ethylphosphorochloridothioate (**5b**) [0.24 g, bp 24–25 °C (0.3 mmHg), $n^{20}_{\rm D}$ 1.4885, $[\alpha]^{20}_{\rm D}$ +52.35° (benzene)].³⁷

(Ethyloxy)ethyloxophosphoranesulfenyl Chloride (2b) with Triphenylphosphine (3f). According to the procedure described above from 2b (3.77 g, 0.02 mol) and 3f (4.6 g, 0.02 mol) a mixture of 4b ($\delta^{31}P$ 45 ppm, 30%), 5b ($\delta^{31}P$ 107.7 ppm, 20%), 6f ($\delta^{31}P$ 42.3 ppm, 30%), and 7f ($\delta^{31}P$ 25.5 ppm, 20%) was obtained. The fraction containing 4b (δ 46.5 ppm, 60%) and 5b (δ 106 ppm, 40%) was obtained after high-vacuum distillation [bp 21–23 °C (0.05 mmHg), n^{20}_{D} 1.4580, [α]²⁰_D +23.4° (neat). This rotation value was changed after 21 h to [α]²⁰_D +23.4° (neat). This

(37) Michalski, J.; Mikołajczyk, M. Chem. Ind. 1964, 661.

fraction was hydrolyzed by standard methods to yield **5b** [bp 23–24 °C (0.2 mmHg), n^{20}_{D} 11.4880, δ^{31} P 106.5 ppm, $[\alpha]^{20}_{D}$ +52.0° (neat)].

(Ethyloxy)ethyloxophosphoranesulfenyl Chloride (2b) with Tris(diethylamino)phosphine (3d). The same procedure was applied to the reaction of 2b (3.77 g, 0.02 mol) and 3d (4.04 g, 0.02 mol). ³¹P NMR analysis of crude reaction mixture, $[\alpha]^{30}_{D}$ +0.96° (neat), revealed the presence of 4b (δ 45 ppm, 48%), 5b (δ 106.2 ppm, 2%), hexaethyloamide of thiophosphoric acid (6d) (δ 79 ppm, 47%), and tris(diethylamino)phosphine oxide (7d) (δ 24 ppm, 3%). High-vacuum distillation afforded the fraction [1.5 g, bp 20–22 °C (0.05 mmHg), $[\alpha]^{22}_{D}$ +0.04° (neat)] which was found to contain 4b (δ 45.2 ppm, 100%). The rotation value of this fraction changed after 40 min to $[\alpha]^{20}_{D}$ -0.07° (neat).

Hydroboration. 88. Borane-1,4-Thioxane. A New, Convenient Hydroborating Agent for the Preparation of Representative Borane Reagents

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Borane-1,4-thioxane (BOT) (1), readily synthesized by adding diborane to 1,4-thioxane (2), is a stable liquid at 25 °C, which crystallizes on cooling to 0 °C, mp 11-15 °C. The neat reagent is 8.0 M in borane. It hydroborates alkenes rapidly in 3:1 mole ratio to form the corresponding trialkylborane in excellent yield. By varying the stoichiometric ratio of alkenes to 1 to 1:1 and 2:1 molar ratios, in certain cases monoalkylboranes, such as thexylborane (7) and monoisopinocampheylborane (8), and dialkylboranes, such as disiamylborane (3), dicyclohexylborane (4), diisopinocampheylborane (6), and 9-borabicyclo[3.3.1]nonane (9-BBN) (5), could be synthesized. The hydroboration reaction can be carried out at 25 °C in a wide variety of solvents, such as tetrahydrofuran (THF), diethyl ether (EE), methylene chloride (CH₂Cl₂), and pentane, or with neat reagents at 0 and 25 °C. It has been demonstrated that the presence of 2 does not interfere with the subsequent in situ utilization of these substituted borane reagents for further transformations. Unlike the ligand methyl sulfide, which is completely insoluble in water, 2 is moderately soluble in water (0.3 M). Consequently, it can be washed out with water from solutions in EE, CH_2Cl_2 , and pentane. Therefore, the organoborane containing 2 can be oxidized selectively to alcohol with a controlled quantity of hydrogen peroxide in the presence of excess sodium hydroxide without attack on 2. 2 in turn can then be removed by washing with water. Alternatively, 2 can be oxidized selectively in the presence of the organoborane by aqueous sodium hypochlorite. The resulting sulfoxide is highly soluble in water and is readily washed away from the organoboranes, thus enabling the organoboranes to be utilized for the many transformations it undergoes. In the case of stable and isolable reagents, such as 9-BBN, 2 can be removed either by decantation along with the solvent or by distillation during neat reaction. The two asymmetric hydroborating agents 8 and 6 were utilized for asymmetric syntheses by the hydroboration-oxidation reaction of 1-methyl-1-cyclopentene and cis-2-butene, respectively, to yield trans-2methylcyclopentanol and 2-butanol in 73% and 97% ee.

The applicability of borane-tetrahydrofuran² (BH₃·TH-F) and borane-methyl sulfide³ (BMS) as valuable hydroborating agents is well recognized. Thus, BH₃·THF and BMS hydroborate essentially all alkenes rapidly and quantitatively to yield a wide variety of fully or partially substituted organoboranes. While the application of the commercially available dilute solution of borane in THF (1 M)⁴ essentially limits its applicability to THF as solvent, BMS (10 M in BH₃) can be utilized in a wide variety of solvents.³ Moreover, BMS is stable at room temperature for long periods of time, whereas BH₃·THF undergoes a slow, but significant, cleavage of THF at room temperature, with loss of hydride.⁵

These advantages of BMS are sometimes negated by the properties of the ligand, dimethyl sulfide, present in the reaction mixture. It is insoluble in water and cannot therefore be removed from the reaction products by washing with water. It is highly volatile and odoriferous, and often draws complaints and criticisms from users of BMS or their neighbors. (On the other hand, it can be considered an excellent warning agent of poor experimental techniques.⁶)

The readily available 1,4-thioxane (2) possesses a lower vapor pressure and a less obnoxious odor than methyl sulfide. It has the additional advantage that it is mod-

⁽¹⁾ Postdoctoral research associate on Grant 2 RO1 GM 10937-14 from the National Institutes of Health.

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(3) (a) Braun, L. M.; Braun, R. A.; Crissman, H. R.; Opperman, M.; Adams, R. M. J. Org. Chem. 1971, 36, 2388. (b) Lane, C. F. Ibid. 1974, 39, 1437. (c) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. Ibid. 1977, 42, 1392.

⁽⁴⁾ Available from Aldrich Chemical Co.

⁽⁵⁾ Kollonitsch, J. J. Am. Chem. Soc. 1961, 83, 1515.

⁽⁶⁾ See Chapter 9 of ref 17 for a review of techniques.

erately soluble in water (0.3 M). Consequently, it can be washed out with water from solutions in EE, CH₂Cl₂, and pentane. In addition, it can be oxidized selectively in the presence of the organoborane by sodium hypochlorite.⁷ The resulting sulfoxide is highly soluble in water and is readily washed away from the organoborane. Accordingly, we attempted to synthesize borane-1,4-thioxane (1) and have recently reported the synthesis and usefulness of 1 toward hydroboration of olefins in the usual 3:1 ratio.⁸ It has been, however, recognized that partially substituted borane reagents, such as disiamylborane (3), dicyclohexylborane (4), 9-borabicyclo[3.3.1]nonane (5), thexylborane (7), etc., are more selective toward hydroboration than borane itself and hence are finding more use in organic syntheses. It is, therefore, desirable to synthesize these borane reagents, making use of the convenient reagent 1. This paper, therefore, deals mainly with convenient methods for the preparation of the above boranes from 1 and suitable olefins in THF, EE, CH₂Cl₂, and pentane at 25 °C and also by mixing the two reagents in stoichiometric amounts at 0 °C. It also describes the preparation of optically active borane reagents like diisopinocampheylborane (6) and monoisopinocampheylborane (8) by the reaction of α -pinene and 1 in 2:1 and 1:1 ratios, respectively, and their subsequent utilizations for asymmetric hydroboration of other olefins. 2 coordinates very weakly with the above dialkylboranes and monoalkylboranes, as is evident from the ¹¹B NMR spectrum of the reagents prepared from 1 and the corresponding olefins. It is therefore demonstrated that its presence does not interfere with the subsequent utilizations of these boranes toward further transformations. In the case of isolations of 9-BBN under neat conditions, 2 (bp 147 °C) was removed by distillation during isomerization at 165 °C.

Results and Discussion

Preparation of Borane-1,4-Thioxane (1). The reagent 1 was conveniently prepared by passing gaseous diborane directly into 2 at 25 °C to saturation (eq 1). The

$$B_2H_6 + 2 O \xrightarrow{25 \circ C} 2 O \xrightarrow{5 \circ BH_3} (1)$$

excess diborane gas was passed through dry THF kept at 0 °C. The liquid thus formed is ~8.0 M in borane. It crystallizes on cooling to 0 °C (mp 11–15 °C). Its ¹¹B NMR spectrum exhibits only one absorption at δ –23.0 (relative to BF₃·OEt₂), supporting the formation of the borane-1,4-thioxane complex by coordination of borane with the sulfur atom (BH₃·SMe₂: δ –20.3; BH₃·THF: δ +1.0). The neat reagent is indefinitely stable at 0 °C. It is also stable at 25 °C for long periods of time, without exhibiting detectable change in the hydride content or in the ¹¹B NMR spectrum.

Like BMS, 1 is miscible with the standard solvents utilized for hydroboration, THF, EE, CH_2Cl_2 , and partially soluble in pentane. Hence, the hydroborations of olefins in different stoichiometric amounts were conducted in the above solvents.

Reaction of Olefins with 1 in a 3:1 Ratio. The hydroboration of olefins of different steric requirements with 1 in a 3:1 ratio proceeds smoothly to completion at 25 °C to yield the trialkylborane. Oxidation with alkaline hydrogen peroxide furnishes the corresponding alcohols in excellent yields.⁸ In the case of terminal olefins, in all four



Figure 1. Reaction in a molar ratio of 2:1 of 2-methyl-2-butene and borane-1,4-thioxane in various solvents at 25 °C.

solvents (THF, EE, CH_2Cl_2 , and pentane), hydroboration proceeds smoothly with the usual distribution of 93–94% of the boron at the terminal position and 6–7% in the internal position. The hydroboration-oxidation reaction with 1 exhibits the same high regio- and stereoselectivity of the earlier reagents, BH_3 -THF and BMS.⁸



Reaction of Olefins with 1 in a 2:1 Ratio. Partially substituted boranes, such as disiamylborane (3), dicyclohexylborane (4), 9-BBN (5), and the optically active diisopinocampheylborane (6), are finding increasing use in recent years because of their greater selectivity toward hydroboration than borane itself. We therefore decided to utilize 1 for the preparation of these borane reagents in a wide variety of solvents, such as THF, EE, CH_2Cl_2 , and pentane, or under neat conditions.

Disiamylborane (3). The reaction of 2-methyl-2-butene with 1 in THF, EE, CH_2Cl_2 , and pentane at 25 °C in the ratio of 2:1 to form 3 is complete within 0.5–1.0 h. The reaction in neat solution utilizes the reagents at 0 to -5 °C for an initial 5 min and then at 25 °C for an additional 15 min (eq 2). The rate of hydroboration was followed



 ⁽⁷⁾ Brown, H. C.; Mandal, A. K. J. Org. Chem. 1980, 45, 916.
 (8) Brown, H. C.; Mandal, A. K. Synthesis 1980, 153.

by the estimation of the residual hydride at different intervals of time (Figure 1). Alternatively, the course of the reaction was followed by ¹¹B NMR, from the disappearance of the absorption due to 1 at δ -23.0 (relative to BF₃·OEt₂) and the appearance of the absorption due to disiamylborane at δ +31.12 (relative to BF₃·OEt₂). Following completion of the reaction, the reaction mixture was oxidized and 3-methyl-2-butanol was obtained in quantitative yield (GC).

The reaction of 2-methyl-2-butene with BMS in THF, EE, CH_2Cl_2 , and pentane is complete within 2-2.5 h at 25 °C.³ From the result of the BOT study, it is evident that the reaction of 2-methyl-2-butene with 1 is faster than that of BMS.

Disiamylborane thus prepared can be utilized as such for organic synthesis or can be converted to methyl disiamylborinate by methanolysis, which is valuable for the synthesis of unsymmetrical diynes.⁹

Application of Disiamylborane (3) for the Regiospecific Hydroboration of Styrene. That the presence of 2 in solution with the reagent 3 does not interfere in its subsequent reaction was demonstrated in the hydroboration of styrene with the reagent. The reagent 3 prepared as above in pentane was reacted with styrene at 25 °C. Following the completion of the reaction, the reaction mixture was oxidized and the composition of the product determined by GC (eq 3).



Dicyclohexylborane (4). The hydroboration of cyclohexene with 1 in a 2:1 ratio in THF, EE, CH_2Cl_2 , and pentane is very fast and is complete within 10-15 min at 25 °C (eq 4). At appropriate intervals of time, aliquots



were withdrawn and analyzed for residual olefin by GC. Thus, the rate of hydroboration was established. The neat reaction is also effected by mixing the reagents at 25 °C. The reaction mixture became solid after mixing and required 5–10 min for completion.

Dicyclohexylborane in solvents is prone to disproportionation with time and hence should be freshly prepared before use.

Application of 4 in Zweifel's cis-Olefin Synthesis.¹⁰ The reagent 4 prepared in EE as before was reacted with 1-hexyne at 0 °C. The vinylborane thus formed was treated with sodium hydroxide and iodine to yield cis-1cyclohexyl-1-hexene in 82% GC yield (eq 5). Hence, the presence of 2 does not interfere with this synthesis.

9-BBN (5). Hydroboration of 1,5-cyclooctadiene with 1 followed by thermal isomerization yielded 9-BBN (5) in



excellent yield. The hydroboration reaction in 2 M THF solution was found to be complete after 0.5 h at 25 °C, as is evident by the analysis of residual olefin after different intervals of time (eq 6).



Oxidation of a small portion of an aliquot with alkaline hydrogen peroxide followed by GC analysis of 1,4- and 1,5-cyclooctane diols revealed the presence of a 33:67 mixture of borabicyclo[4.2.1]- and -[3.3.1]nonanes in the initial hydroboration product. Thermal isomerization in refluxing THF was found to be complete after 1 h, as is evident by the oxidation of an aliquot and analysis by GC for 1,5-cyclooctanediol.

The neat reaction was performed by addition of the diene to 1 at 0 °C. Several individual reaction mixtures were carried out, and after appropriate intervals, the contents of the reaction flasks were methanolyzed to determine the residual hydride and then analyzed for residual olefin by GC. Hydroboration was found to be complete after 0.25 h at 0 °C and 0.25 h at 25 °C. As before, the product is about a 33:67 mixture of the 1.4- and 1.5-isomer. respectively. During isomerization at 165 °C for 1 h, 1,4thioxane (2) distills off from the reaction mixture quantitatively, leaving 9-BBN in the reaction flask.

Since 9-BBN was isolated as a pure, stable crystalline solid, mp 153 °C, from both procedures, its preparation in other solvents was not pursued.

Diisopinocampheylborane (IPC₂BH) (6). The preparation of 6 from α -pinene and diborane was previously studied in diglyme and THF at 0 °C.^{11,12} Asymmetric hydroboration of cis-2-butene with the reagent in diglyme and THF followed by oxidation yielded 2-butanol in 87% and 78% ee, respectively. The lower ee in THF compared to that in diglyme was attributed to the greater solubility of 6 in THF and hence to more dissociation of the reagent in THF to triisopinocampheyldiborane and α -pinene¹³ (eq 7).



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In recent years it has been demonstrated in this laboratory that IPC₂BH (6) approaching almost 100% ee can be prepared from BH₃. THF and BH₃. SMe₂. The reagents thus formed hydroborate *cis*-2-butene to afford after oxidation 2-butanol in 98.4% and 97.2% ee.^{3,14} We therefore decided to utilize the new reagent 1 for this remarkable asymmetric synthesis.

It was observed during BMS study that IPC_2BH made in THF was obtained in higher ee than that made in EE, CH_2Cl_2 , and pentane. Hence, the preparation of IPC_2BH and its utilization for asymmetric hydroboration was conducted in THF. Thus, IPC_2BH in THF was made at 0 °C by adding (+)- α -pinene (94.8% ee) in 15% excess to 1 in 1.0 M THF followed by equilibration at 0 °C for 90 h. Analysis of the supernatant solution for free α -pinene established that the minor isomer had accumulated in this phase as in the previous syntheses involving BH₃·THF¹⁴ and BH₃·SMe₂.³ Consequently, the product must be highly pure material, comparable to that prepared from the earlier two studies.

Application of IPC₂BH (6) for Asymmetric Hydroboration. The utility of the reagent 6 was tested in the hydroboration of *cis*-2-butene at -25 °C. The reaction was allowed to proceed for 5 h. The product after oxidation with alkaline hydrogen peroxide followed by purification by GC yielded pure 2-butanol, $[\alpha]^{23}_{D}$ -13.1°, 97% ee.

IPC₂BH (6) in THF prepared at 25 °C for 14 h followed by 12 h at 0 °C was also utilized for hydroboration of *cis*-2-butene at -25 °C, and the 2-butanol exhibited a rotation of -12.7° corresponding to 94% ee. Hence, this procedure does not have any advantage over the above procedure although it consumes less reaction time.

Reaction of Olefins with 1 in a 1:1 Ratio. Thexylborane (7) and the optically active monoisopinocampheylborane (8) were prepared by reacting 2,3-dimethyl-2-butene and α -pinene, respectively, with 1 at 25 °C.

Thexylborane (7). The hydroboration of 2,3-dimethyl-2-butene with 1 in a 1:1 ratio in THF, EE, CH_2Cl_2 , and pentane to yield 7 is complete within 10–15 min at 25 °C (eq 8). Aliquots of the reaction mixture were with-

$$\begin{array}{c} H_{3}C \\ C = C \\ H_{3}C \\ C H_{3} \end{array} + BH_{3} \cdot S \\ C H_{3} \cdot S \\$$

drawn at definite intervals of time and estimated for residual hydride by hydrolysis. Alternately, the course of the reaction was followed by ¹¹B NMR from the disappearance of the peak due to 1 at δ -23.0 (relative to Et₂O-BF₃) and the appearance of the peak due to thexylborane at δ +24.17 (relative to Et₂O-BF₃).

The reaction with neat reagents is very fast and is complete within 5 min at 25 °C. The reaction course was followed by ¹¹B NMR and also by the residual olefin analysis after methanolysis of aliquots withdrawn after different intervals of time. 1,4-Thioxane (2) can be removed at 25 °C under high vacuum (0.1 mm), and the resulting neat thexylborane (liquid at 25 °C) can be utilized for further transformation.

Application of 7 for the Preparation of Bis[trans-(2-methylcyclopentyl)borane]-TMED Adduct. Thexylborane (7), prepared in EE as above, was converted to the bis(thexylborane)-TMED adduct by adding 0.5 mol of N,N,N',N'-tetramethylethylenediamine (TMED). Reaction with 1-methylcyclopentene in refluxing EE, following the reported procedure, furnished bis[*trans*-(2methylcyclopentyl)borane]-TMED adduct, mp 123-4 °C, in quantitative yield (eq 9).

Monoisopinocampheyiborane (IPCBH₂) (8). In the course of studies directed to other objectives, we have recently reported¹⁶ that the reaction of α -pinene with borane in 1:1 ratio in THF at 25 °C yielded monoisopinocampheylborane (8) in excellent yield. We therefore wanted to see whether such a synthesis of 8 could be achieved with 1.

We now found out that the reaction of α -pinene with 1 in a 1:1 ratio in 0.7 M THF solution attains equilibrium after 120 h at 25 °C, and the equilibrium mixture consisted of 82% IPCBH₂ and 9% each of IPC₂BH and 1. Analysis of the reaction mixture was done as before by low-temperature methanolysis of aliquots followed by ¹H and ¹¹B NMR determination of IPC₂BOMe, IPCB(OMe)₂, and B(OMe)₃. Following the equilibrium, the volatiles were removed and replaced by pentane. Addition of an appropriate amount of TMED to precipitate 1 leads to the precipitation of TMED·2 BH₃, which is removed by filtration. The supernatant solution thus contains >90% of IPCBH₂ and <10% of IPC₂BH (eq 10). However, at the



temperature used for hydroboration, IPC_2BH reacts extremely slowly with the trisubstituted olefin so that the alkene essentially reacts with 8.

Application of 8 for the Asymmetric Hydroboration of 1-Methylcyclopentene. The hydroboration of 1methylcyclopentene with 8 was done at -25 °C for 4 h. Following hydroboration-oxidation, *trans*-2-methylcyclopentanol is obtained in 72% ee.

Conclusion

The present study has demonstrated the usefulness of the new reagent, borane-1,4-thioxane (1) as a hydroborating agent for the preparation of partially substituted borane reagents, such as disiamylborane, dicyclohexylborane, 9-BBN, diisopinocampheylborane, thexylborane,

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and monoisopinocampheylborane, in a wide variety of solvents, e.g., THF, EE, pentane, and CH_2Cl_2 . It also indicates the absence of complications in the utilization for organic synthesis of the reagents so prepared.

Experimental Section

All reactions were carried out in an atmosphere of dry nitrogen. The special techniques employed in handling air-sensitive materials and the usual experimental setup for the utilization of borane reagents were reported elsewhere.¹⁷

borane reagents were reported curves. Materials. Purification of solvents, e.g., THF, EE, CH_2Cl_2 , and pentane, were carried out according to standard procedure.¹⁷ The olefins were distilled from lithium aluminum hydride (LiAlH₄) and stored under nitrogen. (+)- α -Pinene (Dragoco Co.) was used after distillation from LiAlH₄, which exhibited an optical rotation of $[\alpha]^{23}_D$ +48.47° and an optical purity of 94.8%.¹⁸ The active hydride was estimated by the hydrolysis of aliquots using a 1:1:1 mixture of glycerine, THF, and water with the exception of 9-BBN where a 1:1 mixture of methanol and THF was employed. The volume of hydrogen was measured in a gas buret.¹⁷

For GC analysis, the following columns were used: (i) alcohols and olefins, a 6-ft \times 0.25-in. column packed with 10% Carbowax 20M on Chromosorb W 60/80 (A) and a 10-ft \times 0.25-in. column packed with 10% SE-30 on Chromosorb W 60/80 (B); (ii) boranes, a 12-ft \times 0.25-in. column packed with 10% SE-30 on Chromosorb W 60/80 (C); (iii) 1,4- and 1,5-cyclooctanediols as silyl ethers, a 18-ft \times 0.25-in. column packed with 5% neopentyl glycol adipate on Varaport-30 (D).

Preparation of Borane-1,4-Thioxane (BOT) (1) Complex. This is prepared by following procedures cited elsewhere.⁸ Diborane gas, generated by reacting 21.5 g (550 mmol) of sodium borohydride in 14.5 mL of diglyme with 91.2 mL (723.6 mmol) of boron trifluoride etherate, was passed through 56.2 mL (540 mmol) of 1,4-thioxane at 25 °C. The excess diborane gas was passed through dry THF solution. The neat borane-1,4-thioxane thus formed is 8.0 M in borane and crystallizes on cooling to 0 °C mp 11-15 °C. Borane-1,4-thioxane is now commercially available from the Aldrich Chemical Co.

Reaction of 1-Methyl-1-cyclopentene with 1 in a 3:1 Ratio. The reaction procedure in THF, EE, CH₂Cl₂, and pentane is similar. The reaction in THF is described as representative. With the usual experimental setup, the hydroboration was carried out in a 50-mL flask. To a solution of 0.63 mL (5 mmol) of neat 1, 0.78 mL (3.0 mmol) of n-tetradecane (internal standard for GC), and 3.68 mL of THF was added dropwise with stirring 1.58 mL (15 mmol) of 1-methyl-1-cyclopentene slowly at 25 °C. After 1 h at 25 °C, the reaction mixture was found to contain 19% active hydride by hydrolysis of an aliquot. To ensure complete reaction, the reaction mixture was refluxed for an additional 0.25 h. Oxidation was carried out by adding 1.0 mL of water and 5.3 mL (16 mmol) of sodium hydroxide. This is followed by the addition of 2.0 mL (16 mmol) of 30% aqueous hydrogen peroxide slowly dropwise, keeping the temperature of the reaction mixture below 40 °C. After 1 additional h at 50 °C, the reaction mixture was cooled and then saturated with anhydrous potassium carbonate. The organic layer was dried over a powdered molecular sieve (4 Å). GC analysis using column A revealed 94% of trans-2methylcyclopentanol (>99% trans).

Reaction of 2-Methyl-2-butene with 1 in a 2:1 Ratio in THF, EE, CH_2Cl_2 , and *n*-Pentane. The reaction procedure in EE is described as representative. With the usual experimental setup, the flask containing 1.25 mL (10 mmol) of 1 and 0.78 mL (3 mmol) of *n*-tetradecane in 5.95 mL of EE was cooled to -5 °C. Hydroboration was initiated by the dropwise addition of 2.1 mL (20 mmol) of 2-methyl-2-butene while the contents of the flask were stirred. After 5 min the reaction mixture was warmed to room temperature (25 °C). Aliquots were withdrawn at 0.5 h and 1 h and analyzed for residual hydride. Thus, the progress of the reaction was followed. Alternately, this could be followed by ¹¹B NMR from the disappearance of the absorption due to 1 at δ -23.0 (relative to BF₃·OEt₂) and the appearance of a peak at δ +31.12 due to the disiamylborane dimer. After 1 h, the reaction mixture was oxidized by adding 1.0 mL of water to destroy the hydride followed by 3.0 mL of ethanol (as cosolvent), 8.0 mL (24 mmol) of 3 M sodium hydroxide, and 2.12 mL (17 mmol) of hydrogen peroxide. Analysis by GC using column B revealed 100% of 3-methyl-2-butanol.

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

Reaction of Cyclohexene with 1 in a 2:1 Ratio in THF, EE, CH₂Cl₂, and *n*-Pentane. The following procedure in pentane is representative. The hydroboration was carried out in the usual experimental setup on a 10 mmol scale using 2.12 mL (20 mmol) of cyclohexene and 1.25 mL (10 mmol) of 1 containing 0.68 mL (3 mmol) of *n*-dodecane in 2.63 mL of pentane at 25 °C. The reaction mixture is 1.0 M with respect to 1. Aliquots (0.5 mL) were withdrawn at 0.25 and 0.5 h and methanolyzed with excess of methanol. The amount of cyclohexene was then analyzed by GC using column C, and from the amount of olefin consumed, the rate of reaction was established. The reaction mixture was oxidized as before. GC analysis using column A revealed a 100% yield of cyclohexanol.

Reaction of Neat 1 with (a) 2-Methyl-2-butene and (b) Cyclohexene. (a) The addition of 2.1 mL (20 mmol) of 2methyl-2-butene to 1.25 mL (10 mmol) of 1 was done at -5 °C. After ~ 5 min, the reaction mixture was brought to 25 °C. Analysis of the aliquot (0.4 mL) after 0.5 h for residual hydride indicated the formation of disiamylborane to be complete. This is also checked by ¹¹B NMR. Oxidation as before yielded 3-methyl-2butanol (100%) as analyzed by GC using column B.

(b) Two different reactions on a 5 mmol scale were carried out by slowly adding 1.01 mL (10 mmol) of cyclohexene to a stirred solution of 0.63 mL (5 mmol) of 1 in 0.49 mL (2.5 mmol) of *n*-decane at 0 °C. After the reagent was mixed, the reaction mixture became a solid lump. It was brought to 25 °C, and the reaction course was followed both by ¹¹B NMR of the methanolyzed product for dicyclohexylborinate and oxidation after 5 min and 15 min at 25 °C.

Isolation of Disiamylborane (3). The reaction of 2methyl-2-butene with 1 was carried out under neat conditions on a 40 mmol scale. **3** (40 mmol) thus formed can be used in situ as such or can be dissolved in a suitable solvent for further transformation. The dropwise addition of 1.6 mL (40 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.¹⁹

Isolation of Dicyclohexylborane (4). Hydroboration of cyclohexene with 1 to form dicyclohexylborane was carried out on a 40 mmol scale as before in a preweighed 100-mL flask. After the hydroboration was over, the volatiles were removed under vacuum (0.1 mm for 2 h) to yield 6.46 g (90%) of dicyclohexylborane free from 1,4-thioxane, mp 102-4 °C (lit.¹² mp 103-5 °C after sublimation).

The purity of the above dicyclohexylborane was further established by methanolysis. To the above reagent was added 3.0 mL of methanol dropwise at 25 °C. After 0.5 h at 25 °C, the volatiles were removed. The resulting material was pure methyl dicyclohexylborinate, as determined by ¹H NMR. This can be distilled, bp 75-80 °C (0.005 mm), or can be used without distillation.

Application of 3. Hydroboration of Styrene at 25 °C. The reaction in pentane is representative. 3 (10 mmol) in pentane (1.0 M) was prepared from 1 as before. Hydroboration of styrene (10 mmol) was carried out according to the literature procedure¹⁷ at 25 °C. Within 1 h, the hydroboration was found to be complete. Oxidation followed by analysis by GC showed 89.5% alcohol (98% 2-phenylethanol and 2% 1-phenylethanol).

Application of 4. Zweifel's cis-1-Cyclohexyl-1-hexene. The reaction in EE is representative. The reagent 4 (10 mmol) in EE was prepared from 1 as before. Hydroboration of 1-hexyne (10 mmol) to the vinylborane followed by its reaction with iodine was

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carried out following the literature procedure. GC analysis revealed 81.5% yield of *cis*-1-cyclohexyl-1-hexene.

9-BBN (5). A. Rate of Hydroboration in THF. With the usual experimental setup, hydroboration was carried out by adding 2.46 mL (20 mmol) of 1,5-cyclooctadiene dropwise over a wellstirred solution of 2.50 mL (20 mmol) of BOT and 1.30 mL (5 mmol) of *n*-tetradecane (internal standard for GC) in 3.74 mL of THF at 25 °C to make the resulting solution 2.0 M in reactants. The rate of hydroboration was found by methanolyzing a 1.0-mL aliquot each time at 0.5 and 1.0 h intervals and then analyzing the unreacted diene by GC using column C. The hydroboration of cyclooctadiene with 1 was complete after 0.5 h at 25 °C.

B. Rate of Isomerization in THF. From the above reaction mixture, a 1.0-mL aliquot was oxidized to establish the initial hydroboration product. The remaining reaction mixture was then refluxed and at definite intervals 1.0 mL was withdrawn for oxidation. Analysis of the oxidation product for cyclooctane-1,4-and 1,5-diols gives the extent of isomerization. In 1 h, the isomerization was complete.

C. Oxidation of Aliquots. In a 25-mL reaction flask equipped with a reflux condenser was placed a 1.0 mL (2 mmol) aliquot. THF (50 mL) and 2.0 mL of water was then added. After the flask was cooled to 0 °C, 2.0 mL (6 mmol) of 3 M NaOH was added followed by 1.2 mL (12 mmol) of 30% aqueous hydrogen peroxide. After addition of hydrogen peroxide, the reaction mixture was heated to 50 °C for 2 h. The aqueous layer was saturated with anhydrous potassium carbonate, and the organic layer was analyzed by GC.

D. GC Analysis of Diols. A 0.2-mL portion of THF solution from oxidation was taken in a vial, and 0.3 mL of dry pyridine and 0.3 mL of N,O-bis(trimethylsilyl)acetamide (BSA) were added. The mixture was heated for 10-15 min while shaking the vial occasionally. The product was anlayzed by column D. The isomeric disilyl ethers separate nicely. The isomeric distribution of the diols was thus determined from the respective area of the peaks (assuming the same response factor for both diols).

E. Isolation of 5 from Reactions in THF. In a preweighed 100-mL flask equipped with a reflux condenser and usual experimental setup were placed 12.5 mL (100 mmol) of 1 and 25.2 mL of THF. The flask was immersed in a water bath (25 °C), and while the contents of the flask were stirred 12.3 mL (100 mmol) of 1,5-cyclooctadiene was added dropwise and stirring was further continued for 0.5 h at 25 °C followed by 1 h of refluxing. The flask was cooled in an ice-salt mixture when 5 crystallized out. The supernatant liquid was removed by double-ended needle, and the crystals were washed with 25 mL of ice-cold pentane and dried under vacuum, yielding 9.6 g (79%) of 5, mp 148-9 °C. Recrystallization from THF gave a material, mp 153 °C.

F. Rate of Hydroboration under Neat Conditions. Three different reactions were carried out, each on a 5-mmol scale in a 25-mL reaction flask. Reactants were mixed at 0 °C. After fixed intervals, one flask at a time was connected to a gas meter and the contents of the flask were methanolyzed by adding 100 mL of a 1:1 mixture of methanol and THF. Thus, the progress of the reaction was followed by residual hydride estimation. It was also checked by analysis of the residual olefin by GC after methanolysis. Hydroboration was complete after 0.25 h at 0 °C and 0.25 h at 25 °C.

G. Rate of Isomerization under Neat Conditions. The hydroboration was carried out as described in F. Following completion of the reaction, each flask was heated in an oil bath at 165–170 °C for fixed intervals of time. After being cooled, the contents were oxidized as before. GC analysis of the disilyl ethers revealed the isomeric ratio in each case. Isomerization was complete in 1 h.

H. Isolation of 5 from Reaction of Neat Reagents. The apparatus was assembled as described in E. 12.5 mL (100 mmol) of 1 was placed in the flask and cooled to 0 °C. To it was added 12.3 mL of 1,5-cyclooctadiene dropwise over a period of 5 min. After 0.25 h at 0 °C and 0.25 h at 25 °C, the reaction mixture was maintained at 170 °C for 1 h, during which time 2 distilled off quantitatively (96%) leaving 12.3 g (100%) of 5 in the reaction flask. Crystallization from boiling THF yielded 10.06 g (~83%) of 5, mp 147-8 °C. Recrystallization from THF afforded pure crystals, mp 153 °C.

Reaction of α -Pinene with 1 at 0 °C. Preparation of 6. The reaction in THF is representative. With the usual experimental setup, the reaction was carried out in a 250-mL flask. The flask was cooled to 0 °C in an ice bath, and 6.25 mL of 1 (50 mmol) in 25.4 mL of THF was placed in the flask. To it was added dropwise 18.4 mL of (+)- α -pinene (115 mmol) ($[\alpha]^{23}_{D}$ +48.47°, 94.8% ee) over a period of 5 min. After the solution was stirred for 2 h at 0 °C, the reaction flask was kept in the cold room (\sim -2 °C) for 90 h.

Application of 6. Hydroboration of cis-2-Butene at -25 °C. The reaction flask was equipped with a dry ice-acetone condenser. The reaction mixture was cooled to -25 °C, and 5.2 mL of cis-2-butene (57.5 mmol) was added to the reaction mixture by means of a double-ended needle. After 5 h at -25 °C, the reaction mixture was warmed to room temperature. This was followed by the addition of 2 mL of water, 54 mL of 3 M sodium hydroxide, and 23 mL of 30% hydrogen peroxide, maintaining the temperature of the reaction mixture below 40 °C. This was further stirred for 1 h at 50 °C. The reaction mixture was cooled and the aqueous layer extracted thoroughly with ether. The combined organic layer was washed with 2×25 mL of saturated brine solution. This was then dried over anhydrous magnesium sulfate overnight. Distillation using a 30-cm Widmer column afforded 2.94 g of 2-butanol (0.76 g at 85-97 °C (750 mm) and 2.18 g at 97 °C (750 mm)), a yield of 79%. The 97 °C fraction was further purified through preparative GC using a 10% XE-60 column to yield pure 2-butanol, n^{20} 1.3975, $[\alpha]^{23}$ -13.1°, 97% ee.

The α -pinene unreacted was recovered by distillation and purified through a 20% SE-30 column, n^{20}_{D} 1.4661, $[\alpha]^{23}_{D}$ +42.5°, 83% ee.

Reaction of 2,3-Dimethyl-2-butene with 1 in a 1:1 Ratio in THF, EE, CH_2Cl_2 , and Pentane. Preparation of Thexylborane (7). The reaction procedure in EE is representative. With the usual experimental setup, the flask was charged with 1.25 mL (10 mmol) of 1, 0.58 mL (3 mmol) of *n*-decane, and 6.97 mL of EE. To it was added with stirring 1.2 mL (10 mmol) of 2,3-dimethyl-2-butene dropwise at 25 °C. Aliquots (1.0 mL) were withdrawn at 15- and 30-min intervals and estimated for residual hydride by hydrolysis. The reaction was complete after 15 min at 25 °C. Alternatively, the reaction could be followed by ¹¹B NMR as before. The reaction was oxidized as before. GC analysis using column A revealed a 100% yield of 2,3-dimethyl-2-butanol.

Reaction of Neat 1 with 2,3-Dimethyl-2-butene at 25 °C. With the usual experimental setup, the addition of 1.2 mL (10 mmol) of 2,3-dimethyl-2-butene to a solution of 1.25 mL of 1 and 0.58 mL (3 mmol) of *n*-decane was done at 25 °C. Aliquots (0.3 mL) were withdrawn at 5- and 10-min intervals and methanolyzed and then analyzed for 2,3-dimethyl-2-butene by GC using column C. The progress of the reaction was also followed by ¹¹B NMR as before. The reaction mixture was then oxidized as before and then analyzed for 2,3-dimethyl-2-butanol (98%) by GC using column B.

Application of 7. Preparation of Bis[trans-(2-methylcyclopentyl)borane]-TMED Adduct. Thexylborane (7) (10 mmol) in EE was prepared as before. The preparation of bis-[trans-(2-methylcyclopentyl)borane]-TMED was carried out according to the literature procedure, and the product, mp 123-4 °C, was obtained in 91% isolated yield.

Reaction of α -Pinene with 1 at 25 °C in a 1:1 Ratio. Preparation of Monoisopinocampheylborane. With the usual experimental setup, the reaction flask was charged with 6.25 mL (50 mmol) of 1 and 56.1 mL of THF to make the reaction mixture 0.7 M with respect to borane. To it was added 8.0 mL (50 mmol) of (+)- α -pinene ([α]²³_D +48.47°, 94.8% ee) at 25 °C. The reaction mixture was stirred at 25 °C for 120 h. An aliquot (~2.9 mL, 2 mmol) was methanolyzed. Removal of volatiles and analysis of the boronate and borinate by ¹H NMR revealed 82% of monoisopinocampheylborinate and 9% each of diisopinocampheylborinate and methylborate (obtained by difference). This indicates the reaction mixture contains 82% monoisopinocampheylborane, 9% IPC₂BH, and 1. The selective removal of 1 was carried out as follows. The volatile materials were distilled from the reaction mixture under vacuum (2 mm, 3 h), and 40 mL of pentane was added. Then 0.36 mL (2.4 mmol) of $N_{,N,N',-}$ N'-tetramethylethylenediamine (TMED) was added. The precipitation of TMED-2BH₃ was complete within 0.5 h at 25 °C. The precipitate was then removed by centrifugation. The solution now contained ~10% Ipc₂BH.

Application of 8. Asymmetric Hydroboration of 1-Methylcyclopentene. The above reaction mixture was cooled to -25 °C, and 4.25 mL (40 mmol) of 1-methylcyclopentene added with stirring. The hydroboration was allowed to proceed for 4 h at -25 °C. The reaction mixture was then warmed to 0 °C, and 3.0 mL of water added to destroy excess hydride. This was followed by the addition of 16 mL of 3 M sodium hydroxide and 12.5 mL of 30% aqueous hydrogen peroxide. The reaction mixture was stirred at 50 °C for 1 h and cooled to 25 °C and the aqueous layer extracted with ether. The combined organic layer was washed twice with 2×20 mL of saturated brine solution. Following drying over anhydrous magnesium sulfate, the solvent was removed in a rotavapor under 15 mm of pressure. Distillation of the residue yielded 3.0 g (75%) of trans-2-methylcyclopentanol, bp 72-3 °C (16 mm). The alcohol was then purified by preparative GC through a 20% SE-30 column: n^{20}_{D} 1.4494. $[\alpha]^{23}_{D}$ +31.6°, 72% ee.

Methyl Nitrate, Hydrazoic Acid, and Their Conjugate Acids. A **Configuration Interaction Study of the Gas-Phase Proton Transfer** Equilibrium and of Acid-Catalyzed Fragmentation Reactions

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Methyl nitrate, hydrazoic acid, their conjugate acids, and selected reactions were studied with ab initio methods. Potential energy surfaces were explored at the RHF/6-31G* level, and electron correlation effects were estimated with third- or full fourth-order perturbation theory and with configuration interaction methods using the 6-31G*, 6-311G**, and 6-311G (df,p) basis sets. CH₃ONO₂ and its conjugate acids were also studied with semiempirical methods (MNDO, AM1, PM3). Relative isomer stabilities and conformational preferences of protonated CH₃ONO₂ are reported. Ester-O protonation is preferred over O_{term} protonation, and *inter*molecular proton transfer is more likely for their gas-phase isomerization. Aminodiazonium ion is greatly preferred over iminodiazenium ion, by 27.1 kcal/mol at CISD/6-311G**//MP2/6-31G*+AVZPE. In good agreement with experiment, the reaction energy of $\Delta E_3 = 2.9 \text{ kcal/mol was found for the proton-transfer reaction CH₃ONO₂ + H₂N₃⁺ <math>\leftrightarrow$ (CH₃ONO₂)H⁺ + HN₃ at CISD/6-311G**//RHF/6-31G*+ Δ VZPE. At this level, the gas-phase proton affinities of HN₃ and CH₃ONO₂ are $\Delta E_1 = 187.6$ and $\Delta E_2 = 184.7$ kcal/mol, respectively. The PA(HN₃) at this level is within 1 kcal/mol of our best value obtained at CISD/6-311G(d,p)//MP2/6-31G*. These theoretical results suggest that the reported experimental proton affinity of HN₃ (176.6 kcal/mol) might be too low as a consequence of evaluating the proton transfer equilibrium with an underestimated proton affinity of CH₃ONO₂. Ester-O protonated CH₃ONO₂ is best described as methanol-solvated NO_2^+ , and its dissociation requires only 17.5 kcal/mol at CISD/6-311G**// RHF/6-31G*+ Δ VZPE. In sharp contrast to prior semiempirical results, dediazotization of aminodiazonium ion is endothermic by 73.6 kcal/mol at CISD/6-311G(df,p)//RHF/6-31G*+ Δ VZPE.

Introduction

Aliphatic diazonium ions are highly reactive intermediates in various deamination reactions¹ that are pertinent to synthetic organic chemistry as well as to the understanding of toxicological problems.² Since aliphatic diazonium ions have eluded a comprehensive characterization by physical organic techniques,³ we have studied aliphatic diazonium ions with modern theoretical methods. Our studies of the bonding and the stability of prototypical diazonium ions⁴⁻⁶ revealed that the formal charges in the commonly used Lewis structure do not appropriately reflect the actual charge distributions. A new bonding model was proposed that is consistent with their electron density distributions, and this model was shown to apply also to diazonium dication⁷ and to aromatic diazonium ions,⁸ and it was shown to be fully consistent with structural features associated with "incipient nucleophilic attack" in diazonium ions with proximate nucleophiles.⁹ We were able to establish another crucial link between theory and experiment recently with the first single-crystal X-ray structure determination of an aliphatic diazonium ion.¹⁰ Heterosubstituted diazonium ions^{11,12} (XNN)⁺, where X is F, HO, and NH₂,¹³ were studied to further probe the nature of aliphatic diazonium ions and because they allow

for another opportunity to compare theory with experiment. Cacace et al.¹⁴ recently reported a joint ab initio and mass spectrometric study of aminodiazonium ion, and

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