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Olefination and Hydroxymethylation of Aldehydes Using Knochel's (Dialkoxyboryl)methylcopper Reagents

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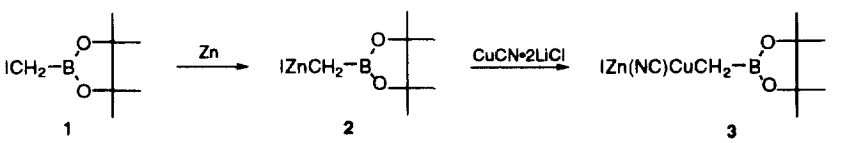
Abstract. The *in-situ* preparation of $[(Me_2C)_2O_2BCH_2]Cu(CN)ZnI$ (**3**) from Knochel's (dialkoxyboryl)-methylzinc reagent (**2**) and CuCN•2LiCl in THF, followed by its addition to aldehydes in the presence of boron trifluoride etherate yielded rather stable β-hydroxyalkylboronates (**5**). The thermal dehydroxyboronation or the alkaline hydrogen peroxide oxidation of **5** gave the corresponding alkenes (**6**) or 1,2-alkanediols (**7**) in high yields. The reaction provides a simple procedure for the olefination or the hydroxymethylation of aldehydes.

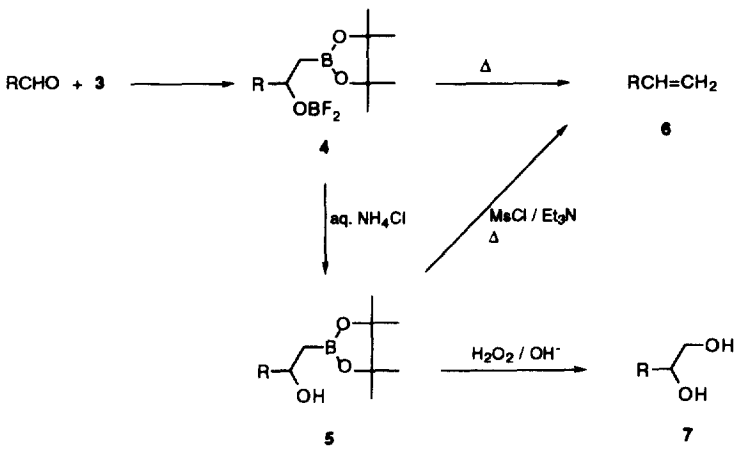
The synthesis of alkenes by the addition of certain lithium or magnesium α-silyl carbanions to aldehydes or ketones followed by the elimination of silanols is referred to as the Peterson olefination.[1] The β-hydroxysilane intermediates are often stable, and can subsequently be converted into the corresponding 1,2-diols on exposure to alkaline hydrogen peroxide.[2] The corresponding boron-Wittig olefination[3] using α-boryl carbanions has been extensively studied by Pelter[4] and Matteson.[5] The condensation of dimesitylboryl carbanions with carbonyl compounds gives either *E*- or *Z*-alkenes, or a mixture of the two in most cases.[4] The addition of a lithio bis(dialkoxyboryl)methane to aldehydes or ketones provides a convenient procedure for producing 1-alkenylboronates from carbonyl compounds.[5] The 1,2-oxaboretaninide intermediate of the boron-Wittig reaction was recently isolated and fully characterized by Okazaki.[6] The reactions are complementary to the Wittig reaction; however, the boryl carbanion may give better results for sterically hindered carbonyl compounds or gives opposite stereoselectivity.



1 2 3 (1)

A preparation of zinc and copper α-boryl carbanions (**2** and **3**)[7] developed by Knochel are able to accommodate various functional groups and display an excellent reactivity toward electrophiles such as allylic halides, acyl halides, and various types of Michael acceptors. We previously reported that the

palladium-catalyzed cross-coupling reaction of **2** offers unique advantages for the syntheses of allylic[8] and benzylic[9] boronates. In connection with these studies, we undertook the addition reaction of the α-boryl carbanions to aldehydes. Terminal alkenes **6** and 1,2-alkandiols **7** are easily obtained in high yields by the addition of **3** to aldehydes in the presence of boron trifluoride etherate, followed by dehydroxyboronation or oxidation with alkaline hydrogen peroxide, respectively (Scheme 1). Although the procedure for hydroxymethylation of 1-naphthaldehyde was first reported by Knochel,[7] we wish to report the scope and the conditions since only limited information was now available on this process.



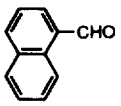
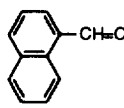
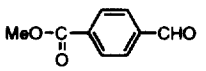
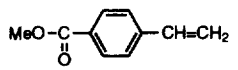
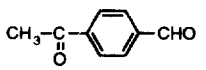
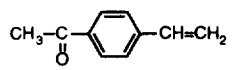
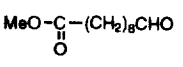
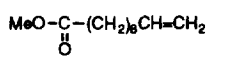
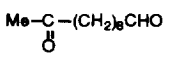
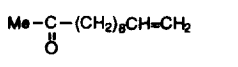
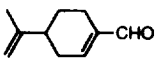
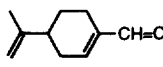
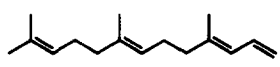
Scheme 1. Addition of Knochel's Borylmethylcopper Reagent to Aldehyde

The conditions were optimized by the addition of **3** to 1-naphthaldehyde giving **6** (R=naphthyl). Two equivalents of **3** were prepared from **2**, CuCN, and two equivalents of LiCl in THF at -30 °C. An aldehyde (1 equiv) and BF_3•OEt_2 (2 equivs) were successively added at -78 °C, the mixture was then slowly warmed to room temperature, and finally refluxed for 1 h to give 1-vinylnaphthalene in a 44% yield. The yield was improved to 84% using four equivalents (two equivalents toward **3**) of BF_3•OEt_2. The reported procedure for the addition of organocopper(I) reagents to aldehydes recommended the use of one equivalent of BF_3•OEt_2 toward the copper reagents;[10] however, an excess of BF_3•OEt_2 can be necessary since the boron-stabilized **3** has a lower nucleophilicity than the usual organocopper(I) reagents. The preparation of **3** from CuBr•SMe_2 gave a 75 % yield of vinylnaphthalene under similar reaction conditions.

Table 1 summarizes the boron-Wittig methylenation of representative aldehydes. The reaction proceeded smoothly for aromatic aldehydes (entries 1-3) and α,β-unsaturated aldehydes (entries 9 and 10). For aromatic or α,β-unsaturated aldehydes, the elimination smoothly occurred by refluxing the reaction mixture for 1 h (*procedure A*). However, lower yields resulted for the aliphatic aldehydes (entries 5-8) since the intermediates **4** are quite stable forward the elimination. Alternatively, higher yields were

achieved by converting the hydroxy group into a better leaving group. The mesylation of **5** with methanesulfonyl chloride (1 equiv) and triethylamine (2 equiv) before refluxing the reaction mixture gave good yields of alkenes (*procedure B*) (entries 6-9). The reaction is available with various functional groups. Aromatic and aliphatic esters are quite inert to the reaction (entries 2 and 7), and no reaction was observed with ketone carbonyls, thus chemoselectively providing a terminal alkene from a ketoaldehyde (entries 3 and 8). Although the olefination of aldehydes with (diarylboryl)methyllithiums suffered from the Cannizzaro-type side reaction,[4] such by-products and Aldol products were noticeably small amounts since the copper reagent **3** has relatively low basicity.

Table 1. Methylenylation of Aldehydes *via* the Boron-Wittig Reaction

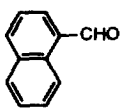
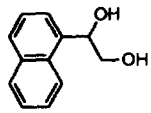
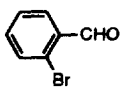
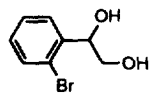
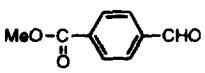
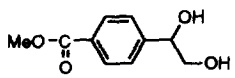
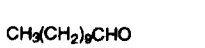
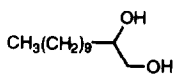
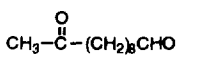
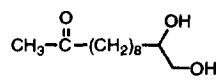
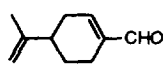
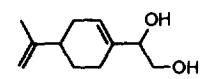
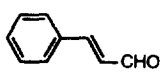
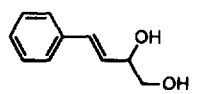
entry	aldehyde	procedure	product	yield/%
1		A		(84)
2		A		84
3		A		64
5	$CH_3(CH_2)_9CHO$	A	$CH_3(CH_2)_9-CH=CH_2$	57
6		B		(86)
7		B		77
8		B		73
9		B		69
10	farnesal	A		78

[a]Procedure A: The intermediate (**4**) was refluxed for 2-7 h.
Procedure B: The isolated **5** was mesylated with $MeSO_2Cl$ and Et_3N in THF and then refluxed for 3 h.
[b]Isolated yields by chromatography and GC yields are shown in the parentheses.

Although the β-elimination from the β-hydroxyboronate is generally very rapid at low temperature,[4a] **5** was unusually stable enough to be isolated due to the low Lewis acidity of boron atom and the steric hindrance of the bulky pinacol moiety. Thus, the isolation of **5** and the subsequent oxidation with alkaline hydrogen peroxide gave 1,2-alkanediols (**7**) in high yields (Scheme 1). The representative results are summarized in Table 2.

Aromatic and aliphatic aldehydes were quantitatively converted to the diols without any difficulties (entries 1-4). α,β-Unsaturated aldehydes such as perillaldehyde and cinnamaldehyde also gave the corresponding diols (entries 6 and 7); however, the reaction with farnesal resulted in a very low yield because the alkene formation from **4** or **5** was very rapid at room temperature. It is interesting to note that **3** selectively added to the carbonyl of α,β-unsaturated aldehydes in contrast to the conjugated 1,4-addition of usual organocopper(I) reagents.[7] Ketoaldehydes such as 10-oxoundecanal shown in entry 5 also resulted in a relatively low yield, presumably due to the competitive Baeyer-Villiger oxidation of the ketone carbonyl during the alkaline hydrogen peroxide oxidation.

Table 2. Synthesis of 1,2-Diols

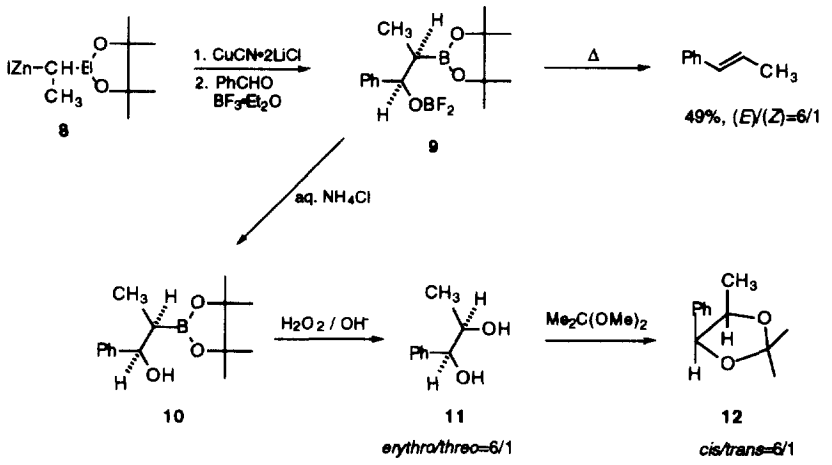
entry	aldehyde	product	yield/%[a]
1			90
2			83
3			93
4			91
5			34 (55)[b]
6			57
7			96

[a] Isolated yields based on the aldehydes. [b] The yield of the corresponding acetone acetal.

The reaction gives a mixture of the expected 1,2-diol and pinacol, separation of which is often difficult by chromatography. The sublimation of pinacol in *vacuo* or the recrystallization of the mixture can be a convenient way to obtain the analytically pure diols; however, the substrates forming solid diols (entries 1-4, 7) may give higher isolated yields than the oily products (entries 5 and 6).

To examine the stereoselectivity, the reaction of a secondary zinc reagent (**8**) with benzaldehyde

was carried out under similar reaction conditions. The stereochemistry of main products and their selectivity are shown in Scheme 2. The addition-dehydroxyboronation sequence gave a mixture of *trans*- and *cis*-1-phenylpropene in a ratio of 6 : 1. The work-up with NH_4Cl solution gave the β-hydroxyboronate intermediate (**10**) as a diastereomeric mixture of 6 : 1. Very interestingly, **10** is unusually stable enough to be isolated by silica gel chromatography or to be analyzed using a GC-mass spectrometer. The ^1H NMR spectrum shows two sets of signals corresponding to *erythro*- and *threo*-**10** (6 : 1) which are in good agreement with the spectrum of the related β-hydroxy(dimesityl)borane analogs.[6] Hydrogen peroxide oxidation of **10** gave a diastereomeric mixture of the diol (**11**) which was then converted to the corresponding acetal (**12**) in quantitative yield. The formation of *cis*-acetal predominates (*cis* : *trans*=6 : 1) as is established by the presence of NOE (3.5%) and the coupling constant (6.8 Hz) between two methine protons at the carbons adjacent to the oxygens.



Scheme 2. Stereochemistry of the Addition of **8**

Thus, the addition of **8** to benzaldehyde predominantly produces the *erythro*-condensation product (**9**) which stereospecifically gives a *trans* rich alkene through an *anti*-elimination.[4a] The *erythro*-selectivity can be best understood by a transition state, where the boron moiety and the carbonyl oxygen ligated with a boron trifluoride, position themselves *anti* to each other, as do phenyl and methyl groups (Figure 1), which is close analogs with the transition state during the addition of dimesitylboryl carbanions to aldehydes.[4]

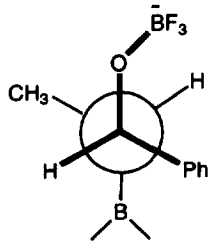


Figure 1. The Transition State

Although it has been reported that β-hydroxyboronates undergo the *syn*-elimination[4,6] of a

hydroxyborane under neutral or basic conditions, the synthesis of *cis*-alkenes from **10** has not yet been studied.

In summary, the sequence of addition of the Knochel's copper(I) boryl carbanions to aldehydes followed by thermal dehydroxyboronation or alkaline hydrogen peroxide oxidation provides new access to alkenes and 1,2-alkanediols from aldehydes. The procedure appears to better tolerate various functional group variations than the related reactions using lithium boryl carbanions. Future investigations will focus on the general utility of the Knochel's reagent for organic synthesis.

Acknowledgment. We are grateful to Prof. R. Okazaki, The University of Tokyo, for sending us the ^{1}H NMR spectrum of dimesityl(2-hydroxypropyl)borane.[6]

EXPERIMENTAL SECTION

All experiments were carried out under a nitrogen atmosphere. The ^{1}H NMR spectra were measured with a Hitachi R-90H (90 MHz) or a JEOL JMN-EX-400 (400 MHz). The mass spectra were recorded using a JEOL JMS-D 300 for high resolution analysis and a Finnigan ITD 800 for GC-mass analysis.

Material. Copper(I) cyanide purchased from Kanto Chemical was used directly. Lithium chloride was dried at 120 °C in *vacuo* (10^{-2} mmHg). THF was dried and distilled from benzophenone ketyl. Boron trifluoride diethyl etherate was distilled from CaH_2 before use. The preparation of the pinacol iodomethylboronic ester (**1**) was previously reported by Matteson.[11] The pinacol (1-iodomethyl)boronic ester was synthesized by the method of Wuts and Thompson.[12] These boronates were converted to the corresponding zinc reagents (**2** and **8**) by the procedure of Knochel.[6] The concentrations of the zinc reagents were estimated by titration with EDTA. The pH of a saturated aqueous NH_4Cl solution was adjusted to pH 8 by the addition of an aqueous NH_3 solution.

Synthesis of terminal alkenes (Table 1). Procedure A: An oven-dried flask was charged with CuCN (0.215 g, 2.4 mmol) and LiCl (0.202 g, 4.8 mmol), and flushed with nitrogen. A 3 ml of THF was added to the flask, and the mixture was then stirred for ca. 1 h to dissolve the solid. A solution of the zinc reagent (**2**) (2.0 mmol) in THF was dropwise added at -30 °C. The flask temperature was slowly warmed to 0 °C to complete the transmetallation to the copper. At -78 °C, an aldehyde (1.0 mmol) and boron trifluoride etherate (0.5 ml, 4 mmol) were successively added. The mixture was stirred for 30 min at -78 °C, warmed to ambient temperature over a period of 2 h, and then refluxed for 2 h. The reaction mixture was treated with saturated NH_4Cl (pH 8) (20 ml) for 1 h at room temperature. The product was extracted with hexane, washed with a NH_4Cl solution and brine, and finally dried over $MgSO_4$. The pure sample was isolated by chromatography over silica gel.

The following compounds were synthesized by the above general procedure.

1-Vinylnaphthalene: ^{1}H NMR ($CDCl_3$) δ 5.45 (dd, 1 H, *J* = 1.8 and 11.8 Hz), 5.78 (dd, 1H, *J* = 1.8 and 17.5 Hz), 7.32-7.83 (m, 8H); IR (neat) 1615, 1605, 1575 cm^{-1}; exact mass calcd for $C_{12}H_{10}$: 154.0782; found 154.0775.

4-Vinylacetophenone: ^{1}H NMR ($CDCl_3$) δ, 2.59 (s, 3 H), 5.39 (d, 1 H, *J* = 10.8 Hz) 5.86 (d, 1 H, *J* = 17.8 Hz), 6.77 (dd, 1 H, *J* = 10.8 and 17.8 Hz), 7.48 (d, 2 H, *J* = 6.6 Hz), 7.94 (d, 2 H, *J* = 6.6 Hz); MS (*m/z*) 77 (36), 103 (51), 115 (2), 131 (100), 146 (26); IR (neat) 1670, 1615, 1590, 1545 cm^{-1}; exact mass calcd for $C_{16}H_{26}$: 218.2034; found 218.2021.

4,8,12-Trimethyl-1,3,7,11-tridecatetraene: ^{1}H NMR ($CDCl_3$) δ, 1.60 (s, 6 H), 1.69 (s, 3 H), 1.76 (s, 3 H), 1.95-2.20 (m, 8 H), 4.96 (t, 1 H, *J* = 10.7 Hz), 5.05-5.15 (m, 3 H), 4.86 (d, 1 H, *J* = 11.0 Hz), 6.58 (ddd, 1 H, *J* = 10.7, 11.0 and 16.8 Hz); MS (*m/z*) 69 (100), 81 (66), 95 (18), 175 (5), 203 (2), 218 (3); exact mass calcd for $C_{10}H_{10}O$: 146.0732; found 146.0712.

Synthesis of terminal alkenes (Table 1). Procedure B: The preparation of the copper reagent (**3**) and its addition to aldehyde is same the procedure A. After being warmed-up to room temperature, the reaction mixture was treated with a saturated NH_4Cl (pH 8) solution (ca. 20 ml) for 1 h at room temperature. The β-hydroxyboronate (**5**) was extracted with ether, washed with brine, and dried over $MgSO_4$. After being filtrated the desiccant, the filtrate was concentrated to give an oily residue of **5**. Methanesulfonyl chloride (2 mmol) and triethylamine (2 mmol) were added at 0 °C to the residue dissolved in THF (6 ml). After being stirred for 1 h at 0 °C, the mixture was refluxed for 3 h. The reaction mixture was diluted with hexane, washed with an aqueous HCl and then an aqueous $NaHCO_3$ solutions, and dried over $MgSO_4$. The product was isolated by chromatography over silica gel.

10-Dodecen-2-one: ^{1}H NMR ($CDCl_3$) δ, 1.20-1.60 (m, 12 H), 2.00 (dt, 2 H, *J* = 6.5 and 7.1 Hz), 2.12 (s, 3 H), 2.41 (t, 2H, *J* = 7.1 Hz), 4.93 (d, 1 H, *J* = 10.1 Hz), 4.97 (d, 1H, *J* = 17.1 Hz), 5.82 (ddt, 1H, *J* = 7.1, 10.1 and 17.1 Hz); IR (neat) 1710, 1630, 900 cm^{-1}; exact mass calcd for $C_{12}H_{22}O$: 182.1671; found 182.1650.

4-(2-Propenyl)-1-vinylcyclohexene: ^{1}H NMR ($CDCl_3$) δ, 1.75 (s, 3 H), 1.60-2.30 (m, 7 H), 4.66 (s, 2 H), 4.90 (d, 1 H, *J* = 10.5 Hz), 5.07 (d, 1 H, *J* = 17.1 Hz), 5.76 (broad s, 1 H), 6.41 (dd, 1 H, *J* = 10.5 and 17.1 Hz); IR (neat) 1645, 1605, 985, 890 cm^{-1}; exact mass calcd for $C_{11}H_{16}$: 148.1252; found 148.1254.

1-Dodecene, methyl 4-vinylbenzoate and methyl 10-undecenoate are directly compared with commercial samples.

Synthesis of 1,2-alkanediols (Table 2). A general procedure: A solution of the zinc reagent (**2**) (3 mmol) in THF was added to the mixture of CuCN (2.4 mmol) and LiCl (4.8 mmol) in THF (3 ml) at -30 °C. The mixture was slowly warmed up to 0 °C over 0.5 h period. At -78 °C, an aldehyde (1 mmol) and BF_3•OEt_2 (4 mmol) were successively added to the mixture. The bath temperature was allowed to warm up to room temperature over 1-2 h period and the mixture was then stirred for 1 h. The reaction mixture was diluted with ether (5 ml) and treated with a saturated NH_4Cl (pH 8) (20 ml) at room temperature for 2 h. The product was extracted with ether, washed with brine, and dried over $MgSO_4$.

After being filtrated the dryer, the filtrate was treated with an aqueous 3 M AcONa (3 ml) and 30% H_2O_2 (2 ml) over night to give **3**. The diol was extracted with ether and dried over $MgSO_4$. Chromatography over silica gel gave a mixture of the expected diol and pinacol. Sublimation of pinacol in vacuo or recrystallization gave an analytically pure compound.

The above general procedure gave the following compounds.

1-Naphthyl-1,2-ethanediol: IR (KBr) 3450 cm^{-1}; ^1H NMR (DMSO) δ, 3.50 (ddd, 1 H, J = 6.0, 7.6, and 11.2 Hz), 3.65 (ddd, 1 H, J = 3.9, 6.0, and 11.2 Hz), 4.87 (t, 1 H, J = 6.0 Hz), 5.33 (ddd, 1 H, J = 3.9, 4.4 and 7.6 Hz), 7.47-8.17 (m, 7 H); Found: C, 76.82; H, 6.57; Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43.

1-(2-Bromophenyl)-1,2-ethanediol: IR (KBr) 3250 cm^{-1}; ^1H NMR (DMSO) δ, 3.30 (dd, 1 H, J = 7.3 and 11.2 Hz), 3.34 (s, 1 H), 3.51 (dd, 1 H, J = 3.1 and 11.2 Hz), 4.85 (dd, 1 H, J = 3.1 and 7.3 Hz), 5.49 (broad s, 1 H), 7.17-7.57 (m, 4 H); Found: C, 44.15; H, 4.27; Calcd for $C_8H_9O_2Br$: C, 44.28, H, 4.18.

1-(4-Methoxycarbonylphenyl)-1,2-ethanediol: IR (KBr) 3400, 1730 cm^{-1}. ^1H NMR ($CDCl_3$) δ, 3.25 (broad s, 2 H), 3.63 (dd, 1 H, J = 8.3 and 11.5 Hz), 3.78 (dd, 1 H, J = 3.4 and 11.5 Hz), 3.91 (s, 3 H), 4.87 (dd, 1 H, J = 3.4 and 8.1 Hz), 7.42 (d, 2 H, J = 8.3 Hz), 8.00 (d, 2 H, J = 8.3 Hz); Found: C, 60.87; H, 6.00; Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17.

1,2-Dodecanediol: IR (KBr) 3320, 3210 cm^{-1}; ^1H NMR ($CDCl_3$) δ, 0.88 (t, 3 H, J = 6.6 Hz), 1.26 (m, 16 H), 1.38 (m, 2 H), 1.97 (broad t, 1 H), 2.08 (broad d, 1 H), 3.43 (m, 1 H), 3.68 (m, 2 H); Found: C, 71.06; H, 12.84; Calcd for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95.

11-Oxo-1,2-dodecanediol: The chromatography over silica gel gave an impure diol which was converted into the corresponding acetone acetal: IR (neat) 1722 cm^{-1}; ^1NMR ($CDCl_3$) δ, 1.29 (s, 6 H), 1.20-1.40 (m, 12 H), 1.57-1.67 (m, 2 H), 2.13 (s, 3 H), 2.42 (t, 2 H, J = 7.6 Hz), 3.25-3.54 (m, 2 H), 4.00-4.10 (m, 1 H); MS (*m/z*) 125 (21), 149 (8), 157 (11), 163 (12), 183 (7), 199 (13), 241 (23), 256 (0.2), 257 (M+1, 2); exact mass calcd for $C_{14}H_{25}O_3$ (M-CH_3): 241.1803; found 241.1813.

[4-(2-Propenyl)cyclohexenyl]-1,2-ethanediol: IR (neat) 3360, 1650, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ, 1.73 (s, 3 H), 1.90-2.30 (m, 7 H), 3.40-4.30 (m, 3 H), 3.60 (bs, 2 H), 4.71 (s, 2 H), 5.79 (bs, 1 H). The corresponding acetone acetal: MS (*m/z*) 72 (100), 147 (18), 164 (16), 207 (9), 222 (12); exact mass calcd for $C_{14}H_{22}O_2$: 222.1620; found 222.1593.

4-Phenyl-3-butene-1,2-diol: IR (KBr) 3350 cm^{-1}; ^1H NMR ($CDCl_3$) δ, 2.10 (s, 1 H), 2.36 (s, 1 H), 3.62 (dd, 1 H, J = 7.3 and 11.2 Hz), 3.75 (d, 1 H, J = 11.2 Hz), 4.44 (s, 1 H), 6.20 (dd, 1 H, J = 6.3 and 16.0 Hz), 6.70 (d, 1 H, J = 16.0 Hz), 7.25-7.45 (m, 5 H); Found: C, 73.25; H, 7.45; Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37.

Syntheses of 10-12 (Scheme 2): The flask was charged with CuCN (0.645 g, 7.2 mmol) and LiCl (0.606 g, 14.4 mmol), and flushed with nitrogen. A 3 ml of THF was added, and the mixture was then stirred for ca. 0.5 h. A solution of the zinc reagent (**8**) in THF (0.57 M, 6.0 mmol) was dropwise added at -30 °C. The temperature was slowly warmed to 0 °C over 1 h. The flask was cooled to

-78 °C and benzaldehyde (1.0 mmol) and boron trifluoride etherate (1.0 ml, 8 mmol) were successively added. The mixture was stirred for 30 min at -78 °C, warmed to ambient temperature over 2 h, and finally refluxed for 3 h. The reaction mixture was treated with a saturated NH_4Cl (pH 8) (40 ml) for 1 h at room temperature. The product was extracted with hexane, washed again with an NH_4Cl solution and brine, and finally dried over $MgSO_4$. The chromatography over silica gel with hexane gave 1-phenyl-1-propene in a yield of 49%. The comparison with authentic samples by GC analysis and by ^1H NMR spectrum indicated the formation of a mixture of (*Z*)- and (*E*)-1-phenyl-1-propene in a ratio of 1 : 6.

The addition of **8** to benzaldehyde in the presence of boron trifluoride etherate was carried out by the same procedure described above. The reaction mixture was diluted with ether (30 ml) and then treated with a saturated NH_4Cl solution (pH 8) (40 ml) at room temperature for 1 h. The β-hydroxyboronate intermediate (**10**) was extracted with ether, washed with a saturated NH_4Cl (pH 8) and brine, dried over $MgSO_4$, and finally concentrated to give an oily residue. Chromatography over silica gel with hexane/ethyl acetate=7/1 (Rf=0.26) gave **10**: The ^1H NMR analysis (400 MHz, $CDCl_3$) indicated the formation of two diastereoisomer in a ratio of 6 : 1. *erythro*-**10**: δ 0.99 (d, 3 H, J = 7.3 Hz), 1.14 (s, 6 H), 1.16 (s, 6 H), 1.25 (s, 1 H), 1.59 (dq, 1 H, J = 4.9 and 7.3 Hz), 2.36 (d, 1 H, J = 4.9 Hz), 7.20-7.40 (m, 5 H). *threo*-**10**: δ, 0.88 (d, 3 H, J = 7.6 Hz), 1.24 (s, 12 H), 1.25 (s, 1 H), 1.53 (dq, 1 H, J = 6. 3 and 7.3 Hz), 2.78 (d, 1 H, J = 6.3 Hz), 7.20-7.40 (m, 5 H); MS (*m/z*) 117 (25), 129 (8), 145 (15), 201 (13), 244 (55), 245 (100), 262 (3).

The β-hydroxyboronate (**10**) was dissolved in THF (5 ml) and treated with 3 M NaOAc (3 ml) and 30% H_2O_2 (2 ml) overnight at room temperature. The diol was extracted with ether (30 ml X 2), washed with brine, and dried over $MgSO_4$. The concentration of the filtrate gave a crude **11** which was converted to the corresponding acetal in boiling benzene (20 ml) overnight with 2,2-dimethoxypropane (5 ml) in the presence of *p*-TsOH. Chromatography over silica gel gave **12** in a yield of 91%. ^1H NMR (400 MHz, $CDCl_3$) δ, 0.80 (d, 3 H, J = 6.4 Hz), 1.47 (s, 3 H), 1.64 (s, 3 H), 4.57 (dq, 1 H, J = 6.4 and 6.8 Hz), 5.20 (d, 1 H, J = 6.8 Hz), 7.26-7.36 (m, 5 H); MS (*m/z*) 77 (49), 91 (64), 105 (56), 115 (19), 117 (23), 119 (23), 135 (50), 148 (100), 176 (9), 192 (1). The GC and ^1H NMR analyses indicated the formation of a mixture of *cis*- and *trans*-**12** in a ratio of 6 : 1. The irradiation of a hydrogen of *cis*-**12** at 4.57 ppm enhanced the signals at 5.20 ppm (3.5%).

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