Chiral Synthesis *via* Organoboranes. 44. Racemic and Diastereo- and Enantioselective Homoallenylboration Using Dialkyl 2,3-Butadien-1-ylboronate Reagents. Another Novel Application of the Tandem Homologation−Allylboration Strategy

Raman Soundararajan, Guisheng Li, and Herbert C. Brown*

H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907

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A highly general and efficient racemic and diastereo- and enantioselective homoallenylboration has been achieved with a novel boron reagent, dialkyl 2,3-butadien-1-ylboronate (dialkyl homoallenylboronate). The starting diisopropyl 2,3-butadien-1-ylboronate is prepared from allenylmagnesium bromide and diisopropyl (halomethyl)boronate. This β,γ-unsaturated boronate reagent reacts readily with aldehydes *via* the usual allylic rearrangement to give the alkyl(1,3-butadien-2-yl)methanols in excellent yield. Among the solvents examined, toluene favored enhanced reaction rates. The reaction is relatively sensitive to steric effects, so that sterically hindered aldehydes react significantly slower. Generally, the reactivities are moderately lower than those of the corresponding simple allylboronates, possibly due to the reduced HOMO electron density of the internal double bond. Also, the reagent exhibits a unique *anti* diastereoselectivity in reaction with α-chiral aldehydes in contrast to the *syn* selectivity observed with a corresponding organosilicon reagent. However, this *anti* selectivity is similar to that observed for the allylboration reactions. We have successfully extended this reaction to the first general synthesis of optically active alkyl(1,3-butadien-2-yl)methanols using chiral tartrate boronate reagents with diisopropyl tartrate (DIPT) and bis(2,4-dimethyl-3-pentyl) tartrate (DMPT) as the chiral modifiers. These reagents react with aldehydes even at −78 °C, albeit slowly, and exhibit remarkable enantioselectivity with all classes of aldehydes examined with the exception of aromatic and α-alkoxy aldehydes. Again, while the selectivity parallels that of the corresponding allylboronate, the reactivities are lower. Also, the double asymmetric homoallenylboration of 2,3-*O*-isopropylidene-D-glyceraldehyde using the DMPT modified boronate reagent gives an excellent 98.5% *anti* selectivity in the matched case and a moderately lower value, 82% *syn* selectivity, in the mismatched case.

A simple, nonasymmetric one-carbon homologation of boronic esters, viz. insertion of a CH_2 group between the carbon and boron atom of the C−B bond, via *in situ* generation and capture of (halomethyl)lithiums, $LiCH_2X$, is an important methodology for a variety of synthetic transformations.[1] The underlying significance of this process is the fact that the rearrangement of the initially formed "ate" complex occurs with absolute stereochemical integrity, thus making it a highly valuable reaction for general asymmetric organic syntheses using organoboranes.[1b] Subsequent to the pioneering report by Matteson *et al.*, we examined in detail the generation and *in situ* capture of $LiCH_2Cl$ as an alternative to the preparation of certain organoboranes not readily available through hydroboration.[1c,2] In spite of the general success of the $LiCH_2Cl$ reagent, occasional problems arising from β−elimination or oxygen migration spurred the development of $LiCH_2Br$ as a better reagent.[3] Though the higher reactivity of the $LiCH_2Br$ compared to that of $LiCH_2Cl$ was indeed more beneficial, functionalized boronic esters and certain other classes of boronic esters failed to give satisfactory results. Recently, Wallace *et al.* introduced $LiCH_2I$ as an improved alternative for homologation of some specific classes of these boronates.[4] With the advent of this report, we undertook a systematic study of all three (halomethyl)lithium reagents ($LiCH_2X$; X = Cl, Br, and I) to compare their reactivity differences in the homologation of representative examples of a wide variety of boronic esters.[5] The results of this study indicated significant reactivity differences among various boronates. Particularly, α,β-unsaturated boronates, such as alkenyl- and alkynylboronates, show opposite trends. The latter reacts much faster with $LiCH_2I$ while the former exhibits little difference in rates among different $LiCH_2X$ (X = Cl, Br, I) reagents.[5] This study led to the first successful synthesis of "higher" propargylboronates in 100% isomeric purity.[6]

Thus, simple one-carbon homologations of α,β-unsaturated boronic esters are not only unique but also synthetically important, owing to the very high reactivity of the product β,γ- unsaturated boronates with carbonyl compounds generally known as allylboration.[7a] Allylboration has reached a certain maturity and is routinely employed in modern asymmetric organic synthesis. In the light of the individual importance of these two methodologies, viz., homologation and allylboration in organic syntheses,

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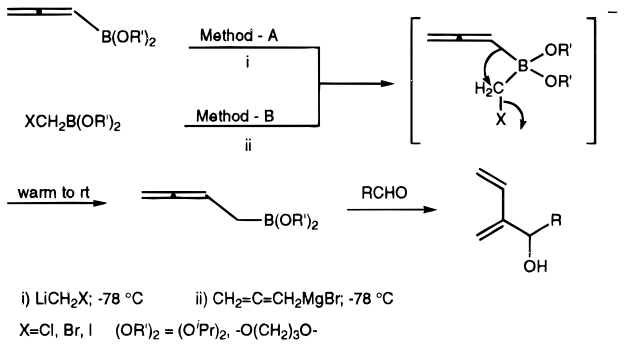
Scheme 1



it appeared possible to us that a unique combination of these two powerful methodologies would provide valuable advances in making possible novel applications which would help extend their usefulness.

This was originally demonstrated in the stereospecific synthesis of "higher" crotylboronates in excellent stereomeric purity.[7b] Thus, for the first time a tandem homologation−allylboration approach was used to synthesize various optically active tetrahydrofurans and tetrahydropyrans in very high enantiomeric purity.[7c] The availability of the "higher" propargyl- and "higher" crotylboronates for the first time in 100% isomeric purity offers significant advantages over other corresponding main group organometallic reagents based on magnesium, silicon, tin, zinc, etc. The fact that all other organometallic reagents suffer mostly from lack of regiomeric integrity, due to rapid 1,3-rearrangement, has precluded any useful applications based on these reagents, especially in asymmetric synthesis. In order to explore further the unique advantage of the tandem homologation−allylboration methodology, we extended the study to allenylboronates.[8] We envisaged that, similar to the behavior of alkenyl- and alkynylboronates, allenylboronates would also rearrange without isomerization to give rise to homoallenylboronates and that these homoallenylboronates, being β,γ-unsaturated, would react with aldehydes in a manner similar to that of simple allylboronates *via* 1,3-rearrangement. This sequence would then give rise to alkyl(1,3-butadien-2-yl)-methanols as the final product. Scheme 1 illustrates the rationale for our approach.

These alkyl(1,3-butadien-2-yl)methanols are valuable starting materials for the syntheses of a variety of natural products.[9] For example, they have been successfully employed for the enantio- and stereocontrolled synthesis of branched chain sugars, such as L-arcanose and L-olivomycose.[9a] These chiral 2-substituted 1,3-dienes are potentially valuable intermediates in providing a new route to the enantioselective synthesis of polyfunctionalized cyclohexanes *via* the Diels−Alder reaction.[9b] However, current methodologies for their synthesis are far from ideal; they suffer from poor regiospecificity, providing a complex mixture of products and low chemical yields.[10] Except for one report by Takano *et al.* describing an asymmetric synthesis of these compounds, albeit in moderate yields, using an expensive chiral reagent, no other procedure is currently available for their general synthesis.[11] Consequently, it was desirable to develop an alternative procedure that would be general and convenient and yet avoid the problems that afflict the existing methodologies. Herein, we describe the racemic and diastereo- and enantioselective syntheses of alkyl(1,3-butadiene-2-yl)methanols using a novel reagent 2,3-butadien-1-ylboronate, readily obtained from diisopropyl (iodomethyl)boronate and allenylmagnesium bromide.

Results and Discussion

The starting diisopropyl 2,3-butadien-1-ylboronate can be prepared by either of the following two approaches (Scheme 1): method A, a one-carbon homologation of allenylboronate using *in situ* generated $LiCH_2X$ or method B, a reaction of allenylmagnesium bromide with (halomethyl)boronates.

Both method A and method B are equally efficient, involving the same intermediate ate complex. Diisopropyl allenylboronate itself is not very stable, and hence, we made the more stable cyclic 1,3-propanediol boronate and subjected it to homologation by method A. In a direct comparison using *in situ* generated $LiCH_2X$, wherein X = Cl, Br, and I, no significant rate differences are noticed. The rearrangement from the initial ate complex was almost complete in less than 5 min after warming to rt. However, method B proved to be much more convenient and gave excellent yields under similar reaction conditions. We have routinely employed method B (in ≥10 g scale) with high isolated yields. In this way, diisopropyl 2,3-butadien-1-ylboronate is readily prepared in excellent isomeric purity. Although, Suzuki *et al.* recently reported comparable yields of a similar intermediate, the relatively inert pinacol esters obtained by their procedure greatly diminishes the possibility of transesterifying the product with other optically active diols.[12,13] In contrast, our reagent, obtained as diisopropyl boronate by a much simpler and more direct route, allows unrestricted transesterification with a large number of diols, including pinacol, tartrate, etc. (*vide infra*), thus making it much more versatile for novel variations and applications.[14]

In contrast to the instability of the diisopropyl allenylboronate, diisopropyl 2,3-butadien-1-ylboronate is a thermally stable compound and can be stored for extended periods of time, with complete exclusion of air and moisture, without noticeable deterioration in quality.

Synthesis of Racemic Alkyl(1,3-butadien-2-yl)-methanols. This boronate reagent readily reacts with a series of aldehydes. The product alkyl(1,3-butadien-2-yl)methanols are obtained exclusively, thus demon-

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(13) All our attempts to transesterify the pinacol 2,3-butadien-1-ylboronate esters with tartrates failed.

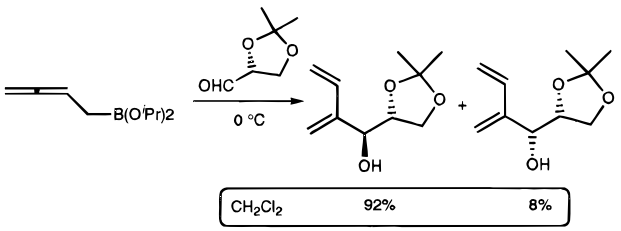
(14) Diisopropyl 2,3-butadien-1-ylboronate can readily be transesterified with pinacol in quantitative yield. The spectral characteristics of this pinacol derivative was identical was reported values.[12]

Table 1. Homoallenylboration of Representative Aldehydes, RCHO, with Diisopropyl 2,3-Butadien-1-ylboronate[a]

no.	R	solvent	time	yield (%)[b]
1	Et	$PhCH_3$	3 h	84
2	Et	neat	1 h	82
3	*i*-Pr	$PhCH_3$	8 h	80
4	*t*-Bu	$PhCH_3$	3 d	60
5	Chx	CH_2Cl_2	30 h	91
6	Chx	$PhCH_3$	4 h	91
7	Chx	neat	1 h	90
8	Ph	$PhCH_3$	0.5 h	85
9	(*E*)-PhCH=CH	CH_2Cl_2	5 h	95
10	$PhCH_2OCH_2$	CH_2Cl_2	3 d	59
11		CH_2Cl_2	12 h	93[c,d]
12		$PhCH_3$	4 h	90[e]

[a] 1.2 equiv of the reagent was used; unless otherwise specified the reactions were carried out at rt. [b] Isolated yields of pure products; all compounds gave satisfactory spectral and analytical data. [c] *Anti*:*syn* = 87:13 at rt; *anti*:*syn* = 92:8 at 0 °C. [d] The *anti*:*syn* ratios were determined by GC analyses and by ^{1}H NMR. [e] *Anti*:*syn* = 89:11.

Scheme 2

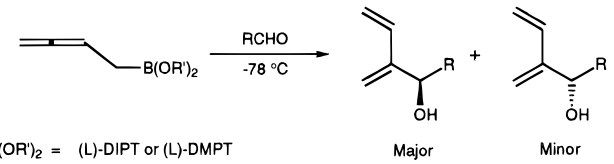


strating that the reaction proceeds *via* a facile 1,3-rearrangement. The reaction can be conveniently monitored by observing at regular intervals the ^{11}B NMR signals (starting boronate: δ 29 ppm; product borate δ 18 ppm).

The results of this reaction with different aldehydes under various conditions are summarized in Table 1. The reactivity of this homoallenylboronate is lower than that of the corresponding allylboronate. This is not unexpected considering the reduced HOMO electron density of the internal π bond with a resultant diminished ability to undergo 1,3-rearrangement. As a result, the reaction times are considerably longer in a given solvent, especially so at lower temperatures. Not surprisingly, the reaction is much faster under neat conditions, presumably due both to the higher concentrations and the enhanced coordination of the boron with the carbonyl oxygen in the transition state, facilitating the rearrangement. The reaction is faster in toluene than in CH_2Cl_2 at all temperatures. Also, sterically hindered aldehydes, such as isobutyraldehyde and pivalaldehyde, react much slower. These results strongly suggest a six-membered cyclic transition state model, such as is generally accepted for allylboration.

Diastereoselective Synthesis. In order to elucidate the diasteroselectivity of the reagent, we examined the reaction with an α-chiral aldehyde, viz., 2,3-O-isopropylidene-D-glyceraldehyde (Scheme 2). The initial lower selectivity obtained in CH_2Cl_2 (87:13; *anti*:*syn*) improved to give a very high *anti* selectivity (92:8; *anti*:*syn*) in excellent chemical yields (Table 1) when the temperature was lowered to 0 °C. The high *anti* selectivity obtained merits some discussion especially in the light of a related

Scheme 3



study by Takano *et al.* using 2,3-butadien-1-yltrimethylsilane. The silicon reagent generally gives high *syn* selectivity in lower yields, in direct contrast to the very high *anti* selectivity and higher yields exhibited by our reagent. The difference in their behavior is due to the presence of chelating Lewis acids such as $TiCl_4$ and $SnCl_4$ used under Takano's conditions, and their behaviors are in good agreement with the expected behavior of both allylboranes and allylsilanes.[15]

Thus, for the first time our reagent offers a unique and complementary procedure for the synthesis of *anti*-substituted derivatives with major advantages over the existing procedures. It is pertinent to note that the 92% ds obtained could probably be improved with another choice of an ester group with modified stereoelectronic factors.

Enantioselective Synthesis. Encouraged by these results we examined the application of this methodology to the enantioselective synthesis. Prompted by the successful use of tartrates as chiral directors in allylboration and in allenylboration studied extensively by Roush and Yamamoto, respectively, we selected diisopropyl tartrate (DIPT) and bis(2,4-dimethyl-3-pentyl) tartrate (DMPT) as chiral modifiers for our study.[16] In light of our earlier results that DMPT proved to be better than DIPT for the higher crotylborations, we initially examined both reagents under otherwise identical conditions (Scheme 3).[7b] The respective tartrate boronates can be conveniently prepared from the diisopropyl 2,3-butadien-1-ylboronate and the two tartrates by a simple transesterification and can be used without isolation in the next step. These readily accessible and synthetically convenient reagents exhibit good to excellent enantioselectivity. The results of this reaction with a series of aldehydes are presented in Table 2.

Once again, we observed that generally DMPT is slightly better than DIPT in terms of selectivity while the chemical yields are identical. It is important to note that the selectivity in terms of absolute configuration of the product alcohols is similar to that observed for allylboration with any given tartrate reagent. Toluene proved to be the solvent of choice, and a slight excess of the chiral tartrate (1.5 equiv) provides better enantioselectivity. But, a further increase in the amount of the chiral reagent (≥2.0 equiv) serves only to accelerate the reaction moderately with negligible effect on the enantioselectivity. Some substrates, such as benzaldehyde and α-alkoxy aldehydes, give lower ee. Surprisingly, DMPT is worse than DIPT for benzaldehyde. Though the reason for this decreased selectivity is unclear, similar results were observed by Yamamoto in the allenylboration of benzaldehyde. A possible explanation

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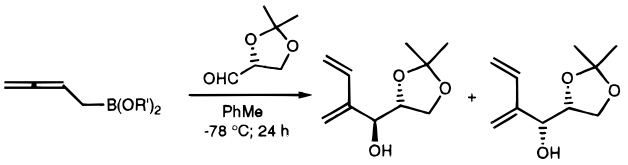
Table 2. Asymmetric Homoallenylboration of Representative Aldehydes, RCHO, Using 2-(2,3-Butadien-1-yl)-1,3,2-dioxaborolane-4,5-dicarboxylates[a]

no.	R	tartrate	yield[b] (%)	ee[c] (%)	abs config[d]	$[\alpha]_D$ (deg) (*c*, $CHCl_3$)
1	Me	L-DMPT	75	61.0	R	+12.10 (4.00)
2	Me	D-DMPT	82	59.8	S	−12.80 (3.50)
3	Et	L-DMPT	-	81.3	R	+10.90 (3.00)
4	Et	D-DMPT	74	81.9	S	−11.20 (5.75)
5	*i*-Pr	L-DMPT	79	87.9	R	−15.76 (6.55)
6	*i*-Pr	D-DMPT	82	88.4	S	+15.76 (6.55)
7	*i*-Pr	L-DIPT	80	80.7	R	−13.60 (3.00)
8	Chx	L-DMPT	94	88.9	R	−6.00 (3.25)
9	Chx	D-DMPT	92	89.6	S	+6.35 (2.30)
10	Chx	D-DIPT	94	84.9	S	
11	Ph	L-DMPT	89	38.3	S	−37.07(2.05)
12	Ph	D-DMPT	86	36.5	R	+35.81(2.15)
13	Ph	L-DIPT	95	43.3	S	−50.10 (5.70)
14	Ph	D-DIPT	90	48.7	R	
15	$BnOCH_2$	D-DMPT	29[e]	48.2	R	+6.40 (0.50)
16	$BnOCH_2$	L-DMPT	36[e]	50.1	S	

[a] See Experimental Section for a representative procedure. [b] Isolated yields of pure products. [c] Determined by capillary GC analyses of the corresponding TFA derivatives on Chiraldex-GTA. [d] The absolute configurations are assigned on the basis of literature data for entry 8, and the others are assigned by analogy to this data. [e] Quenched with $NaBH_4$ at −78 °C and estimated by GC.

Scheme 4



$(OR')_2$	Yield (%)	Anti : Syn
(L)-DMPT	72	98.5 : 1.5
(D)-DMPT	53	18.0 : 82.0

could be an unfavorable interaction between the rich π electron clouds of the proximate allenyl and phenyl groups in the six-membered cyclic transition state.

In comparison to the only other report in the literature for the enantioselective synthesis of alkyl(1,3-butadien-2-yl)methanols by Takano *et al.*, our method is more general and avoids the use of expensive chiral directors while the optical induction obtained is either comparable or even better in most cases.

Double Asymmetric Synthesis. Homoallenylboration of a chiral aldehyde, 2,3-*O*-isopropylidene-D-glyceraldehyde, with DMPT-modified 2,3-butadien-1-ylboronate afforded in high selectivity the *anti* product under similar reaction conditions in the matched case (Scheme 4). We observed that the initial poorer selectivity exhibited by D-DMPT (53:47; *anti:syn*) could be improved provided the reactions were quenched with $NaBH_4$ in EtOH at −78 °C prior to workup.[16a] Thus, we achieved 82% *syn* selectivity with D-DMPT as compared to ≥98.5% *anti* selectivity with L-DMPT.

Conclusions

This is the first detailed report of a novel homoallenylboration including diastereo- and enantioselective studies. We have developed a simple and efficient route for the synthesis of diisopropyl 2,3-butadien-1-ylboronate (homoallenylboronate) in 100% isomeric purity. This homoallenylboronate reagent reacts readily with aldehydes *via* 1,3-rearrangement to give exclusively alkyl(1,3-butadien-2-yl)methanols in excellent yields. With an α-chiral aldehyde, this reagent exhibits a very high *anti* diastereoselectivity. The DIPT- and DMPT-modified tartrate boronate esters of this reagent are readily prepared from the starting diisopropyl 2,3-butadien-1-ylboronate and usually exhibit excellent enantioselectivity with the exception of aromatic aldehydes. The reason for the poorer selectivity in the case of aromatic and alkoxy aldehydes is not readily apparent. However, there is a strong possibility that unfavorable electronic interactions, especially in the transition state, could be responsible for this observation. The double asymmetric homoallenylboration using 2,3-*O*-isopropylidene-D-glyceraldehyde gives 98.5% *anti* selectivity and 82% *syn* selectivity with matched and mismatched tartrate boronate, respectively.

Experimental Section

General Remarks. All air and moisture sensitive reactions were carried out under nitrogen using oven-dried glassware. THF was freshly distilled from sodium benzophenone ketyl. Anhydrous Et_2O and toluene were kept over 4 Å molecular sieves for several days prior to use. Allenylmagnesium bromide was freshly prepared and titrated according to published procedure.[17,18] L- and D-bis(2,4-dimethyl-3-pentyl) tartrate (DMPT) were prepared from the corresponding tartaric acids and 2,4-dimethyl-3-pentanol using CH_3SO_3H as the catalyst.[19] 2,3-*O*-Isopropylidene-D-glyceraldehyde was freshly prepared according to a reported procedure.[20] For homoallenylboration reactions with diisopropyl 2,3-butadien-1-ylboronate and the DIPT ester of 2,3-butadien-1-ylboronic acid, the workup included direct hydrolysis of the reaction mixture with H_2O and extraction with CH_2Cl_2, followed by column chromatography on silica gel using CH_2Cl_2 as the eluent unless otherwise indicated. For those reactions with the DMPT ester of 2,3-butadien-1-ylboronic acid, DMPT was removed either by hydrolysis with excess MeONa/MeOH prior to the usual workup or by Kugelrohr distillation before column chromatographic isolation.

^{11}B chemical shifts (δ) are given in ppm relative to the external standard $BF_3 \cdot Et_2O$. Chiral GC analyses were carried out on Chiraldex-GTA.

Preparation of Diisopropyl (Iodomethyl)boronate. A solution of *n*-BuLi in hexane (40.0 mL, 100 mmol) was slowly transferred to a mixture of $(O^iPr)_3B$ (23.1 mL, 100 mmol) and CH_2I_2 (8.1 mL, 100 mmol) in THF (50 mL) at −78 °C while the solution was stirred. After addition, the mixture was

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stirred at −78 °C for an additional 0.5 h, followed by quenching the reaction with anhydrous HCl in Et_2O (105 mL, 105 mmol). The cold bath was removed, and the mixture was allowed to warm to rt for 1 h. The solid was filtered off under N_2 and washed with Et_2O (3 × 20 mL). The combined ethereal solution was concentrated, and the residue was distilled under reduced pressure in the presence of copper wires (cut into 0.2 cm long) to afford an almost colorless liquid (18.8 g, 92−94 °C at 30 mmHg) in 70% yield. ^{11}B NMR ($CDCl_3$): δ 27.6. ^{1}H NMR ($CDCl_3$): δ 4.39 (septet, 6 Hz, 2H), 2.12 (s, 2H), 1.19 (d, 6 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 66.06, 24.23. IR (neat, cm^{-1}): 2972, 2919, 2872, 1401, 1336, 1284, 1171, 1117, 1021, 907. MS *m*/*z*: (EI) 270 (M^+), (CI) 271 (MH^+), 229 ($MH^+ - C_3H_6$, base). HRMS found 271.0229, calcd for $C_7H_{16}BO_2I$ 271.0366.

Preparation of Diisopropyl 2,3-Butadien-1-ylboronate. Freshly prepared allenylmagnesium bromide (50 mmol, 1.54 M in Et_2O) was slowly added to a precooled solution of $(O^i\text{-}Pr)_2BCH_2I$ (13.60 g, 50 mmol) in THF (30 mL) at −78 °C while the solution was stirred vigorously. The resulting white suspension was stirred at −78 °C for another 0.5 h. The cold bath was then removed, and the mixture was stirred at rt for 20 h. The solution was separated from the solid under N_2 by means of a cannula and was concentrated. The residue was distilled to give a colorless liquid (7.52 g, 58−60 °C /15 mmHg) in 72% yield. ^{11}B NMR ($CDCl_3$): δ 29.3. ^{1}H NMR ($CDCl_3$): δ 5.18 (m, 1H), 4.60 (dt, 7 Hz, 3 Hz, 2H), 4.40 (septet, 6 Hz, 2H), 1.58 (m, 2H), 1.16 (d, 6 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 73.86, 86.60, 65.42, 24.38. IR (neat, cm^{-1}): 1949, 1410, 1340, 1120, 840.

Preparation of the Pinacol Ester of 2,3-Butadien-1-ylboronate. Pinacol (0.328 g, 2.78 mmol) and diisopropyl 2,3-butadien-1-ylboronate (0.506 g, 2.78 mmol) were mixed in dry pentane (5 mL), and the mixture was stirred at rt for 1 h. Removal of pentane and isopropanol under vacuum gave a quantitative yield of the pinacol ester of 2,3-butadien-1-ylboronate. ^{11}B NMR ($CDCl_3$): δ 32.98. ^{1}H NMR ($CDCl_3$):[12] δ 5.15 (m, 1H), 4.63 (dt, 7 Hz, 3 Hz, 2H), 1.61 (m, 2H), 1.26 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 85.37, 83.43, 74.32, 24.80.

Representative Procedure for Reactions of the DMPT Ester of 2,3-Butadien-1-ylboronate with Aldehydes. To a mixture of L-DMPT (0.843 g, 2.43 mmol), powdered molecular sieves (0.5 g), and PhMe (5 mL) was added diisopropyl 2,3-butadien-1-ylboronate (0.25 mL, 1.21 mmol). The reaction mixture was stirred at rt for 1 h, and the apparatus was connected to a vacuum (15 mmHg) for approximately 3 h while the mixture was stirred. ^{11}B NMR indicated diisopropyl 2,3-butadien-1-ylboronate (δ ∼29 ppm) was completely converted to the DMPT ester of 2,3-butadien-1-ylboronic acid (δ ∼34 ppm). Nitrogen was then allowed into the flask, and PhMe (2 mL) was added. The mixture was cooled to −78 °C, and cyclohexanecarboxaldehyde (0.10 mL, 0.82 mmol) was added slowly while the mixture was stirred. After it was stirred for 72 h at −78 °C, the reaction was quenched with excess 25% MeONa in MeOH to hydrolyze DMPT, and the mixture was extracted with Et_2O (3 × 10 mL). The combined ethereal solution was concentrated, and the residue was chromatographed on silica gel with CH_2Cl_2 as the eluent to provide (*R*)-cyclohexyl(1,3-butadien-2-yl)methanol as a colorless oil (0.128 g) in 94% yield. $[\alpha]^{25}_D = -6.0°$ (c, 3.25, $CHCl_3$) (lit.[11] $[\alpha]^{29}_D =$ 5.8°, $CHCl_3$, 88% ee). This alcohol was analyzed by capillary GC as its TFA derivative on a Chiraldex-GTA column at 75 °C to reveal 89% ee in (*R*) isomer. Retention times for the (*R*)- and (*S*)-isomer are 45.18 and 54.26 min, respectively. ^{1}H NMR ($CDCl_3$): δ 6.33 (dd, 18 Hz, 11 Hz, 1H), 5.37 (d, 18 Hz, 1H), 5.20 (s, 1H), 5.09 (d, 11 Hz, 1H), 4.12 (m, 1H), 1.90−1.50 (m, 7H), 1.30−0.95 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 147.93, 136.09, 114.63, 114.32, 76.65, 41.70, 29.81, 27.64, 26.34, 26.23, 25.98. IR (neat, cm^{-1}): 3386, 3085, 1591, 1000, 904. MS *m*/*z*: (EI) 166 (M^+), 55 (base), (CI) 149 ($MH^+ - H_2O$, base). HRMS found 166.1355, calcd for $C_{11}H_{18}O$ 166.1358.

2-Methylene-1-phenyl-3-buten-1-ol.[10d] Colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.32 (dd, 18 Hz, 11 Hz, 1H), 5.47 (d, 4 Hz, 1H), 5.41 (d, 1 Hz, 1H), 5.33 (s, 1H), 5.23 (d, 18 Hz, 1H), 5.04 (d, 11 Hz, 1H), 2.01 (d, 4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 147.44, 141.87, 135.74, 128.37, 127.69, 126.84, 115.62, 115.33, 73.77. IR (neat, cm^{-1}): 3359, 3085, 3025, 1591, 1451, 1014, 764, 697.

3-Methylene-4-penten-2-ol.[21] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 6.36 (dd, 18 Hz, 11 Hz, 1H), 5.33 (d, 18 Hz, 1H), 5.28 (m, 1H), 5.13 (d, 11 Hz, 1H), 5.12 (s, 1H), 4.65 (m, 1H), 1.57 (d, 4 Hz, 1H), 1.37 (d, 6 Hz, 3H), 1.37 (d, 6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 150.31, 136.28, 114.24, 113.25, 67.16, 22.79.

4-Methylene-5-hexen-3-ol. Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 6.35 (dd, 18 Hz, 11 Hz, 1H), 5.34 (d, 18 Hz, 1H), 5.23 (d, 1 Hz, 1H), 5.16 (s, 1H), 5.11 (d, 11 Hz, 1H), 4.36 (m, 1H), 1.89−1.55 (m, 3H), 0.85 (t, 7 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 148.85, 136.21, 114.18, 114.03, 72.81, 29.02, 9.92. IR (neat, cm^{-1}): 3366, 3085, 1591, 981, 904. MS *m*/*z*: (EI) 112 (M^+), 95 ($M^+ - OH$), (CI) 95 (base, $MH^+ - H_2O$). HRMS found 112.0892, calcd $C_7H_{12}O$ 112.0888.

2-Methyl-4-methylene-5-hexen-3-ol.[10a] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 6.34 (d, 18 Hz, 11 Hz, 1H), 5.35 (d, 18 Hz, 1H), 5.20 (s, 1H), 5.17 (s, 1H), 5.10 (d, 11 Hz, 1H), 4.13 (m, 1H), 1.90 (m, 1H), 1.51 (d, 4 Hz, 1H), 0.93 (d, 7 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 148.31, 136.23, 114.59, 114.43, 71.21, 31.95, 19.63, 19.93. IR (neat, cm^{-1}): 3413, 3079, 1591, 1000, 904.

2,2-Dimethyl-4-methylene-5-hexen-3-ol.[10d] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 6.37 (dd, 18 Hz, 11 Hz, 1H), 5.36 (d, 18 Hz, 1H), 5.32 (s, 1H), 5.15 (s, 1H), 5.04 (d, 11 Hz, 1H), 4.15 (d, 3 Hz, 1H), 1.669 (d, 3 Hz, 1H), 0.93 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 148.13, 137.86, 115.50, 113.71, 78.59, 35.39, 26.25.

(1*E*)-4-Methylene-1-phenyl-1,5-hexadien-3-ol.[10d] Viscous oil. ^{1}H NMR ($CDCl_3$): δ 7.80−7.40 (m, 5H), 6.64 (d, 16 Hz, 1H), 6.36 (dd, 18 Hz, 11 Hz, 1H), 6.27 (dd, 16 Hz, 6 Hz, 1H), 5.42 (d, 18 Hz, 1H), 5.35 (s, 1H), 5.23 (s, 1H), 5.13 (d, 11 Hz, 1H), 5.04 (d, 6 Hz, 1H), 2.18 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 147.26, 136.52, 135.78, 131.11, 128.48, 127.66, 126.49, 115.17, 115.09, 72.10.

1-(Benzyloxy)-3-methylene-4-penten-2-ol. Colorless oil (eluent for chromatography was CH_2Cl_2:EtOAc = 20:1). ^{1}H NMR ($CDCl_3$): δ 7.32 (m, 5H), 6.31 (dd, 18 Hz, 11 Hz, 1H), 5.37 (s, 1H), 5.24 (d, 18 Hz, 1H), 5.20 (s, 1H), 5.05 (d, 11 Hz, 1H), 4.67 (m, 1H), 4.55 (s, 2H), 3.64 (dd, 10 Hz, 3 Hz, 1H), 3.37 (dd, 10 Hz, 9 Hz, 1H), 2.87 (d, 3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 144.65, 137.72, 136.27, 128.33, 127.68, 127.64, 115.84, 113.77, 74.21, 73.17, 69.72. IR (neat, cm^{-1}): 3439, 3079, 3025, 1591, 1104, 907, 734, 697. MS *m*/*z*: (EI) 204 (M^+), 91 (base), (CI) 205 (MH^+), 169 (base). HRMS found 205.1219, calcd for $C_{13}H_{16}O_2$ 205.1229.

(2*R*,3*S*)-1,2-*O*-Isopropylidene-4-methylene-5-pentene-1,2,3-triol. Colorless liquid (eluent for chromatography was CH_2Cl_2:EtOAc = 5:1). ^{1}H NMR ($CDCl_3$): δ 6.35 (dd, 18 Hz, 11 Hz, 1H), 5.43 (d, 1 Hz, 1H), 5.32 (18 Hz, 1H), 5.23 (d, 1 Hz, 1H), 4.72 (d, 3 Hz, 1H), 4.31 (dt, 3 Hz, 7 Hz, 1H), 3.91 (dd, 7 Hz, 8 Hz, 1H), 3.81 (dd, 7 Hz, 8 Hz, 1H), 2.47 (br, 1H), 1.48 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 143.75, 136.23, 15.95, 114.08, 109.44, 76.72, 68.94, 63.80, 26.34, 25.00. IR (neat, cm^{-1}): 3459, 3085, 1588, 1061, 907; MS (EI) *m*/*z*: 169 (M − Me), 101 (base); (CI) 185 (MH^+), 167 ($MH^+ - H_2O$). HRMS found 185.1182, calcd for $C_{10}H_{16}O_3$ 185.1178.

(2*R*,3*R*)-1,2-*O*-Isopropylidene-4-methylene-5-pentene-1,2,3-triol. ^{1}H NMR ($CDCl_3$): δ 6.37 (dd, 18 Hz, 11 Hz, 1H), 5.44 (d, 18 Hz, 1H), 5.29−5.28 (m, 2H), 5.15 (d, 11 Hz, 1H), 4.28 (s, 1H), 4.24 (q, 6 Hz, 1H), 3.97 (dd, 6 Hz, 8 Hz, 1H), 3.76 (dd, 6 Hz, 8 Hz, 1H), 2.58 (s, 1H), 1.48 (s, 3H), 1.37 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.00, 135.94, 116.87, 115.18, 109.91, 78.15, 72.59, 66.22, 26.77, 25.31.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR of the optically active alkyl(1,3-butadien-2-yl)methanols (17 pages). This material is contained in libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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