thiooxazolidine-4-carboxylate (**9**) in 5 mL of methylene chloride. After the resultant white slurry was stirred for 3 h, it was concentrated in vacuo at 0 °C. The residue was suspended in 15 mL of tetrahydrofuran at 0 °C, and 7.5 mL of pH 7 phosphate buffer was added. The reaction mixture was stirred at 0 °C for 1.5 h, poured into 100 mL of 1 N aqueous sodium bisulfate, and extracted with three 75-mL portions of methylene chloride. The combined organic extracts were dried over anhydrous sodium sulfate and concentrated to give a white solid and a yellow oil. Purification by flash chromatography (20 × 100 mm silica gel, 30% ethyl acetate/hexane) afforded 455 mg (76%) of the title compound as a clear oil: R_f 0.26 (30% ethyl acetate/hexane); IR (CH_2Cl_2) 3080–2860, 1754, 1438, 1400, 1216, 1048, 970 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.55–5.31 (m, 2 H, C*H*=C*H*), 4.28 (dd, 1 H, J = 4.8, 6.2 Hz, C_5-*H*), 3.97 (d, 1 H, J = 4.8 Hz, C_4-*H*), 3.82 (s, 3 H, CO_2CH_3), 2.91 (s, 3 H, NCH_3), 2.25–2.17 (m, 1 H, C*H*HCH=CH), 2.00–1.83 (m, 2 H, C*H*CH*H*CH=CH), 1.66 (dd, 3 H, J = 1.1, 6.0 Hz, CH=CHCH_3), 0.95 (d, 3 H, J = 6.6 Hz, CHCH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.2, 157.2, 128.0, 127.3, 79.3, 61.8, 52.7, 37.6, 34.2, 30.0, 17.8, 13.8; $[\alpha]_D$ +37.1° (CH_2Cl_2, c 1.51).

Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94. Found: C, 60.14; H, 8.19.

(2*S*,3*R*,6*E*)-3-Hydroxy-4-methyl-2-(methylamino)-6-octenoic Acid (1a). This reaction was carried out according to the procedure of Wenger.[5] A solution of 269 mg (1.11 mmol) of methyl (4*S*,5*R*)-3-methyl-5-((1′*R*,3′*E*)-1′-methyl-3′-pentenyl)-2-oxazolidinine-4-carboxylate (**11**) in 2.5 mL of 2 N aqueous potassium hydroxide solution was heated at 75–80 °C overnight. The solution was allowed to cool to room temperature, and the pH was adjusted to 5 by the addition of 1 N aqueous hydrochloric acid. The solution was concentrated and chromatographed (40 g Sephadex LH-20, methanol) to give 183 mg (82%) of the title compound. An analytical sample was prepared by recrystallization from ethanol/water, which was identical (^1H NMR (250 MHz), melting point, and mixture melting point) with a sample prepared by synthesis from diethyl tartrate:[13] mp 242–243 °C; IR (KBr pellet) 3210, 2960, 2930, 2890, 2700–2200 (broad), 1615, 1585, 1460, 1445, 1430, 1410, 1380, 1320, 1260, 1245, 1140, 1110, 1030, 990, 965, 930, 890, 850, 675 cm^{-1}; ^1H NMR (250 MHz, D_2O) δ 5.52–5.29 (m, 2 H, C*H*=C*H*), 3.65 (t, 1 H, J = 6.0 Hz, C_3-*H*), 3.50 (d, 1 H, J = 5.8 Hz, C_2-*H*), 2.61 (s, 3 H, N-CH_3), 2.15 (br d, 1 H, 13.0 Hz, C_5HH), 1.82–1.70 (m, 1 H, C_5HH), 1.62–1.53 (m, 1 H, C_4-*H*), 1.52 (d, 3 H, J = 5.4 Hz, C_8-*H*), 0.81 (d, 3 H, J = 6.7 Hz, C_4-CH_3); ^{13}C NMR (75.5 MHz, MeOD-d_3, amino acid hydrochloride salt) δ 170.1, 129.9, 128.3, 74.7, 64.9, 37.4, 35.6, 33.6, 18.1, 16.2; $[\alpha]_D$ +11.4° (H_2O at pH 7 (phosphate buffer Titrisol pH 7.00 from Merck), c 0.50) [lit.[5] $[\alpha]_D$ +13.5° (H_2O at pH 7 (phosphate buffer Tritrisol pH 7.00 from Merck), c 0.50)].

Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52. Found: C, 59.59; H, 9.44.

Acknowledgment. Support from the National Science Foundation and the National Institutes of Health is gratefully acknowledged. The NIH BRS Shared Instrumentation Grant Program 1 S10 RRO1748-01A1 is acknowledged for providing NMR facilities.

Chiral Synthesis via Organoboranes. 8. Synthetic Utility of Boronic Esters of Essentially 100% Optical Purity. Synthesis of Primary Amines of Very High Enantiomeric Purities

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Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received May 22, 1986*

Abstract: 2-Alkyl-1,3,2-dioxaborinanes, R*$BO_2(CH_2)_3$, of essentially 100% optical purity, prepared by the asymmetric hydroboration of readily available prochiral olefins with subsequent removal of the chiral auxiliary, can be converted into borinic ester derivatives, R*MeB$O(CH_2)_3$OAc, of essentially 100% ee by reaction with MeLi. The intermediates, R*MeB$O(CH_2)_3$OAc, react readily with hydroxylamine-*O*-sulfonic acid in tetrahydrofuran at 25 °C to provide the corresponding primary amines stereospecifically in very good yields and in very high optical purity. Consequently, it is now possible to convert prochiral olefins into either (+)- or (−)-primary amines of essentially 100% optical purity. The optical purities of the amines were determined by capillary GC analyses of their MTPA amides.

Optically active primary amines are of major biological and synthetic importance. For example, (*R*)-(−)-*sec*-butylamine is present in pharmacologically active species such as β-blockers[2] or central analgesics[3] and possess fungistatic activity.[4] Generally, optically active primary amines are either prepared by resolution of racemic amines[5] or synthesized from optically active precursors.[6] Asymmetric synthesis of primary amines using borane reagents has not yet achieved high enantioselectivity.[7]

Organoboranes are among the most versatile intermediates available to the organic chemist. Our studies have established that organoboranes transfer the alkyl group to essentially most of the other elements of synthetic interest, including carbon, with complete maintanence of stereochemical integrity.[8] Several reactions are known where an alkyl group is transferred from organoborane to nitrogen leading to primary amine derivatives. We previously reported that trialkylboranes, on treatment with chloramine or hydroxylamine-*O*-sulfonic acid (HSA), give primary amines in 40–60% yield (eq 1).[9] Recently a new reagent, *O*-

$$R_3B + NH_2X \rightarrow 2\ RNH_2 \qquad (X = Cl,\ OSO_3H) \qquad (1)$$

mesitylenehydroxylamine, has been developed for the conversion of organoboranes into primary amines in 20–50% yield.[10a] Reaction of trialkylboranes with chloramine generated *in situ* has been reported to give primary amines in 25–60% yield.[10b] An alkyl

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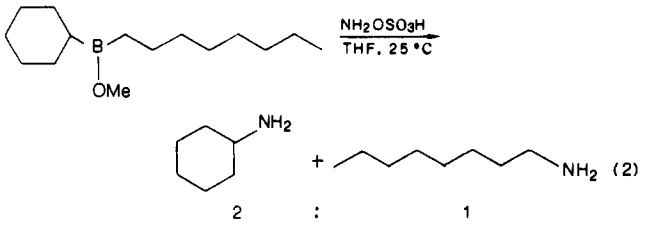
group can also be transferred from boron to nitrogen by using chloramine-T.[10c]

Reaction of *B-sec*-butylisopinocampheylborane with HSA in diglyme at 90 °C has been reported to give [*R*]-(−)-*sec*-butylamine in 75% optical purity and in 13% chemical yield.[7a]

Boranes derived from α-pinene exhibit great potential for converting commercially available prochiral olefins into optically active derivatives. A recent development offers promise of providing both chiral organoborane intermediates and all organic compounds containing a chiral center in essentially 100% optical purity in both (+)- and (−)-isomers.[11] Recently this development has been utilized for the synthesis of α-chiral aldehydes, β-chiral alcohols, and α-chiral acid.[12] We describe here a stereospecific conversion of optically active boronic esters into the corresponding primary amines of essentially 100% optical purity.

Results and Discussion

The reaction of trialkylboranes with HSA is sensitive to stereoelectronic factors so that, at best, only two of the three alkyl groups can be utilized. This was confirmed by the isolation of alkylboronic acid from the reaction mixture. We also found that various monoalkylborane derivatives such as $RBO_2(CH_2)_3$, $RB(OAc)_2$, RBX_2, RBHX, and RBH_2 do not react with HSA. We then discovered that HSA reacts readily with borinic esters in THF at 25 °C, transferring one of the alkyl groups from boron to nitrogen. Even though HSA is insoluble in tetrahydrofuran (THF), the reaction resulted in a clear solution at the end of the reaction. We were seeking a way of overcoming this limitation to quantitative utilization of alkyl residues by utilizing mixed organoboranes, such as RR^1BOR^2, in which the group R shows significantly greater migratory aptitude. Accordingly, we reacted various mixed borinates with HSA. Thus, the reaction of methyl cyclohexyl-*n*-octylborinate with HSA gives a mixture of amines, which indicates that the cyclohexyl group migrates twice as fast as the *n*-octyl group (eq 2).



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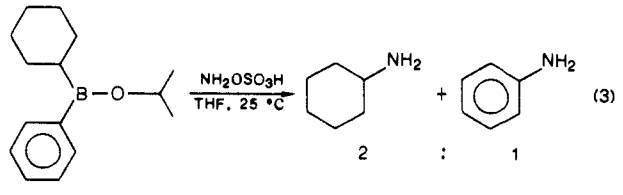
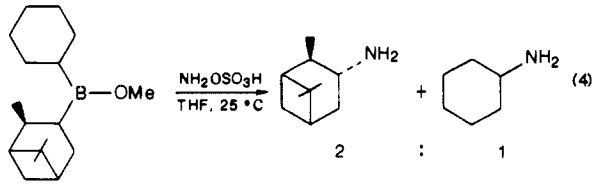
Similarly, the reaction of isopropyl cyclohexylphenylborinate gives a mixture of amines, which indicates that the cyclohexyl group migrates twice as fast as the phenyl group (eq 3). On the



(3)

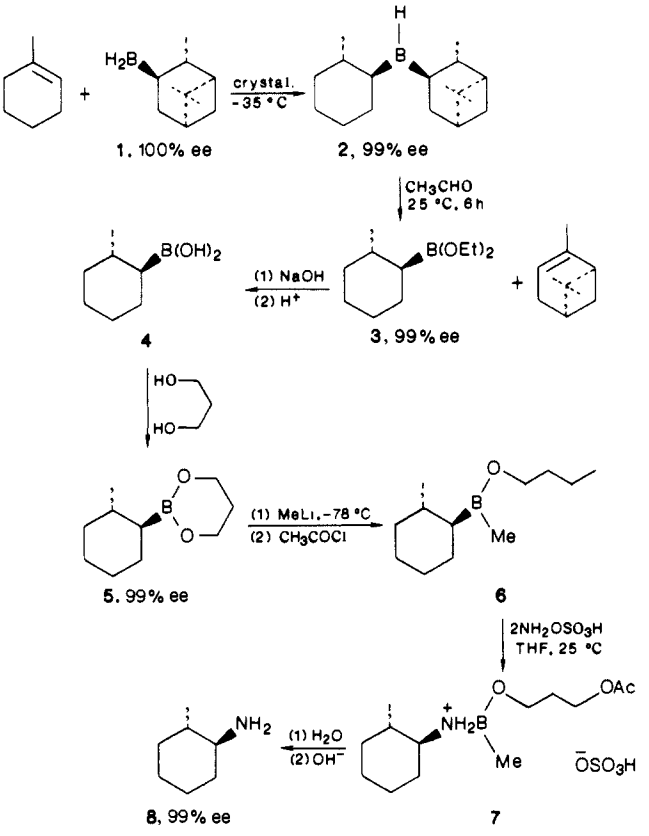
other hand, methyl cyclohexylisopinocampheylborinate gives a mixture of amines, which indicates that the isopinocampheyl group migrates twice as readily as the cyclohexyl group (eq 4). This



(4)

migratory aptitude of the isopinocampheyl group may be one of the reasons for the low yield of [*R*]-(−)-*sec*-butylamine realized previously from the reaction of *B-sec*-butyldiisopinocampheylborane and HSA.[7a] Unfortunately, thexylalkylborinates failed to react with HSA under a variety of reaction conditions.

Scheme I



Since secondary groups migrate preferentially in the reaction of organoboranes with HSA, we checked the possibility of utilizing the methyl group as a nonmigrating blocking group. We synthesized the cyclohexylmethylborinate derivative from 2-cyclohexyl-1,3,2-dioxaborinane and methyllithium by the procedure reported previously.[13] This borinate derivative readily reacted with HSA in THF to give cyclohexylamine in 88% yield.

Encouraged by this result, we turned our attention to the synthesis of optically active amines. Optically active organoborane intermediates, needed for the synthesis of optically active amines, were prepared by the asymmetric hydroboration of prochiral olefins with monoisopinocampheylborane, $IpcBH_2$ (**1**), prepared from (+)-α-pinene. Thus, the asymmetric hydroboration of prochiral olefins with **1** in the molar ratio 1:1, followed by crystallization, provides the chiral isopinocampheylalkylboranes, IpcR*BH (e.g., **2**), in essentially 100% optical purity. Treatment of these dialkylboranes with acetaldehyde under mild conditions results in the selective, facile elimination of the chiral auxiliary, providing the corresponding boronic ester (e.g., **3**) in very high optical purity. The optically active 2-alkyl-1,3,2-dioxaborinanes were then prepared by esterification[14] of the corresponding boronic acids with 1,3-propanediol (e.g., **4** → **5**) (Scheme I).

The optical purities of these 2-alkyl-1,3,2-dioxaborinanes were determined by measuring the rotations of the alcohols obtained following alkaline hydrogen peroxide oxidation and comparing the values with the maximum reported rotations. The enantiomeric excesses of most of these alcohols were also determined by ^{19}F NMR of their MTPA esters[15] and/or by ^{31}P NMR with use of the Anderson and Shapiro reagent[16] and/or by capillary

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Table I. Primary Amine Hydrochlorides of Very High Optical Purity

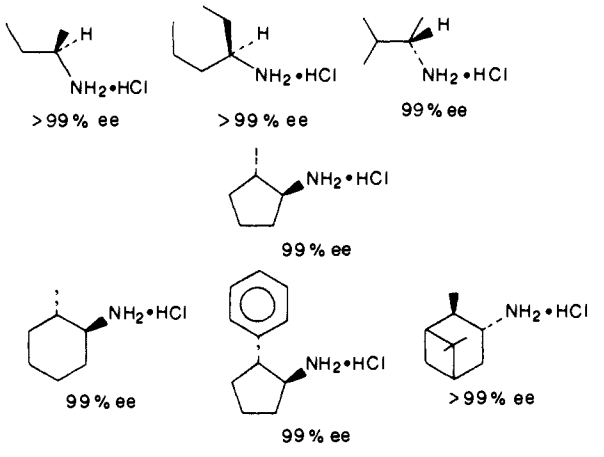
R* of R*NH_2·HCl	yield, % (isolated)	mp, °C	$[\alpha]^{23}D$, deg (*c* 4, MeOH)	% ee[a]	config. of R*NH_2·HCl
2-butyl	77	140–142	+2.64 ± 0.02	>99	*R*
3-hexyl	83	232–234	−3.73 ± 0.02	>99	*R*
3-methyl-2-butyl	80	213–214	−2.19 ± 0.03	99	*S*
trans-2-methylcyclopentyl	77	196–198	+29.2. ± 0.03	99	1*S*,2*S*
trans-2-methylcyclohexyl	76	>250	+26.36 ± 0.04	99	1*S*,2*S*
trans-2-phenylcyclopentyl	77	200–202	+68.15 ± 0.03	99	1*S*,2*R*
3-isopinocampheyl	72	>250	−23.68 ± 0.04	>99	1*R*,2*S*,3*R*,5*R*

[a] Optical purity was determined by capillary GC analyses of the MTPA amides.

GC analyses of their MTPA esters or their menthyl carbonates.[17]

The optically active 2-alkyl-1,3,2-dioxaborinanes were then converted to the optically active alkylmethylborinate esters by reaction with methyllithium at −78 °C, followed by treatment with acetyl chloride (e.g., **5** → **6**).[18] The crude borinate esters were then reacted with 2 equiv of HSA at 25 °C in THF. Hydroxylamine-*O*-sulfonic acid slowly dissolved to give a clear solution. The reaction mixture was stirred at 25 °C for 12 h to ensure complete reaction (e.g., **6** → **7**). Water was added to decompose the intermediate (e.g., **7**), and the acidic aqueous solution containing the amine was separated from the organic phase containing the unreacted boronic acid derivative. The acidic aqueous layer was made strongly alkaline, and the amines were isolated and converted into amine hydrochlorides by standard procedures.

Using this general procedure, the following representative primary amine hydrochlorides were prepared in very high optical purities (Table I).



The reaction proceeds with retention of configuration at the migrating carbon atom, as observed in other related 1,2-migration reactions of organoboranes. Thus, the *trans* geometry in 2-([1*S*,2*S*]-*trans*-2-methylcyclohexyl)-1,3,2-dioxaborinane (**5**), obtained by the asymmetric hydroboration of 1-methylcyclohexene, is retained in the product [1*S*,2*S*]-*trans*-2-methylcyclohexylamine (**8**). The isomeric purity of all of the cyclic amines was confirmed by gas chromatographic analyses on a 50-m methylsilicone capillary column.

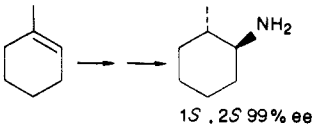
In this study, we have given the yield of the optically pure amines starting from the optically active alkylmethylborinate esters (e.g., **6**). The overall yield of the optically pure amine starting from the corresponding olefin is variable, depending on the magnitude of the asymmetric induction in the hydroboration stage. For example, in the case of *cis*-2-butene, the initial induction is very high (>95% ee). Consequently, the corresponding optically pure boronic acid derivatives (e.g., **4** and **5**) are obtained in high yield, and the overall yield of the optically pure 2-butylamine, based on the alkene or the hydroborating agent, is 62%. On the other hand, in cases where the initial asymmetric induction is moderate, ~70% ee, this lower induction will in turn be reflected in a lower yield of the corresponding optically pure boronic acid derivatives. Consequently, the overall yield of the optically pure *trans*-2-methylcyclohexylamine from 1-methylcyclohexene or the hydroborating agent is ~48%. However, it should be pointed out that we have not as yet undertaken to optimize the yield of the optically active boron derivatives from the alkenes.

Some of the amine hydrochlorides, reported here, have not been described previously in optically pure form, and the others have small specific rotations. Consequently, the optical purities of these amine hydrochlorides could not be determined by chiroptical comparison. It has been reported that *N*-(trifluoroacetyl)-[*S*]-prolyl chloride can be used to resolve racemic amines by gas chromatography.[19] Unfortunately, commercially available *N*-(trifluoroacetyl)-[*S*]-prolyl chloride is not optically pure. We then utilized the readily available MTPA acid chloride as the chiral derivatizing agent. Following the general procedure, we converted racemic 2-alkyl-1,3,2-dioxaborinanes into the corresponding racemic amine hydrochlorides. The racemic amine hydrochlorides reacted readily with MTPA acid chloride in the presence of pyridine to form the corresponding racemic MTPA amides. These racemic amides were analyzed by capillary GC using a 20-m Supelcowax capillary column and were well resolved to give two peaks of equal intensity. The optically active amine hydrochlorides were then converted into the corresponding MTPA amides, and analyses by capillary GC on a 20-m Supelcowax capillary column indicated that they were essentially optically pure (Table I).

Conclusion

The methodology described in this study provides a convenient, simple, and high-yielding procedure for the synthesis of various primary amines in essentially 100% optical purities. Both (+)- and (−)-α-pinenes are readily available. Consequently, both enantiomers of the amines are readily synthesized. Incidently, the asymmetric synthesis of optically pure *trans*-2-phenylcyclopentylamine (cypenamine), an antidepressant,[20] has been achieved for the first time.

This primary amine synthesis from methylalkylborinic esters, when combined with the asymmetric hydroboration reaction, provides a new method for introducing an amine functionality into olefins in regio-, stereo-, and enantioselective manners (eq 5).



(5)

Experimental Section

All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[8] The spectra were obtained in an inert atmosphere. The ^{11}B NMR spectra were recorded on a Varian FT-80A spectrometer and the chemical shifts are in δ relative to EE·BF_3 with chemical shifts downfield from EE·BF_3 assigned as positive. The ^1H NMR spectra were scanned on a Varian T-60 spectrometer, and the ^{13}C NMR spectra were obtained on a Varian FT-80A instrument. Chemical shifts, all in D_2O, are in δ relative to external Me_4Si for ^1H and ^{13}C NMR spectra. Gas chromatographic analyses were carried out with a Varian 1400 FID instrument equipped with a Hewlett-Packard 3390A integrator/plotter

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using a 6 ft × 0.125 in. column of 10% Carbowax 20M–2% KOH on Chromosorb W and an internal standard. Capillary gas chromatographic analyses were carried out with a Hewlett-Packard 5890 chromatograph. Optical rotations were measured on a Rudolph Polarimeter Autopol III. Elemental analyses were done in the Purdue University Microanalytical Laboratory. Melting points are uncorrected.

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Anhydrous diethyl ether (EE) was purchased from Mallinckrodt, Inc., and was used directly. Hydroxylamine-*O*-sulfonic acid obtained from Aldrich Chemical Co. was used as such. (*R*)-MTPA was purchased from Aldrich Chemical Co. and was converted to the acid chloride[15] and distilled. The boronic esters, used in this study, were prepared by procedures described previously[12] starting from (+)-α-pinene.

Generation of Monoisopinocampheylborane from TMED·2BH$_2$Ipc in EE. A 250-mL flask with a magnetic stirring bar and septum was charged with 20.85 g of TMED·2BH$_2$Ipc (50 mmol)[21] and EE (67.2 mL). While the slurry was stirred at 25 °C, 12 mL (98 mmol) of EE·BF$_3$ was added dropwise, and the reaction mixture was allowed to stir at 25 °C for 2 h. Meanwhile, a 250-mL flask with a septum inlet, magnetic stirring bar, and a filtration chamber was assembled under dry nitrogen and cooled to 25 °C. The resulting slurry from the reaction flask was transferred under nitrogen to the filtration chamber. The solid TMED·2BF$_3$ was washed with EE (2 × 36 mL). The combined filtrate was analyzed for IpcBH$_2$ by hydrolysis with 1:1:1 glycerol:water:THF as the hydrolyzing mixture and found to be 0.723 M; 110 mL (79.5 mmol), 79% yield; ^{11}B NMR (decoupled) +22.4 (singlet); $[\alpha]^{23}$D −39.93° (*c* 11.6, EE). The standard solution of IpcBH$_2$[22] in EE can be stored at 0 °C for at least 20 days without any isomerization or loss of hydride activity.

Isopinocampheyl-[1*S*,2*S*]-*trans*-2-methylcyclohexylborane (2). With the usual experimental setup, 3.5 mL (30 mmol) of 1-methylcyclohexene was added to 34.6 mL (25 mmol) of 0.723 M IpcBH$_2$ in EE at −35 °C. The reactants were mixed together well and left at −35 °C without stirring for 12 h. The crystalline dialkylborane was isolated, washed with cold (−35 °C) EE (2 × 5 mL), and dried: 5.24 g (21.3 mmol, 85% yield). The dialkylborane was 89% optically pure. It was suspended in 16 mL of THF so as to give a 1.0 M slurry and allowed to age for 12 h at 0 °C. The supernatant solution was decanted by using a double-ended needle. The solid isopinocampheyl-[1*S*,2*S*]-*trans*-2-methylcyclohexylborane (**2**)[22] was washed with cold (0 °C) EE (2 × 3 mL) and dried: 4.66 g (18.9 mmol, 75% yield). The dialkylborane was methanolyzed, oxidized, and worked up following the literature procedure.[11] The [1*S*,2*S*]-*trans*-2-methylcyclohexanol obtained was purified by using a 10% Carbowax column to furnish a GC-pure sample: $[\alpha]^{23}$D +42.9° (± 0.1) (*c* 1, MeOH), ≥99% ee.

Preparation of 2-Alkyl-1,3,2-dioxaborinanes of Very High Optical Purity. The following procedure for the preparation of (+)-2-(1*S*,2*S*)-*trans*-2-methylcyclohexyl-1,3,2-dioxaborinane (**5**) is typical. Acetaldehyde (4 mL, 75 mmol) was added to a suspension of the dialkylborane **2** (25 mmol) in 20 mL of EE at 0 °C. After the vigorous initial reaction, 2 mL of acetaldehyde was added, and the reaction mixture was stirred at 25 °C for 6 h. Water (5 mL) was added and stirred for 0.5 h. Excess acetaldehyde was evaporated (25 °C, 12 mmHg, 1 h), and pentane (30 mL) was added. The boronic acid was extracted with 3 M NaOH (3 × 15 mL) in a separating funnel. The combined aqueous phase was cooled to 0 °C, acidified with 3 M HCl, extracted with EE (3 × 25 mL), and dried over anhydrous MgSO$_4$. Ethyl ether was evaporated, and the boronic acid was reesterified with 1,3-propanediol following the published procedure.[14] The ester was purified by distillation (3.87 g, 85% yield): bp 80–82 °C (2.5 torr); $[\alpha]^{23}$D +24.2° ± 0.02° (*c* 7, THF); ^{11}B NMR +30.9 (singlet); ^{1}H NMR ($CDCl_3$) 0.4–0.7 (*m*, 1 H), 0.85 (*d*, *J* = 6.5 Hz, 3 H), 1.1–1.8 (*m*, 9 H), 1.9 (*p*, *J* = 6 Hz, 2 H), 3.93 (*t*, *J* = 6 Hz, 4 H). Oxidation of the ester with alkaline hydrogen peroxide gave [1*S*,2*S*]-(+)-*trans*-2-methylcyclohexanol, which exhibited $[\alpha]^{23}$D +42.8° (*c* 1, MeOH), suggesting >99% ee for the ester.[11] The above alcohol was derivatized by using Anderson and Shapiro reagent.[16] The ^{31}P NMR analysis showed only a single peak.[12]

Synthesis of Optically Active Borinic Esters, R*MeBO(CH$_2$)$_3$OAc, of Very High Optical Purity. The following procedure for the preparation of the optically active borinic ester **6** is representative.[13] To a 0.5 M EE solution of (+)-2-[1*S*,2*S*]-*trans*-2-methylcyclohexyl-1,3,2-dioxaborinane (**5**, 20 mmol) at −78 °C, methyllithium in EE (1.47 *M*, 24 mmol) was added with stirring. Care was taken to maintain the temperature at −78 °C. The reaction mixture was stirred at −78 °C for 3.0 h, acetyl chloride (1.7 mL, 24 mmol) was added at −78 °C, and the reaction mixture was allowed to reach 25 °C gradually. The solvent was evaporated at 25 °C under reduced pressure (12 torr). The residue was dissolved in *n*-pentane (20 mL), and the slurry was transferred to a centrifuge vial. Lithium chloride was centrifuged, and the clear supernatant solution containing the product was transferred to another flask by using a double-ended needle. Solid lithium chloride was washed with *n*-pentane (2 × 10 mL), and the washings were combined with the solution of the product. Solvent *n*-pentane was evaporated (25 °C, 12 torr) to give the crude borinic ester **6** in essentially quantitative yield. The ^{11}B NMR spectrum of the product showed a peak at δ +56.0 (br s) due to the borinate ester and trace amount of unreacted boronic ester. The crude borinic ester was used in the amine synthesis without further purification.

Synthesis of Optically Active Primary Amine Hydrochlorides. The following procedure for the synthesis of [1*S*,2*S*]-(+)-*trans*-2-methylcyclohexylamine hydrochloride is typical. The crude borinic ester **6** (20 mmol) was dissolved in THF so as to give a 1.0 M solution, and solid hydroxylamine-*O*-sulfonic acid (4.52 g, 40 mmol) was added by using a solid addition tube. The reaction mixture was stirred at 25 °C, and the initial slurry became a clear solution after 8 h. The reaction mixture was stirred overnight to ensure complete reaction. Water (10 mL) and EE (20 mL) were added, and the ^{11}B NMR of the organic phase showed a peak at δ +31 due to boronic acid derivative. The acidic aqueous layer was separated, cooled to 0 °C, and layered with EE (20 mL). It was then made strongly alkaline by adding solid sodium hydroxide (80 mmol) with stirring. The organic phase was separated, and the aqueous layer was extracted with EE (20 mL). The combined organic phase was dried over anhydrous magnesium sulfate and filtered. The filtrate was reacted with ethereal hydrogen chloride (2 M, 10 mL) to precipitate amine **8** as its hydrochloride. The solid thus obtained was isolated, washed with EE (2 × 5 mL), and dried (25 °C, 12 torr): 2.3 g (76% yield); mp > 250 °C; ^{1}H NMR 1.05 (*d*, *J* = 6 Hz, 3 H), 1.2–2.2 (*m*, 9 H), 2.7–3.1 (*m*, 1 H), 4.70 (*s*, 3 H); ^{13}C NMR 20.5, 27.0, 27.5, 33.4, 36.0, 38.6, 59.4. Anal. Calcd for $C_7H_{16}NCl$: C, 56.2; H, 10.8; N, 9.4; Cl, 23.7. Found: C, 56.0; H, 11.1; N, 9.0; Cl, 23.8.

[2*R*]-(+)-2-Butylamine Hydrochloride. ^{1}H NMR 1.0 (*t*, *J* = 7 Hz, 3 H), 1.32 (*d*, *J* = 7 Hz, 3 H), 1.62 (quintet, *J* = 7 Hz, 2 H), 3.37 (unresolved sextet, *J* = 7 Hz, 1 H), 4.70 (*s*, 3 H); ^{13}C NMR 11.8, 20.1, 29.9, 52.1. Anal. Calcd for $C_4H_{12}NCl\cdot{}^1/_8H_2O$: C, 43.0; H, 11.0; N, 12.5; Cl, 31.7. Found: C, 42.9; H, 11.3; N, 12.7; Cl, 31.9.

[3*R*]-(−)-3-Hexylamine Hydrochloride. ^{1}H NMR 0.95–1.30 (*m*, 6 H), 1.4–2.2 (*m*, 6 H), 3.38 (unresolved quintet, 1 H), 4.73 (*s*, 3 H); ^{13}C NMR 11.5, 15.9, 20.6, 27.7, 36.3, 55.8. Anal. Calcd for $C_6H_{16}NCl\cdot{}^1/_4H_2O$: C, 50.7; H, 11.7; N, 9.9; Cl, 24.9. Found: C, 51.0; H, 12.0; N, 9.8; Cl, 25.0.

[2*S*]-(−)-3-Methyl-2-butylamine Hydrochloride. ^{1}H NMR 1.04 (*d*, *J* = 7 Hz, 6 H), 1.31 (*d*, *J* = 7 Hz, 3 H), 2.0 (*m*, 1 H), 3.3 (*m*, 1 H), 4.73 (*s*, 3 H); ^{13}C NMR 17.4, 19.5, 20.6, 33.8, 55.9. Anal. Calcd for $C_5H_{14}NCl\cdot{}^1/_8H_2O$: C, 47.7; H, 11.4; N, 11.1; Cl 28.2. Found: C, 47.7; H, 11.7; N, 11.3; Cl, 28.3.

[1*S*,2*S*]-(+)-*trans*-2-Methylcyclopentylamine Hydrochloride. ^{1}H NMR 1.05 (*d*, *J* = 7 Hz, 3 H), 1.1–2.3 (*m*, 7 H), 3.0–3.3 (*m*, 1 H), 4.7 (*s*, 3 H); ^{13}C NMR 20.1, 24.7, 32.9, 35.0, 41.7, 61.4. Anal. Calcd for $C_6H_{14}NCl\cdot{}^1/_4H_2O$: C, 51.4; H, 10.4; N, 10.0; Cl, 25.3. Found: C, 51.3; H, 10.5; N, 10.0; Cl, 25.0.

[1*S*,2*R*]-(+)-*trans*-2-Phenylcyclopentylamine Hydrochloride. ^{1}H NMR 1.65–2.55 (*m*, 6 H), 2.95–3.95 (*m*, 2 H), 4.73 (*s*, 3 H), 7.32 (*s*, 5 H); ^{13}C NMR 24.9, 32.8, 36.1, 53.1, 61.3, 130.0, 130.3, 131.7, 143.6. Anal. Calcd for $C_{11}H_{16}NCl$: C, 66.8; H, 8.2; N, 7.1; Cl, 17.9. Found: C, 66.7; H, 8.4; N, 7.1; Cl, 18.2.

[1*R*,2*S*,3*R*,5*R*]-(−)-3-Isopinocampheylamine Hydrochloride. ^{1}H NMR 1.07 (*s*, 3 H), 1.13 (*d*, *J* = 7 Hz, 3 H), 1.33 (*s*, 3 H), 1.7–2.9 (*m*, 7 H), 3.63 (*m*, 1 H), 4.7 (*s*, 3 H); ^{13}C NMR 22.6, 25.7, 30.1, 35.5, 36.1, 40.8, 43.5, 44.5, 50.0, 52.7. Anal. Calcd for $C_{10}H_{20}NCl$: C, 63.3; H, 10.6; N, 7.4; Cl, 18.7. Found: C, 62.8; H, 10.8; N, 7.4; Cl, 18.6.

Preparation of MTPA Amides. The [*R*]-(+)-MTPA acid was converted to the acid chloride[15] and distilled. The amine hydrochloride (0.1 mmol), methylene chloride (0.3 mL), and pyridine (0.6 mL) were mixed together in a vial fitted with a rubber septum. The MTPA acid chloride (26 μL) was then injected into the vial, and the mixture was stirred for 1.0 h at 25 °C. It was then diluted with EE (10 mL) and washed with aqueous HCl (1.0 M, 5 mL) and the ether solution of the MTPA amide was dried over anhydrous magnesium sulfate. This ether solution was analyzed by capillary GC by using a 20-m Supercowax capillary column.

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(22) These organoboranes actually exist in the solution as the dimers, that is, as derivatives of the diborane molecules. However, it is convenient to refer to them as simple borane derivatives.