Hydroboration. 91. Improved Procedure for the Synthesis of Optically Pure Bis-adducts, *N,N,N',N'*-Tetramethylethylenediamine·2-organylapoisopinocampheylboranes, from the Corresponding 2-Organylapopinenes of Lower Optical Purity. Conversion of These Adducts into 2-Organylapoisopinocampheylboranes, Useful Asymmetric Hydroborating Reagents

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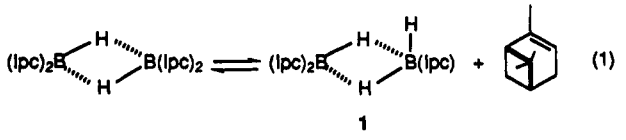
The higher analogues of α-pinene, such as 2-ethyl-, 2-*n*-propyl-, 2-isobutyl-, 2-phenyl-, and 2-isopropylapopinenes, were treated with borane–methyl sulfide (BMS) in the stoichiometry of 1.2:1, respectively, in anhydrous tetrahydrofuran (THF) at 25 °C, obtaining an equilibrium mixture of 2-organylapoisopinocampheylboranes (2-R-apoisopinylborane, $RapBH_2$) as major and bis(2-organylapoisopinocampheyl)borane [bis(2-R-apoisopinyl)borane, Rap_2BH] as minor constituents. Treatment of the equilibrium mixture of boranes with tetramethylethylenediamine (TMEDA) at 34 °C readily and selectively provided the optically pure bis(2-organylapoisopinocampheylborane)·TMEDA adducts, $(RapBH_2)_2$·TMEDA, in satisfactory yield. This reaction is quite general and appears to be broadly applicable to the conversion of the sterically bulkier 2-organylapopinenes (2-R-apopinenes) with widely varied steric requirements and lower optical purity (87–92% ee) into the corresponding optically pure $(RapBH_2)_2$·TMEDA derivatives, approaching ≥99% ee. Treatment of the crystalline bis-adduct in ethyl ether with BF_3·EE precipitates $(BF_3)_2$·TMEDA and provides $RapBH_2$ of essentially ≥99% ee, enantiomerically purer than the 2-R-apopinenes of 87–92% ee utilized for these preparations.

One of the most fundamental processes encountered in asymmetric synthesis is the stereoselective construction of a new chiral center or centers on a prochiral substrate. The best asymmetric syntheses occur in nature *via* enzymatic reactions. However, in recent years considerable research efforts have been expended by organic chemists to achieve comparable results.[2,3] A decade ago, we focused our efforts on the development of chiral, pinene-based borane reagents to bring about asymmetric transformations, such as the hydroboration of prochiral olefins,[4] reduction of prochiral ketones,[5] asymmetric allyl- and crotylboration,[6] asymmetric opening of *meso*-epoxides,[7] and asymmetric homologation.[8]

The versatile hydroborating agent Ipc_2BH[9] is readily available from the reaction of α-pinene with BMS.[10] It reacts with *cis*-disubstituted alkenes with excellent chiral induction in the range of 80–90% ee, in many cases.[4c] However, the hydroboration of trisubstituted and *trans*-disubstituted alkenes proceeds more slowly, in a complex manner, involving displacement of α-pinene, to give the species 1 (eq 1). As a result, the degree of chiral induction is dramatically lowered to about 14–22%.[11]



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The difficulty encountered in hydroborating more hindered olefins with Ipc_2BH was circumvented, in part, by the synthesis of the sterically less hindered and more reactive isopinocampheylborane, $IpcBH_2$ (**3a**).[4c] It reacts with aliphatic-[4c] or phenyl-substituted cyclic trisubstituted and *trans*-disubstituted alkenes providing, after oxidation, product alcohols with enantiomeric purities in the range of 50 to ≥99%.[4e] These results and the current activity

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(9) This moiety actually exists in solution as a dimer, a derivative of the diborane molecule. However, it is convenient to refer to it in terms of the simple monomer constituent.

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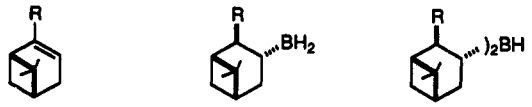


2a R = Me 2d R = *i*-Bu
2b R = Et 2e R = Ph
2c R = Pr 2f R = *i*-Pr

3a-f

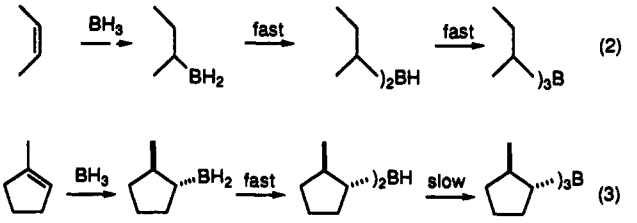
4a-f

in this area have prompted us to search for improved, easily available chiral auxiliaries and reagents in the hope of optimizing the steric requirements of the reagent with those of the prochiral substrate. Introduction of an ethyl group at the 2-position of apopinene provided a new pinene-based chiral auxiliary, 2-ethylapopinene.[4f] The 2-ethylapoisopinylborane, $EapBH_2$ (**3b**),[9] derived from 2-ethylapopinene (**2b**) was used in the hydroboration of a series of representative prochiral alkenes and provided modestly improved enantiomeric purity of the resulting alcohols[4f] as compared to those derived from $IpcBH_2$. Encouraged by these early results, we undertook an extensive program to modify apopinene at the 2-position to produce a number of sterically bulkier chiral auxiliaries. The synthesis of 2-*n*-propyl- (**2c**),[12a] 2-isobutyl- (**2d**),[13a] 2-phenyl- (**2e**),[13b] and 2-isopropylapopinenes (**2f**)[13a] has now been achieved and described.

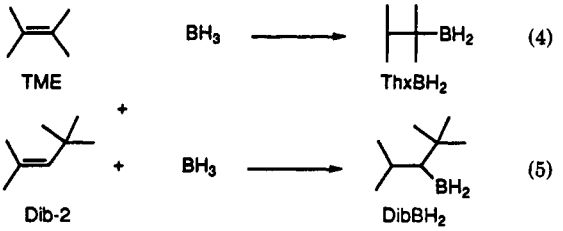
As part of our ongoing program in this area, the present importance of these chiral auxiliaries in the asymmetric synthesis *via* organoboranes and the nonavailability of a convenient general procedure to synthesize the sterically more demanding 2-R-apoisopinylboranes ($RapBH_2$) from these potential chiral auxiliaries (**2b–f**) inspired us to develop such a general procedure, applicable to the preparation of a wide variety of sterically bulkier $RapBH_2$. We now report the development of an improved procedure for the conversion of sterically bulkier 2-R-apopinenes **2b–f** of lower optical purity (87–91% ee) to the optically pure (≥99% ee) bis-adducts of $RapBH_2$ with TMEDA. This procedure has several advantages over the earlier procedures.[4f,13b,14] The reaction appears to be general and provides a simple economical approach for the synthesis of sterically demanding bis(2-organylapoisopinocampheylborane)·TMEDA [$(RapBH_2)_2$·TMEDA, **5b-f**] adducts in satisfactory yield and their ready conversion into the desired $RapBH_2$ reagents.

Results and Discussion

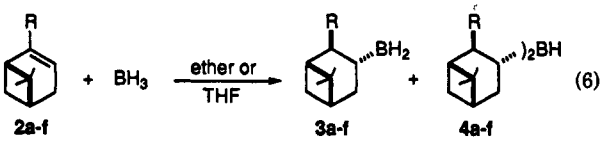
The applicability of borane–methyl sulfide (BH_3·SMe_2, BMS)[15] and borane–THF (BH_3·THF)[16b] is well documented. It has been demonstrated that the reaction of simple olefins with BH_3·THF or BMS generally proceeds rapidly past the monoalkylborane stage to the dialkyl- or trialkylborane stage (eq 2).[16] In the case of more hindered alkenes, such as 1-methylcyclopentene, it is possible to proceed rapidly to R_2BH and slowly on to R_3B (eq 3).[16]



As a result, it is generally not possible to obtain monoalkylborane of interest by the direct reaction of olefins with boranes (BMS or BH_3·THF). However, in the case of certain highly hindered olefins, such as tetramethylethylene (TME) or 2,4,4-trimethyl-2-pentene (diisobutylene-2 = Dib-2), it is possible to control the hydroboration so as to achieve the synthesis of the monoalkylboranes.[17] In this way thexylborane ($ThxBH_2$)[18] and DIBborane ($DibBH_2$)[19] can be readily prepared (eqs 4 and 5).



Earlier, we reported[13a] that the hydroboration of 2-R-apopinenes **2a–f** with boranes in different stoichiometry at room temperature generally yields a mixture of products. However, in case of phenyl- (**2e**), isopropyl- (**2f**), and to some extent isobutylapopinenes (**2d**), hydroboration leads predominantly to the corresponding 2-R-apoisopinylborane ($RapBH_2$, **3e–f**),[9] as much as ≥95% (eq 6).



Under these conditions, it is generally not possible to obtain either bis(2-R-apoisopinyl)borane, Rap_2BH **4a–f**,[9] or $RapBH_2$ **3a–f** essentially exclusively.[13a] Similarly, the presence of a small amount of Rap_2BH or unreacted BH_3 in the reaction mixture will lower the optical induction in the asymmetric hydroboration of prochiral olefins. It is essential, therefore, to develop a convenient procedure for the synthesis of the sterically more demanding $RapBH_2$ **3b–f** in good chemical yield, coupled with high stereochemical purity approaching >99% ee. It has been established that under normal conditions the hydroboration of α-pinene cannot be stopped at the monoalkylborane stage.[17] Therefore, several syntheses were explored to provide a convenient preparation of this desirable reagent. A detailed account of the different syntheses of

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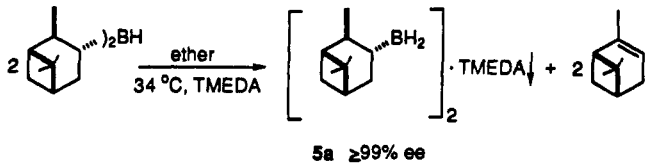
Scheme 1



5a ≥99% ee

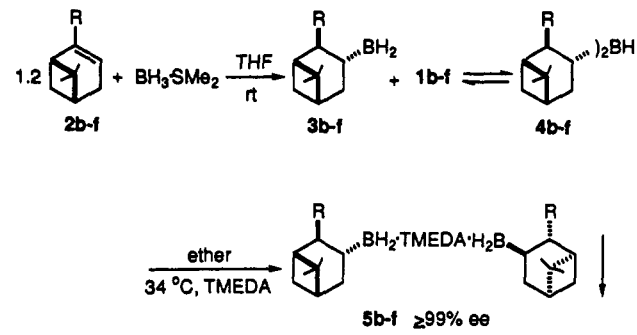
$IpcBH_2$ developed is reported elsewhere.[20] The discovery that monoalkylborane forms a crystalline adduct with TMEDA[21] made available the most convenient synthesis of $(IpcBH_2)_2$·TMEDA (**5a**). In this procedure, the reaction of a 2-fold excess of α-pinene with 1 equiv of BMS in ether at 34 °C rapidly furnishes Ipc_2BH.[22] This compound, upon treatment with 0.5 equiv of TMEDA, liberates α-pinene to yield crystalline $(IpcBH_2)_2$·TMEDA in good chemical and optical yield[23] (Scheme 1). However, this procedure suffers from a limitation that it uses excess α-pinene. A similar excess of 2-ethylapopinene (**2b**) is utilized in the earlier synthesis of $(EapBH_2)_2$·TMEDA (**5b**).[4f]

It is observed that the reaction of 2-R-apopinenes **2c–f** with BMS (0.5 M in each) under mild conditions at room temperature produces $RapBH_2$ in ≥90%, except for 2-ethylapopinene (**2b**) which gave only 86% of the desired 2-R-apoisopinylborane.[13a] On the contrary, these 2-R-apopinenes **2b–f** on reaction with borane–THF (0.5 M in each) produced substantial amount of Rap_2BH (**4b–d**, 11–25%), with the exception of 2-phenyl- and 2-isopropylapopinenes, in which cases <5% of the Rap_2BH **4e–f** formed.[13a] It is inferred from these results that the borane–THF, as a hydroborating agent, is less advantageous than the corresponding borane–methyl sulfide which permits a more economical utilization of the valuable 2-R-apopinenes **2b–f** to provide a higher percentage of $RapBH_2$ **3b–f**. Another advantage of BMS is that it is stable at room temperature for long periods of time, whereas borane–THF undergoes a slow, but significant, cleavage of THF at ambient temperature with a loss of hydride.[24]

Therefore, the present procedure utilizes BMS in THF for the easy conversion of the sterically bulkier 2-R-apopinenes **2b–f** to the equilibrium mixture of $RapBH_2$ as major and Rap_2BH as minor components. The reaction of this mixture with TMEDA gives the bis-adducts **5b–f**, which upon reaction with BF_3·EE remove the TMEDA from the product (Scheme 2).

Thus, 2-R-apopinenes **2b–f** (1.2 equiv) were treated with BMS (1.0 equiv) in THF at room temperature for 24–36 h. The total concentration of the solution was maintained at 1.0–1.1 M. The ^{11}B NMR of the reaction mixture at this stage showed the complete hydroboration of 2-R-apopinenes resulting in an equilibrium mixture of $RapBH_2$ and Rap_2BH, with the latter being the minor component. The percentage of Rap_2BH present was inversely proportional to the bulk at the 2-position of apopinene.[13a] The reaction of BMS with 2-R-apopinenes **2d–f** provided $RapBH_2$ in >90% yield, while in the case of 2-ethylapopinene (**2b**), the $EapBH_2$ (**3b**) was formed in a slightly lower yield (86%). The reaction of the mixture of 2-R-apoisopinylboranes **3b–f** and **4b–f** with TMEDA in THF

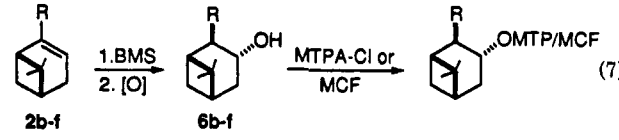
Scheme 2



furnished bis-adducts **5b–f** in considerably lower yields. However, the use of diethyl ether as solvent improved the yield without affecting the desired optical improvement achieved by selective crystallization. Consequently, THF was stripped off from the reaction mixture after complete hydroboration of the 2-R-apopinenes and replaced by diethyl ether. The addition of 0.5 equiv of TMEDA to the reaction mixture at 34 °C led to the rapid reaction with $RapBH_2$ **2b–f** and Rap_2BH to furnish the desired bis-adducts **5b–f**, with displacement of the second 2-R-apopinene moiety from Rap_2BH. The reaction mixture upon cooling provided the bis-adducts **5b–f** as a crystalline solid. The bis-adducts **5b–f** were isolated in ~70–78% yield (Scheme 2).

The spectral (^1H, ^{13}C and ^{11}B NMR) data revealed that the bis-adducts **5b–f** were quite pure. Methanolysis of **5b–f** provided pure boronate esters, $RapB(OMe)_2$, and the alkaline peroxide oxidation provided the corresponding 2-R-apoisopinocampheols **6b–f**. The optical rotation values of **6b–f** corresponded to the values for the alcohols provided by hydroborating 2-R-apopinenes of ≥99% ee, indicative of ≥99% optical purity of the bis-adducts **5b–f**.

In another method, both (+)- and (−)-2-R-apopinenes **2b–f** were hydroborated with BMS and oxidized to provide the corresponding enantiomeric 2-R-apoisopinocampheols **6b–f**. A racemic mixture of the two enantiomeric alcohols was derivatized with (−)-menthyl chloroformate (MCF)[25a] or (−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA-Cl),[25b] and the resulting two diastereomers separated cleanly on a SPB-5 capillary GC column. Thus, we were able to confirm the ≥99% ee value for the optically pure 2-R-apoisopinocampheols derived from the bis-adducts **5b–f** of ≥99% (eq 7).



(7)

It is demonstrated that the addition of TMEDA not only serves to obtain chemically pure $(RapBH_2)_2$·TMEDA **5b–f** adducts but also helps to upgrade the optical purity of the resulting bis-adducts to >99%, the synthesis having started with 2-R-apopinenes **2b–f** of only 87–92% ee. This is due to the preferential crystallization of bis-adducts **5b–d,f** of two (2*S*,3*R*)-$RapBH_2$ moieties [resulting from (+)-2-R-apopinenes] over that of the mixed adduct containing both (2*S*,3*R*)-$RapBH_2$ and (2*R*,3*S*)-$RapBH_2$ components. The amount of adduct resulting from two

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Table 1. Melting Points and $[\alpha]_D$ of Bis-adducts [$(RapBH_2)_2$·TMEDA, 5a–f] and 2-R-Apoisopinocampheols (RapOH, 6a–f)

	$(RapBH_2)_2$·TMEDA		RapOH	
R	mp, °C	$[\alpha]_D$ (T) c = 1[a]	mp, °C	$[\alpha]_D$ (T) c = 1[a]
Me	140–42	−69.0 (20)[b]	51–3	−35.8 (27)[c]
Et	138–39	−50.4 (21)[d]	80[e]	−24.3 (23)[e]
Pr	136–38	−66.6 (22)	43–4	−34.8 (24)
i-Bu	110–13	−65.1 (20)	92–3	−33.9 (24)
Ph[f]	136–38	+31.8 (20)	108–9	+24.8 (20)
i-Pr	120–21	−33.6 (20)	75–6	−16.4 (20)

[a] $[\alpha]_D$ was measured in degrees in THF for bis-adducts and in MeOH for RapOH or otherwise mentioned. [b] (c 9.31, THF), while in the literature[4e] it is reported as $[\alpha]^{23}_D$ +69.0 (c 9.33, THF) (see ref 23). [c] (c 0.9, C_6H_6).[14] [d] $[\alpha]_D$ was measured in C_6H_6. [e] Boiling point at 0.5 mmHg while $[\alpha]_D$ value (c 3, $CHCl_3$) was taken from ref 4f. [f] 2-Phenylapopinene (2e) was synthesized from (−)-β-pinene.[13b]

(2*R*,3*S*)-$RapBH_2$ species present would be negligible. This hypothesis requires the $(RapBH_2)_2$·TMEDA present in solution to be much lower in optical purity than the crystallized product.

The melting points and the $[\alpha]_D$ values of the bis-adducts [$(RapBH_2)_2$·TMEDA, **5a–f**] and of the 2-R-apoisopinocampheols (RapOH, **6a–f**) are summarized in Table 1.

It has been proved that amine–boranes[4b] react sluggishly with olefins at 25 °C. Therefore, removal of TMEDA from the bis-adducts forms a necessary step to facilitate the hydroboration reaction. It is known that TMEDA readily reacts with BF_3·EE to yield $(BF_3)_2$·TMEDA as a clean solid mass in ether medium (eq 8).[21]

$$\underset{\textbf{5b–f}}{(RapBH_2)_2\cdot TMEDA} + 2BF_3\cdot EE \xrightarrow[1\text{–}2\ h]{\text{ether, rt}} 2RapBH_2 + (BF_3)_2\cdot TMEDA\downarrow \quad (8)$$
$$\geq 99\%\ ee$$

Thus, the addition of BF_3·EE to the ethereal solution of bis-adducts **5b–f** at 25 °C separated $(BF_3)_2$·TMEDA in 1–2 h, leaving $RapBH_2$ **3b–f** of ≥99% ee in solution ready for hydroboration of olefins. Filtration of the reaction mixture yielded $RapBH_2$ as a solution in ether in nearly quantitative yield (eq 8). The molarity of this solution was conveniently determined by hydride analysis of an aliquot.[16d] The utility of optically pure $RapBH_2$ **3c,d,f** and the corresponding RapBHCl (Rap = **2a–f**) for the asymmetric hydroboration of prochiral olefins is under investigation.

Conclusions

This new improved procedure describes a convenient general method for the synthesis of a family of asymmetric hydroborating reagents $(RapBH_2)_2$·TMEDA of variable steric requirements with high stereochemical purity approaching >99% ee. This procedure is efficient and makes economical use of chiral auxiliaries, of only 87–92% ee, to produce optically pure bis-adducts. These adducts are stable and can be stored at room temperature for a considerable period of time without any loss of its chemical and optical purity. The chiral hydroborating reagent $RapBH_2$ can readily be obtained from the bis-adduct by treatment with BF_3·EE in essentially quantitative yield. It has been previously demonstrated that the borane reagents incorporating the 2-ethyl- and 2-*n*-propylapopinenes have been proved to enhance the optical purity of asymmetric syntheses involving these chiral auxiliaries.[4f,12a] Therefore, on the basis of these results, it is anticipated that the chiral borane reagents such as *n*-propyl-, isobutyl-, and isopropylapoisopinocampheylboranes (**3c,d,f**) and the corresponding RapBHCl (Rap = **2a–f**) will serve as a family of promising chiral hydroborating reagents of favorable steric requirements to provide an improved steric fit with prochiral alkenes to achieve better optical inductions than those derived from $IpcBH_2$ and $EapBH_2$. The results of this ongoing research will be reported when the study has been completed.

Experimental Section

All glassware was dried at 140 °C overnight, assembled hot, and cooled to ambient temperature in a stream of nitrogen.[16d] All reactions involving air- or moisture-sensitive compounds were performed under a static pressure of dry nitrogen.[16d] Reported melting points are uncorrected. ^{11}B NMR spectra were recorded at 96 MHz and were referenced relative to BF_3·EE. ^1H and ^{13}C NMR spectra for all new compounds were recorded at 200 and 50 MHz, respectively, relative to internal tetramethylsilane (TMS). Chemical shifts in the ^1H and ^{13}C NMR spectra are reported as parts per million (ppm) downfield from TMS. Optical rotations were measured on a digital polarimeter in a 1-dm cell. Capillary GC analyses were performed using the SPB-5 column (30 m).

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and used as required. Commercial BMS was used as such without any further purification. TMEDA was distilled over CaH_2 prior to use. Anhydrous diethyl ether was used without purification. The 2-R-apopinenes **2b–f** were synthesized by known procedures.[4f,12a,13] The 2-R-apopinenes **2b–d,f** were derived from (+)-α-pinene, while 2-phenylapopinene (**2e**) was synthesized from (−)-β-pinene.

A Typical General Procedure for the Preparation of the Bis-adducts of 2-Organylapoisopinocampheylboranes with TMEDA [$(RapBH)_2$·TMEDA, 5b–f] from the 2-R-Apopinenes of 87–92% Optical Purity. All operations were carried out under nitrogen. A dry 500-mL flask was charged with BMS (10 M, 42-50 mmol) and dry THF (32–35 mL). 2-R-Apopinene (50–60 mmol) was added dropwise with stirring while the reaction temperature was maintained at 35 °C. The reaction mixture was maintained at 1.0–1.1 M with respect to BMS. The reaction was continued at 25 °C for 24–36 h. An aliquot of the reaction was methanolyzed and analyzed by ^{11}B NMR which showed the equilibrium mixture of $RapBH_2$ **2c–f** and Rap_2BH **2c–d** in >90% and <10%, while in case of 2-ethylapopinene (**2b**), $EapBH_2$ was formed in >86% along with trace amount (<1%) of $B(OMe)_3$. THF and the volatiles were removed in vacuo (12 mmHg, 50–55 °C, 1 h). The residue was redissolved in diethyl ether (32–35 mL), and the solution was refluxed for 0.5 h. TMEDA (21–25 mmol) was added *dropwise* to the refluxing solution of mixture of boranes. Once the addition was complete, the solution was maintained at reflux for an additional 0.5 h. Sometime during the addition of TMEDA, solid separated which then dissolved in the solution following completion of the addition of TMEDA. The solution was cooled to room temperature and kept at 0 °C overnight (12–14 h) to ensure complete crystallization of $(RapBH)_2$·TMEDA **5b–f**. The supernant liquid was removed by the double-ended needle, and the white solid was washed with cold pentane (50–100 mL) and filtered.

The solid was dried under vacuum to give 70–78% yield of **5b–f** with chemical and optical purity approaching >99%. Small amounts of bis-adducts **5b–f** were subjected to the alkaline peroxide oxidation to obtain the corresponding alcohols **6b–f**, derivatized as the MTPA (of **6e**) or menthyl carbonate (of **6b–d,f**). These derivatives were analyzed on a SPB-5 capillary GC column, revealing optical purities of ≥99% ee, in comparison with the equal diastereomeric mixture of derivatives of the alcohols **6b–f** obtained from hydroboration–oxidation of the corresponding racemic 2-R-apopinenes **2b–f**.

[EapBH$_2$]$_2$·TMEDA (5b). Prepared from (+)-2-ethylapopinene (91% ee). ^{1}H and ^{13}C NMR spectra are in accordance with that reported.[4f]

2-Ethylapoisopinocampheol (6b). ^{1}H and ^{13}C NMR spectra are in accordance with the reported values.[4f]

[PraBH$_2$]$_2$·TMEDA (5c): ^{1}H NMR δ 3.05–3.35 (m, 4H), 2.65 (s, 6H), 2.60 (s, 6H), 1.75–2.30 (m, 12H), 1.25–1.50 (m, 10H), 1.05–1.25 (m, 2H), 1.19 (s, 6H), 1.10 (s, 6H), 0.75–0.95 (m, 6H); ^{13}C NMR δ 57.62, 51.38, 51.16, 47.92, 44.46, 43.60, 39.57, 39.27, 38.66, 33.9, 28.87, 23.04, 21.89, 15.25. Anal. Calcd for $C_{30}H_{62}B_2N_2$: C, 76.27; H, 13.23; B, 4.58; N, 5.93. Found: C, 75.88; H, 13.58; B, 4.82; N, 6.27.

2-*n*-Propylapoisopinocampheol (6c): ^{1}H NMR δ 4.00–4.15 (m, 1H), 2.30–2.60 (m, 2H), 1.91 (br d, 2H), 1.65–1.85 (m, 3H), 1.30–1.60 (m, 4H), 1.20 (s, 3H), 1.05 (d, J = 9.6 Hz, 1H), 0.90 (t, J = 6.9 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR δ 70.73, 53.21, 45.42, 41.71, 39.19, 38.12, 37.96, 33.72, 27.57, 23.77, 21.44, 14.41. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 78.84; H, 12.10.

[^{i}BapBH$_2$]$_2$·TMEDA (5d): ^{1}H NMR δ 3.00–3.40 (m, 4H), 2.65 (s, 6H), 2.60 (s, 6H), 2.00–2.30 (m, 4H), 1.75–2.00 (m, 6H), 1.20–1.70 (m, 9H), 1.15 (s, 6H), 1.10 (s, 6H), 0.75–0.95 (m, 15H); ^{13}C NMR δ 57.43, 51.48, 51.13, 46.65, 45.14, 44.42, 43.57, 39.26, 38.68, 33.90, 26.03, 25.25, 28.89, 23.51, 22.25. Anal. Calcd for $C_{32}H_{66}B_2N_2$: C, 76.79; H, 13.29; B, 4.32; N, 5.60. Found: C, 76.54; H, 13.66; B, 4.11; N, 5.22.

2-Isobutylapoisopinocampheol (6d): ^{1}H NMR δ 3.90–4.10 (m, 1H), 2.30–2.60 (m, 2H), 1.82–1.98 (m, 3H), 1.60–1.80 (m, 3H), 1.22–1.49 (m, 2H), 1.20 (s, 3H), 1.08 (d, J = 9.8 Hz, 1H), 0.87–0.95 (m, 9H); ^{13}C NMR δ 71.44, 50.91, 45.73, 45.60, 41.93, 39.54, 38.18, 33.96, 27.81, 26.00, 23.99, 23.28, 22.89. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.51; H, 12.68.

[PapBH$_2$]$_2$·TMEDA (5e). 2-Phenylapopinene (**2e**) used for this preparation was synthesized from (−)-β-pinene:[15a] ^{1}H NMR δ 7.35–7.50 (m, 4H), 7.00–7.30 (m, 6H), 2.95 (m, 2H), 2.85 (s, 4H), 2.40 (s, 12 H), 2.35 (s, 2H), 2.10–2.25 (m, 4H), 1.80–2.00 (m, 5H), 1.35–1.50 (bm, 2H), 1.00–1.10 (m, 1H), 1.10 (s, 6H), 1.15 (s, 6H); ^{13}C NMR δ 150, 129.41, 129.32, 128.16, 125.27, 57.29, 54.08, 51.30, 49.82, 43.35, 39.06, 38.08, 35.01, 28.74, 24.41. Anal. Calcd for $C_{36}H_{58}B_2N_2$: C, 79.99; H, 10.84; B, 4.00; N, 5.18. Found: C, 80.26, H, 10.50; B, 3.95; N, 5.23.

2-Phenylapoisopinocampheol (6e): ^{1}H NMR δ 7.10–7.40 (m, 5H), 4.40-4.55 (m, 1H), 3.21 (br d, 1H), 3.08 (br s, 1H), 2.45–2.65 (m, 3H), 1.75–2.05 (m, 2H), 1.30 (bs, 4H), 0.79 (s, 3H); ^{13}C NMR δ 145.61, 127.95, 126.96, 125.66, 70.66, 55.83, 44.80, 39.22, 37.65, 33.85, 27.38, 24.61. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.01; H, 9.59.

(^{i}PraBH$_2$)$_2$·TMEDA (5f): ^{1}H NMR δ 3.25 (s, 4H), 2.65 (s, 6H), 2.60 (s, 6H), 2.00–2.25 (m, 6H), 1.65–1.95 (m, 6H), 1.25–1.40 (m, 2H), 1.15 (s, 6H), 1.00 (s, 6H), 0.95 (br d, 6H), 0.82 (br d, 6H); ^{13}C NMR δ 58.50, 54.10, 50.84, 44.23, 43.30, 38.74, 38.41, 34.17, 31.91, 28.35, 23.88, 23.65, 22.69. Anal. Calcd for $C_{30}H_{62}B_2N_2$: C, 76.27; H, 13.23; B, 4.58; N, 5.97. Found: C, 75.88; H, 13.53; B, 4.39; N, 5.64.

2-Isopropylapoisopinocampheol (6e): ^{1}H NMR δ 4.07–4.19 (m, 1H), 2.45-2.62 (m,1H), 2.29–2.42 (m, 1H), 2.10–2.20 (m, 1H), 1.55–2.00 (m, 4H), 1.31–1.45 (m, 1H), 1.20 (s, 3H), 1.10 (d, J = 9.8 Hz, 1H), 1.05 (d, J = 6.5 Hz, 3H), 0.89 (d, J = 6.7 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR δ 69.57, 61.21, 43.58, 41.81, 39.77, 38.00, 32.74, 32.44, 27.77, 24.09, 22.78, 21.95. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 78.75; H, 11.79.

For convenience, the melting points and $[\alpha]_D$ values for bis-adducts **2b–f** together with 2-R-apoisopinocampheols (RapOH, **6b-f**) are summarized in Table 1.

A Typical Procedure for the Preparation of 2-Organylapoisopinocampheylboranes (RapBH$_2$, 3b–f) from 5b–f. To a dry 250-mL round-bottom flask, flushed with nitrogen, containing bis-adducts **5b–f** (25 mmol) in 75 mL ether, was added BF_3·EE (48.8 mmol) dropwise at 25 °C, and the mixture was stirred for 1–2 h. The resulting slurry was transferred with a double-ended needle to a filtration chamber attached to a round-bottom flask flushed with nitrogen. The solid $(BF_3)_2$·TMEDA was washed with cold ether (2 × 10 mL), and the filtrate was analyzed for hydride content by hydrolyzing an aliquot with a 1:1:1 hydrolyzing mixture of glycerol/water/THF[16d] and found to be 0.48–0.51 M (95–90 mL, 91–92% yield) (^{11}B NMR δ 21–23). The solution is best stored under nitrogen at 0 °C. Under these conditions no appreciable loss of active hydride was observed in 10–15 days.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for new compounds described in the Experimental Section (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.