme and THF at 0 °C.[30,31] The use of the reagent in asymmetric synthesis was studied via hydroboration of *cis*-2-butene, followed by oxidation.[15] The optical purities of 2-butanol realized in diglyme and THF were 87 and 78%, respectively. The lower optical purity in THF compared to that in diglyme was attributed to the greater solubility of IPC_2BH in THF than in diglyme, involving more dissociation in THF to triisopinocampheyldiborane and α-pinene[15] (eq 9).



(9)

In the preceding paper of this series[17] from our laboratory, it was demonstrated that the reaction of excess α-pinene with borane in THF at 0 °C attains equilibrium in 2–3 days with almost quantitative (~99.5%) formation of diisopinocampheylborane. The minor isomer of α-pinene accumulates in the solution, so that the product is almost pure diisopinocampheylborane, enriched in the major isomer. The 2-butanol obtained in the hydroboration of *cis*-2-butene with this pure reagent, followed by oxidation, revealed an optical purity of 98.4%, an almost complete asymmetric induction.

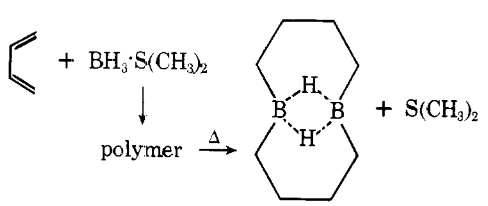
The question arose as to whether the more convenient reagent, BMS, can be utilized for this remarkable asymmetric synthesis. (+)-α-Pinene (optical purity of 95.2%) in 15% excess was slowly added at 0 °C to BMS in sufficient THF to make the final concentration of borane 1.0 M. The reaction mixture was then brought to 25 °C and maintained at that temperature for 14 h, and then kept in the cold room (~−2 °C) for another 10 h. Analysis of the supernatant solution for free α-pinene established that the minor isomer had accumulated in this phase, as in the previous synthesis involving BH_3·THF.[17] Consequently, the product must be the highly pure material, comparable to that prepared from BH_3·THF.[17]

Application of Diisopinocampheylborane to Asymmetric Hydroboration. The utility of this reagent was tested in the hydroboration of *cis*-2-butene. The flask and its contents from a typical preparation, as described above, were cooled to −25 °C and treated with a slight excess of *cis*-2-

butene. The reaction was allowed to proceed for 6 h. The product was then oxidized in the usual manner with alkaline hydrogen peroxide. Distillation provided (−)-2-butanol in a yield of 73%. Following purification by GC, the material exhibited a rotation of $[\alpha]^{25}_D$ −13.12°, an optical purity >97.2%.

The preparation of diisopinocampheylborane could also be achieved with BMS in the other solvents, EE, CH_2Cl_2, and pentane. However, there appears to be no advantage over THF to the use of these solvents for the synthesis of diisopinocampheylborane and its application for asymmetric hydroboration.

1,6-Diboracyclodecane. The primary product of the hydroboration of 1,3-butadiene with BMS is mainly a polymeric material, similar to that obtained with $BH_3 \cdot THF$.[22] Three procedures were employed for the hydroboration: (a) addition of BMS to a solution of diene in THF at 0 °C; (b) passing the diene into a solution of BMS in THF;[39] and (c) passing the diene into neat BMS at 0 °C (eq 10). In all of these methods, after mixing the reactants at 0 °C, the reaction mixture was stirred for 1 h at room temperature to ensure the completion of hydroboration. Depolymerization was effected by heating to 150 °C under reduced pressure, when the product distilled. The distillate contained a small quantity of active hydride impurity which could be easily removed by washing with cold, dilute alkaline hydrogen peroxide.



(10)

Conclusions

The present study has indicated the reaction conditions for the convenient synthesis of borane reagents, e.g., thexylborane, disiamylborane, dicyclohexylborane, catecholborane, 9-BBN, diisopinocampheylborane, and 1,6-diboracyclodecane, via hydroboration with BMS in a wide variety of solvents (e.g., THF, EE, CH_2Cl_2, and pentane). It also indicates the absence of complications in the utilization in organic syntheses of reagents so prepared.

Experimental Section

Since the boron hydrides are extremely sensitive to air and moisture, all reactions were carried out in the atmosphere of dry nitrogen. Special techniques employed in handling the air-sensitive materials and the usual experimental setup for hydroboration reaction or the subsequent utilization of organoboranes are described elsewhere.[40]

Materials. The olefins were distilled from lithium aluminum hydride and stored under nitrogen. High-purity catechol (Eastman Kodak) was sublimed and dried under vacuum. (+)-α-Pinene (Dragoco Co.) was used after distillation from $LiAlH_4$, which showed an optical rotation of $[\alpha]^{26.5}_D$ +48.7°, an optical purity of 95.2%.[41] However, after purification through GC using SE-30 column, it revealed $[\alpha]^{25.5}_D$ +49.48°, an optical purity of 97.4%. Purifications of EE, THF, CH_2Cl_2, and pentane were carried out according to standard methods.[40] BMS (Aldrich) was analyzed for hydride concentration and used directly. It was found to be nearly 10 M in BH_3 (±5% for different samples). For the active hydride estimation, the aliquot was hydrolyzed using a mixture of glycerine, THF, and water (1:1:1 ratio), except in case of 9-BBN, where a 1:1 mixture of CH_3OH and THF was employed. The volume of hydrogen evolved was measured in a gas buret.[40]

The following columns were utilized for the GC analysis: (A) for the analysis of alcohols, a 6 ft × 0.25 in. column packed with 10% Carbowax 20M on Chromosorb W; (B) for the separation of 1,4- and 1,5-cyclooctanediols as silyl ethers, a 18 ft × 0.125 in. column packed with 5% neopentyl glycol adipate on Varaport-30; (C) for the analysis of olefins and ketones, a 6 ft × 0.25 in. column packed with 10% SE-30 on Chromosorb W.

Reaction of 2,3-Dimethyl-2-butene (1.0 M) with BMS (1.0 M) in THF, EE, CH_2Cl_2, and Pentane at 0 °C. The reaction procedure in all of these solvents is similar. The reaction in THF is described as representative. With the usual experimental setup,[40] the hydroboration is carried out on a 10-mmol scale in a 50-mL flask. The reaction mixture containing a solution of 1.0 mL (10 mmol) of neat BMS, 1.14 mL (5 mmol) of *n*-dodecane (internal standard for GC) in 6.67 mL of THF was cooled to 0 °C in an ice bath. Hydroboration was initiated by dropwise addition of 1.19 mL (10 mmol) of 2,3-dimethyl-2-butene while stirring the contents of the flask at 0 °C. The total volume was 10 mL (1.0 M in both olefin and BMS). Aliquots (1.0 mL) were withdrawn at intervals of 0.5, 1.0, 1.5, 2.0, and 2.5 h and analyzed for residual hydride by hydrolysis. After 2.5 h, when the reaction was essentially complete, the reaction mixture was oxidized by the careful addition of 0.4 mL of water (at 0 °C), 0.6 mL of 3 M NaOH, 3.0 mL of THF, 1.0 mL of ethanol, and finally 1.0 mL of 30% aqueous H_2O_2 (at 25 °C). The reaction mixture was stirred at 55 °C for 2 h. The aqueous layer was saturated with anhydrous K_2CO_3 and the organic layer then dried over anhydrous $MgSO_4$ and molecular sieve (3 Å). GC analysis using column A revealed a 99.4% yield of 2,3-dimethyl-2-butanol.

As revealed in Figure 1, only minor variations in the rates of hydroboration in the different solvents are observed.

Reaction of 2-Methyl-2-butene with BMS in THF, EE, CH_2Cl_2, and Pentane at 25 °C. The reaction procedure in pentane is described as representative. The usual experimental setup was employed and the reaction flask containing 1.0 mL (neat, 10 mmol) of BMS and 2.43 mL (10 mmol) of *n*-tridecane in 4.4 mL of pentane was cooled to −10 °C. The contents of the flask were stirred and 2.17 mL (20 mmol) of 2-methyl-2-butene was added dropwise to it. The total volume was 10 mL (1.0 M in BMS). The reaction mixture was stirred at −10 °C for an additional 5 min and then the ice–salt bath was replaced by a water bath (25 °C). Aliquots (1 mL) were withdrawn at 0.5, 1.0, 1.5, and 2.0 h as before and analyzed for residual hydride. After 2 h, the reaction mixture was oxidized as before and analysis by GC using column A revealed a 98.5% yield of 3-methyl-2-butanol.

As in the previous case, variation of the solvent resulted in only minor changes in the observed rates of hydroboration.

Reaction of Cyclohexene with BMS in THF, EE, CH_2Cl_2, and Pentane at 0 °C. The following procedure for the rate of the reaction of cyclohexene with BMS in EE at 0 °C is representative. With the usual experimental setup, the hydroboration on 10-mmol scale was carried out as described above using 1.0 mL (10 mmol) of neat BMS and 2.02 mL (20 mmol) of cyclohexene containing 1.62 mL (10 mmol) of *n*-octane in 5.36 mL of EE. The reaction mixture was 1.0 M with respect to BMS. Aliquots (1 mL) of the clear supernatant solution were withdrawn at 0.5, 1.0, 2.0, and 3.0 h and quenched in an ice–water mixture; 3 M NaOH was added at 0 °C and the organic material extracted into EE. The EE layer was dried and analyzed for cyclohexene by GC using column C. From the amount of the olefin consumed, the rate of the reaction was estimated.

A modified procedure was utilized to follow the reaction in THF. Four different reactions were carried out on 10-mmol scale in four different 50-mL flasks by the dropwise addition of 2.02 mL (20 mmol) of cyclohexene to a stirred solution of 1.0 mL (10 mmol) of neat BMS in 6.98 mL of THF at 0 °C. Methanol (0.8 mL, 20 mmol) was added at 0.5, 1.0, 1.5, and 2.0 h intervals and each reaction mixture was stirred at 25 °C for 0.5 h. Solvent was removed at 15 mm, 0.44 mL (5 mmol) of benzene (internal standard for NMR analysis) was added, and methyl dicyclohexylborinate was analyzed by NMR. From these data, the rate of the hydroboration was established. The reaction was complete in 0.5 h. Here also, only minor variations in the time required for complete reaction were observed for the various solvents.

Reaction of Neat BMS with (a) 2,3-Dimethyl-2-butene at 0 °C; (b) 2-Methyl-2-butene at (−10 to 25 °C); (c) Cyclohexene at 0 °C. A. Four different reactions were carried out in individual reaction flasks cooled at 0 °C. The flasks were charged with 1.0 mL (10 mmol) of neat BMS and 1.14 mL (5 mmol) of *n*-dodecane. 2,3-Dimethyl-2-butene (1.19 mL, 10 mmol) was added dropwise while stirring the contents of the flask. The reaction mixtures were oxidized at 0.25, 0.5, 1.0, and 2.0 h by the addition of 10 mL of THF, 3 mL of ethanol, 1 mL of water, 2 mL of 6 M NaOH, and 3.5 mL of 30% aqueous H_2O_2. After stirring for 2 h at 50 °C, the reaction mixtures were cooled and the aqueous layer saturated with anhydrous K_2CO_3. The organic layer was dried and analyzed for 2,3-dimethyl-2-butanol by GC using column A. Thus the rate of hydroboration was determined.

B. The reaction procedure is similar to that described above. The addition of 2-methyl-2-butene (20 mmol) to BMS (10 mmol) was done at −10 °C. After keeping at −10 °C for 0.25 h, the reaction mixture was brought to 25 °C and then as before in A.

C. Three different reactions of 5-mmol scale were carried out by slowly adding 1.01 mL (10 mmol) of cyclohexene to a stirred solution of 0.5 mL (5 mmol) of neat BMS in 1.215 mL (5 mmol) of tridecane at 0 °C. The reaction course was followed by oxidation at 0.25, 0.5, and 1.0 h as described before in A. The hydroboration was complete in 0.25 h.

Preparation and Isolation of Thexylborane. The hydroboration of 2,3-dimethyl-2-butene with BMS was carried out under neat condition. With the usual experimental setup, 10 mL (neat, 100 mmol) of BMS was placed in a preweighed 100-mL flask fitted with a connecting tube and cooled to −10 °C in an ice–salt bath. 2,3-Dimethyl-2-butene (12 mL, 100 mmol) was then added dropwise while stirring the contents of the flask. After the addition was complete, the ice–salt bath was replaced by an ice bath (0 °C) and the reaction mixture was stirred for 2 h at this temperature. Volatile products were pumped off at 25 °C under aspirator vacuum (14 mm) and condensed in a trap cooled in dry ice–acetone (−78 °C). Analysis of the volatile products by GC showed only methyl sulfide and no 2,3-dimethyl-2-butene. the residue in the flask is pure thexylborane (9.6 g, 99%).

The purity of thexylborane was further established by methanolysis. To a solution of 4.25 g (43.8 mmol) of thexylborane in 3 mL of THF, there was added with stirring 7 mL (176 mmol) of methanol dropwise at 25 °C. After stirring for 0.5 h at 25 °C, THF, an excess of methanol was pumped off at 25 °C under 14 mm pressure and the residue was distilled to yield 5.59 g of pure dimethyl thexylboronate, bp 56–57 °C (14 mm), a yield of 82%.

Preparation and Isolation of Disiamylborane. The reaction of 2-methyl-2-butene with BMS can be carried out in THF, EE, CH_2Cl_2, or pentane to obtain disiamylborane. The preparation in THF is representative.[34] In a 500-mL flask with the usual hydroboration setup, 50 mL of THF and 10.2 mL (9.8 M, 100 mmol) of BMS) were placed. The flask was immersed in an ice–salt bath and 22.3 mL (14.7 g, 210 mmol) of 2-methyl-2-butene was added dropwise via a syringe. The reaction mixture was stirred at room temperature for 2 h. Disiamylborane thus obtained in quantitative yield can be used in situ. For example, the dropwise addition of 4.1 mL (3.2 g, 100 mmol) of methanol to the above product, followed by stirring for 1 h, provides methyl disiamylborinate, which can be utilized in situ in the unsymmetrical diyne synthesis.[24]

Preparation and Isolation of Dicyclohexylborane. Hydroboration of cyclohexene with BMS in THF, EE, CH_2Cl_2, and pentane gave almost the same results. The reaction in EE is described as representative.[36] In a 250-mL flask with the usual hydroboration setup, 10.0 mL (100 mmol) of BMS and 75 mL of EE were placed. The flask was cooled in an ice bath and 20.2 mL (16.4 g, 200 mmol) of cyclohexene was added dropwise during 15 min with vigorous stirring. Hydroboration was completed in 3 h at 0 °C. On pumping off the solvent, a quantitative yield of crystalline dicyclohexylborane (17.8 g) free from methyl sulfide was obtained, mp 103–104 °C (lit.[36] 103–105 °C) after sublimation.

The purity of this material was further established by methanolysis. The preparation of dicyclohexylborane was carried out as described above. When the reaction was complete (3 h, 0 °C), 15 mL of methanol was added slowly (~2.5 L of H_2 liberated). The reaction flask was brought to room temperature and solvent pumped off. The resulting material was >95% pure methyl dicyclohexylborinate, as determined by NMR. This can be distilled, bp 75–80 °C (0.005 mm), or can be used without distillation.

Application of Thexylborane. Synthesis of Cyclopentyl *n*-Pentyl Ketone. Thexylborane (10 mmol) in THF (1 M) was prepared from BMS as before. Thexylcyclopentyl-*n*-pentylborane (10 mmol) in THF was prepared following a similar procedure described in the literature.[33] Preparation of thexylcyclopentyl-*n*-pentylcyanoborohydride, its acylation with trifluoroacetic anhydride, and oxidation to cyclopentyl *n*-pentyl ketone were carried out following literature procedure.[32] The yield of cyclopentyl *n*-pentyl ketone, as analyzed by GC using column C, was 95%. The presence of the methyl sulfide created no difficulties, either in the hydroboration or the cyanidation stages.

Application of Disiamylborane. Hydroboration of Styrene in THF, EE, CH_2Cl_2, and Pentane. The experimental procedure for the reaction in pentane is representative. Disiamylborane (10 mmol) in pentane (1 M) was prepared from BMS as before. Hydroboration of styrene with the reagent was carried out following the literature procedure.[5] Analysis by GC showed 90% of alcohol (98% 2-phenylethanol and 2% 1-phenyl-1-ethanol).

Application of Dicyclohexylborane. Zweifel's *cis*-1-Cyclohexyl-1-hexene Synthesis.[37] The reaction in EE is representative. Dicyclohexylborane (10 mmol) in EE was prepared from BMS as before. Hydroboration of 1-hexyne with this reagent to the vinylborane followed by its reaction with iodine was performed following Zweifel's procedure.[37] GC analysis revealed 83% of *cis*-1-cyclohexyl-1-hexene.

Reaction of Catechol with BMS in EE. Preparation of Catecholborane. A. At 25 °C. With the usual experimental setup, the reaction was carried out in a 250-mL three-necked round-bottom flask fitted with a dropping funnel. The flask was immersed in a water bath (25 °C) and 20 mL (200 mmol) of neat BMS and 20 mL of dry EE were placed in the reaction flask. The solution of 22 g (200 mmol) of catechol in 55 mL of EE was introduced in the dropping funnel using a double-ended needle. The catechol solution was added dropwise to the stirred solution of borane over a period of 3 h. The reaction mixture was further stirred for 1 h when hydrogen evolution ceased (as monitored by gas meter). EE and methyl sulfide were removed under reduced pressure (50 mm) at 25 °C and the residue was distilled using a 60-cm Vigreux column to yield 17.22 g of pure catecholborane (72.3% yield), bp 80–81 °C (85–88 mm).

B. At 0 °C. The reaction procedure for 0 °C is similar to that described above in A. The reaction took 10 h for completion. Distillation yielded 75% of pure catecholborane.

9-BBN. A. Rate of Hydroboration in THF. With the usual experimental setup,[40] hydroboration was carried out in a 50-mL flask immersed in a water bath. To a well-stirred solution of 2.0 mL (20 mmol) of BMS in 5.54 mL of THF (to make 2 M in reactants) was added dropwise 2.46 mL (20 mmol) of 1,5-cyclooctadiene during 10 min. After the complete addition, a 1.0-mL aliquot was hydrolyzed at definite intervals of time and the volume of hydrogen liberated was measured. This gives the residual hydride concentration in the reaction mixture. The hydroboration of cyclooctadiene was thus found to be complete in 1 h.

B. Rate of Isomerization in Refluxing THF. Hydroboration of 1,5-cyclooctadiene was carried out as described in A. After completion of the reaction, 1.0 mL of the aliquot was oxidized. The remaining solution was refluxed and at definite intervals a 1.0-mL aliquot was withdrawn for oxidation. Analysis of the oxidation product for cyclooocane-1,4- and -1,5-diols gives the extent of isomerization. In 2 h, the isomerization was complete.

C. Oxidation of Aliquots. In a 50-mL flask equipped with reflux condenser, a 1.0-mL aliquot (2 mmol) was introduced with a syringe. Then 10 mL of THF, followed by 2 mL of water, were added. The flask was cooled in an ice bath and 1 mL (3 mmol) of 3 N sodium hydroxide was added, followed by a dropwise addition of 1.0 mL (8 mmol) of 30% hydrogen peroxide (100% excess). After the initial vigorous reaction subsided, the flask was maintained at 50 °C for 2 h. The aqueous layer was saturated with anhydrous potassium carbonate and the organic layer was used for GC analysis.

D. GC Analysis of Diols. Two drops of the THF solution from oxidation was taken in a vial, and 0.1 mL of dry pyridine and 0.1 mL (excess) of *N,O*-bis(trimethylsilyl)acetamide (BSA) were added. The mixture was thoroughly shaken and heated for 5 min. The product was injected into column B. The isomeric disilyl ethers separate nicely. Integration shows the isomer distribution (assuming the same response ratios for both isomers) of the two diols.

E. Isolation of 9-BBN from Reaction in THF. In a 250-mL flask equipped with a reflux condenser, and usual setup, 20 mL (200 mmol) of BMS and 55.4 mL of THF were introduced. The flask was immersed in a water bath, and while stirring vigorously, 24.6 mL (200 mmol) of 1,5-cyclooctadiene was added dropwise (exothermic), and stirring was continued for 1 h followed by 2 h of refluxing. The flask was cooled in an ice–salt mixture, when the 9-BBN crystallized. The supernatant liquid was decanted through a double-ended needle, and the crystals were washed with 50 mL of ice-cold pentane and dried under vacuum, yielding 21 g (86%) of product, mp 148 °C. Recrystallization from THF gave a material, mp 152–153 °C. Most of the 9-BBN can be recovered from the washings.

F. Rate of Hydroboration under Neat Conditions. Five different reactions were carried out, each on a 5-mmol scale in 25-mL flasks. Reactants were mixed at 0 °C. After fixed intervals, one flask at a time was connected to a gas meter and the contents were hydrolyzed by adding 15 mL of a 1:1 mixture of methanol and THF. Thus, the progress of hydroboration was followed by residual hydride estimation. Hydroboration was complete after 0.5 h at 0 °C followed by 0.5 h at room temperature.

G. Rate of Isomerization under Neat Conditions. The hydroboration was carried out as described in F. When the reaction was complete, each flask was heated in an oil bath at 160 °C for fixed intervals of time. After cooling, the contents were oxidized as described in C. GC analysis of the disilyl ethers revealed the isomer ratio in each case. Isomerization was thus found to be complete in 1 h.

H. Isolation of 9-BBN from Reaction of Neat Reagents. The apparatus was assembled as described in E, except that neat BMS was taken in the flask, cooled in an ice bath, and the diene was carefully added dropwise (exothermic). After 0.5 h at 0 °C, the contents were allowed to warm to room temperature and stirred for an additional 0.5 h. Distillation equipment was attached to the flask and isomerization was carried out by heating in an oil bath for 1 h at 160 °C, when methyl sulfide distilled almost quantitatively (11.7 g, 94%). The resulting solid (24.4 g, 100%) was crystallized from boiling THF, yield 20 g (82%), mp 146–147 °C. Recrystallization from THF afforded pure crystals, mp 153 °C.

Reaction of α-Pinene with BMS at 25 °C. Preparation of Diisopinocampheylborane (IPC_2BH). The experimental procedure for the preparation of IPC_2BH in THF, EE, CH_2Cl_2, and pentane is similar. The reaction in THF is described as representative. With the usual experimental setup, the reaction was carried out in a 300-mL, three-necked, round-bottom flask fitted with a dry ice–acetone condenser. The flask was cooled to 0 °C in an ice bath and was then charged with 39.7 ml (100 mmol) of 2.52 M BMS in THF and 23.5 mL of THF. (+)-α-Pinene (31.4 g, 230 mmol) ($[\alpha]^{23}{}_D$ +48.7°, an optical purity of 95.2%) was added dropwise over a period of 20 min. The ice bath was replaced by a water bath (25 °C) and the reaction mixture was stirred for another 2 h and then allowed to stand at this temperature for 14 h (the white precipitate of IPC_2BH was observed after 0.5 h). The reaction mixture was then kept in the cold room (∼−2 °C) for an additional 10 h.

Application of Diisopinocampheylborane (IPC_2BH). Hydroboration of *cis*-2-Butene at −25 °C. The reaction flask and its contents, from above, were then cooled to −25 °C (dry ice–CCl_4 bath) and 6.5 g (115 mmol) of *cis*-2-butene was added to the reaction mixture by means of a double-ended needle. The reaction mixture was stirred for 6 h at −25 °C and then warmed up to room temperature, followed by addition of 3 mL of water, 33 mL of 3 M NaOH, and 36 mL of 30% aqueous H_2O_2 (added dropwise) maintaining the temperature of the solution below 40 °C. It was further stirred for 2 h at 40 °C. The reaction mixture was then cooled, 33 mL of 3 M NaOH was added, and the aqueous layer was saturated with anhydrous K_2CO_3. The organic layer was separated and the aqueous layer was extracted with four 50-mL portions of ether. The combined ether extracts were washed twice with 20 mL of saturated NaCl solution and finally dried over anhydrous Na_2SO_4 overnight. It was further dried over anhydrous $MgSO_4$ for 4 h and then distilled using a 30-cm Widmer column. There was obtained 5.402 g of (−)-2-butanol [1.452 g at 84–97 °C (752 mm) and 3.950 g at 97 °C (752 mm)], a yield of 73%. The 97 °C fraction was further purified through preparative GC using 20% SE-30 and 10% SE-60 columns, $n^{20.5}{}_D$ 1.3975, $[\alpha]^{25}{}_D$ −13.12°, an optical purity of 97.2%.[42]

The α-pinene unreacted was recovered by distillation and purified through a 20% SE-30 column, $n^{20.5}{}_D$ 1.4660, $[\alpha]^{26.5}{}_D$ +39.6°, an optical purity of 76.2%.

1,6-Diboracyclodecane. A. Addition of BMS to Diene in THF. In a 250-mL flask fitted with the usual setup, 100 mL of THF was placed and the flask was cooled in an ice bath. A 25-mL graduated test tube was cooled in a dry ice–acetone bath (see Figure 9.22 in ref 2), and 14.8 mL (200 mmol, *d* 0.73 at −78 °C, bp −44 °C) of 1,3-butadiene was condensed. Then it was gradually allowed to distill into the reaction flask to prepare a solution of 1,3-butadiene in THF. To the diene solution in THF at 0 °C was slowly added 20 mL (200 mmol) of BMS during 15 min. After complete addition, the progress of the reaction was followed by the residual hydride estimation for 1 mL of aliquot each time. Reaction was complete after stirring for 1 h at 0 °C followed by 1 h at room temperature.

The solvent was distilled off at atmospheric pressure, and depolymerization was carried out by distillation under reduced pressure (18 mm). No liquid distilled until the oil bath temperature reached 140 °C. Almost all material distilled at 92–94 °C (18 mm) (bath temperature, 150 °C): yield 10.8 g; $n^{20}{}_D$ 1.4795; IR 2520, 1610, 1560 cm^{-1} absorptions due to >B–H, It contains an active hydride species as impurity, which can be removed by purification as described in the literature.[22] The yield of pure distilled 1,6-diboracyclodecane was 8.5 g (62%): bp 88–89 °C (16 mm), $n^{20}{}_D$ 1.4888, IR 1610 cm^{-1} in the region expected for >B–H absorption.

Addition of Diene to BMS in THF. The experimental setup is the same as in A, but in the reaction flask, 20 mL (200 mmol) of BMS and 80 mL of THF were placed. 1,3-Butadiene, condensed into the graduated test tube, was then allowed to distill slowly into the flask. The rest of the procedure was the same. After the workup, 1,6-diboracyclodecane was distilled: bp 88–89 °C (16 mm), yield 8.8 g (65%); $n^{20}{}_D$ 1.4895; IR 1610 cm^{-1} is the only >B–H absorption.

C. Addition of Diene to Neat BMS. The same procedure was followed as in B, but neat BMS was taken in the reaction flask. Since the reaction was very vigorous, an ice–salt mixture was used to cool the flask. After the usual workup, 1,6-diboracyclodecane was distilled: yield 8.7 g (64%); bp 88–89 ° C (16 mm); $n^{20}{}_D$ 1.4886; IR only 1610 cm^{-1} in the >B–H absorption region.

Registry No.—2,3-Dimethyl-2-butene, 563-79-1; BMS, 13292-87-0; 2-methyl-2-butene, 513-35-9; cyclohexene, 110-83-8; thexylborane, 61505-80-4; methanol, 67-56-1; dimethyl thexylboronate, 56118-62-8; disiamylborane, 61484-00-2; dicyclohexylborane, 61484-01-3; methyl dicyclohexylborinate, 32705-46-7; catechol, 120-80-9; catecholborane, 274-07-7; 9-BBN, 21205-91-4; 1,5-cyclooctadiene, 111-78-4; diisopinocampheylborane, 61997-72-1; (+)-α-pinene, 7785-70-8; *cis*-2-butene, 590-18-1; (−)-2-butanol, 14898-79-4; 1,6-diboracyclodecane, 34629-70-4; 1,3-butadiene, 106-99-0.

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