there are stable ground-state forms, these species are not exciplexes.

**Thermodynamic Parameters.** Only the two-equilibrium constant model successfully explains all of our data. Using the equilibrium constants determined at 25 and 6 °C, we evaluated $\Delta H$ and $\Delta S$. These are summarized in Table II.

In keeping with many other exciplexes, we assume that the complex is stabilized largely by a charge transfer interaction. Formation of the charge transfer stabilized 1:1 $*RuL_3^{2+}|Ag^+$ exciplex results from the affinity of $Ag^+$ for the electron in the partially filled $\pi$-antibonding orbitals of polypyridyl ligands.

At first, even the existence of $*DAg_2^{2+}$ species was puzzling. The *D excited state has only a single electron promoted from a metal to a ligand $\pi^*$ orbital and the electron is largely localized in a single ligand. Thus, it was difficult to envision binding of a second silver ion either to a second ligand or to the one already associated with a silver ion. Further, the $\Delta H$ for the second binding is remarkably high for an apparently unfavorable process.

We believe that this apparent anomaly can be explained by the well-known tight binding of $Ag^+$ to $Ag^0$:

$$Ag^+ + Ag^0 \rightarrow Ag_2^+$$

Indeed, the dimeric species is far and away the most stable form of $Ag^0$ in the presence of an excess of $Ag^+$.[8] Thus, we suggest that charge transfer to the first bound $Ag^+$ is sufficient to give considerable $Ag^0$ character. Then the driving force for formation of $*DAg_2^{2+}$ is not binding of a second $Ag^+$ to a second ligand ring, but rather the coupling of the two silvers to form an $*D^+|Ag_2^+$ species. Thus, the large $\Delta H_2$'s arise predominantly from the silver dimerization and not from interaction with an aromatic ring.

**Comparison with Other Exciplex Systems.** Exciplexes have been well-studied in organic systems.[23] There is one charge transfer stabilized organic exciplex of silver ion (acceptor) with a pyrene (donor)[24a] as well as perylene–$Ag^+$ exciplexes.[24b,c] A rare termolecular excited state interaction has been proposed for the naphthalene–naphthalene–dicyanobenzene exciplex.[25]

Much less is known about inorganic exciplexes. The only other exciplex involving a platinum metal photosensitizer appears to be $Re(phen)(CO)_3Cl$ with dimethylaniline.[26] Our results seem to involve the first documented case of exciplex formation involving the widely used Ru(II) polypyridine photosensitizers. Further, a termolecular exciplex in inorganic systems is completely new.

Exciplexes differ widely in the relative contributions of $\Delta H$ and $\Delta S$ to their stability. In the perylene–$Ag^+$–acetonitrile system, the relatively small $\Delta H$ contribution of −1 kcal/mol suggests that there is only a weak charge transfer interaction. While the −5 kcal/mol for Ru(II)/$Ag^+$ and −5.7 kcal/mol for Re(I)/DMA indicates much more charge transfer. The stability of the *perylene/$Ag^+$ exciplex is driven mainly by $\Delta S$ factors associated with the decrease in ordering of solvent around the $Ag^+$ upon exciplex formation. The stabilities of the Ru(II)/$Ag^+$ and Re(I)/DMA exciplexes are largely due to $\Delta H$ factors, and $\Delta S$ is counterproductive. Due to the current paucity of inorganic exciplexes, it remains to be seen whether these trends will hold.

## Conclusions

We report the first example of an exciplex based entirely on inorganic species. The earlier reported luminescence "quenching" by $Ag^+$ is shown to be incorrect and formation of both dimeric and trimeric Ru(II)–$Ag^+$ exciplexes in water accounts for all observations. $Ag^0$ formation was undetectable in our experiments and the yield for its formation appears to be very low (<0.02 in water and <0.05 in acetonitrile); this severely limits any practical applications of $Ag^0$ formed by this system.

We suspect that inorganic exciplexes will prove to be much more pervasive than the literature to date has indicated. Further, we suggest that exciplexes may make useful new, excited state reactants. Further work is in progress.

**Acknowledgment.** We gratefully acknowledge support by the National Science Foundation (CHE 86-00012). We thank Professor D. G. Whitten for his comments.

**Registry No.** $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(4,7\text{-}Me_2phen)_3^{2+}$, 24414-00-4; $Ag^+$, 14701-21-4.

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# Chiral Synthesis via Organoboranes. 12. Conversion of Boronic Esters of Essentially 100% Optical Purity into Monoalkylthexylboranes Providing Convenient Synthetic Routes to *trans*-Olefins, *cis*-Olefins, Alkynes, and Ketones of Very High Enantiomeric Purities

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*Contribution from the H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907.* *Received June 8, 1987*

**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 transformed into the lithium monoalkylborohydrides $R^*BH_3Li$ of essentially 100% ee by reaction with lithium aluminum hydride. These monoalkylborohydrides are converted into optically active monoalkylthexylboranes R*ThxBH through the intermediate formation of the corresponding optically active monoalkylboranes $R^*BH_2$. The synthetic potential of optically active R*ThxBH is demonstrated by carrying out various reactions leading to *trans*-olefins, *cis*-olefins, alkynes, and ketones of very high optical purities. Since both (+)- and (−)-alkylboronic esters are available in essentially 100% optical purity, it is now possible to synthesize (+)- and (−)-*cis*- and *trans*-olefins, -alkynes, and -ketones in very high optical purities.

Organoboranes have become one of the most significant classes of organometallics in organic synthesis.[2] Our studies have established that organoboranes transfer the alkyl group to essentially most other elements of synthetic interest, including carbon, with

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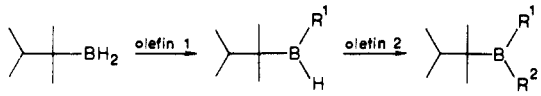
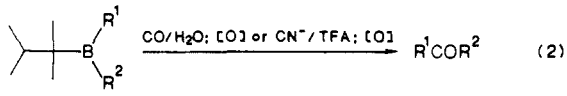
complete maintenance of stereochemical integrity. However, when the organoborane is applied to organic synthesis, it is often undesirable to use symmetrical trialkylboranes ($R_3B$). First, these symmetrical trialkylboranes are not, in most cases, applicable to the synthesis of unsymmetrical organic compounds such as ketones, alkenes, and secondary and tertiary alcohols.[2] Second, many reactions of organoboranes involve utilization of only one of the three alkyl groups. Use of symmetrical trialkylboranes in these reactions limits the maximum yield of products to 33.3%. Use of the partially alkylated boranes is effective in circumventing these difficulties. It may be stated that selection of the most suitable partially alkylated borane is the key to the successful application of organoboranes to organic synthesis. One of the partially alkylated boranes is the thexylborane ((2,3-dimethyl-2-butyl)borane, $ThxBH_2$).

Synthetically, the most important derivatives of thexylborane are those obtained by its reaction with olefins. Thexylborane reacts with olefins in two distinct stages: first, to form the mono (RThxBH), and then the dialkylthexylborane (eq 1).[3] The



(1)

discovery that the thexyl group does not migrate competitively in the carbonylation or cyanidation reactions in the manner exhibited by primary and secondary alkyl groups makes it possible to convert two olefins cleanly into the corresponding ketone $R^1COR^2$ (eq 2).[4] However, the scope of this approach is limited



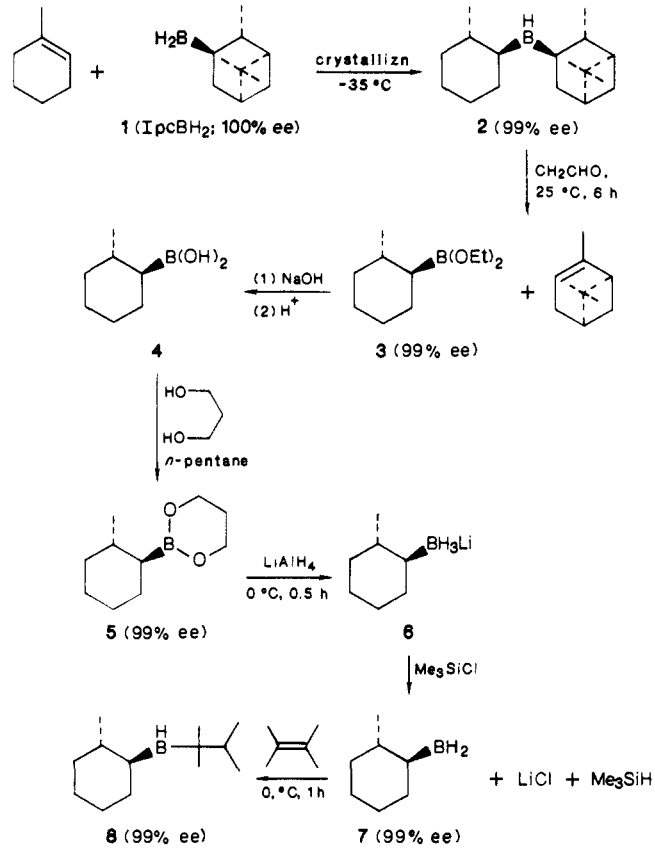
(2)

by the availability of suitable RThxBH. Only alkenes with intermediate steric requirements form RThxBH cleanly. This limitation has been recently circumvented by the use of thexylchloroborane.[5] Unfortunately, neither thexylborane nor thexylchloroborane can be used to prepare optically active monoalkylthexylborane (R*ThxBH), where R* is an optically active alkyl group, either (+)- or (−)-isomer. Yet, they are very valuable intermediates in organic synthesis. A recent development offers promise not only of providing any RThxBH but also of making these intermediates in essentially 100% optical purity.[6]

## Results and Discussion

Optically active organoborane intermediates needed for the synthesis of optically active monoalkylthexylboranes R*ThxBH were prepared by the asymmetric hydroboration of prochiral olefins with diisopinocampheylborane ($Ipc_2BH$; (99% ee)[7] and monoisopinocampheylborane ($IpcBH_2$, **1**; 100% ee),[8,9] prepared from (+)-α-pinene. Thus, asymmetric hydroboration of prochiral olefins with I in the molar ratio of 1:1, followed by crystallization, provides the chiral isopinocampheylalkylboranes IpcR*BH (e.g., **2**)[9] 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 enantiomeric purity. The optically active 2-alkyl-1,3,2-dioxaborinanes were then

**Scheme I**




prepared by esterification of the corresponding boronic acids with 1,3-propanediol (e.g., **4** and **5**; Scheme I). The optical purities of all of these boronic esters were determined by $^{19}F$ NMR or $^{31}P$ NMR or capillary GC analyses of the appropriate derivatives of the alcohols obtained following alkaline hydrogen peroxide oxidation.[10]

Chiral alkylboronic esters are exceptionally promising intermediates for carbon–carbon bond-forming reactions. Recently, we utilized these boronic esters for the synthesis of α-chiral aldehydes, β-chiral alcohols, α-chiral acids,[10] and α-chiral amines.[11] Yet the versatility of these boronic esters would greatly extend if the boron–oxygen bonds in these intermediates are converted into boron–hydrogen bonds. It was a real breakthrough when we discovered that lithium aluminum hydride ($LiAlH_4$) readily converted these relatively inert boronic esters into very active lithium monoalkylborohydrides $R^*BH_3Li$ of very high optical purity (e.g., **5** and **6**).[12] Diethyl alkylboronate esters (e.g., **3**) can also be converted into $R^*BH_3Li$, but we routinely used esters **5** because of the ease of isolation of the product. These $R^*BH_3Li$ are very stable and can be stored under nitrogen, even at 25 °C, without any hydride loss, redistribution, isomerization, or racemization of the alkyl groups. The monoalkylboranes ($R^*BH_2$, **7**)[9] are generated from the $R^*BH_3Li$ by a conveniently simple reaction with trimethylsilyl chloride (e.g., **6** and **7**). Reaction of optically active monoalkylboranes with a 10% excess of 2,3-dimethyl-2-butene at 0 °C afforded the desired optically active monoalkylthexylborane (R*ThxBH, **8**). Conversion of the boronic ester (e.g., **5**) to the R*ThxBH (e.g., **8**) proceeds in essentially quantitative yields. This reaction sequence represents a new general synthesis of monoalkylthexylborane intermediates. This methodology not only permits the synthesis of monoalkylthexylboranes containing primary alkyl groups but also

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(7) Brown, H. C.; Singaram, B. *J. Org. Chem.* **1984**, *49*, 945.
(8) Brown, H. C.; Schwier, J. R.; Singaram, B. *J. Org. Chem.* **1978**, *43*, 4395.
(9) These organoboranes actually exist in solution as dimers, that is, as derivatives of diborane molecules. However, it is convenient to refer to them as simple borane derivatives.
(10) Brown, H. C.; Imai, T.; Desai, M. C.; Singaram, B. *J. Am. Chem. Soc.* **1985**, *107*, 4980.
(11) Brown, H. C.; Kim, K.-W.; Cole, T. E.; Singaram, B. *J. Am. Chem. Soc.* **1986**, *108*, 6761.
(12) Brown, H. C.; Singaram, B.; Cole, T. E. *J. Am. Chem. Soc.* **1985**, *107*, 460.

**Table I.** Monoalkylthexylboranes of High Optical Purity[a]

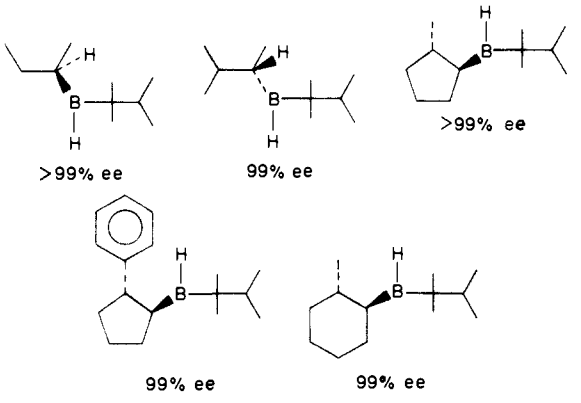
| dialkylboranes R*ThxBH, R* | % yield[b] | % ee[c] | $^{11}$B NMR: chemical shift, δ monomer[h] ($J_{BH}$, Hz) | $^{11}$B NMR: chemical shift, δ dimer[i] | IR: $\nu_{BH}$, cm$^{-1}$ monomer | IR: $\nu_{BH}$, cm$^{-1}$ dimer | monomer:dimer[j] |
|---|---|---|---|---|---|---|---|
| (*R*)-2-butyl | 80 | >99 | +78 (100) | 32 | 2435 | 1610 | 75:25 |
| (*S*)-3-methyl-2-butyl | 70 | 99[d,e] | +80 (110) | 32 | 2460 | 1580 | 95:5 |
| (1*S*,2*S*)-*trans*-2-methylcyclopentyl | 75 | 99[f,g] | +78 (105) | 33 | 2474 | 1590 | 85:15 |
| (1*S*,2*S*)-*trans*-2-methylcyclohexyl | 78 | 99[f,g] | +80 (95) | 33 | 2439 | 1542 | 95:5 |
| (1*S*,2*S*)-*trans*-2-phenylcyclopentyl | 75 | 99[e] | +81 (95) | 32 | 2495 | 1570 | 95:5 |

[a] Organoborane intermediates were prepared starting from (+)-α-pinene. [b] Determined by hydride analysis and $^{11}$B NMR spectroscopy. Calculated starting from IpcR*BH (e.g., **2**). [c] See ref 6a. [d] Analyzed by $^{19}$F NMR. [e] Analyzed by capillary GC of the MTPA ester of the alcohol obtained following oxidation. [f] Analyzed by $^{31}$P NMR. [g] Analyzed by capillary GC of the menthylcarbonate of the alcohol obtained following oxidation. [h] Unresolved doublets. [i] Broad singlets. [j] Determined by $^{11}$B NMR spectroscopy.

permits the preparation of monoalkylthexylboranes in optically active form.

Dialkylboranes previously studied exist as dimers, that is, as the tetraalkyldiboranes, either under neat conditions or in various solvents such as diethyl ether and tetrahydrofuran. Thus, disiamylborane, dicyclohexylborane, diisopinocampheylborane, borinane, and 9-borabicyclo[3.3.1]nonane[2] all exist as dimers, as established by the strong absorption in the 1600–1500-cm$^{-1}$ region characteristic of the B–H–B stretching. They also exhibit a broad singlet of approximate δ +32 in the $^{11}$B NMR spectrum. As observed previously,[13] the IR spectra of the monoalkylthexylboranes described in the present study reveal the presence of the IR band (~2470 cm$^{-1}$) attributable to monomeric dialkylboranes in varying intensities. Examination of the $^{11}$B NMR spectra of these R*ThxBH shows a doublet of approximate δ +80 ($J$ = 100 Hz), establishing the presence of monomeric dialkylboranes, along with a broad singlet of approximate δ +32 attributable to the dimeric dialkylboranes. The ratio of intensities of the peak δ +80 to that δ +32 increases in the following order and seems to correlate with the steric requirements of the alkyl groups: 2-butyl < *trans*-2-methylcyclopentyl < *trans*-2-methylcyclohexyl ≈ *trans*-2-phenylcyclopentyl < 3-methyl-2-butyl (Table I). These results strongly suggest that these monoalkylthexylboranes exist as the monomer–dimer equilibria and that the large steric requirements of the two alkyl groups are primarily responsible for the existence of such monomeric dialkylboranes.

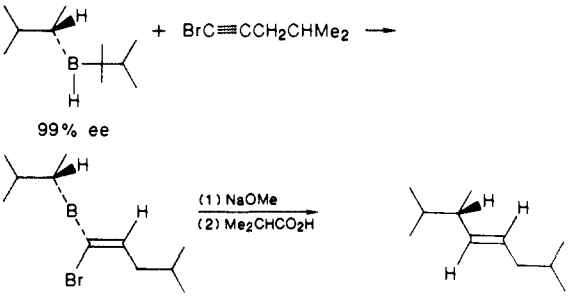
By use of the general procedure described above, the following representative monoalkylthexylboranes were prepared in very high optical purities.




The optical purity of all of these R*ThxBH was 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 excess of most of these alcohols was also determined by $^{19}$F NMR of their MTPA esters[14] and/or by $^{31}$P NMR with the use of the Anderson and Shapiro reagent[15] and/or by capillary GC analyses of their MTPA esters or their menthyl carbonates.[16]

With the availability of monoalkylboranes of very high optical purity, we carried out typical reactions of RThxBH to demonstrate the synthetic potentials of these valuable intermediates.

**Application of R*ThxBH in the Synthesis of *trans*-Olefin of Very High Optical Purity.**[17] (*S*)-(+)-*trans*-2,3,7-Trimethyl-4-octene was synthesized from the reaction of (*S*)-(3-methyl-2-butyl)thexylborane with 1-bromo-4-methyl-1-pentyne, followed by treatment with sodium methoxide and protonolysis (eq 3). The




99% ee, 72% yield, >99% *trans*

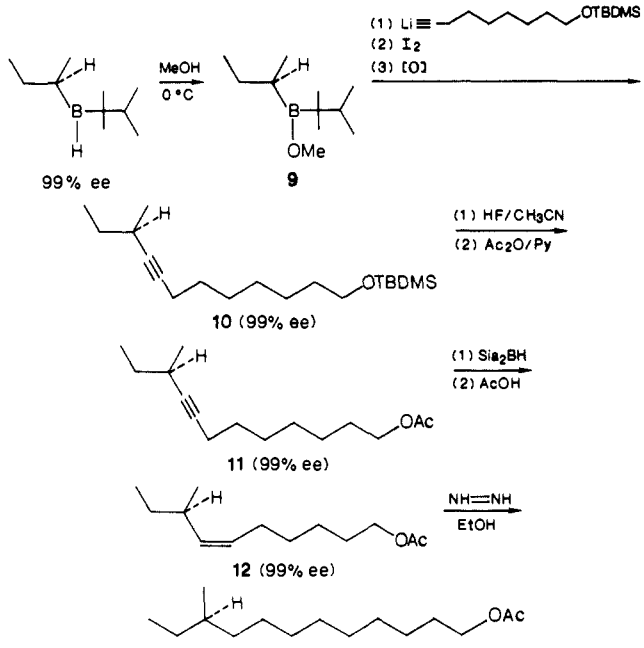
optical purity of the *trans*-olefin was determined by comparing the optical rotation with that of the *trans*-olefin prepared previously from isobutylthexylborane and optically active (*S*)-3,4-dimethyl-1-pentyne.[18] Isomeric purity of the optically active *trans*-olefin was determined by $^{13}$C NMR and capillary gas chromatographic comparison with the (±)-*cis*-2,3,7-trimethyl-4-octene obtained from disiamylborane and 4-methyl-1-pentyne.[19]

**Application of R*ThxBH in the Synthesis of Alkyne and *cis*-Olefin of Very High Enantiomeric Purity. Synthesis of the Sex Pheromone of the Lesser Tea Tortrix Moth *Adoxopheyes spp*.** Methanolysis of (*R*)-2-butylthexylborane furnished the borinate ester **9**. The addition of [9-[(*tert*-butyldimethylsilyl)oxy]-1-nonyl]lithium to the borinate **9** followed by the addition of iodine and oxidation gave the alkyne **10**.[20] Deprotection using hydrogen fluoride and esterification with acetic anhydride gave the alkyne **11**. The *cis*-olefin **12** was prepared from the alkyne **11** by hydroboration with disiamylborane ($Sia_2BH$) followed by protonolysis. In order to determine the optical purity of the alkynes **10** and **11** and the *cis*-olefin **12**, the *cis*-olefin was converted to the sex pheromone of the lesser tea tortrix moth by the reduction of the double bond with diimide. The optical purity of the pheromone was found to be essentially 100% by chiroptical comparison (Scheme II).[21]

**Application of R*ThxBH in the Synthesis of Optically Active Ketones.** Monoalkylthexylboranes can be converted into ketones

(13) Brown, H. C.; Negishi, E.; Katz, J.-J. *J. Am. Chem. Soc.* **1975**, *97*, 2791.
(14) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.
(15) Anderson, R. C.; Shapiro, M. *J. Org. Chem.* **1984**, *49*, 1304.
(16) Racemic alcohols give two signals, which are well resolved.
(17) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086.
(18) Caporusso, A. M.; Giacomelli, G.; Lardicci, L. *Gazz. Chim. Ital.* **1976**, *106*, 879.
(19) Zweifel, G.; Arzoumanian, H.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 3652.
(20) Sikorski, J. A.; Bhat, N. G.; Cole, T. E.; Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 4521.
(21) Hjalmarsson, M.; Högberg, H.-E. *Acta Chem. Scand., Ser. B* **1985**, *B39*, 793.

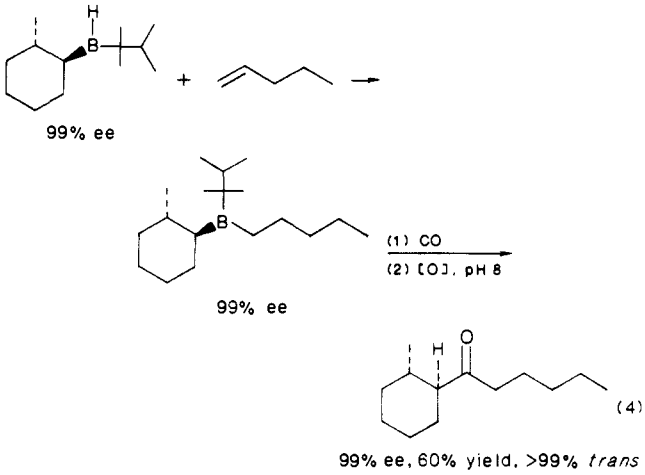
**Scheme II**




(*R*)-(−)-10-methyl-1-dodecanol acetate 99% ee, 70% yield from **9**

by three different methods. The first two routes involve hydroboration of an olefin with R*ThxBH leading to a trialkylborane. This sequence represents a stepwise hydroboration wherein two different alkyl groups can be attached to thexylborane. The trialkylboranes thus obtained can be readily converted into ketones either by carbonylation or by cyanidation reaction.[4] In the third procedure, R*ThxBH is converted into ketone R*COR by use of 1-halo-1-alkyne.[22]

(i) **Carbonylation.** (1*S*,2*S*)-*trans*-(2-Methylcyclohexyl)thexylborane (**8**) was readily converted with 1-pentene to the corresponding trialkylborane (1 h, 0 °C). Carbonylation of this trialkylborane, followed by oxidation, furnished optically active (1*S*,2*S*)-*trans*-2-methylcyclohexyl *n*-pentyl ketone (eq 4).

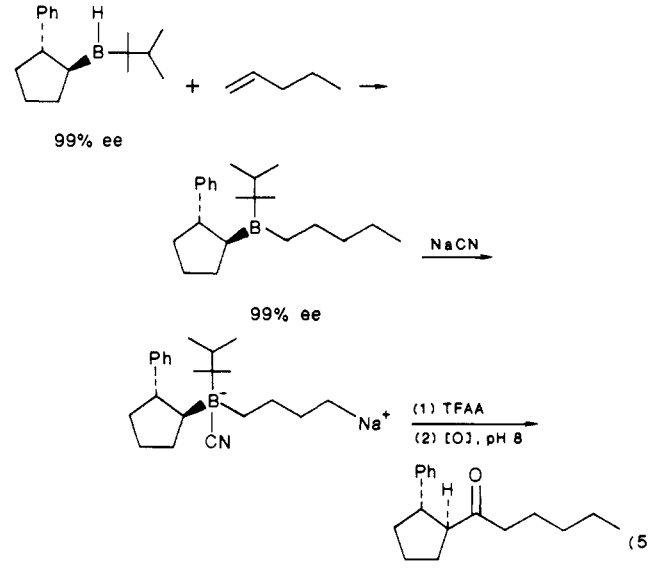



(4)

99% ee, 60% yield, >99% *trans*

Capillary GC analysis using a 50-m methyl silicone column showed that the ketone was diastereomerically pure.[23] The diastereomeric purity of the ketone in turn reflects its enantiomeric purity.

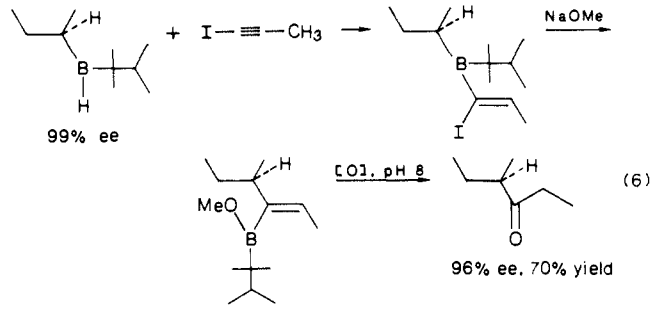
(ii) **Cyanidation.** Reaction of lithium (1*S*,2*S*)-*trans*-(2-phenylcyclopentyl)borohydride with trimethylsilyl chloride in the presence of 2,3-dimethyl-2-butene cleanly produced the corresponding R*ThxBH. Hydroboration of 1-pentene with R*ThxBH furnished (1*S*,2*S*)-(2-phenylcyclopentyl)-*n*-pentylthexylborane. Treatment with sodium cyanide (NaCN), however, did not produce the desired trialkylcyanoborate. Careful examination revealed that the lithium chloride, produced during the conversion of LiR*$BH_3$ to R*ThxBH (e.g., **6** and **7**), interferes with the cyanidation reaction. This difficulty was circumvented by isolating the trialkylborane from the reaction mixture and then carrying out the cyanidation reaction. Alternatively, the lithium chloride present in the trialkylborane solution was removed by stirring the solution with NaCN. Trialkylborane solution, free from LiCl, was then separated by centrifugation and treated with fresh NaCN to get the trialkylcyanoborate. Acylation with trifluoroacetic anhydride (TFAA), followed by oxidation, afforded optically active (1*S*,2*S*)-*trans*-2-phenylcyclopentyl *n*-pentyl ketone (eq 5).




(5)

99% ee, 75% yield, 99% *trans*

(iii) **Haloalkyne Route.** Hydroboration of 1-iodo-1-propyne with (2*R*)-2-butylthexylborane proceeded cleanly at −25 °C with the formation of the desired (α-iodovinyl)borane. The base-induced migration of the 2-butyl group to the adjacent carbon followed by oxidation with hydrogen peroxide and pH 8 buffer, provided (*R*)-(−)-4-methyl-3-hexanone of high optical purity (eq 6). This ketone was found to be 96% optically pure by chiroptical




(6)

96% ee, 70% yield

comparison.[24] Evidently, there was ~2% racemization of the ketone during the oxidation step. The intermediate vinylthexylborinates are relatively resistant to oxidation, often requiring higher temperatures for the completion of the reaction.[22] Care has to be taken in oxidizing these optically active vinylthexylborinates to avoid extensive racemization.

## Conclusion

The present study provides a simple procedure for the synthesis of various optically active monoalkylthexylboranes. These are valuable reagents, especially promising for chiral synthesis pro-

(22) Kulkarni, S. U.; Lee, H. D.; Brown, H. C. *Synthesis* **1982**, 193.
(23) Authentic cis–trans mixture (62:38) of the ketone was prepared by hydroboration of 2-methylhexylidenecyclohexane, followed by oxidation with $CrO_3$.
(24) Enders, D.; Eichenauer, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 397.

ceeding through boron intermediates. Both (+)- and (−)-α-pinenes are readily available. Consequently, both enantiomers are readily synthesized. The synthetic potential of these monoalkylthexylboranes was demonstrated by carrying out a few typical reactions leading to the synthesis of optically active *trans*-olefin, *cis*-olefin, alkyne, and ketone.

## Experimental Section

**General Methods.** All operations were carried out under nitrogen atmosphere with oven-dried glassware.[2] Spectroscopic measurements (NMR, $^1H$, $^{11}B$, $^{13}C$, $^{19}F$, $^{31}P$; IR) and optical rotations were made with standard instruments. Gas chromatographic analyses and capillary gas chromatographic analyses were carried out with Hewlett-Packard 5750 and 5890 chromatographs, respectively. All new compounds gave satisfactory elemental analyses.

**Materials.** Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Anhydrous ethyl ether (EE) was purchased from Mallinckrodt, Inc., and was used directly. Lithium aluminum hydride (1.0 M) in EE was purchased from Aldrich Chemical Co. Optically active organoborane intermediates were prepared starting from (+)-α-pinene.

**(1*S*,2*S*)-*trans*-Isopinocampheyl-(2-methylcyclohexyl)borane (2).** A 100-mL flask fitted with a rubber septum and a magnetic stirring bar was charged with 34.6 mL of $IpcBH_2$[6a] in EE (0.723 M, 25 mmol) and the resultant mixture cooled to −35 °C. 1-Methylcyclohexane (3.5 mL, 30 mmol) was added to it. The reactants were mixed together well and left at −35 °C without stirring for 12 h. The crystalline dialkylborane was isolated, washed with cold EE (−35 °C; 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 with a double-ended needle. The solid (1*S*,2*S*)-*trans*-isopinocampheyl-(2-methylcyclohexyl)borane (**2**)[9] was washed with cold EE (0 °C; 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.[6a] The (1*S*,2*S*)-*trans*-2-methylcyclohexanol obtained was purified by preparative GC: $[\alpha]^{23}D$ +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 the borinate ester **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 resultant mixture was stirred for 6 h at 25 °C. Water (5 mL) was then added, and the resultant mixture was stirred for 0.5 h. Excess acetaldehyde was evaporated (25 °C, 12 Torr, 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. 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 δ +30.9 (s); $^1H$ NMR ($CDCl_3$) δ 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 (quintet, *J* = 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.[6a] The above alcohol was derivatized with Anderson and Shapiro reagent,[15] and the $^{31}P$ NMR analysis showed only a single peak.[16] The optical purity of the above alcohol was further confirmed by capillary GC analysis of its menthylcarbonate with a 50-m methyl silicone column.

**Preparation of Optically Active Lithium Monoalkylborohydrides.** The following procedure for the preparation of lithium [1*S*,2*S*]-*trans*-(2-methylcyclohexyl)borohydride (**6**) is representative. A 250-mL flask fitted with a rubber septum and a magnetic stirring bar was charged with 60 mL of a 0.5 M solution of **5** (30 mmol) in *n*-pentane and the mixture cooled to 0 °C. A 1.0 M solution of $LiAlH_4$ in EE (30 mL, 30 mmol) was added with vigorous stirring. The stirring was continued for 0.5 h at 0 °C, and the solvent was evaporated under reduced pressure (12 Torr) at 25 °C. The residue containing the desired borohydride and alkoxyaluminohydride was stirred with *n*-pentane (50 mL) and filtered under nitrogen. The solid alkoxyaluminohydride was washed with *n*-pentane (3 × 10 mL), and the washings were combined with the filtrate. The solvent was evaporated at 25 °C under reduced pressure (12 mmHg). The residue (5.0 g) was dissolved in THF (25 mL) and estimated by hydride analysis:[2] 0.95 M, 95% yield; $^{11}B$ NMR δ −25.5 (q, $J_{BH}$ = 74 Hz); IR ν 2180 $cm^{-1}$. No signal attributable to the presence of aluminum compounds in the solution could be detected in either $^{27}Al$ NMR or the IR spectrum. The borohydride solution was quenched with methanol and then oxidized with alkaline hydrogen peroxide. The product alcohol (1*S*,2*S*)-(+)-*trans*-2-methylcyclohexanol exhibited $[\alpha]^{23}_D$ +42.8° (*c* 1, MeOH), suggesting 99% ee for the borohydride.

**Synthesis of Monoalkylthexylboranes of Very High Optical Purity.** The following procedure for the synthesis of (1*S*,2*S*)-*trans*-(2-methylcyclohexyl)thexylborane (**8**) is typical. A 100-mL flask fitted with a rubber septum and a magnetic stirring bar was charged with 40 mL of a 0.5 M THF solution of **6** and cooled to 0 °C. 2,3-Dimethyl-2-butene (2.02 g, 24 mmol) and trimethylsilyl chloride (2.39 g, 22 mmol) were added successively with stirring. The reaction mixture was stirred for 1 h at 0 °C, and then the lithium chloride precipitate was allowed to settle. The clear supernatant solution was withdrawn and estimated by hydride analysis:[2] 0.43 M, 98% yield; $^{11}B$ NMR δ +80 (unresolved d, $J_{BH}$ = 95 Hz), +33 (br s); IR ν 2439, 1542 $cm^{-1}$. The dialkylborane was quenched with methanol and then oxidized. The product alcohol (1*S*,2*S*)-(+)-*trans*-2-methylcyclohexanol exhibited $[\alpha]^{23}_D$ +42.8° (*c* 1, MeOH), suggesting 99% ee for the dialkylborane (Table I).

**(*S*)-(+)-*trans*-2,3,7-Trimethyl-4-octene.** To a 0.5 M EE solution of (*S*)-(3-methyl-2-butyl)thexylborane (99% ee, 20 mmol) at −25 °C was added 1-bromo-4-methyl-1-pentyne (3.21 g, 20 mmol) with stirring. The reaction mixture was stirred at −25 °C for 1 h. Methanolic sodium methoxide (4.54 M, 6 mL) was then added, and the reaction mixture was stirred at 25 °C for 1 h. The solvent was evaporated at 25 °C under reduced pressure (12 Torr), and the residue was taken up in isobutyric acid (25 mL). The reaction mixture was heated under reflux for 60 h and worked up as described before.[17] The *trans*-olefin was purified by distillation: 2.2 g (72% yield); bp 68–70 °C (15 Torr); $^1H$ NMR ($CDCl_3$) δ 0.9 (m, 15 H), 1.4–2 (m, 5 H), 5.3 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) δ 17.6, 19.5, 19.8, 22.2, 28.5, 33.0, 42.1, 43.0, 127.9, 135.7.

The *trans*-olefin was further purified by preparative GC. The (*S*)-(+)-*trans*-2,3,7-trimethyl-4-ocetene thus obtained exhibited $[\alpha]^{23}_D$ +35.9° (neat), suggesting 99% ee for the olefin.[18] Racemic *cis*-2,3,7-trimethyl-4-octene was prepared from disiamylborane and 4-methyl-1-pentyne following the literature procedure.[19] Analyses on capillary GC using a 50-m methyl silicone column showed that (*S*)-(+)-*trans*-2,3,7-trimethyl-4-octene was >99% isomerically pure.

**(*R*)-(−)-10-Methyl-8-dodecynyl Acetate (11).** To a 1.0 M EE solution of (*R*)-2-butylthexylborane (25 mmol) at 0 °C was added methanol (50 mmol), and the reaction mixture was stirred at 0 °C for 1 h. The solvent was evaporated at 25 °C under reduced pressure (12 Torr), and the residue was dissolved in THF (25 mL). lithium [1-[(*tert*-butyldimethylsilyl)oxy]-8-nonyl]acetylide (25 mmol) was then added at 0 °C and the resultant mixture then cooled to −78 °C. Iodine (6.35 g, 25 mmol) in THF (20 mL) was added slowly, and the reaction mixture was stirred at −78 °C for 1 h and at 25 °C for 2 h. The reaction mixture was then oxidized with alkaline hydrogen peroxide (NaOH, 30 mmol; $H_2O_2$, 30 mmol). The reaction product was extracted with *n*-pentane, washed with water (3 × 50 mL), and dried over anhydrous $MgSo_4$. The solvent was evaporated to get the crude alkyne **10**.

The crude alkyne **10** was dissolved in a 5% acetonitrile solution (100 mL) of hydrogen fluoride (48% aqueous solution) and kept at 0 °C for 0.5 h. The reaction mixture was extracted with chloroform, washed with water, and dried over anhydrous $MgSO_4$. The residue, obtained after evaporation of the solvent, was dissolved in acetic anhydride (4.71 mL, 50 mmol) and pyridine (3.9 g, 50 mmol) and stirred at 25 °C for 12 h. It was then poured into water (100 mL), extracted with *n*-pentane (150 mL), washed with water (2 × 25 mL), and dried over $MgSO_4$. The solvent was evaporated, and the residue was distilled to give (*R*)-(−)-10-methyl-8-decynyl acetate (**11**) as a colorless oil: 4.8 g (82%); bp 96–100 °C (0.05 Torr); $^1H$ NMR ($CDCl_3$) δ 0.9 (t, *J* = 6 Hz, 3 H), 1.1 (d, *J* = 6 H, 3 H), 1.3–2.3 (m, 15 H), 2.03 (s, 3 H), 4.1 (t, *J* = 6 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) δ 11.7, 18.7, 20.9, 21.0, 25.8, 27.6, 28.6, 28.7, 29.1, 30.3, 64.6, 80.2, 84.8, 171.1; $[\alpha]^{23}_D$ −18.91° (*c* 2, MeOH).

**(*R*)-(−)-*cis*-10-Methyl-8-dodecenyl Acetate (12).** The alkyne **11** (10 mmol) was added to a 1.0 M THF solution of disiamylborane (10 mmol) at −10 °C. The resultant mixture was then stirred for 1 h at 25 °C. Acetic acid (10 mL) was added, and the stirring was continued for another 2 h at 25 °C. The reaction mixture was poured into water (100 mL), extracted with *n*-pentane (3 × 25 mL), and washed with water (2 × 25 mL). The organic layer was oxidized with hydrogen peroxide (20 mmol) and pH 8 buffer (10 mL). The organic phase was separated, washed with water, and dried. Evaporation of the solvent afforded (*R*)-(−)-*cis*-10-methyl-8-dodecenyl acetate: 2.25 g, 94% yield. The *cis*-olefin was further purified by preparative GC: $^1H$ NMR ($CDCl_3$) δ 0.8–1.1 (m, 6 H), 1.3–2.3 (m, 15 H), 2.07 (s, 3 H), 4.05 (t, *J* = 7 Hz, 2 H), 5.05–5.4 (m, 2 H); $[\alpha]^{23}_D$ −10.4° (*c* 1, MeOH).

**(*R*)-(−)-10-Methyl-1-dodecanol Acetate.** Through a well-stirred mixture of (*R*)-(−)-10-methyl-8-dodecenyl acetate (1.21 g, 5 mmol), copper sulfate (0.2 g), hydrazine (97%, 2 g), and ethyl alcohol (40 mL) was bubbled air slowly for 12 h at 25 °C. The reaction mixture was then filtered, ethanol was distilled off, and the residue was extracted with EE (3 × 25 mL). The organic layer was washed with water (3 × 10 mL)

and dried over anhyrous $MgSO_4$. Evaporation of the solvent under reduced pressure (12 Torr) at 25 °C afforded (*R*)-(−)-10-methyldodecanol acetate: 1.1 g (90% yield); $^1H$ NMR ($CDCl_3$) $\delta$ 0.9 (m, 6 H), 1.3 (br s, 19 H), 2.03 (s, 3 H), 4.07 (t, $J$ = 6 Hz, 2 H). The acetate was further purified by preparative GC. The acetate exhibited $[\alpha]^{23}_D$ −5.93° (*c* 10, $CHCl_3$), suggesting 99% ee for the alkyne **11** and the *cis*-olefin **12**.[21]

**Preparation of (1*S*,2*S*)-*trans*-2-Methylcyclohexyl *n*-Pentyl Ketone by Carbonylation Reaction.** To a 1.0 M THF solution of the dialkylborane **8** (20 mmol) was added 1-pentene (22 mmol) at 0 °C and the resultant mixture stirred for 2 h. Water (1 mL) was then added, and the reaction mixture was transferred into an autoclave under nitrogen. Carbonylation was achieved by filling the autoclave with carbon monoxide to 1000 psi and stirring the reaction mixture at 50 °C for 4 h. The reaction mixture was transferred to a flask, 17 mL of pH 8 buffer was added, and oxidation was carried out by the addition of 5 mL of 30% hydrogen peroxide. The reaction mixture was stirred at 25 °C for 12 h. The aqueous layer was saturated with potassium carbonate, and the organic phase was separated. The aqueous phase was extracted with ether. After the combined extracts were dried, distillation yielded (1*S*,2*S*)-(+)-*trans*-2-methylcyclohexyl *n*-pentyl ketone: 2.2 g (60% yield); bp 70–72 °C (0.1 Torr); $^1H$ NMR ($CDCl_3$) $\upsilon$ 0.9 (m, 6 H), 1.1–2.2 (m, 18 H); IR, 1708 $cm^{-1}$; $[\alpha]^{23}_D$ +18.6° (*c* 6, EtOH).

Racemic *cis*- and *trans*-2-methylcyclohexyl *n*-pentyl ketones were prepared from 2-methyl-7-*n*-pentylmethylenecyclohexane[23] and capillary GC analysis using a 50-m methyl silicone column showed that the optically active *trans*-ketone is >99% diastereomerically pure.

**Synthesis of (1*S*,2*S*)-(+)-*trans*-2-Phenylcyclopentyl *n*-Pentyl Ketone by Cyanidation Reaction.** To a 1.0 M THF solution of lithium [1*S*,2*S*]-*trans*-(2-phenylcyclopentyl)borohydride at 0 °C was added 2,3-dimethyl-2-butene (2.02 g, 24 mmol) and trimethylsilyl chloride (2.39 g, 22 mmol), successively, and the reaction mixture was stirred at 0 °C for 1 h. 1-Pentene (1.54 g, 22 mmol) was then added, and the reaction mixture was stirred further for 1 h. The solvent was evaporated at 25 °C under reduced pressure (12 Torr), and the residue was taken up in *n*-pentane (50 mL) to precipitate the lithium chloride. The reaction mixture was centrifuged, and the clear *n*-pentane solution containing the desired trialkylborane was transferred to another flask. The solvent was evaporated, and the neat trialkylborane thus obtained was dissolved in THF (20 mL) and reacted with sodium cyanide (1.0 g, ~20 mmol) at 25 °C for 1 h. $^{11}B$ NMR spectrum of the reaction mixture showed a single peak at $\delta$ −15, indicating the clean formation of the trialkylcyanoborate. The reaction mixture was cooled at −78 °C and acylated with trifluoroacetic anhydride (3.4 mL, 25 mmol) and the resultant mixture stirred at −78 °C for 1 h. It was then warmed to 25 °C and oxidized by using pH 8 buffer (20 mL) and 30% hydrogen peroxide (10 mL). The reaction mixture was stirred at 25 °C for 8 h to ensure complete oxidation. The reaction mixture was extracted with EE (3 × 20 mL) and dried. Distillation afforded (1*S*,2*S*)-(+)-*trans*-2-phenylcyclopentyl *n*-pentyl ketone: 3.5 g (75% yield); bp 112–114 °C (0.05 Torr); $^1H$ NMR ($CDCl_3$) $\delta$ 0.83 (t, $J$ = 6 Hz, 3 H), 1.1–2.3 (m, 14 H), 2.7–3.2 (m, 2 H), 7.2 (s, 5 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.8, 22.4, 23.2, 25.4, 30.2, 31.4, 35.6, 43.0, 49.1, 59.6, 126.3, 127.2, 128.5, 144.6, 212.8; IR, 1705 $cm^{-1}$.

The ketone was further purified by preparative GC and the sample thus obtained exhibited $[\alpha]^{23}_D$ +117.8° ± 0.2 (*c* 6, EtOH). Capillary GC analysis using 50-m methyl silicone column showed that the ketone was 99% diastereomerically pure.

**Synthesis of (*R*)-4-Methyl-3-hexanone by Haloalkyne Route.** 1-Iodo-1-propyne (20 mmol) was hydroborated (1 h, −25 °C) with (*R*)-2-butylthexylborane (20 mmol) in ethyl ether. Methanolic sodium methoxide (5.5 mL, 25 mmol) was added, and the reaction mixture was stirred at 25 °C for 2 h. the reaction mixture was washed with water (3 × 25 mL), and the organic layer was oxidized with hydrogen peroxide and pH 8 buffer (25 °C, 6 h). The reaction mixture was extracted with EE, washed with water, and dried. The solvent was distilled off, and the crude product was isolated by distillation: 1.6 g (70% yield); bp 74–77 °C (100 Torr); $^1H$ NMR ($CDCl_3$) $\delta$ 0.75–1.2 (m, 9 H), 1.3–1.9 (m, 2 H), 2.35–2.7 (m, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 7.6, 11.5, 15.9, 26.0, 34.2, 47.5, 214.9; IR, 1720 $cm^{-1}$.

The ketone was further purified by preparative GC. (*R*)-(2)-4-Methyl-3-hexanone thus obtained exhibited $[\alpha]^{23}_D$ −30.8° (*c* 4, EE), suggesting 96% ee for the ketone.[24]

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**Registry No. 1**, 64234-27-1; **2**, 88947-07-3; **3**, 112398-76-2; **4**, 97235-31-9; **5**, 97235-25-1; **6**, 93984-87-3; **7**, 93984-85-1; **8**, 112398-77-3; **9**, 112398-78-4; **10**, 112398-79-5; **11**, 112398-80-8; **12**, 112398-81-9; ((*R*)-2-butyl)ThxBH, 112398-82-0; ((*S*)-3-methyl-2-butyl)ThxBH, 112398-83-1; ((1*S*,2*S*)-*trans*-2-methylcyclopentyl)ThxBH, 112529-26-7; ((1*S*,2*S*)-*trans*-2-phenylcyclopentyl)ThxBH, 112398-84-2; $[((1R)$-2-butyl)ThxBH$]_2$, 112398-88-6; $[((1S)$-3-methyl-2-butyl)ThxBH$]_2$, 112398-89-7; $[((1S,2S)$-*trans*-2-methylcyclopentyl)ThxBH$]_2$, 112398-90-0; $[((1S,2S)$-*trans*-2-methylcyclohexyl)ThxBH$]_2$, 112398-91-1; $[((1S,2S)$-*trans*-2-phenylcyclopentyl)ThxBH$]_2$, 112421-41-7; ((1*R*)-2-butyl)$BH_3Li$, 112457-47-3; ((1*S*)-3-methyl-2-butyl)$BH_3Li$, 94062-94-9; ((1*S*,2*S*)-*trans*-2-methylcyclopentyl)$BH_3Li$, 94062-95-0; ((1*S*,2*S*)-*trans*-2-phenylcyclopentyl)$BH_3Li$, 112398-92-2; ((1*S*,2*S*)-*trans*-2-phenylcyclopentyl)$B(Thx)_2CN{\cdot}Na$, 112398-93-3; 1-methylcyclohexene, 591-49-1; (1*S*,2*S*)-*trans*-2-methylcyclohexanol, 15963-37-8; acetaldehyde, 75-07-0; 2,3-dimethyl-2-butene, 563-79-1; (*S*)-(+)-*trans*-2,3,7-trimethyl-4-octene, 52763-13-0; 1-bromo-4-methyl-1-pentyne, 55944-42-8; lithium [1-[(*tert*-butyldimethylsilyl)oxy]-8-nonyl]acetylide, 112398-85-3; disyamylborane, 1069-54-1; (*R*)-(−)-10-methyl-1-dodecanol acetate, 71777-34-9; (1*S*,2*S*)-(+)-*trans*-2-methylcyclohexyl *n*-pentyl ketone, 112570-99-7; 1-pentene, 109-67-1; (±)-*cis*-2-methylcyclohexyl *n*-pentyl ketone, 112457-44-0; (±)-*trans*-2-methylcyclohexyl *n*-pentyl ketone, 112457-45-1; 2-methyl-7-*n*-pentylmethylenecyclohexane, 112398-86-4; (1*S*,2*S*)-(+)-*trans*-2-phenylcyclopentyl *n*-pentyl ketone, 112457-46-2; *n*-pentyl((1*S*,2*S*)-*trans*-2-phenylcyclopentyl)thexylborane, 112398-87-5; (*R*)-(−)-4-methyl-3-hexanone, 77858-08-3; 1-iodo-1-propyne, 624-66-8; 1,3-propanediol, 504-63-2.