8.4 Hz, 6-H), 7.74 (1 H, d, J = 7.7 Hz, 4-H), 7.82 (1 H, dd, J = 1.3 and 7.6 Hz, 5-H), 12.09 (1 H, s, 8-OH), and 12.39 (1 H, s, 1-OH); MS, m/z 254 $(M)^+$.

1-Hydroxy-8-methoxy-2-methylanthraquinone (Isochrysophanol 8-(Methyl ether)) (11b). A mixture of 3-chloro-5-methoxynaphthoquinone[47] (223 mg, 1.00 mmol) and diene **1f** (172 mg, 1.10 mmol) in dry benzene (11 mL) was stirred at room temperature for 1 h and heated to reflux for 24 h. Oxidation of the adduct by method B (room temperature, 4 h) and purification by chromatography (C_6H_6–AcOEt 5:1) gave anthraquinone **11b** (243 mg; 91%): mp 196–198 °C (ethanol) (lit.[32] mp 192–193 °C); UV λ_{max} (MeOH) 224, 255, 280 sh, 416, and 438 nm (log ϵ 4.62, 4.41, 4.03, 4.04, and 3.93); IR ν_{max} (KBr) 1670, 1635, 1590, and 1570 cm^{-1}; NMR δ ($CDCl_3$) 2.37 (3 H, s, 2-CH_3), 4.08 (3 H, s, 8-OCH_3), 7.35 (1 H, dd, J = 1.1 and 8.4 Hz, 7-H), 7.48 (1 H, d, J = 7.7 Hz, 3-H), 7.69 (1 H, d, J = 7.7 Hz, 4-H), 7.73 (1 H, dd, J = 7.7 and 8.4 Hz, 6-H), 7.96 (1 H, dd, J = 1.1 and 7.7 Hz, 5-H) and 13.29 (1 H, s, 1-OH); MS, m/z 268 $(M)^+$ (Found: C, 71.49; H, 4.53. $C_{16}H_{12}O_4$ requires: C, 71.64, H, 4.51.

1,5-Dihydroxy-2-methylanthraquinone (Isozyganein) (11c). The usual procedure applied to 2-chlorojuglone (**7b**) (209 mg, 1.00 mmol) and diene **1f** (172 mg, 1.10 mmol) in dry benzene (7 mL) (room temperature, 24 h) gave the adduct which was oxidized (method B, room temperature for 4 h). Purification by chromatography (C_6H_6) gave isozyganein (**11c**) (187 mg; 74%): mp 186–187 °C (ethanol) (lit.[18] mp 189–190 °C); UV λ_{max} (MeOH) 226, 254, 278, 288, 422, and 436 nm (log ϵ 4.70, 4.49, 4.09, 4.10, 4.14, and 4.14); IR ν_{max} (KBr) 1625 br, 1605, and 1580 cm^{-1}; NMR δ ($CDCl_3$) 2.38 (3 H, s, 2-CH_3), 7.29 (1 H, dd, J = 1.1 and 8.4 Hz, 6-H), 7.53 (1 H, br d, J = 7.7 Hz, 3-H), 7.66 (1 H, dd, J = 7.7 and 8.4 Hz, 7-H), 7.73 (1 H, d, J = 7.7 Hz, 4-H), 7.82 (1 H, dd, J = 1.1 and 7.7 Hz, 8-H), 12.70 (1 H, s, 5-OH), and 12.97 (1 H, s, 1-OH); MS, m/z 254 $(M)^+$.

1-Hydroxy-5-methoxy-2-methylanthraquinone (Isozyganein 5-(Methyl ether)) (11d). A similar reaction involving 2-chloro-5-methoxynaphthoquinone[48] (223 mg, 1.00 mmol) and diene **1f** (1.10 mmol) in benzene (11 mL) (room temperature, 40 h), after oxidation (method B, room temperature for 3.5 h) and chromatography (C_6H_6–AcOEt 5:1), gave anthraquinone **11d** (235 mg; 88%): mp 183–184 °C (ethanol) (lit.[34] mp 189–191 °C); UV λ_{max} (MeOH) 224, 253, 280, and 412 nm (log ϵ 4.57, 4.39, 4.00, and 3.99); IR ν_{max} (KBr) 1670, 1640, and 1590 cm^{-1}; NMR δ ($CDCl_3$) 2.35 (3 H, s, 2-CH_3), 4.04 (3 H, s, 5-OCH_3), 7.34 (1 H, d, J = 8.4 Hz, 6-H), 7.50 (1 H, br d, J = 7.7 Hz, 3-H), 7.66–7.75 (2 H, m, 4,7-H), 7.96 (1 H, dd, J = 1.1 and 7.7 Hz, 8-H), and 12.98 (1 H, s, 1-OH); MS, m/z 268 $(M)^+$ (Found: C, 71.54; H, 4.49. $C_{16}H_{12}O_4$ requires: C, 71.64; H, 4.51).

1,6-Dihydroxy-2-methylanthraquinone (Soranjidiol) (11e). To a solution of juglone **7g** (222 mg, 1.00 mmol) in dry benzene (10 mL) was added 2-(trimethylsiloxy)butadiene (**8a**) (156 mg, 1.10 mmol) in the same solvent (2 mL). After the mixture was refluxed for 24 h, the adduct was oxidized according to method C (3 days). Purification of the crude product by chromatography gave soranjidiol (75 mg, 30%): mp 286–287 °C (EtOH–CCl_4) (lit.[49] mp 283 °C); NMR δ (DMSO-d_6) 2.28 (3 H, s, 2-CH_3), 7.23 (1 H, dd, J = 2.6 and 8.8 Hz, 7-H), 7.46 (1 H, d, J = 2.6 Hz, 5-H), 7.58 (1 H, d, J = 7.7 Hz, 3-H), 7.64 (1 H, d, J = 7.7 Hz, 4-H), 8.10 (1 H, d, J = 8.8 Hz, 8-H), 11.18 (1 H, s, 6-OH), and 13.11 (1 H, s, 1-OH).

Acknowledgment. We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada and the Fonds F.C.A.R. (Gouvernement du Québec) as well as bursaries (to L.B.) from the Fonds Georges-Elie Amyot. We also wish to thank Prof. S. Neelakantan for a sample of barleriaquinone.

Registry No. **1a**, 1515-76-0; **1b**, 72808-94-7; **1c**, 17616-47-6; **1d**, 17616-45-4; **1e**, 6651-43-0; **1f**, 98670-68-9; **1g**, 65420-54-4; **1h**, 72237-32-2; **2a**, 615-93-0; **2b**, 697-91-6; **2c**, 1633-14-3; **2d**, 19643-45-9; **2e**, 24605-23-0; **2f**, 54490-80-1; **2g**, 19832-87-2; **2h**, 1123-64-4; **4a**, 1010-60-2; **4b**, 87170-63-6; **4c**, 87170-62-5; **4d**, 87170-60-3; **4e**, 87170-61-4; **4f**, 87170-64-7; **4g**, 87170-65-8; **4h**, 78758-29-9; **4i**, 57855-16-0; **4j**, 482-70-2; **5b**, 115077-55-9; **5c**, 65120-69-6; **6a**, 68963-22-4; **6b**, 68963-23-5; **6c**, 34641-56-0; **6d**, 22225-63-4; **6e**, 6219-65-4; **6f**, 70063-64-8; **6g**, 115077-54-8; **7a**, 18855-92-0; **7b**, 4923-57-3; **7c**, 115077-56-0; **7d**, 115077-57-1; **7e**, 62993-89-9; **7f**, 62993-88-8; **7g**, 95393-69-4; **7h**, 78308-30-2; **7i**, 15254-76-9; **7j**, 481-42-5; **7k**, 115077-58-2; **8a**, 38053-91-7; **8b**, 54781-39-4; **8c**, 54781-31-6; **8d**, 17616-46-5; **10a**, 69119-29-5; **10b**, 76665-65-1; **10c**, 115077-59-3; **10d**, 115077-60-6; **10g**, 115077-61-7; **10h**, 115077-62-8; **10i**, 104904-71-4; **11a**, 34425-60-0; **11b**, 51996-00-0; **11c**, 64809-73-0; **11d**, 64809-72-9; **11e**, 518-73-0; tectoquinone, 84-54-8; 2-chloro-5-methoxynaphthoquinone, 95684-12-1.

(47) Giles, R. G. F.; Roos, G. H. P. *J. Chem. Soc., Perkin Trans 1* **1976**, 2057; prepared from **7b** (CH_3I–Ag_2O).
(48) Guay, V.; Brassard, P. *Tetrahedron* **1984**, *40*, 5039.
(49) de Silva, S. O.; Watanabe, M.; Snieckus, V. *J. Org. Chem.* **1979**, *44*, 4802.

Hydroboration of Terpenes. 9. A Simple, Improved Procedure for Upgrading the Optical Purity of Commercially Available α- and β-Pinenes. Conversion of (+)-α-Pinene to (+)-β-Pinene via Hydroboration–Isomerization

Herbert C. Brown* and Navalkishore N. Joshi[1]

H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received February 24, 1988

An improved method for the preparation of optically pure diisopinocampheylborane (Ipc_2BH) from commercially available (+)- and (−)-α-pinene (91–92% ee) is described. The procedure, which is based on selective incorporation of the major enantiomer of α-pinene in crystalline dialkylborane, is both simple and efficient. Treatment with benzaldehyde liberates the parent olefin in very high enantiomeric excess (>99.5%). The intermediate Ipc_2BH can be thermally isomerized (130 °C, 12 h) to dimyrtanylborane, which is readily converted into the otherwise inaccessible (+)-β-pinene (>99.5% ee). In the course of this study it was established that the optical purification of commercial (−)-β-pinene too can be easily achieved by the formation and recrystallization of tri-*cis*-myrtanylborane. Thus, simple manipulations via hydroboration provide easy access to all four enantiomers of α- and β-pinenes in very high optical purity.

α-Pinene, in both (+)- and (−)-isomeric forms, is one of the most easily accessible optically active terpenes. With the advances in boron chemistry, α-pinene has become an extremely versatile intermediate for asymmetric synthesis.

0022-3263/88/1953-4059$01.50/0

Hydroboration of α-pinene provides mono- and diisopinocampheylboranes. Complementing each other, these reagents hydroborate a wide range of olefins furnishing organoboranes of high optical purity. These can be subsequently transformed into an array of optically active compounds.[2] Besides asymmetric hydroboration, the reagents derived from α-pinene have proved remarkably useful for asymmetric allylboration and reduction.[3] Unfortunately, the commercially available α-pinene has at best only 90–92% ee. Recently Bir and Kaufmann have reported[4] upgrading the optical purity of commercial α-pinene by crystallization at −130 °C. However, the more convenient and efficient method for optical purification of α-pinene still appears to be via diisopinocampheylborane (Ipc_2BH). The first report on the preparation of this compound in high enantiomeric purity was from our laboratory.[5] The method was based on an "exchange" process in which the major (desired) enantiomer of α-pinene becomes selectively incorporated into the solid Ipc_2BH. The original procedure, requiring borane in THF, was later modified[6] so as to employ the commercially available borane methyl sulfide (BMS). However, this method involved the inconvenience of performing the reaction at 0 °C for 72 h, as well as the need to remove methyl sulfide. A procedure that provided Ipc_2BH in easy to handle and in optically purer crystalline form was later developed.[7] This method too had limitations, especially in terms of decreased yields and difficulties in scaling up to large preparations. It was therefore decided to reexamine all of these procedures critically in the hope of finding optimum parameters for preparing optically pure Ipc_2BH in high yields. Such high purity Ipc_2BH would also provide high purity α-pinene.

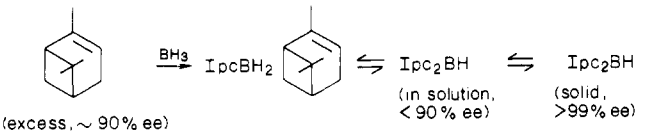
β-Pinene is an important raw material for various perfumes and polyterpene resins. Unlike α-pinene, only the (−) isomer of β-pinene is commerically available. Numerous procedures for the preparation of (+)-β-pinene have been reported,[8] mainly on the basis of (+)-α-pinene as the starting material. Unfortunately, none of the reported methods can provide high purity product in satisfactory yield. The only procedure that does provide optically pure β-pinene proceeds in only 6% overall yield.[9]

Our group has earlier shown[10] that hydroboration–isomerization–displacement can be a convenient synthetic route for converting endocyclic olefins to the exocyclic ones. Applied to α-pinene, the reaction sequence was shown to yield a mixture of β- and α-pinenes, albeit with a substantial amount of isomeric species. A better understanding of these reactions today, and also the present importance of these terpenes in asymmetric synthesis, inspired us to explore this method for the preparation of optically pure (+)-β-pinene. The other enantiomer, although commercially available, is of 91–93% ee. It was therefore worth examining the possibility of upgrading the optical purity of this product as well.

The present paper therefore describes the optical purification of commercially available (+)-/(−)-α-pinene, (−)-β-pinene, and the conversion of (+)-α-pinene to (+)-β-pinene via organoborane isomerization.

Results and Discussion

Preparation of Ipc_2BH and (+)-/(−)-α-Pinene of Very High Optical Purity. Hydroboration of α-pinene with BMS provides Ipc_2BH, a solid (eq 1). One of the



(1)

ways for upgrading the optical purity of this product would be selective crystallization.[7] However, the "exchange" process (selective incorporation of the major enantiomer) appears far more attractive.[5] Under ideal conditions, one could obtain a quantitative yield of optically pure Ipc_2BH by this method. In principle at least, the hydroboration of α-pinene and also the exchange reaction can be driven to completion. The obvious way to enhance both processes would be to use excess α-pinene and perform the reaction at higher temperature, e.g., 25 °C instead of 0 °C. However, at this temperature and at standard concentration, a large portion of Ipc_2BH remains undissolved, rendering the exchange ineffective. On the other hand, use of more concentrated reaction mixtures or less polar solvents (e.g., ether or hexane instead of THF) leads to almost complete precipitation of Ipc_2BH. Such highly insoluble Ipc_2BH makes enrichment by exchange very slow.

After examining various reaction parameters, it was concluded that the use of THF as solvent, a concentration of 1.25 M (in borane), 25% excess α-pinene, and reaction at room temperature, were the optimum conditions. The reaction (monitored by ^{11}B NMR and hydride estimation) attains equilibrium at the end of ~16 h. At that point, ~10% of the total hydride remains in solution, mainly as Ipc_2BH. Only very small amounts of $IpcBH_2$ and essentially no BMS was detectable. The product, separating as a crystalline mass (90–91% yield), had an optical purity of >99.5%, as judged from the rotation of displaced α-pinene.[11] It was interesting to find that the Ipc_2BH remaining in solution possesses a comparable optical purity. This indicates that the optical enrichment had taken place through exchange rather than through selective crystallization. Further confirmation was provided by the residual α-pinene, which exhibited 84–85% ee. Surprisingly, the presence of dimethyl sulfide did not have any detrimental effect, as reported by the earlier workers.[6] Perhaps the coordination of dimethyl sulfide with Ipc_2BH is reduced at room temperature, permitting the dissociation needed for exchange.

Having solved the problem of making optically pure Ipc_2BH in high yield, it was important to liberate α-pinene quantitatively. The method reported earlier[12] called for heating with benzaldehyde at 100 °C for 20 h. Despite these rigorous conditions, 10–15% of α-pinene remained

(1) Postdoctoral research associate on Grant GM 10937-24 of the National Institutes of Health.

(2) For a recent review, see: Brown, H. C.; Jadhav, P. K.; Singaram, B. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, Heidelberg, 1986; Vol. 4, p 308.

(3) (a) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352. (b) Brown, H. C.; Pai, G. G. *J. Org. Chem.* **1985**, *50*, 1384.

(4) Bir, G.; Kaufmann, D. *Tetrahedron Lett.* **1987**, *28*, 777.

(5) Brown, H. C.; Yoon, N. M. *Isr. J. Chem.* **1977**, *15*, 12.

(6) Brown, H. C.; Desai, M. C.; Jadhav, P. K. *J. Org. Chem.* **1982**, *47*, 5065.

(7) Brown, H. C.; Singaram, B. *J. Org. Chem.* **1984**, *49*, 945.

(8) (a) Lavalee, P.; Bouthillier, G. *J. Org. Chem.* **1986**, *51*, 1362. (b) Andrianome, M.; Delmond, B. *J. Chem. Soc., Chem. Commun.* **1985**, 1203. (c) Zaidlewicz, M. J. *Organomet. Chem.* **1985**, *293*, 139 and references cited therein.

(9) Kirmse, W.; Gruber, W. *Chem. Ber.* **1972**, *105*, 2764.

(10) Brown, H. C.; Bhatt, M. V.; Munekata, T.; Zweifel, G. *J. Am. Chem. Soc.* **1967**, *89*, 567.

(11) Based on maximum rotation reported for (+)-α-pinene, $[\alpha]^{23}_D$ +51.6°: Johnson, W. S.; Frei, B.; Gopalan, A. S. *J. Org. Chem.* **1981**, *46*, 1512.

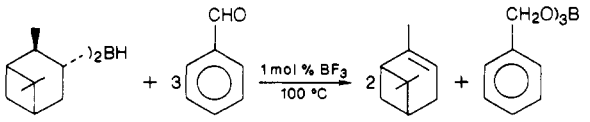
(12) Brown, H. C.; Jadhav, P. K.; Desai, M. S. *J. Org. Chem.* **1982**, *47*, 4583.

Table I. Effect of Olefin:Hydride Ratio[a]

α-pinene, mmol	BMS, mmol	excess hydride, %	% composition[b] β	α	others	approx ratio β/α
30	12	20	71	23	6	3
30	15	50	76	11	13	7
30	20	100	69	14	17	5

[a] Triglyme as solvent, 160 ± 5 °C, 2 h. [b] ±1%, determined by GC following oxidation with alkaline H_2O_2.

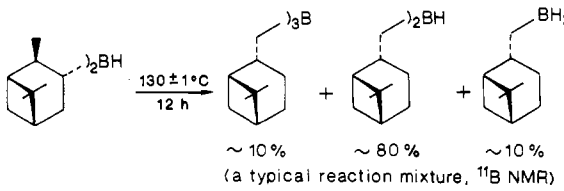
unrecovered. We have now found that the reaction is greatly accelerated by BF_3 as catalyst (eq 2). The reaction, conducted in the presence of 1 mol % BF_3·Et_2O, was complete within 1 h at 100 °C.



(2)

Thermal Isomerization of Ipc_2BH. Conversion of (+)-α-Pinene to (+)-β-Pinene. Previous studies[13] dealing with thermal isomerization of organoboranes have revealed that the rate as well as the position of equilibrium is strongly dependent on the concentration of "excess" hydride, the temperature, and the structure of the olefin. Consequently, a general procedure utilizing 20% excess of hydroborating agent and a reaction temperature of 160 °C for 2–4 h was employed for the contrathermodynamic isomerization. However, in the case of sensitive molecules, such as Δ^3-carene and α-pinene, these reaction conditions are known to induce several side reactions.[13] Since our aim was to prepare (+)-β-pinene of high optical purity and high yield, it was imperative to avoid isomeric impurities in the product. A systematic study was therefore undertaken to control the reaction to achieve a clean reaction product. The reactions were monitored by ^{11}B NMR, and the product composition was established by GC, following oxidation with alkaline H_2O_2.

It was found that increasing the excess hydride from 20% to 50% had a favorable effect on the rate of reaction. However, the use of a very large excess of hydride (100%) proved detrimental. It was interesting to find that a higher temperature (160 °C) provided a better ratio of β-:α-pinene, unfortunately, along with a substantial amount of byproducts. A lower temperature (100 °C), on the other hand, led to a cleaner reaction but with a less favorable equilibrium. After a careful study of these parameters (Tables I and II), it was concluded that using 50% excess hydride and performing the reaction at 130 °C for 12 h provided the most suitable conditions (eq 3). Isomerization thus performed gave an organoborane product containing a ~5:1 mixture of moieties derived from β- and α-pinene, along with <3% byproducts. Identical results were obtained when preformed Ipc_2BH was used.



(3)

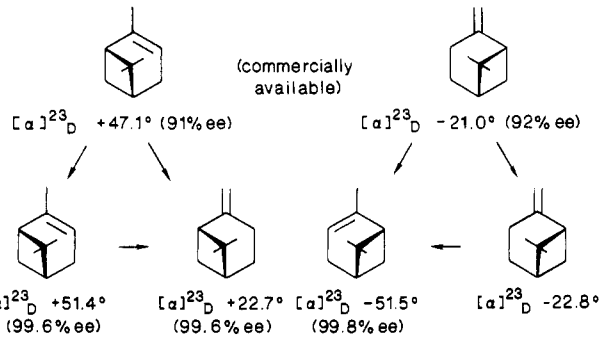
Recovery of (+)-β-pinene from the isomerized product proved rather difficult. Displacement[10] with even 100% excess 1-dodecene was very slow and incomplete. Treatment with benzaldehyde rapidly liberated the first mole of β-pinene. The second equivalent, however, could not be recovered, even after heating at 170 °C for several hours. The problem was fortunately solved by prior treatment with 1-hexene. The resulting trialkylborane now readily reacts with benzaldehyde liberating >90% of available β-pinene within 3 h at 170 °C (eq 4).

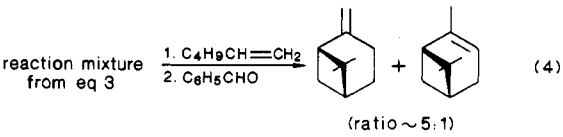
Table II. Effect of Temperature[a]

temperature, °C	time,[b] h	% composition β	α	others	approx ratio β/α
160	2	76	11	13	7
140	8	78	13	9	6
120	24	77	18	5	4
100	48	76	24	<1	3

[a] 50% excess hydride, i.e., α-pinene:BMS = 2:1. [b] Optimum time giving best ratio of β-:α-pinene.

Scheme I





(4)

The (+)-β-pinene thus obtained was accompanied by 15–20% of unisomerized (+)-α-pinene. These could be separated by fractional distillation with a spinning band column. This represented a very efficient transformation of (+)-α-pinene to (+)-β-pinene in 53% overall yield and the product had >99.5% ee.[9]

Upgrading Optical Purity of Commercially Available (−)-β-Pinene. The commercially available (−)-β-pinene is of approximately 91–93% ee. During the course of our work on isomerization, an authentic sample of *cis*-myrtanol was needed. It was obtained by hydroboration of β-pinene, followed by oxidation of the resulting trialkylborane. A significant observation was made that tri-*cis*-myrtanylborane is a solid, and a simple crystallization yielded pure diastereomer [(−)(−)(−)]. Unlike the product from isomerization, which is the less strained and hence stable *trans*-myrtanyl derivative, the cis isomer readily reacts with 1-dodecene or benzaldehyde to give all 3 mol of β-pinene. The product thus obtained exhibited a rotation value higher than the maximum value previously reported.[14] Isomerization (with KAPA)[15] of such optically

(13) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1967**, *89*, 561. Brown, H. C.; Bhatt, M. V.; Munekata, T.; Zweifel, G. *J. Am. Chem. Soc.* **1967**, *89*, 567.

(14) Maximum rotation reported for (−)-β-pinene: $[\alpha]^{25}_D$ −22.7°: Comyns, A. E.; Lucas, H. J. *J. Am. Chem. Soc.* **1957**, *79*, 4339.

pure (−)-β-pinene can be an alternate method for preparing high purity (−)-α-pinene. Scheme I summarizes the transformations and purifications achieved.

Conclusion

Diisopinocampheylborane of very high purity can now be easily made from commercial α-pinene (91% ee) in excellent yield. Besides asymmetric hydroboration, this intermediate can be used for the preparation of optically pure (+)-α-pinene, as well as the relatively rare (+)-β-pinene. A simple method for optical purification of (−)-β-pinene has also been established. Thus, an easy access to all four enantiomers of α- and β-pinenes with essentially 100% ee has been achieved.

Experimental Section

All operations were carried out in oven-dried glassware assembled under a nitrogen atmosphere. ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. GC analyses were performed with a Hewlett-Packard 5750 chromatograph with a 12 ft × 0.25 in. column packed with 10% SP-2100 on Chromosorb W. For preparative GC, a 6 ft × 0.25 in. column packed with 10% tricresyl phosphate on Chromosorb W was used. The optical rotations were measured on a Rudolph Autopol III polarimeter.

Materials. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. $BH_3 \cdot Me_2S$, (+)-α-pinene of 91% ee and (−)-β-pinene of 92% ee were purchased from the Aldrich Chemical Co. (−)-α-Pinene was prepared by isomerization of (−)-β-pinene with KAPA.[15] The pinenes were distilled over a small amount of $LiAlH_4$ and stored under nitrogen. Triglyme was distilled over $LiAlH_4$ under reduced pressure.

Preparation of Ipc_2BH. Reaction of BMS with 91% ee (+)-α-Pinene. A 250-mL flask equipped with a septum inlet, magnetic stirring bar, and a reflux condenser was charged with 30 mL of THF and 40 mL (250 mmol) of (+)-α-pinene ($[\alpha]^{23}_D$ +47.1° (neat), 91% ee). The reaction flask was immersed in a water bath and maintained at 20–25 °C. To this, 10 mL (10 M, 100 mmol) of BMS was added dropwise while the reaction mixture was stirred vigorously. The reaction is mildly exothermic and kept under control by the rate of addition. At times the Ipc_2BH starts precipitating before the addition is over. In such cases the reaction mixture was warmed (50–55 °C) to redissolve the solid. The clear solution was allowed to stand undisturbed at room temperature. It was monitored periodically by estimation of hydride. After about 16 h, the supernatant solution was found to have a balance of ~30 mmol hydride, which did not decrease significantly over the next 4 h. The reaction mixture was then cooled in an ice bath for about 2 h, and the supernatant solution was removed with a double-ended needle. The crystalline mass of Ipc_2BH was broken and washed with 20 mL of pentane, and the solid was dried under reduced pressure, 25.9 g (91% yield).

The product obtained by this procedure was found to be quite stable. As long as the product was stored at 0 °C under nitrogen, no significant disproportionation or loss of hydride activity was observed even after several months.

Preparation of (+)-α-Pinene of >99.5% ee. Reaction of Ipc_2BH with Benzaldehyde. A 50-mL flask fitted with a septum inlet, magnetic stirring bar, and the usual distillation unit was charged with 14.3 g (50 mmol) of Ipc_2BH. To this was added 15.2 mL (150 mmol) of benzaldehyde cautiously (exothermic!). Once the initial reaction subsided, the reaction mixture was slowly heated to 100 °C (bath temperature). By this time, ^{11}B NMR shows the formation of a clean boronate (δ 31), indicating elimination of the first α-pinyl group. To the reaction mixture was added 0.06 mL (0.5 mmol) of $BF_3 \cdot Et_2O$, and stirring was continued for 1 h at 100 °C. The second equivalent of α-pinene is liberated within this period. The product was distilled off by applying reduced pressure. A simple distillation over a small amount of $LiAlH_4$ provides pure (+)-α-pinene: 11.7 g (84% yield); bp 74–75 °C (50 mmHg). A sample freshly purified by preparative GC exhibited $[\alpha]^{23}_D$ +51.4° (neat), 99.6% ee.[11]

Upgrading Optical Purity of 92% ee (−)-α-Pinene. Following the procedure described above, (−)-α-pinene ($[\alpha]^{23}_D$ −47.5° (neat), 92% ee) was used to prepare Ipc_2BH, which upon treatment with benzaldehyde, furnished (−)-α-pinene, $[\alpha]^{23}_D$ −51.5° (neat), 99.8% ee.

Thermal Isomerization of Ipc_2BH. Conversion of (+)-α-Pinene to (+)-β-Pinene. A 100-mL side-arm flask was equipped with the usual distillation assembly and provided with a nitrogen atmosphere. The flask was charged with 14.3 g (50 mmol) of Ipc_2BH and 10 mL of anhydrous triglyme. The mixture was gradually heated to 130 °C (bath temperature) and stirred at that temperature for 12 h. Thereafter, the reaction mixture was cooled to room temperature and treated cautiously with 6 mL (50 mmol) of 1-hexene. The reaction mixture was stirred at room temperature for 2 h by which time ^{11}B NMR indicated a clean formation of trialkylborane (δ 86).

To the above reaction mixture was then added 10 mL (100 mmol) of benzaldehyde, and the mixture was heated to 170 ± 5 °C. After the mixture was stirred at that temperature for 2 h, the liberated β-pinene was distilled off under reduced pressure. The distillate, which is a ~4.5:1 mixture of β- and α-pinene, along with some benzaldehyde and triglyme, was fractionally distilled on a spinning band or 90-cm Helipack column: 8.0 g (59% yield); bp 97–98 °C (100 mmHg). A sample further purified by preparative GC exhibited $[\alpha]^{23}_D$ +22.7°, 99.6% ee.[9]

Upgrading the Optical Purity of 92% ee (−)-β-Pinene. (A) Hydroboration. To a stirred and cooled (0–5 °C) solution of 25 mL (157 mmol) of (−)-β-pinene ($[\alpha]^{23}_D$ −21.0° (neat), 92% ee) in 15 mL of hexane was added 5 mL (10 M, 50 mmol) of BMS dropwise. Following the addition, the cooling bath was removed and the reaction mixture was stirred at room temperature for 1 h. By that time, a thick precipitate of tri-*cis*-myrtanylborane had appeared. The reaction flask was immersed in a warm (55–60 °C) water bath, and the reaction mixture was stirred until all of the solid had dissolved. The resulting clear solution was allowed to stand undisturbed at room temperature for about 4 h. Large crystals of *cis*-myrtanylborane start separating by then. Crystallization was completed by cooling the reaction flask in an ice bath for 4 h. The supernatant solution was removed with a double-ended needle; the solid was dried under reduced pressure: 18.1 g (86% yield).

(B) Recovery of Optically Pure (−)-β-Pinene. A 50-mL flask fitted with a Vigreaux column (15 cm) and the usual distillation assembly was charged with 8.4 g (20 mmol) of tri-*cis*-myrtanylborane, 26.6 mL (120 mmol, 100% excess) of 1-dodecene, and 6 mL of triglyme. The reaction mixture was heated until the liberated (−)-β-pinene slowly started distilling out. The temperature was maintained until completion of the distillation: 7.4 g (91% yield). A small amount of sample was further purified by preparative GC: $[\alpha]^{23}_D$ −22.7°.[14]

Alternatively, the recovery of (−)-β-pinene was also done as follows. The reaction unit described above was charged with 12.6 g (30 mmol) of tri-*cis*-myrtanylborane and 9 mL (90 mmol) of benzaldehyde. The reaction was mildly exothermic, and the first mole of (−)-β-pinene was eliminated within 0.5 h at room temperature. The reaction mixture was then gradually heated and monitored by ^{11}B NMR. The second pinyl group was removed by the time the temperature reached 100 °C. However, removal of the third unit needed heating at 170 ± 5 °C for 2 h. The product was distilled off under reduced pressure and purified by distillation over a small amount of $LiAlH_4$: 10.2 g (83% yield); bp 81–82 °C (40 mmHg). A freshly purified sample exhibited $[\alpha]^{23}_D$ −22.8°.[14]

Acknowledgment. We thank the National Institutes of Health for supporting this research program through Grant GM 10937-24.

(15) Brown, C. A. *Synthesis* **1978**, 754.