Effect of Solvent. The effect of solvent was studied both in the presence and absence of ultrasound. All experiments were performed (viz., the preparation of n-Bu_3B from n-BuBr) at 0.25 M concentration in ether, THF, and pentane on a 10-mmol scale. The yields were established by GC analysis, as described above. The quantitative formation of ate complex in THF was determined by ^{11}B NMR.

Effect of Alkyl Halide. The effect of alkyl halide was examined only in the presence of ultrasound. The formation of n-Bu_3B from n-BuCl, n-BuBr, and n-BuI was compared in anhydrous ether at 0.25 M on a 10-mmol scale. In every experiment, n-dodecane was used as internal standard. By determining the yield of n-butyl alcohol by gas chromatography, the yield of n-Bu_3B was ascertained in each case.

Effect of Metal. The metals Li and Mg were compared. Formation of n-Bu_3B from n-BuBr, Mg turnings, and BF_3·OEt_2 works almost quantitatively (99%) in anhydrous ether at 0.25 M, as already described. However, when lithium wire was used instead of magnesium and the procedure was repeated under identical conditions, no n-Bu_3B formation was observed in the presence of ultrasound and only coupled products were obtained. No attempt was made to estimate the yield of the coupled products.

Acknowledgment. We thank the National Science Foundation (Grant CHE 8414171) for the financial support of this research.

Registry No. $(CH_3)_3B$, 593-90-8; $(C_2H_5)_3B$, 97-94-9; $(n\text{-}C_3H_7)_3B$, 1116-61-6; $(i\text{-}C_3H_7)_3B$, 1776-66-5; $(n\text{-}C_4H_9)_3B$, 122-56-5; $(sec\text{-}C_5H_{11})_3B$, 1069-78-9; $(c\text{-}C_6H_{11})_3B$, 1088-01-3; Ph_3B, 960-71-4; $(1\text{-}C_{10}H_7)_3B$, 6962-78-3; $(PhCH_2)_3B$, 1694-84-4; $(H_2C{=}CHCH_2)_3B$, 688-61-9; $(n\text{-}C_7H_{15})_3B$, 3244-73-3; CH_3I, 74-88-4; C_2H_5Br, 74-96-4; $n\text{-}C_3H_7Br$, 106-94-5; $i\text{-}C_3H_7Br$, 75-26-3; $n\text{-}C_4H_9Br$, 109-65-9; $sec\text{-}C_5H_{11}Br$, 10422-35-2; $c\text{-}C_6H_{11}Br$, 108-85-0; PhBr, 108-86-1; $1\text{-}C_{10}H_7Br$, 90-11-9; $PhCH_2$, 100-44-7; $H_2C{=}CHCH_2$, 107-05-1; $n\text{-}C_7H_{15}I$, 4282-40-0; BF_3·OEt_2, 109-63-7; THF, 109-99-9; $n\text{-}C_5H_{12}$, 109-66-0; n-BuCl, 109-69-3; n-BuI, 542-69-8.

Chiral Synthesis via Organoboranes. 5. Asymmetric Allylboration via Chiral Allyldialkylboranes. Synthesis of Homoallylic Alcohols with Exceptionally High Enantiomeric Excess

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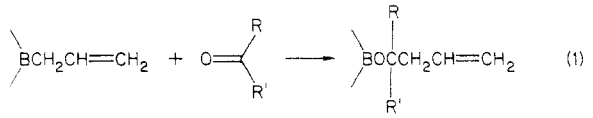
Allyldiisopinocampheylborane, prepared readily by treatment of methoxydiisopinocampheylborane with allylmagnesium bromide, adds smoothly to aldehydes with remarkable enantioselectivity, transferring an allyl group to the carbonyl carbon with boron going to the oxygen. The enantioselectivity in allylboration varies with the reaction temperature, increasing considerably by decreasing the temperature from 0 °C to −78 °C. However, the enantioselectivity achieved does not vary significantly with the structure of the aldehyde. The enantioselectivity in the condensation of the reagent with representative ketones is less favorable, but in selected cases the results are promising (as high as 75% ee). Condensation of methallyldiisopinocampheylborane and (3,3-dimethylallyl)diisopinocampheylborane with aldehydes proceeds with equally high asymmetric induction, indicating that wide variations in the structure of the allylic moiety can be accommodated. The effect of changes in the chiral ligand on boron has also been studied.

Allylboranes are extremely reactive organoborane intermediates.[1] The high reactivity of allylboranes is manifested in their reactions with water, alcohols, and amines, which occur even at room temperature.[1a] This feature distinguishes them markedly from trialkylboranes, which react with the same substrates only at elevated temperatures. Over the past decade, Mikhailov and coworkers[1a] have extensively examined the chemistry of the simple triallylboranes. They have reported that such allylboranes add smoothly to various carbonyl derivatives in the usual organometallic fashion, transferring an allyl group to the carbonyl carbon with boron going to the oxygen (eq 1). Such allylborations of aldehydes and ketones



(1)

proceed simply, utilizing all three allyl groups in the former case but only two allyl moieties in the latter. The allylboration of other carbonyl derivatives such as nitriles and quinones are not as straightforward, being accompanied by subsequent reactions of the initial products. *B*-Allyl derivatives of 9-borabicyclo[3.3.1]nonane (9-BBN) are known to possess unique advantages over simple triallylboranes in many synthetic applications. Consequently, *B*-allyl derivatives of 9-BBN were systematically investigated in our laboratory.[1b,c]

Allylboranes are extremely valuable intermediates in organic synthesis, particularly for carbon–carbon bond formation. Use of chiral allylboranes for asymmetric carbon–carbon bond formation was not recognized until recently.[2,3] Hoffmann and co-workers[2] used chiral allylboronates for asymmetric carbon–carbon bond formation. We have developed allyldiisopinocampheylborane derivatives for asymmetric allylboration. These chiral allylboranes are highly effective intermediates for asymmetric carbon–carbon bond formation. A portion of our study has appeared in the form of preliminary communica-

(1) (a) Mikhailov, B. M. *Organomet. Chem. Rev Sec. A* **1972**, *8*, 1. (b) Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2292; (c) *J. Organomet. Chem.* **1977**, *132*, 9.

(2) (a) Herold, T.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768. (b) Herold, T.; Schrott, U.; Hoffmann, R. W. *Chem. Ber.* **1981**, *114*, 359. (c) Hoffmann, R. W.; Herold, T. *Ibid.* **1981**, *114*, 375.

(3) Midland, M. M.; Preston, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 2330.

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Table I. Allylboration of Aldehydes with *B*-Allyldiisopinocampheylborane.[a] Preparation of Homoallylic Alcohols 8

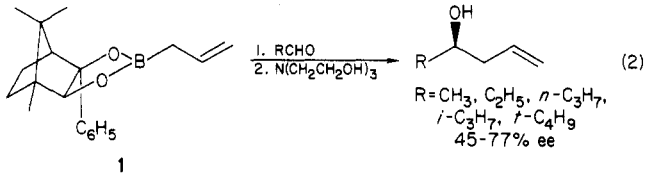
		homoallylic alcohols				
entry	aldehyde	alcohol	isolated yield, %	$[\alpha]^{23}_D$, deg	% ee	config
A	acetaldehyde	4-penten-2-ol	74	−9.08 (*c* 9.18, Et_2O)	93	*R*[b]
B	*n*-propionaldehyde	5-hexen-3-ol	71	+5.30 (*c* 10.76, benzene)	86	*R*[b]
C	*n*-butyraldehyde	1-hepten-4-ol	72	+12.52 (*c* 10.22, benzene)	87	*R*[b]
D	2-methylpropionaldehyde	2-methyl-5-hexen-3-ol	86	−3.36 (*c* 11.82, benzene)	90	*S*[b]
E	2,2-dimethylpropionaldehyde	2,2-dimethyl-5-hexen-3-ol	88	−9.80 (*c* 10.88, benzene)	83	*S*[b]
F	benzaldehyde	1-phenyl-3-buten-1-ol	81	−44.92 (*c* 7.38, benzene)	96	*S*[b]

[a] (+)-α-Pinene was used to prepared the reagent. [b] Based on ref 2c.

tions.[4-7] We now describe in full the results of our systematic investigation on asymmetric allylboration.

Results and Discussion

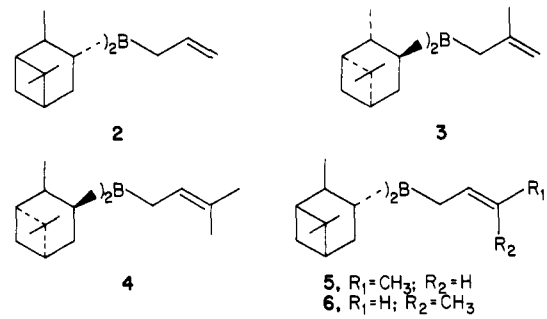
Herold and Hoffmann[2a] prepared chiral allylboronate **1** in several steps from (+)-camphor. Condensation of



(2)

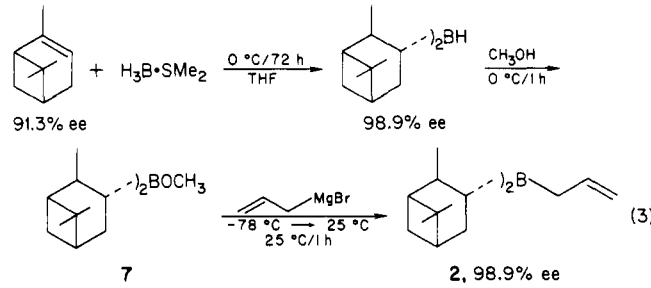
1

aldehydes with **1** followed by triethanolamine workup provides secondary homoallylic alcohols in 45–77% enantiomeric excess. We envisioned that allyldiisopinocampheylborane derivatives **2–6** might prove superior to



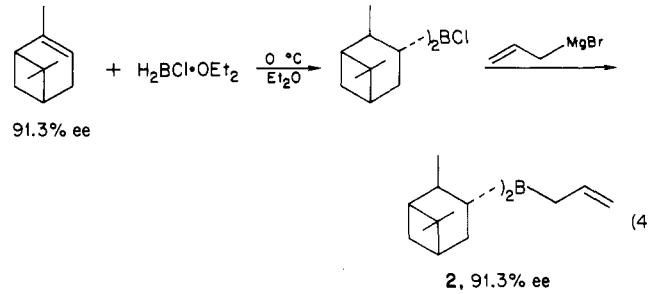
the chiral allylboronates utilized by Hoffmann and coworkers for the following reasons. The allyldialkylboranes are much more reactive toward aldehydes, permitting a lower reaction temperature and improved chirality. The preparation of the allyldiisopinocampheylboranes appears considerably simpler than that of the chiral allylboronates. The products of both absolute configurations can be readily obtained from the appropriate diisopinocampheylborane derivative. In chiral allylboronate **1**, the boron is one oxygen atom removed from the chiral centers. Therefore, the direct attachment of boron to the chiral centers in the isopincoampheyl groups in **2–6** might result in improved enantioselectivity. These considerations prompted us to study the scope and limitations of allyldiisopinocampheylboranes.

Allyldiisopinocampheylborane (2). Preparation of allyldiisopinocampheylborane ($Ipc_2BCH_2CH{=}CH_2$) is extremely simple.[4] Thus methanolysis of diisopinocampheylborane (Ipc_2BH) of 99% ee[8] proceeds cleanly to methoxydiisopinocampheylborane (Ipc_2BOCH_3). This intermediate, on treatment with allylmagnesium bromide, provides $Ipc_2BCH_2CH{=}CH_2$ (^{11}B NMR δ + 78; eq 3).



(3)

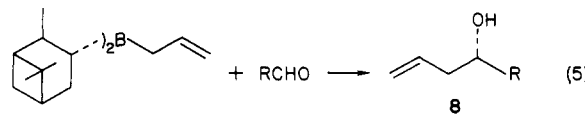
An alternative procedure involves hydroboration of α-pinene with monochloroborane etherate[9] ($H_2BCl{\cdot}OEt_2$) in ethyl ether at 0 °C to give Ipc_2BCl, followed by treatment with allylmagnesium bromide to provide cleanly $Ipc_2BCH_2CH{=}CH_2$ (eq 4).



(4)

Preparation of $Ipc_2BCH_2CH{=}CH_2$ involving use of Ipc_2BH (eq 3) is advantageous over that involving use of Ipc_2BCl (eq 4) because one can prepare $Ipc_2BCH_2CH{=}CH_2$ of 98.9% ee starting with α-pinene of 91.3% ee. The reagent can be readily isolated as the neat liquid, free of magnesium salts and solvent, by passing the reaction mixture through a filtration chamber, followed by pumping off the solvent. However, it is generally more convenient to react the reagent with aldehyde without prior isolation.

Condensation with Aldehydes. $Ipc_2BCH_2CH{=}CH_2$ reacts with various aldehydes such as propionaldehyde, *n*-butyraldehyde, 2-methylpropionaldehyde, and 2,2-dimethylpropionaldehyde at −78 °C to furnish the corresponding secondary homoallylic alcohols in remarkably high enantiomeric excess (Table I). The % ee of the alcohols are comparable in all cases and apparently do not depend on the steric requirements of the aldehydes. The asymmetric induction in the case of benzaldehyde, 96% ee, is highly gratifying in comparison to the earlier report of ~30% ee.[10] The absolute configurations of the homoallylic alcohols are known in the literature.



(5)

(4) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092.
(5) Brown, H. C.; Jadhav, P. K.; Perumal, P. T. *Tetrahedron Lett.* **1984**, *25*, 5111.
(6) Brown, H. C.; Jadhav, P. K. *Tetrahedron Lett.* **1984**, *25*, 1215.
(7) Brown, H. C.; Jadhav, P. K. *J. Org. Chem.* **1984**, *49*, 4089.
(8) Brown, H. C.; Desai, M. C.; Jadhav, P. K. *J. Org. Chem.* **1982**, *47*, 5065.
(9) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1972**, *94*, 2112.
(10) Hoffmann, R. W.; Herold, T. *Chem. Ber.* **1981**, *114*, 375.

Table II. Allylboration of Ketones with *B*-Allyldiisopinocampheylborane.[a] Preparation of Homoallylic Alcohols 9

		homoallylic alcohols				
entry	ketone	alcohol	isolated yield, %	$[\alpha]^{23}_D$, deg (neat)	% ee	config
A	2-butanone	3-methyl-5-hexen-3-ol	68	−2.63	50[b]	*R*[c]
B	3-buten-2-one	3-methyl-1,5-hexadien-3-ol	79	+1.46	35	*R*[c]
C	acetophenone	2-phenyl-4-penten-2-ol	63	−0.91	5	*S*[d]
D	3-butyn-2-one	3-methyl-5-en-1-hexyn-3-ol	76	−14.89	75	*S*[c]

[a] (+)-α-Pinene was used to prepare the reagent. [b] The % ee is obtained by catalytic (5% Pt on C) hydrogenation of **9a** into the corresponding saturated alcohol.[19] [c] The absolute configurations are obtained by catalytic (5% Pt on C) hydrogenation of homoallylic alcohols into their corresponding saturated alcohol.[19] [d] The absolute configuration is predicted in analogy to the configurations of the products obtained by *B*-allyldiisopinocampheylborane with aldehyde.

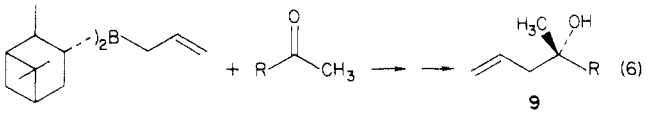
Table III. Allylboration of Acetaldehyde with *B*-Allyldiisopinocampheylborane.[a] Temperature Studies in the Preparation of Homoallylic Alcohol (4-Penten-2-ol)[b]

temp, °C	yield, %	$[\alpha]^{23}_D$, deg	% ee
−100	74	−9.24 (*c* 9.18, Et_2O)	94.7
−78	74	−9.08 (*c* 9.18, Et_2O)	93.0
−50	72	−8.79 (*c* 9.18, Et_2O)	90.1
−25	70	−8.30 (*c* 9.18, Et_2O)	85.1
0	67	−7.75 (*c* 9.18, Et_2O)	79.4

[a] (+)-α-Pinene was used to prepare the reagent. [b] All reactions were carried out in ether.

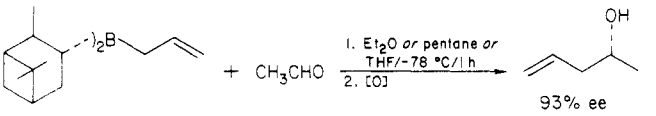
Condensation with Ketones. Asymmetric allylboration of ketones with $Ipc_2BCH_2CH{=}CH_2$ provides tertiary homoallylic alcohols. Aliphatic ketones, α,β-unsaturated ketones, α,β-acetylenic ketones, and aromatic ketones exhibit distinctly different behavior in asymmetric synthesis. Therefore, 2-butanone, 3-buten-2-one, 3-butyn-2-one, and acetophenone were chosen as representative examples from each of the above mentioned classes of ketones for asymmetric allylboration study. The results are summarized in Table II.

Condensation of $Ipc_2BCH_2CH{=}CH_2$ with 2-butanone, followed by oxidative workup, provides 3-methyl-5-hexen-3-ol in 50% ee. Asymmetric allylboration of 3-buten-2-one and acetophenone with $Ipc_2BCH_2CH{=}CH_2$ furnished the corresponding tertiary homoallylic alcohols in 35% and 5% ee. However, condensation of 3-butyn-2-one with $Ipc_2BCH_2CH{=}CH_2$ proceeded with relatively good asymmetric induction to give 3-methyl-5-hexen-1-yn-3-ol in 75% ee (eq 6).



9 (6)

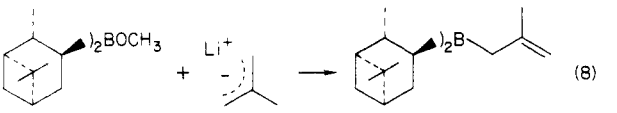
Effect of Solvent. In order to find the most effective solvent for asymmetric allylboration of acetaldehyde with $Ipc_2BCH_2CH{=}CH_2$, the reaction was carried out in pentane, ethyl ether (Et_2O), and tetrahydrofuran (THF). Thus, $Ipc_2BCH_2CH{=}CH_2$, on treatment with acetaldehyde in Et_2O at −78 °C, undergoes condensation to provide, after the usual alkaline hydrogen peroxide workup, 4-penten-2-ol in 93% ee (eq 7). Similar treatment of $Ipc_2BCH_2CH{=}CH_2$ with acetaldehyde in either pentane or THF did not have a significant effect on the % ee of 4-penten-2-ol, indicating no significant solvent effect on the enantioselectivity of the reaction.



2 (7)

Effect of Temperature. Condensation of $Ipc_2BCH_2CH{=}CH_2$ with acetaldehyde in Et_2O at 0 °C provides 4-penten-2-ol in 79% ee. Enantioselectivity of the reaction increased by decreasing the temperature from 0 °C to −78 °C. However, a further decrease in temperature from −78 °C to −100 °C did not produce any major improvement in the enantiomeric excess of 4-penten-2-ol (Table III). These results suggest that the convenience of −78 °C makes it the preferred temperature for asymmetric allylboration.

Methallyldiisopinocamphenylborane. The introduction of methyl groups into the allyl moiety of allyldiisopinocampheylborane leads to substituted allyldiisopinocampheylborane derivatives. These chiral allylboranes can then be used for the enantioselective synthesis of appropriately substituted secondary homoallylic alcohols.[5] Methallyldiisopinocampheylborane (**3**) is readily prepared by treatment of methoxydiisopinocampheylborane with methallyllithium (eq 8).



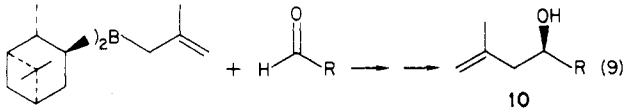
3 (8)

Methallyldiisopinocampheylborane, on condensation with a variety of aldehydes, provides, after oxidative workup, methallylated products in >90% ee (eq 9). The results are summarized in Table IV.

Table IV. Allylboration of Aldehydes with Methallyldiisopinocampheylborane (3).[a] Preparation of Homoallylic Alcohols 10

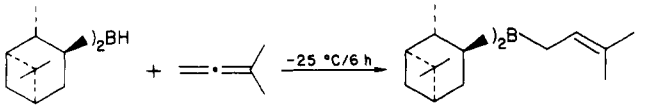
		homoallylic alcohols				
entry	aldehyde	alcohol	isolated yield,[b] %	$[\alpha]^{23}_D$, deg (neat)	% ee	config[c]
A	acetaldehyde	4-methyl-4-penten-2-ol	56	+4.94	90	*S*
B	*n*-propionaldehyde	5-methyl-5-hexen-3-ol	54	−3.07	90	*S*
C	*n*-butyraldehyde	2-methyl-1-hepten-4-ol	56	−9.53	91	*S*
D	2-methylpropionaldehyde	2,5-dimethyl-5-hexen-3-ol	57	+2.84	96	*R*
E	2,2-dimethylpropionaldehyde	2,2,5-trimethyl-5-hexen-3-ol	55	−0.65	90	*R*
F	acrolein	5-methyl-1,5-hexadien-3-ol	57	−20.62	92	*R*

[a] (−)-α-Pinene was used to prepare the reagent. [b] We believe that the chemical yields approach 90% with losses primarily involved in isolated (silica gel chromatography) of the highly volatile alcohols. We made no attempt to maximize chemical yields. [c] Configurations are predicted in analogy to the configurations of the products obtained with *B*-allyldiisopinocampheylborane.



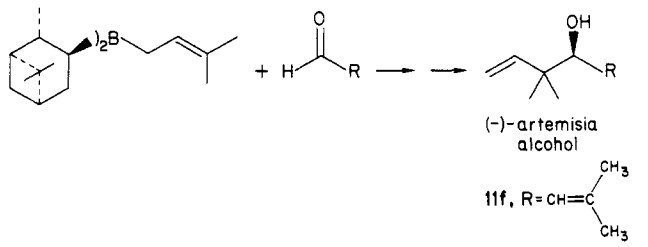
10 (9)

(3,3-Dimethylallyl)diisopinocampheylborane. Preparation of allyl- or methyallyldiisopinocampheylborane involves use of organomagnesium or organolithium reagents. However, hydroboration of appropriate dienes is perhaps the most simple and convenient route to some of the allyldiisopinocampheylborane derivatives.[6] Thus, hydroboration of 3-methyl-1,2-butadiene with Ipc_2BH cleanly proceeds to give (3,3-dimethylallyl)diisopinocampheylborane (4) (eq 10).



4 (10)

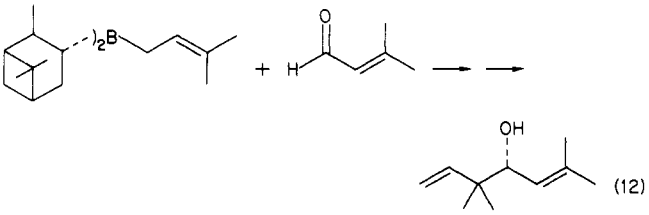
We have demonstrated that $Ipc_2BCH_2CH{=}C(CH_3)_2$ is an excellent reagent for chiral isoprenylation of aldehydes.[6] The great majority of terpenes can be represented by the head-to-tail union of isoprene units. However, there are a few less common terpenes such as (−)-artemisia alcohol[11] (11) that must be represented by non-head-to-tail union of the isoprene units. We demonstrated the use of $Ipc_2BCH_2CH{=}C(CH_3)_2$ for the first asymmetric synthesis of (−)- and (+)-artemisia alcohols, the acyclic monoterpene alcohols isolated from *Artemisia annua* L. and *Aremisia herba-alba*, respectively.[12] Thus, condensation of $Ipc_2BCH_2CH{=}C(CH_3)_2$ [derived from (−)-α-pinene] with 3-methyl-2-butenal, followed by oxidative workup, furnished (−)-artemisia alcohol (11), $[\alpha]_D$ −32.12° (neat), 96% ee in 85% isolated yield (eq 11).



(−)-artemisia alcohol

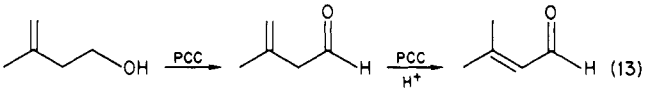
11f, R = CH=C(CH3)2 (11)

Smilarly, (+)-artemisia alcohol (11e), $[\alpha]_D$ +32.10° (neat), was prepared in 96% ee by condensing 3-methyl-2-butenal with $Ipc_2BCH_2CH{=}C(CH_3)_2$ derived from (+)-α-pinene (eq 12).



11e, (+)-artemisia alcohol (12)

3-Methyl-2-butenal was prepared by oxidation of 3-methyl-3-buten-1-ol with pyridinium chlorochromate (PCC), followed by concurrent isomerization of disubstituted double bond to trisubstituted olefinic linkage (eq 13).[13]

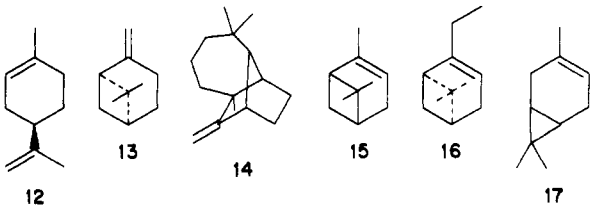


(13)

The reagent 4 is generally applicable to a variety of aldehydes such as acetabldehyde, *n*-butyraldehyde, 2-methylpropionaldehyde, and acrolein. The results are summarized in Table V.

Effect of Chiral Auxiliary. $Ipc_2BCH_2CH{=}CH_2$, $Ipc_2BCH_2C(CH_3){=}CH_2$, and $Ipc_2BCH_2CH{=}C(CH_3)_2$ are excellent allylborating agents. In order to see if we could improve upon these highly promising results, we undertook exploration of other chiral *B*-allyldialkylboranes and studied the effect of the chiral ligand in this asymmetric allylboration reaction.[7]

Allyldialkylboranes were prepared from (+)-limonene (12), (−)-β-pinene (13), (+)-longifolene (14), (+)-α-pinene (15), (−)-10-methyl-α-pinene (16), and (+)-3-carene (17).

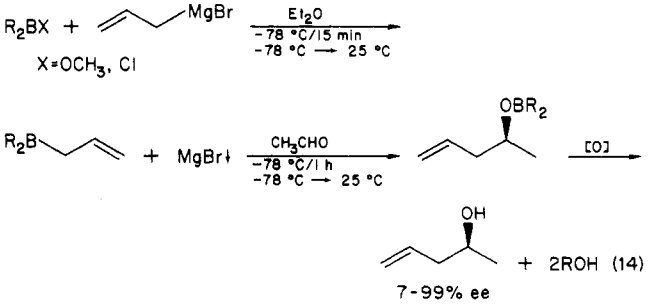


12 13 14 15 16 17

The preparation of allyldialkylboranes in all of these cases, except for (+)-limonene and (−)-β-pinene, is straightforward. Thus the terpene hydrocarbon is hydroborated with borane–methyl sulfide complex ($BH_3{\cdot}SMe_2$) to the R_2BH stage and the resulting dialkylborane is methanolyzed to provide the allyldiisopinocampheylborane. This intermediate on subsequent treatment with allylmagnesium bromide, provides the desired allyldialkylborane. In the case of (−)-β-pinene, however, hydroboration with $BH_3{\cdot}SMe_2$ cannot be stopped at the dialkylborane stage. Consequently, it was hydroborated with monochloroborane etherate ($H_2BCl{\cdot}OEt_2$) to provide *B*-chloro-10-pinanylborane. This intermediate readily reacts with allylmagnesium bromide to furnish the desired allyldi-10-pinanylborane. *B*-(Chlorolimonyl)borane was prepared by using the cyclic hydroboration procedure reported earlier and treated with allylmagnesium bromide to provide (allyllimonyl)borane.

Formation of the allyldialkylboranes was indicated by precipitation of the magnesium salts and confirmed by ^{11}B NMR (δ +78–85).

In all cases the allyldialkylboranes were prepared following the appropriate procedure and condensed in situ with acetaldehyde at −78 °C, and the resulting borinates were oxidized with alkaline hydrogen peroxide to provide 4-penten-2-ol (eq 14).



7-99% ee (14)

The results achieved by asymmetric allylboration of acetaldehyde with various allyldialkylboranes are summarized in Table VI. The results indicate that asymmetric inductions observed with allylboranes derived from (+)-limonene, (−)-β-pinene, and (+)-longifolene are less satis-

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(12) Segal, R.; Breuer, A.; Feuerstein, I. *Phytochemistry* **1980**, *19*, 2761.
(13) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

Table V. Allylboration of Aldehydes with (3,3-Dimethylallyl)diisopinocampheylborane.[a] Preparation of Homoallylic Alcohols 11

		homoallylic alcohols				
entry	aldehyde	alcohol	isolated yield, %	$[\alpha]^{23}_D$, deg (neat)	% ee	config[c]
A	acetaldehyde	3,3-dimethyl-4-penten-2-ol	73	−5.95	91	*S*
B	*n*-butyraldehyde	3,3-dimethyl-1-hepten-4-ol	79	−38.56	92	*S*
C	2-methylpropionaldehyde	2,4,4-trimethyl-5-hexen-3-ol	73	−27.95	89	*S*
D	acrolein	4,4-dimethyl-1,5-hexadien-3-ol	70	−41.53	95	*S*
E	3-methyl-2-butenal	3,3,6-trimethyl-1,5-heptadien-4-ol	85	−32.12	96	*S*
F	3-methyl-2-butenal	3,3,6-trimethyl-1,5-heptadien-4-ol[b]	83	+32.10	96	*R*

[a] (−)-α-Pinene was used to prepare the reagent. [b] (+)-α-Pinene was used to prepare the reagent. [c] Configurations are predicted in analogy to the configurations of the products obtained with *B*-allyldiisopinocampheylborane.

Table VI. Allylboration of Acetaldehyde with Chiral *B*-Allyldialkylboranes[a]

		4-penten-2-ol			
entry	R_2B-allyl	isolated yield, %	$[\alpha]^{23}_D$, deg (*c* 9.18, Et_2O)	% ee	config
18	*B*-allyllimonylborane	72	−0.70	7[b]	*R*
19	*B*-allyldi-10-pinanylborane	65	+1.07	11[b]	*S*
20	*B*-allyldilongifolylborane	67	+3.34	34[b]	*S*
2	*B*-allyldiisopinocampheylborane	74	−9.08	93	*R*
21	*B*-allylbis(10-methylisopinocampheyl)borane[c]	72	+9.06	93 (99)[d]	*S*
22	*B*-allyldiisocaranylborane	72	−9.75	>99	*R*

[a] (+)-Limonene, $[\alpha]^{23}_D$ +120° (*c* 1, CH_3OH); (−)-β-pinene, $[\alpha]^{23}_D$ −21.1° (neat); (+)-longifolene, $[\alpha]^{23}_D$ +44.2° (*c* 4.6, $CHCl_3$); (−)-10-methyl-α-pinene, $[\alpha]^{23}_D$ −42.2° (neat); (+)-3-carene, $[\alpha]^{23}_D$ +18° (neat) were used to prepare the reagents. [b] No correction has been made for the enantiomeric purity of the starting terpenes. [c] Alkene **16** was readily prepared by reductive detosylation of nopol tosylate with lithium aluminum hydride. [d] Corrected value for enantiomerically pure **16**.

Table VII. Allylboration of Aldehydes with *B*-Allyldiisocaranylborane (22)

	homoallylic alcohols				
aldehyde	alcohol	isolated yield, %	$[\alpha]^{23}_D$, deg	% ee[a]	config
acetaldehyde	4-penten-2-ol	72	−9.75 (*c* 9.16, Et_2O)	>99 (93)	*R*
propionaldehyde	5-hexen-3-ol	76	+5.59 (*c* 10.75, benzene)	91 (86)	*R*
n-butyraldehyde	1-hepten-4-ol	73	+12.74 (*c* 10.21, benzene)	89 (87)	*R*
2-methylpropionaldehyde	2-methyl-5-hexen-3-ol	73	−3.62 (*c* 11.8, benzene)	97 (90)	*S*
2,2-dimethylpropionaldehyde	2,2-dimethyl-5-hexen-3-ol	80	−10.4 (*c* 10.89, benzene)	88 (83)	*S*
acrolein	1,5-hexadien-3-ol	79	+17.84 (*c* 8.57, Et_2O)	86	*S*

[a] Figures in parentheses are % ee of the homoallylic alcohols obtained by using *B*-allyldiisopinocampheylborane.

factory. The probable reason would be, in these allylboranes, that the boron atom is not directly attached to the chiral center. Moreover, (allyllimonyl)borane does not have an element of C_2 symmetry. On the other hand, the boron atom is directly attached to the chiral centers in the case of allyldialkylboranes derived from **15**, **16**, and **17**. These allyldialkylboranes provide 4-penten-2-ol in exceptionally high enantiomeric excess.

Allyldiisocaranylborane proved to be the most satisfactory reagent among the allyldialkylboranes examined thus far, achieving >99% asymmetric synthesis. Consequently, its scope was explored in greater detail. These results are summarized in Table VII.

In general, higher values of enantiomeric excess are realized compared to allyldiisopinocampheylborane. Allylboration of acrolein (α,β-unsaturated aldehyde) also occur with high asymmetric induction (86% ee) in comparison to the literature achievement of only 50% ee.[2c]

Unfortunately only (+)-3-carene is readily available from natural sources. However, both (+)- and (−)-α-pinene are readily available. Consequently, we recommend use of α-pinene as chiral auxiliary for asymmetric allylboration.

(3-Methylallyl/crotyl)diisopinocampheylborane. (3-Methylallyl)diisopinocampheylborane was readily prepared by hydroboration of 1,2-butadiene with diisopinocampheylborane. However, asymmetric allylboration of acetaldehyde with the reagent proceeds to give a mixture of threo and erythro alcohols, presumably because (3-methylallyl)diisopinocampheylborane exists as a mixture of ((*E*)-3-methylallyl)diisopinocampheylborane (**5**) and ((*Z*)-3-methylallyl)diisopinocampheylborane (**6**). Fortunately, we have recently solved the problem of preparing pure **5** and **6** and the results of this study will shortly be communicated.[14]

Conclusion

In the present paper we have clearly demonstrated the use of allyldiisopinocampheylboranes for enantioselective synthesis of secondary homoallylic alcohols in both enantiomeric form and with exceptionally high enantomeric excess. The present paper also demonstrates the superior chiral-directing property of the 3-pinanyl group in asymmetric synthesis. Asymmetric allylboration is quite general and apparently does not depend on the nature of aldehyde. It accommodates wide variations in the structure of the allylic moiety, as is evident from the successful applications of methallyldiisopinocampheylborane and (3,3-dimethylallyl)diisopinocampheylborane. The absolute stereochemistry is the same in all cases examined. (+)-3-Carene has emerged as a superior chiral auxiliary during the exploration for the most effective chiral allyldialkylborane. Its applications for other asymmetric syntheses appear promising.

The present method provides a simple and convenient route to a one-pot synthesis of chiral homoallylic alcohols from readily available starting materials. It appears to be

(14) Research of H. C. Brown and K. S. Bhat.

a valuable advance in the area of asymmetric organic synthesis.

Experimental Section

The reaction flasks and other glass equipment were dried in an oven (140 °C, 12–18 h) and assembled in a stream of dry nitrogen gas. All reactions were carried out under an atmosphere of nitrogen. Special experimental techniques used in handling air-sensitive materials are described in detail elsewhere.[15]

Spectra. ^{11}B NMR spectra were recorded by using a Varian FT-80A instrument. The chemical shifts are in δ relative to $BF_3{\cdot}OEt_2$. ^1H NMR (90 MHz) and ^{13}C NMR spectra were recorded on Perkin-Elmer R-32 and FT-80A spectrometers, respectively.

GC analyses were carried out with a Hewlett-Packard 5750 chromatography using (a) 9 ft × 0.125 in. column packed with 10% Carbowax 20M on Chromosorb W (100–120 mesh) or (b) 9 ft × 0.125 in. column packed with 10% SE-30 on Chromosorb W (100–120 mesh). All homoallylic alcohols were purified to 100% GC pure by preparative GC using either (a) 6 ft × 0.5 in. column packed with 10% Carbowax W (60–80 mesh) or (b) 6 ft × 0.5 in column packed with 20% SP-2100 on Chromosorb W (60–80 mesh).

Optical Purity Determination. The following methods were followed for the optical purity determination: (a) using ^{19}F NMR of the MTPA esters of the alcohols using a Varian XL-200 spectrometer; (b) using ^1H NMR in the presence of chiral shift reagent, $Eu(hfc)_3$.

Preparation of *B*-Allyldiisopinocampheylborane (2) ($Ipc_2BCH_2CH{=}CH_2$). Method A. Diisopinocampheylborane (Ipc_2BH) of 98.9% ee was prepared from $BH_3{\cdot}SMe_2$ and (+)-α-pinene [$[\alpha]^{23}_D$ +47.1° (neat), 91.3% ee] by following the reported procedure.[8] Ipc_2BH (50 mmol) in THF was treated at 0 °C with methanol (4.0 mL, 100 mmol). After complete addition of methanol, the reaction mixture was warmed to room temperature and was stirred at 25 °C for 1 h. The solvents were removed under vacuum (14 mmHg, 1 h; 1 mmHg, 2 h). The residue was dissolved in anhydrous ethyl ether (50 mL) and the solution was cooled to −78 °C. To the borinate (*B*-methoxydiisopinocampheylborane) was then added dropwise allylmagnesium bromide in ethyl ether (1.18 M, 42.3 mL, 50 mmol). The reaction mixture, after 15 min of stirring −78 °C, was removed from a dry ice–acetone bath and allowed to warm to 25 °C (~1 h). The formation of $Ipc_2BCH_2CH{=}CH_2$ is indicated by precipitation of the magnesium salts as well as by ^{11}B NMR (δ + 78). The reagent can be readily isolated as the neat liquid, free of magnesium salts and solvent, by passing the reaction mixture through a filtration chamber, followed by pumping off the solvents. However, it is generally used for the condensation reactions with various aldehydes, without prior isolation.

Method B. A 250-mL flask equipped with a septum inlet, a magnetic stirring bar, and a bent tube adaptor was charged with monochloroborane etherate[9] in ethyl ether (1 M, 50 mL, 50 mmol). It was cooled to 0 °C and (−)-α-pinene [15.8 mL, 100 mmol, $[\alpha]^{25}_D$ −48.3° (neat), 93.6% ee] was added dropwise. The reaction mixture was kept at 0 °C for 16 h, ^{11}B NMR (δ +76). It was then cooled to −78 °C and allylmagnesium bromide in ethyl ether (1.18 M, 42.3 mL, 50 mmol) was added dropwise. The reaction mixture, after being stirred for 1 h at −78 °C, was removed from the dry ice–acetone bath and allowed to warm to 25 °C (~1 h). The formation of $Ipc_2BCH_2CH{=}CH_2$ is indicated by ^{11}B NMR (δ +78). This was used as such for condensation with various aldehydes.

4-Penten-2-ol (8a). The $Ipc_2BCH_2CH{=}CH_2$ in ethyl ether (50 mmol, method A) was cooled to −78 °C, and acetaldehyde (2.9 mL, 50 mmol) was added dropwise with stirring. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C (~1 h). The completion of the reaction was evident from ^{11}B NMR (δ +55). The reaction mixture was treated with 3 N NaOH (36.6 mL, 110 mmol) and 30% H_2O_2 (15 mL) and the contents were refluxed for 1 h. The organic layer was separated and washed with water (30 mL) and brine (30 mL) and dried over anhydrous $MgSO_4$. The residue, after removal of the solvent, was distilled under vacuum at 100–120 °C (bath, 20 mmHg) and the distillate free from isopinocampheol was collected in a dry ice–acetone trap. The distillate was passed through silica gel to remove any α-pinene (elution with pentane). Elution with a mixture of ethyl ether and pentane (1:4) furnished **8a** (3.2 g, 74% yield): bp 115 °C (746 mmHg); $[\alpha]^{23}_D$ −9.08° (*c* 9.18. Et_2O); 93% ee (method A).

5-Hexen-3-ol (8b). With the usual experimental setup, propionaldehyde (3.6 mL, 50 mmol) was added slowly to $Ipc_2BCH_2CH{=}CH_2$ in ethyl ether (50 mmol, method A) and cooled at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C (~1 h). The reaction mixture was oxidized and worked up as described in the experiment with 4-penten-2-ol to provide **8b** (3.5 g, 71% yield): bp 130–131 °C (750 mmHg); $[\alpha]^{23}_D$ +5.30° (*c* 10.76, benzene); 86% ee (method A).

1-Hepten-4-ol (8c). The *n*-butyraldehyde (4.4 mL, 50 mmol) was added slowly to $Ipc_2BCH_2CH{=}CH_2$ in ethyl ether (50 mmol, method A) and then cooled at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C (~1 h). The reaction mixture was oxidized and worked up as described in the experiment for 4-penten-2-ol to provide **8c** (4.1 g, 72% yield): bp 102 °C (95 mmHg); $[\alpha]^{23}_D$ +12.52° (*c* 10.22, benzene); 87% ee (method A).

2-Methyl-5-hexen-3-ol (8d). The 2-methylpropionaldehyde (4.53 mL, 50 mmol) was added slowly to $Ipc_2BCH_2CH{=}CH_2$ in ethyl ether (50 mmol, method A) and then cooled at −78 °C. The reaction mixture was oxidized and worked up as described in the experiment for 4-penten-2-ol to provide **8d** (4.9 g, 86% yield): bp 98–100 °C (97 mmHg); $[\alpha]^{23}_D$ −3.36° (*c* 11.82, benzene); 90% ee (method A).

2,2-Dimethyl-5-hexen-3-ol (8e). The 2,2-dimethylpropionaldehyde (5.42 mL, 50 mmol) was added slowly to $Ipc_2BCH_2CH{=}CH_2$ in ethyl ether (50 mmol, method A) and then cooled at −78 °C. After complete addition of aldehyde, the reaction mixture was stirred for 2 h at −78 °C and then allowed to warm to 25 °C (~1 h). The reactrion mixture was oxidized and worked up as described in the experiment for 4-penten-2-ol to provide **8e** (5.6 g, 88% yield): bp 94 °C (92 mmHg); $[\alpha]^{23}_D$ −9.80° (*c* 10.88, benzene); 83% ee (method A).

1-Phenyl-3-buten-1-ol (8f). The benzaldehyde (5.1 mL, 50 mmol) was added slowly to $Ipc_2BCH_2CH{=}CH_2$ (50 mmol, method A) and then cooled at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C. The reaction mixture was oxidized and worked up as described in the experiment for 4-penten-2-ol to furnish **8f** (6.0 g, 81% yield): bp 105–110 °C (15 mm); $[\alpha]^{23}_D$ −44.92° (*c* 7.38, benzene); 96% ee (method B).

3-Methyl-5-hexen-3-ol (9a). 2-Butanone (4.48 mL, 50 mmol) was added dropwise to a stirred solution of **2** in ethyl ether (50 mmol, method A) at −78 °C. Stirring was continued at −78 °C for 3 h and then allowed to warm to 25 °C (~1 h). The completion of the reaction was evident from ^{11}B NMR (δ +53). The reaction mixture was passed through a filtration chamber and the filtrate was treated with ethanolamine (4.52 mL, 75 mmol) at 0 °C. It was slowly warmed to 25 °C and stirred at 25 °C for 5 h. The reaction was followed by ^{11}B NMR (δ +10). The residue after removal of ether was distilled at 100–120 °C (bath temperature) (20 mmHg) and the distillate was collected in a dry ice–acetone trap. The distillate was further fractionated by distillation under reduced pressure to furnish **9a** (3.9 g, 68% yield): bp 85 °C (90 mmHg); 100% GC pure compound was obtained by preparative GC using a column, 20% SP-2100 over Chromosorb W 60/80; $[\alpha]^{25}_D$ −2.63° (neat); 50% ee (method, see Table II).

3-Methyl-1,5-hexadien-3-ol (9b). To the cooled solution (−78 °C) of **2** in ethyl ether (50 mmol, method A) was added 3-buten-2-one (4.05 mL, 50 mmol) dropwise with stirring. Stirring was continued for 4 h at −78 °C and then allowed to warm to 25 °C (~1 h). The reaction mixture was worked up as described in the experiment for 3-methyl-5-hexen-3-ol to provide **9b** (4.4 g, 79% yield): bp 65–68 °C (70 mmHg); $[\alpha]^{23}_D$ +1.46° (neat); 35% ee (method B).

2-Phenyl-4-penten-2-ol (9c). Acetophenone (5.82 mL, 50 mmol, was added dropwise to a stirred solution of **2** in ethyl ether

(15) For handling air- and moisture-sensitive compounds, see: Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-interscience: New York, 1975; p 191.

(16) Akiyama, S.; Hooz, J. *Tetrahedron Lett.* **1973**, 4115.

(50 mmol, method A) at −78 °C. The contents were stirred at −78 °C for 4 h and allowed to warm to 25 °C (~1 h). The reaction mixture was then worked up as described in the experiment for 3-methyl-5-hexen-3-ol to furnish **9c** (5.1 g, 63% yield): bp 81 °C (1 mmHg); $[\alpha]^{25}_D$ −0.91 (neat); 5% ee (method B).

3-Methyl-5-hexen-1-yn-3-ol (9d). 3-Butyn-2-one (3.4 g, 50 mmol) was added dropwise to a stirred solution of **2** in ethyl ether (50 mmol, method A) at −78 °C. Stirring was continued at −78 °C for 3 h and allowed to warm to 25 °C (~1 h). The reaction mixture was worked up as described in the experiment for 3-methyl-5-hexen-3-ol to provide **9d** (4.18 g, 76% yield): bp 71–73 °C (85 mmHg); $[\alpha]^{23}_D$ −14.89° (neat); 75% ee (method B).

Preparation of *B*-Methallyldiisopinocampheylborane (3) [$Ipc_2BCH_2C(CH_3)=CH_2$]. To the stirred solution of *B*-methoxydiisopinocampheylborane (50 mmol, 99% ee) prepared according to the method described in the preparation of *B*-allyldiisopinocampheylborane (method A) in 50 mL of anhydrous ethyl ether at −78 °C was added methallyllithium[16] (50 mmol) dropwise. The addition completed, the reaction mixture was stirred at −78 °C for 1 h and then allowed to warm to 25 °C (~1 h). The formation of $Ipc_2BCH_2C(CH_3)=CH_2$ was indicated by ^{11}B NMR (δ +84). This reagent was used as such for condensation reactions with various aldehydes.

4-Methyl-4-penten-2-ol (10a). To the cooled (−78 °C) solution of $Ipc_2BCH_2C(CH_3)=CH_2$ (50 mmol, prepared as above) was added acetaldehyde (2.8 mL, 50 mmol) dropwise with stirring. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C. The completion of the reaction was evident from ^{11}B NMR (δ +54). The organoboron intermediate was treated with 3 M NaOH (18 mL, 54 mmol), followed by 30% H_2O_2 (18 mL), and the contents were stirred at 30 °C for 3 h. After the usual workup, the residue was distilled under vacuum at 100–120 °C (bath, 20 mmHg) and the distillate was collected in a dry ice–acetone trap. The distillate was then passed through a small silica gel column. Elution with pentane removed the α-pinene and elution with ethyl ether provided **10a** (2.8 g, 56% yield): bp 72–74 °C (76 mmHg); $[\alpha]^{23}_D$ +4.94° (neat); 90% ee (method B).

5-Methyl-5-hexen-3-ol (10b). To the cooled solution (−78 °C) of **3** in ethyl ether/*n*-hexane (50 mmol) was added propionaldehyde (3.6 mL, 50 mmol) slowly. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C. The reaction mixture was oxidized and worked up as described in the experiment for 4-methyl-4-penten-2-ol to provide **10b** (3.0 g, 54% yield): bp 78–80 °C (60 mmHg); $[\alpha]^{23}_D$ −3.07° (neat); 90% ee (method B).

2-Methyl-1-hepten-4-ol (10c). To the cooled solution (−78 °C) of **3** in ethyl ether/*n*-hexane (50 mmol, prepared as above) was added *n*-butyraldehyde (4.4 mL, 50 mmol) slowly. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C. The reaction mixture was oxidized and worked up as described in the experiment for 4-methyl-4-penten-2-ol to provide **10c** (3.6 g, 56% yield): bp 104 °C (80 mmHg); $[\alpha]^{23}_D$ −9.53° (neat); 91% ee (method B).

2,5-Dimethyl-5-hexen-3-ol (10d). To the cooled solution (−78 °C) of **3** in ethyl ether/*n*-hexane (50 mmol, prepared as above) was added 2-methylpropionaldehyde (4.53 mL, 50 mmol) slowly. After complete addition of aldehyde, the reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 25 °C. The reaction mixture was oxidized and worked up as described in the experiment for 4-methyl-4-penten-2-ol to provide **10d** (3.6 g, 57% yield): bp 88–90 °C (54 mmHg); $[\alpha]^{23}_D$ +2.84° (neat); 96% ee (method B).

2,2,5-Trimethyl-5-hexen-3-ol (10e). To the cooled solution (−78 °C) of 3 in ethyl ether/*n*-hexane (50 mmol, prepared as above) was added 2,2-dimethylpropionaldehyde (5.42 mL, 50 mmol) slowly. The reaction mixture was stirred for 2 h at −78 °C and allowed to warm to 25 °C (~ 1 h). Then it was oxidized and worked up as described in the experiment for 4-methyl-4-penten-2-ol to provide **10e** (3.9 g, 55% yield): bp 94 °C (60 mmHg); $[\alpha]^{23}_D$ −0.65 (neat); 90% ee (method B).

5-Methyl-1,5-hexadien-3-ol (10f). To the cooled solution (−78 °C) of **3** in ethyl ether/*n*-hexane (50 mmol, prepared as above) was added acrolein (3.34 mL, 50 mmol) slowly. After complete addition of aldehyde, the contents were stirred for 1 h at −78 °C and then warmed up to 25 °C. The reaction mixture was oxidized and worked up as described in the experiment for 4-methyl-4-penten-2-ol to provide **10f** (2.8 g, 57% yield): bp 84–86 °C (70 mmHg); $[\alpha]^{23}_D$ −20.62° (neat); 92% ee (method B).

Preparation of (3,3-Dimethylallyl)diisopinocampheylborane (4) [$Ipc_2BCH_2CH=C(CH_3)_2$]. To the cooled (−25 °C) suspension of (+)-Ipc_2BH[8] (175 mmol, THF, 99% ee) prepared from (−)-α-pinene [$[\alpha]^{23}_D$ −47.20° (neat), 92% ee], was added 3-methyl-1,2-butadiene (17.5 mL, 175 mmol) slowly, and the reaction mixture was stirred at −25 °C for 6 h. The formation of $Ipc_2BCH_2CH=C(CH_3)_2$ is indicated by ^{11}B NMR (δ +81). The THF was pumped off at 25 °C (14 mmHg)/1 h, 25 °C (0.5 mm)/2 h and the residue was dissolved and diluted to 250 mL using ethyl ether. This standard solution of **4** in ethyl ether was used for condensation reaction with various aldehydes.

3,3-Dimethyl-4-penten-2-ol (11a). Acetaldehyde (1.4 mL, 25 mmol) was added dropwise to a stirred solution of **4** (25 mmol, 0.7 M in ethyl ether) at −78 °C. Stirring was continued at −78 °C for 12 h and then allowed to warm to 25 °C (~1 h). The completion of the reaction was evident from ^{11}B NMR (δ +55). The reaciton mixture was then treated with 3 N NaOH (36.6 mL, 100 mmol) followed by 30% H_2O_2 (15 mL), and the contents were refluxed for 2 h. The organic layer was separated and washed with water (50 mL) and brine (50 mL) and dried over anhydrous $MgSO_4$. The residue, after removal of the solvent, was distilled under vacuum at 100–120 °C (bath, 20 mmHg) and the distillate was collected in a dry ice–acetone trap. The distillate was then passed through a small silica gel column. Elution with pentane removed the α-pinene and elution with a mixture of ethyl ether and pentane (1:1) furnished **11a** (2.1 g, 73% yield): bp 86 °C (107 mm); $[\alpha]^{23}_D$ −5.95° (neat); 91% ee (method B); ^1H NMR ($CDCl_3$) δ 1.00 (s, 6 H), 1.13 (d, 3 H, J = 9 Hz), 1.71 (br s, 1 H), 3.55 (q, 1 H, 9 Hz), 5.00–5.20 (m, 2 H), 5.75–6.08 (m, 1 H); ^{13}C NMR ($CDCl_3/Me_4Si$), δ 17.58, 21.91, 22.95, 41.50, 73.94, 112.91, 145.32.

3,3-Dimethyl-1-hepten-4-ol (11b). To the cooled solution (−78 °C) of $Ipc_2BCH_2CH=C(CH_3)_2$ (25 mmol, 0.7 M in ethyl ether) was added *n*-butyraldehyde (2.2 mL, 25 mmol) slowly. After complete addition of the aldehyde, the contents were stirred at −78 °C for 12 h and then allowed to warm to 25 °C. The reaction mixture was oxidized and worked up as described in the experiment for 3,3-dimethyl-4-penten-2-ol to provide **11b** (2.8 g, 79% yield): bp 104 °C (86 mmHg); $[\alpha]^{23}_D$ −38.56° (neat); 92% ee (method B); ^1H NMR ($CDCl_3$) δ 0.85–1.10 (m, 9 H), 1.15–1.71 (m, 4 H), 3.35 (m, 1 H), 4.95–5.25 (m, 2 H), 5.73–6.10 (m, 1 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 13.98, 20.08, 22.50, 22.77, 33.69, 41.56, 78.00, 112.68, 145.62.

2,4,4-Trimethyl-5-hexen-3-ol (11c). To the cooled solution (−78 °C) of **4** (25 mmol, 0.7 M in ethyl ether) was added 2-methylpropionaldehyde (2.3 mL, 25 mmol) slowly. The contents were stirred for 12 h at −78 °C and then allowed to warm to 25 °C. The reaction mixture was worked up as described in the experiment for 3,3-dimethyl-4-penten-2-ol to provide **11c** (2.6 g, 73% yield): bp 91 °C (45 mmHg); $[\alpha]^{23}_D$ −27.95° (neat); 89% ee (method B); ^1H NMR ($CDCl_3$) δ 0.90 (d, 3 H, J = 3 Hz), 1.10 (m, 9H), 1.62 (d, 1 H, J = 9 Hz)8 1.80–2.10 (m, 1 H), 3.20 (m, 1 H), 5.00–5.22 (m, 2 H), 5.88–6.18 (m, 1 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 16.73, 23.13, 23.93, 24.17, 29.24, 42.00, 82.17, 111.50, 145.87.

4,4-Dimethyl-1,5-hexadien-3-ol (11d). Acrolein (1.66 mL, 25 mmol) was added dropwise to a stirred solution of **4** (25 mmol, 0.7 M in ethyl ether) at −78 °C. The contents were stirred for 12 h at −78 °C and then allowed to warm to 25 °C. The reaction mixture was worked up as described in the experiment for 3,3-dimethyl-4-penten-2-ol to provide **11d** (2.2 g, 70% yield): bp 140–141 °C (740 mmHg); $[\alpha]^{23}_D$ −41.53° (neat); 95% ee (method B); ^1H NMR ($CDCl_3$) δ 1.05 (s, 6 H) 1.83 (br s, 1 H), 3.85 (m, 1 H), 5.00–5.45 (m, 4 H), 5.80–6.10 (m, 2 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 22.11, 23.26, 41.14, 79.47, 113.10, 116.39, 137.51, 144.95.

3,3,6-Trimethyl-1,5-heptadien-4-ol: Artemisia Alcohol (11e). 3-Methyl-2-butenal[13] (1.9 g, 20 mmol) was added dropwise to a stirred solution of **4** (20 mmol, 0.7 M in ethyl ether) at −78 °C. After complete addition of aldehyde, the contents were stirred at −78 °C for 12 h and then allowed to warm to 25 °C. The reaction mixture was worked up as described in the experiment for 3,3-dimethyl-4-penten-2-ol to furnish **11e** (2.5 g, 85% yield): bp 98 °C (28 mmHg); $[\alpha]^{23}_D$ −32.12° (neat); 96% ee (method B); ^1H NMR ($CDCl_3$) δ 1.00 (s, 6 H), 1.50 (br s, 1 H), 1.70 (s, 3 H), 1.75 (s, 3 H) 4.10 (d, 1 H, J = 15 Hz), 5.00–5.35 (m, 3 H), 5.85–6.18

(m, 1 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 18.43, 21.49, 23.81, 25.95, 41.87, 74.64, 112.98, 124.45, 135.98, 145.25.

Preparation of *B*-(Allyllimonyl)borane (18). To the cooled solution (−78 °C) of *B*-(chlorolimonyl)borane[17] (5.53 g, 30 mmol) in ethyl ether (35 mL) was added allylmagnesium bromide in ethyl ether (25.4 mL, 1.18 M, 30 mmol) dropwise with stirring. The contents after stirring at −78 °C for 15 min were allowed to warm to 25 °C (~1 h). The formation of *B*-(allyllimonyl)borane was evident by ^{11}B NMR (δ +85). This reagent was then treated with acetaldehyde at −78 °C to furnish 4-penten-2-ol.

Preparation of *B*-Allyldi-10-pinanylborane (19). β-Pinene [16.8 mL, 105 mmol, $[\alpha]^{23}_D$ −21.4° (neat)] was added dropwise to the stirred solution of $H_2BCl{\cdot}OEt_2$[9] (50 mL, 1 M, 50 mmol) at 0 °C. The contents were stirred at 0 °C for 2 h to furnish *B*-chlorodi-10-pinanylborane; ^{11}B NMR (δ +77). It was then cooled to −78 °C and allylmagnesium bromide in ethyl ether (42.3 mL, 1.18 M, 50 mmol) was added dropwise. Stirring was continued for 15 min at −78 °C and the reaction mixture was allowed to warm to room temperature (~1 h). Formation of **19** was indicated by ^{11}B NMR (δ +86). **19** was then used for condensation reaction at −78 °C with acetaldehyde to furnish 4-penten-2-ol.

***B*-Allyldilongifolylborane (20).** The stirred suspension of dilongifolylborane[18] (21.1 g, 50 mmol, prepared from longifolene; $[\alpha]^{23}_D$ +42.2° (*c* 4.6, $CHCl_3$) in THF (50 mL) was treated with methanol (4 mL, 100 mmol). The residue after removal of solvents (14 mmHg/1 h; 1 mmHg/1 h) was dissolved in anhydrous ethyl ether (40 mL) and the resulting solution was cooled to −78 °C. To this was added allylmagnesium bromide in ethyl ether (42.3 mL, 1.18 M, 50 mmol) dropwise with stirring. After complete addition of allylmagnesium bromide, the reaction mixture was allowed to warm to room temperature (~1 h). The formation of **20** was then used for the condensation reaction with acetaldehyde at −78 °C to furnish 4-penten-2-ol.

***B*-Allylbis(10-methylisopinocampheyl)borane (21).** 10-Methyl-α-pinene [9.2 mL, 52.5 mmol, $[\alpha]^{23}_D$ −42.2° (neat)] was added to the stirred solution of $H_2BCl{\cdot}OEt_2$[9] (25 mL, 1 M, 25 mmol) at 0 °C. After complete addition of 10-methyl-α-pinene, the reaction mixture was stirred for 1 h at 0 °C to furnish *B*-chlorobis(10-methylisopinocampheyl)borane. It was then cooled to −78 °C and allylmagnesium bromide in ethyl ether (21.2 mL, 1.18, 25 mmol) was added dropwise. Stirring was continued for 15 min at −78 °C and then it was allowed to warm to room temperature (~1 h). The formation of *B*-allylbis(10-methylisopinocampheyl)borane was indicated by ^{11}B NMR (δ +85). **21** was then used for the condensation reaction at −78 °C with acetaldehyde to furnish 4-penten-2-ol.

***B*-Allyldiisocaranylborane (22).** To the stiirred solution of $BH_3{\cdot}SMe_2$ (5 mL, 50 mmol) in THF (20 mL) at 0 °C was added dropwise 3-carene [18.25 mL, 115 mmol, $[\alpha]^{23}_D$ +18° (neat)]. The mixture was stirred at 0 °C for 1 h and stored at 0 °C for 15 h. The resulting dialkylborane was treated with methanol (4 mL, 100 mmol) at 0 °C (15 min, 25 °C/1 h). The reaction was indicated by ^{11}B NMR (δ +55). The solvents were removed under vacuum (14 mmHg/1 h; 1 mmHg/2 h). The residue was dissolved in anhydrous ethyl ether (40 mL) and the clear solution was cooled to −78 °C. Allylmagnesium bromide in ethyl ether (42.3 mL, 1.18 M, 50 mmol) was then added dropwise with stirring. After 15 min at −78 °C, the reaction mixture was allowed to warm to 25 °C (~1 h). The formation of **22** was indicated by ^{11}B NMR (δ +85.8). **22** was then used for condensation reactions with various aldehydes.

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Hydroboration. 75. Directive Effects in the Hydroboration of Vinyl and Propenyl Heterocycles with Representative Hydroborating Agents

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The hydroboration of representative heterocyclic compounds bearing a vinyl or propenyl substituent with borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane (Chx_2BH), and disiamylborane (Sia_2BH) was investigated systematically to establish directive effects in the hydroboration. The directive effects observed for 2-vinylfuran and 2-vinylthiophene are similar to those realized in styrene. The hydroboration of vinylpyridine required an excess of borane hydroborating agent. Alternatively, the nitrogen atom could be protected by complexing with boron trifluoride. When the vinyl group is ortho or para to the pyridine nitrogen, α-organoboranes are the major products in the hydroboration. However, when the vinyl group is meta to the pyridine nitrogen, β-organoboranes are formed predominantly. Hydroboration of the vinylpyridine–BF_3 complexes results in an increase in the formation of α-organoboranes, as compared to β. The distribution of boron in the hydroboration of 2-propenyl heterocyclic compounds compared to that of *trans*-1-propenylbenzene showed that the effect of the heterocycle is pronounced in directing the boron atom strongly to the α-carbon atom.

The regioselectivity of borane addition to alkenes is dependent upon both steric and electronic effects exerted by the substituents on the hydrocarbon and also on the bulkiness of the hydroborating agent.[2,3] Electronic effects, viz., both inductive and mesomeric effects, play a major role in the hydroboration of functionalized olefins in directing the boron atom.[4-6] Vinyl substituents with strong +M effects direct the boron to the β-position and many

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