the m/z 130 ion when $^{18}O_2^{-}\cdot$ is used; (4) when phenyl benzoate is used as substrate, no m/z 126 ion is formed because ketene elimination has been blocked by substitution of phenyl for methyl and the requisite acidic hydrogen is no longer present. Thus, superoxide reacts with phenyl benzoate to give four anionic products: m/z 121 (benzoate), m/z 93 (phenoxide), m/z 108 (**2**), and m/z 137 (peroxybenzoate). As before, use of $^{18}O_2^{-}\cdot$ shifts the m/z 108 ion quantitatively to m/z 110, m/z 121 to m/z 123, and m/z 137 to m/z 141, which indicates that the products are formed by a mechanism similar to that for the phenyl acetate reaction.

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Registry No. 1, 85029-12-5; **2**, 20526-43-6; phenyl acetate, 122-79-2; phenyl benzoate, 93-99-2; superoxide, 11062-77-4; acetate, 71-50-1; peroxyacetate, 35683-46-6; phenoxide, 3229-70-7; peroxybenzoate, 35683-46-6; oxygen, 7782-44-7; propylene, 115-07-1; water, 7732-18-5; phenyl acetate-CD_3, 22705-27-7; $^{18}O_2^{-}$, 52227-59-5.

(17) Collision induced dissociation (CID) in FT MS involves the selection of the desired parent ion by ejection of all other ions prior to its translational excitation by "tickling" at its resonance frequency in the presence of a collision gas at a suitable pressure (ca. 10^{-6} torr).[18-20]

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Asymmetric Carbon-Carbon Bond Formation via *B*-Allyldiisopinocampheylborane. Simple Synthesis of Secondary Homoallylic Alcohols with Excellent Enantiomeric Purities

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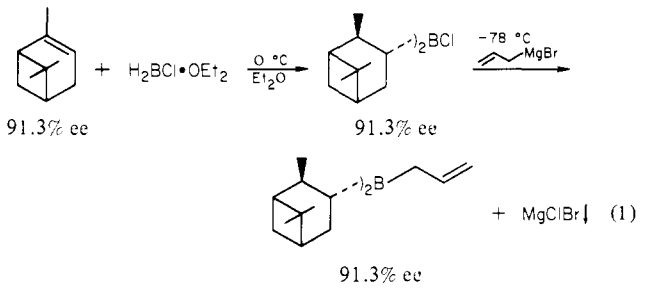
A new chiral allylborane, *B*-allyldiisopinocampheylborane ($Ipc_2BCH_2CH{=}CH_2$), has been conveniently prepared and successfully utilized for asymmetric carbon-carbon bond formation. Thus, *B*-chlorodiisopinocampheylborane (Ipc_2BCl), readily prepared by the hydroboration of α-pinene with chloroborane etherate ($H_2BCl{\cdot}OEt_2$), on treatment with allylmagnesium bromide, provides $Ipc_2BCH_2CH{=}CH_2$. Alternatively, it is prepared by the hydroboration-methanolysis of α-pinene, followed by the reaction of the borinate with allylmagnesium bromide. The new chiral allylborane undergoes condensation with a variety of aldehydes to furnish secondary homoallylic alcohols with enantiomeric purities in the range 83-96%.

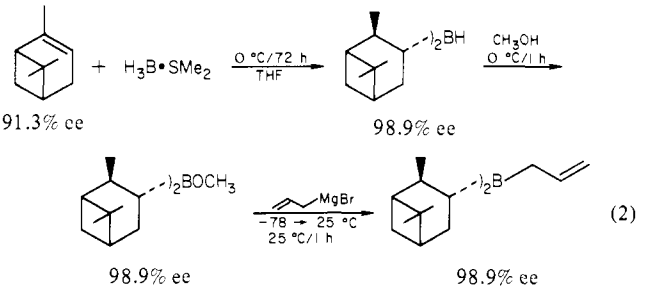
Allylboranes are extremely valuable intermediates in organic synthesis, particularly for carbon-carbon bond formation.[2] Use of chiral allylboranes for asymmetric carbon-carbon bond formation was not known until recently. Chiral allylboronates derived from camphor glycols have been successfully used for condensation with aldehydes.[3] In this reaction, the chirality of the boron ligand induces chirality at the new asymmetric center. In another report, chirality located in the allyl side chain of a borinic acid is efficiently transferred to form a new asymmetric center.[4] We now report a new chiral reagent, *B*-allyldiisopinocampheylborane, for the enantioselective, one-pot synthesis of a wide range of secondary homoallylic alcohols with excellent enantiometric purities.

Preparation of the chiral allylborane is extremely simple. Thus hydroboration of (+)-α-pinene with monochloroborane etherate[5] ($H_2BCl{\cdot}OEt_2$) in ethyl ether at 0 °C proceeds cleanly to Ipc_2BCl. This intermediate, on treatment with allylmagnesium bromide, at −78 °C, provides $Ipc_2BCH_2CH{=}CH_2$ (^{11}B NMR δ +78; eq 1).



91.3% ee 91.3% ee 91.3% ee

An alternative procedure involves hydroboration of (+)-α-pinene with $BH_3{\cdot}SMe_2$,[6] equilibration at 0 °C for 3 days to give a reagent approaching 100% ee,[7] followed by methanolysis of the Ipc_2BH to Ipc_2BOCH_3. the reaction of allylmagnesium bromide with Ipc_2BOCH_3 is slow at −78 °C but rapid at room temperature (eq 2). The reagent can be readily isolated as the neat liquid, free



91.3% ee 98.9% ee 98.9% ee 98.9% ee

of magnesium salts and solvent, by passing the reaction mixture through a filtration chamber,[8] followed by pumping off the solvents. However, it is generally more convenient to react the reagent with the aldehyde without prior isolation.

Thus, *B*-allyldiisopinocampheylborane, on treatment with acetaldehyde at −78 °C, undergoes condensation to provide, after the usual alkaline hydrogen peroxide workup, 4-penten-2-ol in 93% ee (eq 3, R = CH_3).

Similarly, propionaldehyde, *n*-butyraldehyde, 2-methylpropionaldehyde, and 2,2-dimethylpropionaldehyde readily react at −78 °C with $Ipc_2BCH_2CH{=}CH_2$ to furnish, after oxidation, the corresponding homoallylic alcohols with remarkable enantiomeric purities (Table I). The percent 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.[3]

The following experimental procedure is representative.[8] Diisopinocampheylborane 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

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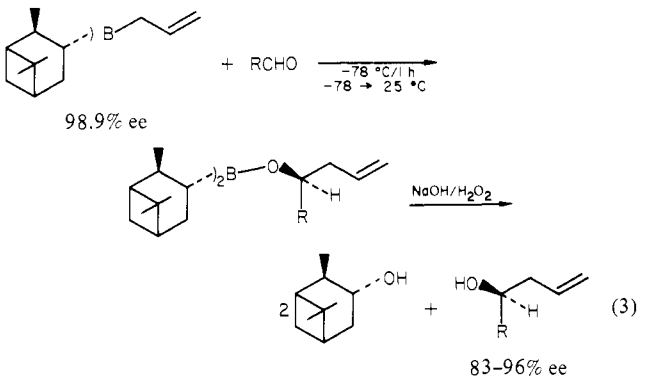
Table I. Allylboration of Aldehydes with *B*-Allyldiisopinocampheylborane

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

[a] The percent ee were independently determined by ^{19}F NMR of the MTPA esters[10] of the alcohols by using a Varian XL-200 spectrometer and found in close agreement with the literature[3] except in the case of 1-phenyl-3-buten-1-ol. [b] The percent ee is confirmed both by ^1H NMR in the presence of chiral shift reagent $Eu(hfc)_3$ and by ^{19}F NMR of the MTPA ester[10] by using a Varian XL-200 spectrometer. [c] Based on ref 3c. In all cases the addition of the allyl group to the aldehyde takes place in the same stereochemical sense, but the Cahn-Ingold-Prelog notations for the products differ because of peculiarities in the priority assignments.



(3)

R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $(CH_3)_3C$, Ph

the reported procedure.[6] Ipc_2BH (50 mmol) in THF was treated at 0 °C with 4.0 mL (100 mmol) of methanol (**Caution**: H_2 evolution). The reaction mixture was stirred at 25 °C for 1 h, the solvents were removed under vacuum (14 mm, 1 h; 1 mm, 2 h), and the residue was dissolved in anhydrous ethyl ether (50 mL) and then cooled to −78 °C. To the borinate was then added dropwise 42.3 mL (50 mmol) of 1.18 M allylmagnesium bromide in ethyl ether. The reaction mixture, after stirring for 15 min 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 precipitation of the magnesium salts as well as by ^{11}B NMR (δ +78). The allylborane was cooled to −78 °C, and 2.8 mL (50 mmol) of acetaldehyde was added dropwise with stirring. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm up to 25 °C (~1 h). The completion of the reaction was evident from ^{11}B NMR (δ +55). The reaction mixture was treated with 36.6 mL (110 mmol) of 3 N NaOH and 15 mL of 30% H_2O_2, 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 and passed through silica gel to remove any α-pinene (elution with pentane). Elution with a mixture of ethyl ether and pentane (1:4) furnished 4-penten-2-ol: bp 115 ° (746 mmHg); 3.2 g (74%); $[\alpha]^{23}_D$ −9.08° (c 9.18, Et_2O); 93% ee.

The present communication once again demonstrates the superior chiral-directing property of the 3-pinanyl group in asymmetric synthesis.[9] The reaction is apparently quite general and apparently does not depend on the nature of the aldehyde. Even the aldehyde with sp^2 CHO linkage provides alcohol of very high ee (Table I, entry 6) in contrast to the earlier conclusion.[3] The absolute stereochemistry is the same in all cases examined. This one-pot method is operationally very simple, makes use of readily available chemicals, and provides access to both enantiomers by selecting the proper antipode of α-pinene for preparation of the reagent. The effect of the change in the chiral ligand on boron and structural changes in the allyl side chain are matters of considerable interest, and we are actively investigating their effects.

Acknowledgment. The financial support from the National Institutes of Health is gratefully acknowledged (Grant GM 10937-20). The Varian XL-200 spectrometer was purchased with funds from NSF Grant CHE-8004246. This support is also gratefully acknowledged.

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