Chiral Synthesis via Organoboranes. 27. Remarkably Rapid and Exceptionally Enantioselective (Approaching 100% ee) Allylboration of Representative Aldehydes at -100 °C under New Salt-Free Conditions

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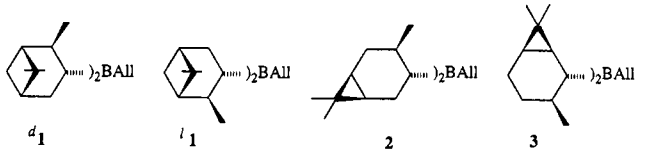
In the absence of magnesium salts (from the synthesis of the reagents), our chiral *B*-allylditerpenylborane reagents (Ter_2*$BCH_2CH{=}CH_2$, **1-3**) react with representative aldehydes (RCHO, R = Me, *n*-Pr, *i*-Pr, *t*-Bu, vinyl, and Ph) practically instantaneously at -100 °C to give homoallylic alcohols (R*$CH(OH)CH_2CH{=}CH_2$) with optical purities approaching 100% ee. The exceptional reaction rate achieved at -100 °C indicates that these allylborations are among the fastest reactions presently known to the organic chemist. The short reaction time adopted (≤0.5 h) greatly facilitates maintaining the reaction temperature at -100 °C. In this way, *B*-allyldiisopinocampheylborane (^{d}Ipc_2BAll, ^{d}**1**) gives homoallylic alcohols of ≥96-99% ee, *B*-allylbis(4-isocaranyl)borane (4-^{d}Icr_2BAll, **2**) affords alcohols of ≥98% ee and *B*-allylbis(2-isocaranyl)borane (2-^{d}Icr_2BAll, **3**) provides alcohols of ≥99% ee. The enantioselectivities (≥99% ee) achieved in allylboration by the reagent **3** are essentially perfect, making this one of the most stereoselective reactions currently known in organic chemistry.

Our standard method for the asymmetric allylboration of aldehydes involves the reaction of representative aldehydes with *B*-allyldiisopinocampheylborane (^{d}Ipc_2BAll, ^{d}**1**, and ^{l}Ipc_2BAll, ^{l}***1***), *B*-allylbis(4-isocaranyl)borane (4-^{d}Icr_2BAll, **2**), and *B*-allylbis(2-isocaranyl)borane (2-^{d}Icr_2BAll, **3**) at -78 °C in Et_2O, in the presence of Mg^{2+} salts (procedure A, Scheme I). The reactions performed in this manner require 1-3 h for completion.[1,2]

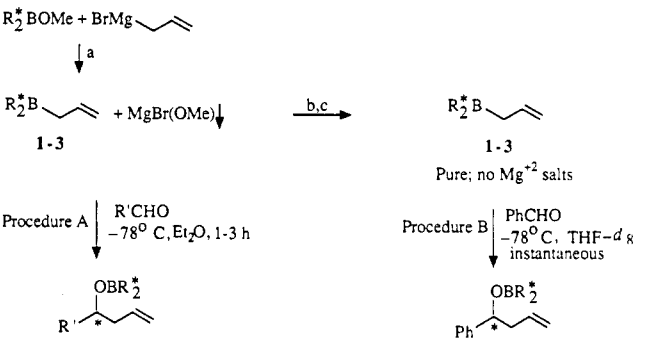


^{d}**1** ^{l}**1** **2** **3**

Recently, we reported a high-field variable-temperature ^1H and ^{11}B NMR spectroscopic study of the factors which control the rate of allylboration.[3] For this study, we needed to remove the suspended magnesium salts so as to have homogeneous solutions for the rate measurements. To our surprise, we found that the rates of allylboration of benzaldehyde with ^{d}Ipc_2BAll (^{d}**1**), ^{l}Ipc_2BAll (^{l}**1**), 4-^{d}Icr_2BAll (**2**), and 2-^{d}Icr_2BAll (**3**) are essentially instantaneous at -78 °C (procedure B, Scheme I). Clearly, we had discovered an unexpected phenomenon. Under the standard allylboration conditions, which we have so far been utilizing (viz., -78 °C, MgBrOMe salt present), our reactions require much longer reaction periods (1-3 h) for completion, whereas the allylborations are practically instantaneous under the NMR experimental conditions (-78 °C, MgBrOMe salt absent).

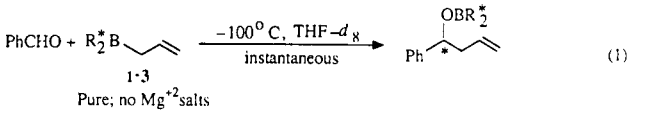
We reasoned that *in our standard procedure,[1,2] the rate of allylboration must be inhibited by the Mg^{2+} salts present in the reaction mixture, whereas the true rates of allylboration[4] at -78 °C by our reagents **1-3** were revealed only in the absence of Mg^{2+} salts* (*Note*: We refer to MgBrOMe as Mg^{2+} salts because we do not know whether it exists in the reaction mixture as a single component or as an equilibrium mixture of salts).

Scheme I[a]



[a] (a) -78 °C, 1 h; -78 to 25 °C, 1 h; (b) pentane extraction; (c) pentane evaporation (10 Torr).

The exceptional reactivity exhibited by our reagents **1-3** in the absence of Mg^{2+} salts at -78 °C prompted us to explore the allylborations of benzaldehyde with these reagents at -100 °C, under identical conditions. In fact, by 200-MHz ^1H NMR spectroscopy, we found that, *in the absence of magnesium salts, benzaldehyde undergoes practically instantaneous allylborations in THF-d_8 with $^{d\,or\,l}$$Ipc_2$BAll (**1**), 4-^{d}$Icr_2$BAll (**2**), and 2-^{d}$Icr_2$BAll (**3**), even at -100 °C*[4] (eq 1).



(1)

Consequently, we examined the allylborations of representative aldehydes with *B*-allyldiisopinocampheylborane (^{d}Ipc_2BAll, ^{d}**1**) at -100 °C in ether,[4] in the absence of Mg^{2+} salts. We were gratified to observe that all of the allylborations are exceptionally facile.[5] At the same time, major increases in optical purities of the product homoallylic alcohols are also achieved. Thus, the % ee of the

(1) Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432.
(2) Brown, H. C.; Randad, R. S.; Bhat, K. S.; Zaidlewicz, M.; Racherla, U. S. *J. Am. Chem. Soc.* **1990**, *112*, 2389.
(3) Brown, H. C.; Racherla, U. S.; Pellechia, P. J. *J. Org. Chem.* **1990**, *55*, 1868.
(4) In a model study (see ref 3), we established that allylborations occur most rapidly in Et_2O, while THF slows down the rate: viz., $Et_2O \geq CS_2 \geq CHCl_3 \geq CH_2Cl_2 >$ toluene $\gg$ THF. However, in our ^1H NMR studies on the rates of allylborations of **1-3**, THF-d_8 was used as it was readily available.
(5) Although ^1H NMR studies showed the rates of allylborations at -100 °C to be instantaneous, we adopted a standard reaction time of 0.5 h in all of our bench-scale allylborations at -100 °C as a precautionary measure to permit the complete utilization of less reactive aldehydes.

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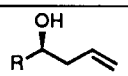
Table I. Comparison of the Percent Enantioselectivities Achieved in the Allylborations of Representative Aldehydes with ^{d}Ipc$_2$BAll (1)[a] at −78 °C and −100 °C in Et$_2$O

aldehyde (RCHO)	R		% ee −78 °C[b]	% ee −100 °C[c]
acetaldehyde	Me	(*R*)-4-penten-2-ol	92[d]	≥99[d]
n-butyraldehyde	*n*-Pr	(*R*)-1-hepten-4-ol	86[e]	96[e]
isobutyraldehyde	*i*-Pr	(*S*)-2-methyl-5-hexen-3-ol	88[d]	96[d]
pivalaldehyde	*t*-Bu	(*S*)-2,2-dimethyl-5-hexen-3-ol	83[f]	≥99[d]
acrolein	vinyl	(*S*)-1,5-hexadien-3-ol	92[d]	96[d]
benzaldehyde	Ph	(*S*)-1-phenyl-3-buten-1-ol	94[d]	96[d]

[a] Use of ^{l}Ipc$_2$BAll [^{l}*I* derived from (−)-α-pinene] provides products of opposite absolute configuration. [b] 1 h, Mg^{2+} salts present. See ref 1. [c] Instantaneous, Mg^{2+} salts absent. [d] Determined by capillary GC analysis of the corresponding (+)-Mosher ester. [e] Determined by capillary GC analysis of the methylcarbonates. See ref 18b. [f] Determined by the comparison of optical rotations.

homoallylic alcohols produced could be raised from 83–94% ee at −78 °C to ≥96–99% ee at −100 °C. Table I summarizes these results.

Encouraged by the remarkable enantioselectivities achieved with ^{d}Ipc$_2$BAll (^{d}**1**) at −100 °C, we extended the study to the allylborations of representative aldehydes with *B*-allylbis(4-isocaranyl)borane (4-^{d}Icr$_2$BAll, **2**) and *B*-allylbis(2-isocaranyl)borane (2-^{d}Icr$_2$BAll, **3**), also at −100 °C in Et$_2$O, in the absence of Mg^{2+} salts. We hoped that these two complementary reagents[6] might achieve still higher enantioselectivities. Indeed, 4-^{d}Icr$_2$BAll (**2**) provided chiral homoallylic alcohols of ≥98% ee and 2-^{d}Icr$_2$BAll (**3**) afforded homoallylic alcohols of ≥99% ee. The percent enantioselectivities realized in allylboration by 2-^{d}Icr$_2$BAll (**3**) are the highest described in the literature.[2,7] These results are described in Table II.

The Role of Mg^{2+} Salts. The 200-MHz ^{1}H NMR spectroscopic experiments conducted at −78 °C and −100 °C clearly established that the allylborations with our reagents **1–3** are instantaneous in the absence of Mg^{2+} salts. However, if the allylborations are conducted in the presence of Mg^{2+} salts formed during the synthesis of our reagents, the reactions require 1–3 h for completion at −78 °C.[1,2] Similarly, we also found that, in the presence of Mg^{2+} salts, our allylborations require even longer reaction periods (5–7 h) for 100% completion at −100 °C.[8a]

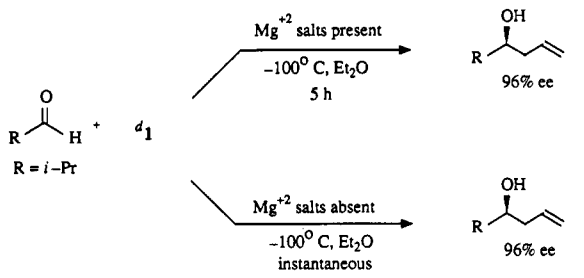
Perhaps, it is desirable to clarify this point. Normally, one maintains a reaction bath at −100 °C by frequent additions of liquid nitrogen to ethanol in a Dewar, and keeping a constant vigil on the reaction temperature. Indeed, it is very difficult to maintain a large Dewar at −100 °C in this manner, for any appreciable length of time. Consequently, performing allylborations at −100 °C for 5–7 h is extraordinarily painful and inconvenient. Fortunately, the allylborations are essentially instantaneous at −100 °C in the absence of Mg^{2+} salts.[5] Therefore, removal of the Mg^{2+} salts from the reaction mixture is extremely important.

(6) 4-^{d}Icr$_2$BAll (2) and 2-^{d}Icr$_2$BAll (3) afford homoallylic alcohols of opposite absolute configurations in allylborations of aldehydes (Table II). See ref 2.

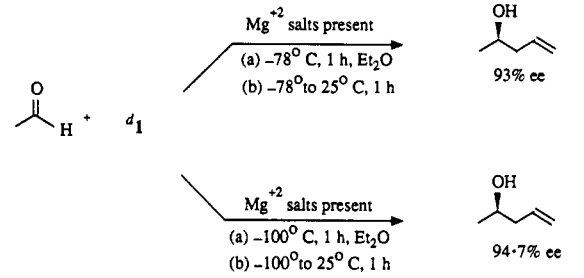
(7) (a) Hoffmann, R. W.; Herold, T. *Chem. Ber.* **1981**, *114*, 375. (b) Reetz, M. T.; Zierke, T. *Chem. Ind.* **1988**, 663. (c) Roush, W. R.; Walts, A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186. (d) Roush, W. R.; Banfi, L. *Ibid.* **1988**, *110*, 3979. (e) Short, R. P.; Masamune, S. *Ibid.* **1989**, *111*, 1892. (f) Corey, E. J.; Yu, C.-M.; Kim, S. S. *Ibid.* **1989**, *111*, 5495.

(8) (a) Brown, H. C.; Randad, R. S. unpublished results. (b) Brown, H. C.; Perumal, P. T. Unpublished results.

Scheme II



Scheme III



Further, we also investigated the effect of Mg^{2+} salts on the percent enantioselectivity of allylboration at −100 °C. We established that the presence or absence of Mg^{2+} salts in the reaction mixture has absolutely no effect on the percent enantioselectivity of allylboration (Scheme II).

In the past, we examined the effect of temperature on the percent enantioselectivity realized in allylboration.[1,8b] During that study, we compared the allylborations of acetaldehyde with ^{d}Ipc$_2$BAll (^{d}**1**), at −78 °C and −100 °C, *in the presence of Mg^{2+} salts*. In two separate experiments, (a) acetaldehyde was added to ^{d}Ipc$_2$BAll (^{d}**1**), in Et$_2$O at −78 °C and −100 °C, in the presence of the Mg^{2+} salts; (b) the reaction mixture was stirred for 1 h, at −78 °C and −100 °C, and (c) the reactions were warmed up to 25 °C, over a period of 1 h.[1,8b] While the allylboration at −78 °C afforded (*R*)-(−)-4-penten-2-ol in 93% ee, the experiment at −100 °C provided a product of 94.7% ee (Scheme III).[1]

As there was no significant improvement in the % ee of products, by decreasing the allylboration temperature from −78 °C to −100 °C, we recommended the −78 °C temperature for the allylboration of aldehydes with our reagents. However, at that time, we did not recognize the major effect of Mg^{2+} salts. Clearly, the reaction at −100 °C must be only partially complete in 1 h, in the presence of Mg^{2+} salts (see Scheme II), and most of the reaction must have occurred at higher temperature, as the reaction mixture was warmed up. It is important to note that we can now achieve the allylboration of acetaldehyde with ^{d}Ipc$_2$BAll (^{d}**1**) at −100 °C by the new salt-free procedure, essentially instantaneously, and obtain (*R*)-(−)-4-penten-2-ol in ≥99% ee (Table I).

Our study establishes the following: (1) *Allylborations with the reagents* **1–3** *are essentially instantaneous at −78 °C or −100 °C, only in the absence of Mg^{2+} salts.* (2) *By going from −78 °C to −100 °C, we achieve major enhancements in the percent enantioselectivities in allylboration, approaching 100%.* (3) *The presence or absence of Mg^{2+} salts in the reaction mixture has no effect on the percent enantioselectivities in allylboration.*

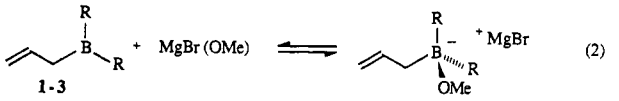
These results may be rationalized as follows: In the standard procedure (procedure A, Scheme I), our reagents **1–3** were utilized for allylborations of aldehydes at −78 °C, in the presence of Mg^{2+} salts. Under such conditions, MgBr(OMe) must complex with the highly electrophilic boron atom in our reagents (eq 2). The resulting complex

Table II. Comparison of the Percent Enantioselectivities Achieved in the Allylborations of Representative Aldehydes with 4-^{d}Icr$_2$BAll (2) and 2-^{d}Icr$_2$BAll (3) at −100 °C and Those Achieved by Other Reagents under Various Conditions

	% ee (achieved by various reagents)								
aldehyde (RCHO)	4[a] (Hoffmann)[b]	5[a] (Reetz)[c]	6[a] (Roush)[d]	7[a] (Roush)[e]	8[a] (Masamune)[f]	9[a] (Corey)[g]	10[a] (Masamune)[h]	2[i]	3[i]
acetaldehyde	86	96						≥99, *R*	≥99, *S*
n-butyraldehyde	72	96	(79)[j]	(94)[k]	(93)[l]	(95)[m]	(96)[l]	98, *R*	≥99, *S*
isobutyraldehyde	70	94			85		96	98, *S*	≥99, *R*
cyclohexanecarboxaldehyde			87	97	88	97	96		
pivalaldehyde	45	88	82	96	86		97	≥99, *S*	≥99, *R*
acrolein						(98)[n]	(97)[o]	98, *S*	≥99, *R*
benzaldehyde		88	71	85		95		98, *S*	≥99, *R*

[a] For structures of 4–10, see ref 2. [b] −78 °C → room temperature overnight (ref 7a). [c] −78 °C, 2 h; −78 °C → room temperature (ref 7b). [d] −78 °C, 1 h (ref 7c). [e] −78 °C, 2–3 days (ref 7d). [f] −78 °C, 1 h; −78 °C → room temperature, 1 h (ref 7e). [g] −78 °C, 2 h (ref 7f). [h] −100 °C, 3 h (ref 7e). [i] −100 °C, essentially instantaneous. [j] For 1-decanal. [k] For (TBDPS)OCH$_2$CH$_2$CHO. [l] For 1-propanal. [m] For 1-hexanal. [n] For cinnamaldehyde. [o] For crotonaldehyde.

will become more stable, the lower the reaction temperature. Therefore, the rate of allylboration can slow down at −78 °C (1–3 h), in presence of the Mg^{2+} salts, due to low concentration of the free and reactive species, viz., the uncomplexed allylborane.



(2)

These effects should become even more pronounced at −100 °C. Indeed, the allylborations of aldehydes with these reagents are significantly slower at −100 °C (5–7 h), in the presence of this Mg^{2+} salt. On the contrary, the new allylboration procedure utilizes the reagents **1–3**, completely free of the Mg^{2+} salts. Under these salt-free conditions, the reagents are exceptionally reactive. They undergo practically instantaneous reactions with aldehydes at −78 °C, and even at −100 °C. Further, we can also understand why the percent enantioselectivities in allylboration are not affected by the presence or absence of Mg^{2+} salts. The species, which undergoes allylboration (viz., the uncomplexed allylborane reagent), is the same under both of those conditions. *Thus, there are two major effects: Instantaneous allylborations at −100 °C, realized entirely due to the absence of the MgBr(OMe) salt, and major enhancements in the percent enantioselectivities at −100 °C, attributable solely to the temperature effect.* The discovery of the magnesium salt effect makes practical, for the first time, the allylboration of aldehydes at −100 °C.

In this study, we developed improved procedures for the methanolysis of the *Ter$_2$BH (^{d}Ipc$_2$BH, ^{l}Ipc$_2$BH, 4-^{d}Icr$_2$BH, and 2-^{d}Icr$_2$BH) derivatives. We also simplified the procedures for the preparation of ^{d}Ipc$_2$BAll (^{d}**1**), ^{l}Ipc$_2$BAll (^{l}*1*), 4-^{d}Icr$_2$BAll (**2**), and 2-^{d}Icr$_2$BAll (**3**). Finally, we developed a simple procedure for the removal of MgBr(OMe) from our reagents. These procedures are fully described in the experimental section.

In summary, we describe a highly convenient procedure for the asymmetric allylboration of a variety of representative aldehydes with ^{d}Ipc$_2$BAll (^{d}**1**), ^{l}Ipc$_2$BAll (^{l}**1**), 4-^{d}Icr$_2$BAll (**2**), and 2-^{d}Icr$_2$BAll (**3**) at −100 °C in Et$_2$O, in the absence of Mg^{2+} salts. Under the new salt-free conditions, allylborations occur both instantaneously and with exceptional selectivity. Thus, while ^{d}Ipc$_2$BAll (^{d}**1**) affords homoallylic alcohols of ≥96–99% ee, 4-^{d}Icr$_2$BAll (**2**) provides alcohols of ≥98% ee, and 2-^{d}Icr$_2$BAll (**3**) affords alcohols of ≥99% ee. Further, our reagents **1–3** can be prepared by simple and efficient methods from readily available optically active terpenes.[9] Consequently, we believe that this allylboration procedure will become even more valuable for stereoselective natural product synthesis.[10] In conclusion, this study describes one of the fastest and probably the most stereoselective asymmetric synthesis currently known in organic chemistry.

Experimental Section

All reaction flasks and equipment were dried in an oven at 150 °C for at least 12 h and assembled hot while cooling under a stream of dry nitrogen gas. Special techniques for handling the air-sensitive materials are described elsewhere.[11] All solvents were distilled over $LiAlH_4$ and stored under nitrogen. Borane–methyl sulfide was purchased from Aldrich Chemical Company, and its molarity was determined by the automatic gasimeter prior to use.[11] The capillary GC analyses for the determination of optical purities of the derivatized product alcohols were performed on a Hewlett-Packard 5890 gas chromatograph.

Preparation of *B*-Methoxydiisopinocampheylborane (^{d}Ipc$_2$BOMe). To a solution of (+)-α-pinene (32.7 g, 240 mmol, $[\alpha]^{23}_D$ = +47.1° (neat), 91% ee) in THF (30 mL) was added rapidly borane–methyl sulfide (10.2 mL, 9.8 M, 100 mmol), while the reaction mixture was stirred. During the addition, the reaction flask was immersed in a water bath, held at 20–25 °C. Immediately following the addition, stirring was discontinued, and a positive pressure of nitrogen was maintained for 1 h. The reaction mixture was then allowed to stand overnight (≥12 h) to obtain a crystalline solid of diisopinocampheylborane (^{d}Ipc$_2$BH). Next, the flask was cooled in an ice bath for 1 h, and the supernatant liquid (containing excess α-pinene and methyl sulfide) was transferred into another flask. The solid was washed with anhydrous pentane (2 × 25 mL) and dried under vacuum (15 Torr; 1 h) to obtain a pure and white crystalline solid of ^{d}Ipc$_2$BH (24.3 g, 85%).[12] This solid is quite stable. It can be stored at 0 °C for several months, under nitrogen. Next, anhydrous ether (50 mL) was added to ^{d}Ipc$_2$BH (14.3 g, 50 mmol),[13] and the resulting suspension was cooled in an ice bath for 1 h. While stirring the reaction mixture, anhydrous methanol (1.92 g, 60 mmol, which was also precooled to 0 °C) was added dropwise over a period of 0.5 h. After the evolution of hydrogen ceased (0 °C, ≤ 2 h), a clear homogeneous solution was formed, indicating the completion of methanolysis (experience has shown that the methanolysis of ^{d}Ipc$_2$BH in Et$_2$O is faster and more convenient than the earlier procedure[1] in THF). Finally, the solvent, and excess methanol

(9) (+)-α-Pinene, (+)-3-carene, and (+)-2-carene, of very high optical purity, are available at low cost from the Aldrich Chemical Company.

(10) (a) Khandekar, G.; Robinson, G. C.; Stacey, A. N.; Steel, P. G.; Thomas, E. J.; Vather, S. *J. Chem. Soc., Chem. Commun.* **1987**, 877. (b) Merifield, E.; Steel, P. G.; Thomas, E. J. *Ibid.* **1987**, 1826. (c) Boeckman, R. K., Jr.; Charette, A. B.; Asberom, T.; Johnson, B. H. *J. Am. Chem. Soc.* **1987**, *109*, 7553. (d) Ireland, R. E.; Wipf, P.; Roper, T. D. *J. Org. Chem.* **1990**, *55*, 2284. (e) Merifield, E.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1990**, 464.

(11) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

(12) Brown, H. C.; Joshi, N. N. *J. Org. Chem.* **1988**, *53*, 4059.

(13) ^{d}Ipc$_2$BH was transferred into the reaction flask using a glovebag, under nitrogen. Alternatively, if one wishes to avoid this operation, the scale of preparation of ^{d}Ipc$_2$BH from (+)-α-pinene can be appropriately modified.

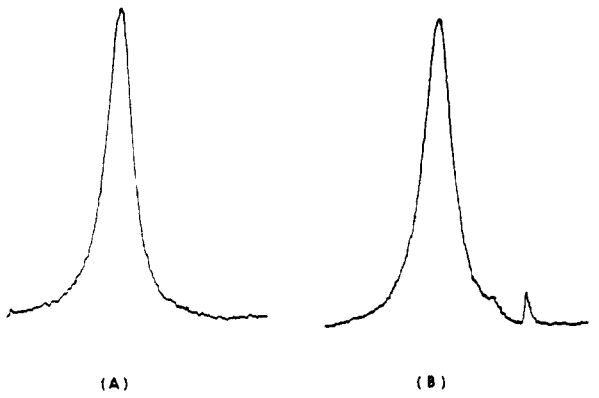


Figure 1. (a) $^{d}Ipc_2BOMe$ ($^{d}1$) in pure form; (b) $^{d}Ipc_2BOMe$ ($^{d}1$) in impure form, contaminated by the disproportionation products.

were stripped off under vacuum (15 Torr), to obtain a quantitative yield of *B*-methoxydiisopinocampheylborane ($^{d}Ipc_2BOMe$) of ≥99% optical purity.

CAUTION! Methanolysis of $^{d}Ipc_2BH$ is exothermic. If the methanolysis is carried out as described above, the ^{11}B NMR spectrum shows a single peak at δ 52, corresponding to *B*-methoxydiisopinocampheylborane, $^{d}Ipc_2BOMe$ (Figure 1A). On the other hand, a rapid addition of methanol, and/or insufficient cooling of the reaction mixture during methanolysis, results in the disproportionation of $^{d}Ipc_2BOMe$, by approximately 5–10% (Figure 1B). However, the reagent is more stable to disproportionation if 10–15% excess of α-pinene is added to the reaction mixture prior to methanolysis. It is important to note that contamination of $^{d}Ipc_2BOMe$ by such disproportionation products (viz., $RB(OMe)_2$, and $B(OMe)_3$ species) results in a reagent that is unsatisfactory. If such impure reagent is utilized further for the preparation of *B*-allyldiisopinocampheylborane ($^{d}1$), and subsequently in asymmetric allylborations, the percent enantioselectivities achieved will be significantly lower.

Preparation of *B*-Methoxybis(4-isocaranyl)borane (4-$^{d}Icr_2BOMe$). To a solution of (+)-3-carene (32.7 g, 240 mmol, $[\alpha]^{20}_D$ =+15° (neat), 85% ee) in THF (200 mL), which was cooled to 0 °C, was added dropwise borane–methyl sulfide (10.2 mL, 9.8 M, 100 mmol), while the reaction mixture was stirred. Following completion of the addition, stirring was discontinued, and the reaction mixture was maintained at 0 °C for 24 h. A white crystalline solid of bis(4-isocaranyl)borane (4-$^{d}Icr_2BH$) separated out. Once again, pure 4-$^{d}Icr_2BH$ (24 g, 84%)[14] was obtained by following the standard procedure described for $^{d}Ipc_2BH$. Methanolysis was also conducted in Et_2O, exactly as described above, to finally obtain a quantitative yield of *B*-methoxybis(4-isocaranyl)borane (4-$^{d}Icr_2BOMe$) of ≥99% optical purity.[15]

Preparation of *B*-Methoxybis(2-isocaranyl)borane (2-$^{d}Icr_2BOMe$). To a solution of borane–methyl sulfide (10.2 mL, 9.8 M, 100 mmol) in THF (200 mL), which was cooled to 0 °C, was added (+)-2-carene (32.7 g, 240 mmol), $[\alpha]^{20}_D$ = +92° (neat), over a period of 10 min, while the reaction mixture was stirred. Stirring was discontinued soon after the addition, and the reaction mixture was stored at 0 °C for 24 h. White needles of 2-$^{d}Icr_2BH$ separated out. The isolation of pure 2-$^{d}Icr_2BH$ (27.2 g, 86%)[16] was carried out by the same procedure described for $^{d}Ipc_2BH$. The methanolysis of 2-$^{d}Icr_2BH$ was also performed in Et_2O, in the same manner, to obtain a quantitative yield of *B*-methoxybis(2-isocaranyl)borane (2-$^{d}Icr_2BOMe$) or ≥99% optical purity.[15]

Preparation of the Allylborane Reagents $^{d}1$, $^{l}1$, 2, and 3 Free of MgBr(OMe). The following experimental procedure for 2-$^{d}Icr_2BAll$ (3) is representative for the preparation of all allylborane reagents. (This is an improvement over the earlier procedure,[1] which involved the addition of the Grignard reagent to the methoxy derivative at −78 °C.) Allylmagnesium bromide in ether (48 mL, 1.0 M, 48 mmol) was added dropwise to a well-stirred solution of *B*-methoxybis(2-isocaranyl)borane[2] (15.8 g, 50 mmol) at 0 °C. Following completion of addition, the reaction mixture was vigorously stirred for 1 h at 25 °C, and the solvents were pumped off under vacuum (14 mm, 2 h). The residue was extracted with pentane (2 × 100 mL) under nitrogen, and stirring was discontinued to permit the MgBr(OMe) salt to settle. The clear supernatant pentane extract (free from the magnesium salts) was transferred into another flask using a double-ended needle through a Kramer filter.[11] Evaporation of pentane (14 mm, 1 h; 2 mm, 1 h) afforded pure *B*-allylbis(2-isocaranyl)borane (2-$^{d}Icr_2BAll$, 3) in nearly quantitative yield.

Typical Procedure for the Allylboration of Representative Aldehydes with the Reagents $^{d}1$, $^{l}1$, 2, and 3. The following experimental procedure, described for the allylboration of acrolein with 2-$^{d}Icr_2BAll$ (3) in Et_2O at −100 °C, in the absence of Mg^{2+} salts, is representative. Anhydrous ether (100 mL) was added to 2-$^{d}Icr_2BAll$ (3), and the resulting solution was cooled to −100 °C. A solution of acrolein (2.8 g, 50 mmol) in ether (50 mL), maintained at −78 °C, was slowly added along the side of the flask to the solution of 2-$^{d}Icr_2BAll$ (3) at −100 °C. The reaction mixture was stirred for 0.5 h at −100 °C,[5] and methanol (1 mL) was added. The reaction mixture was then brought to room temperature (1 h) and treated with 3 N NaOH (20 mL) and 30% H_2O_2 (40 mL). The completion of oxidation was ensured by refluxing the reaction mixture for 3 h. The usual workup and distillation afforded (*R*)-1,5-hexadien-3-ol (bp 54 °C at 20 mm), yield 4.17 g (82%).[17] GC analysis of its Mosher ester [18] on a capillary Supelcowax column (15 m × 0.25 cm) established the alcohol to be ≥99% ee.

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