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Borabicyclo[3.3.2]decanes and the Stereoselective Asymmetric Synthesis of 1,3-Diol Stereotriads from 1,3-Diborylpropenes

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Abstract: The synthesis of mixed borabicyclodecane (BBD)-derived 1,3-diborylpropenes (*trans*-**1**) is described. These new bimetallic reagents are effective for the selective asymmetric allylboration first of ketones (or ketimines) and second of aldehydes (or aldimines). Formed as a thermodynamic mixture of trans regioisomers from *cis*-**1** through a series of 1,3-borotropic shifts, only *trans*-**1** undergoes the monoallylation of ketones. After this single addition, this process is effectively shut down after the reaction of the 10-Ph-9-BBD portion in **1**. Serving as a molecular gate, the rearranged 10-TMS-9-BBD *trans*-allylborane intermediate **11** reacts only after an aldehyde (or aldimine) is added. This allylation fixes the last two stereogenic centers of the 2-vinyl-1,3-diol stereotriad, ultimately resulting in **16** (or 1,3-amino alcohols) in 50−72% yield (>98% ee) as single observable diastereomers. These reagents **1** uniquely function as the equivalent of 1,1-bimetallic allylic reagents, adding sequentially first to ketones and second to aldehydes.

Introduction

Ranking among the most important asymmetric processes, the allylboration of carbonyl compounds provides easy access to homoallylic alcohols having extremely high optical purities. Numerous variations upon this central theme are now known, including the use of bimetallic reagents in which two metals displaying differing reactivities can be used in selective processes. This concept was used initially for the synthesis of *anti*-1,2-diols,[1] with Brown and Narla's use of *trans*-1,3-diborylpropenes serving as a representative example.[1e] Roush and co-workers[2a−c] recognized the potential for these 1,3-diborylpropenes to serve as double-allylating agents, resulting in a convenient entry to 1,5-diols. Related chemistry was reported by Barrett et al.,[2d] who employed diborylated isobutylene to effectively construct symmetrical 1,5-diols. Recently, Peng and Hall[2e] reported a B/Si-based α-CH_2TMS allylic borolidine reagent that exhibits a greater chemoselectivity than the above diboryl reagents. Moreover, while the Ipc_2B-derived reagents are not suitable for ketone substrates, these new reagents provide a novel entry to tetrahydrofurans in high ee (>95%) and dr (12:1) through the sequential addition of aldehydes and ketones.

Recent studies in our laboratories have chronicled the remarkable selectivities of the *B*-allyl derivatives of 10-TMS-9-BBD and 10-Ph-9-BBD (9-BBD = 9-borabicyclo[3.3.2]decane) in the asymmetric allylboration of aldehydes and ketones, respectively.[3] The 10-TMS systems are much less reactive toward ketones than their 10-Ph counterparts, a phenomenon that can be attributed to the difference in the sizes of these groups together with their impact on the preferred ring conformations in the reacting species.[3b] We envisaged the incorporation of these borane components into a single reagent that would permit the sequential allylation first of ketones and second of aldehydes. It was felt that only the 10-Ph-9-BBD portion would react with ketones, whereas the 10-TMS-9-BBD moiety would serve as a molecular gate, reacting only with an aldehyde after it is added. Both the allenylborane **3** and the hydroborating agent **4** are readily prepared through simple, essentially one-step procedures from air-stable crystalline complexes.[3e,f] Through their chemoselective use in sequential processes, we hoped that troublesome product mixtures could be completely avoided and that isomerically pure, highly complex molecular assemblies could be constructed in a single operation.

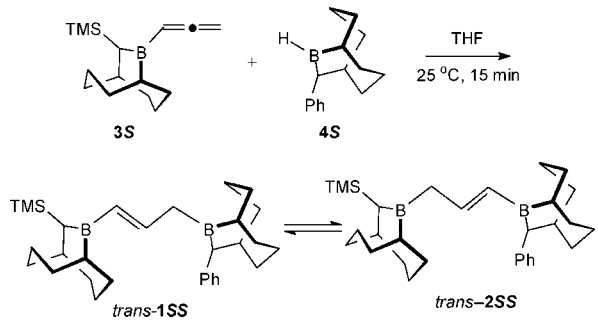
Results and Discussion

Synthesis of 1,3-Diborylpropene Reagents 1, 7, and 8. To access our new *trans*-1,3-diborylpropene reagents (**1**), we chose to employ a variation of Brown and Narla's hydroboration protocol[1e] using 10-Ph-9-BBD-H (**4*S***) to selectively hydroborate the stable allenylborane **3*S*** (Scheme 1). We were surprised to find that two regioisomeric *trans*-1,3-diborylpropenes, *trans*-

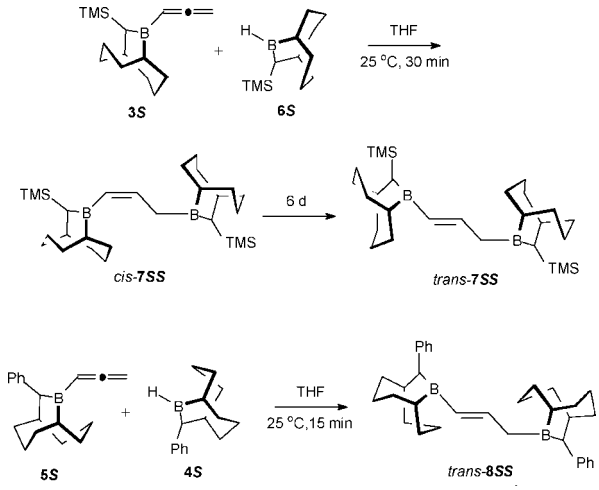
(1) For the synthesis of *anti*-1,2-diols see: (a) Roush, W. R.; Grover, P. T. *Tetrahedron* **1992**, *48*, 1981. (b) Roush, W. R.; Grover, P. T. *Tetrahedron Lett.* **1990**, *31*, 7567. (c) Hunt, J. A.; Roush, W. R. *J. Org. Chem.* **1997**, *62*, 1112. (d) Barrett, A. G. M.; Malecha, J. W. *J. Org. Chem.* **1991**, *56*, 5243. (e) Brown, H. C.; Narla, G. *J. Org. Chem.* **1995**, *60*, 4686.

(2) For bimetallic double-allylating reagents, see: (a) Roush, W. R.; Pinchuk, A. N.; Micalizio, G. C. *Tetrahedron Lett.* **2000**, *41*, 9413. (b) Flamme, E. M.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 13644. (c) Flamme, E. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 1411. (d) Barrett, A. G. M.; Braddock, D. C.; de Koning, P. D.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2000**, *65*, 375. (e) Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 3070, and references cited therein.

Scheme 1

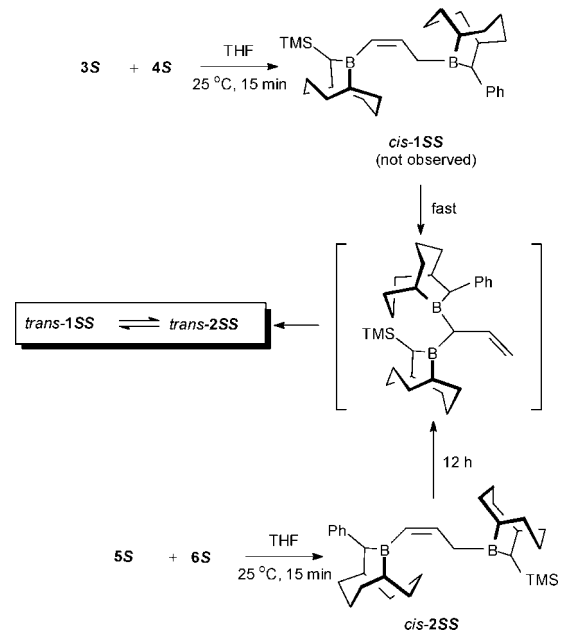


Scheme 2



1*SS* and *trans*-**2*SS***, were formed in a 59:41 ratio in this process. These isomeric boranes exhibited distinctly different ^{1}H NMR signals for their α-vinylic hydrogens [δ 5.96 (d, J = 17.1 Hz) and 5.82 (d, J = 17.2 Hz), respectively] and *B*-broadened ^{1}H-decoupled ^{13}C NMR signals in the same area ratio at δ 135.9 and 137.2, respectively.[4] HMQC NMR experiments confirmed these assignments. It seemed highly unlikely that this mixture (*trans*-**1** and *trans*-**2**) was obtained directly from the hydroboration of **3** with **4**.[5] Moreover, it is counterintuitive that this process would result in the formation of the trans adducts. In an attempt to clarify these issues, we examined the hydroboration of (*S*)-*B*-allenyl-10-TMS-9-BBD (**3*S***) with (*S*)-*B*-H-10-TMS-9-BBD (**6*S***) (Scheme 2). This combination would eliminate regioisomeric adducts, thereby simplifying the interpretation of the results. As expected, only one bis(TMS)diboryl species

Scheme 3



(**7**) was produced. The ^{1}H NMR spectrum of **7** revealed a telling doublet for its α-vinylic hydrogen at δ 5.64 (J = 13.7 Hz), corresponding to the *cis*-vinylborane adduct (*cis*-**7*SS***).[6] Furthermore, monitoring this mixture by NMR revealed the smooth production of *trans*-**7*SS*** [^{1}H NMR: α-vinylic hydrogen, δ 5.82 (d, J = 17.1 Hz)] at the expense of *cis*-**7*SS***, a process that was complete after 6 days. These results suggest that this process proceeds through the initial formation of a *cis*-1,3-diborylpropene, which slowly isomerizes through 1,3-borotropic rearrangements to the more thermodynamically stable *trans*-1,3-diborylpropene product *trans*-**7** via a 1,1-diborylpropene intermediate.

We chose to examine these processes further. We carried out the hydroboration of **5*S*** with **4*S***, which yielded only *trans*-**8*SS*** [^{1}H NMR: α-vinylic hydrogen, δ 5.96 (d, J = 17.3 Hz)] with no observable formation of *cis*-**8*SS*** (Scheme 2). Moreover, we felt that if our view of this process was accurate, an ~60:40 mixture of *trans*-**1** and *trans*-**2** should result from the hydroboration of **5*S*** with **6*S***. However, the ^{1}H NMR spectrum of this mixture revealed the sole formation of *cis*-**2*SS*** [α-vinylic hydrogen, δ 5.63 (J = 13.8 Hz)]. After 3 h, this was fully isomerized into a 59:41 *trans*-**1*SS***/*trans*-**2*SS*** mixture, fully consistent with the proposed mechanism. Thus, the *cis*-1,3-diborylpropenes evidently rearrange to their trans counterparts much faster with a 10-Ph-9-BBD group than with a 10-TMS-9-BBD group in the allylic position. However, from the hydroboration of either **3** with **4** or **5** with **6**, once the first 1,3-borotropic rearrangement occurs, the same 1,1-diboryl species is formed, and accordingly, the same ratio of *trans*-1,3-diborylpropene reagents (*trans*-**1** and *trans*-**2**) is ultimately produced (Scheme 3). For the proposed studies, we chose to utilize reagents **3** and **4** as precursors to *trans*-**1** and *trans*-**2** because of the greater stability of **3** compared with **5** and the enhanced reactivity of **4** compared with **6**.[3f]

Synthesis of 1,3-Diols 16. With an understanding of the identities of our reagents, it remained to be seen whether

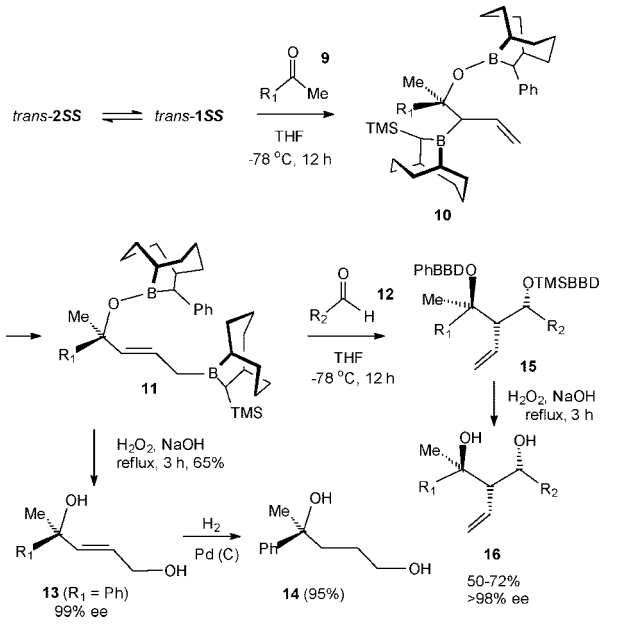
(3) (a) Burgos, C.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044. (b) Canales, E.; Prasad, K. G.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 11572. (c) Hernandez, E.; Canales, E.; González, E.; Soderquist, J. A. *Pure Appl. Chem.* **2006**, *78*, 1389. (d) Canales, E.; Hernandez, E.; Soderquist, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 8712. Hernandez, E.; Burgos, C. H.; Alicea, E.; Soderquist, J. A. *Org. Lett.* **2006**, *8*, 4089. (e) Lai, C.; Soderquist, J. A. *Org. Lett.* **2005**, *7*, 799. (f) Gonzalez, A. Z.; Román, J. G.; Gonzalez, E.; Martinez, J.; Medina, J. R.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 9218.

(4) In the notation for *trans*-**1*SR*** and all related compounds, the first letter gives the stereochemical assignment of the 10-position in the 10-Ph-9-BBD moiety and the second letter that in the 10-TMS-9-BBD moiety [e.g., *trans*-**1*SR*** contains (*S*)-10-Ph-9-BBD and (*R*)-10-TMS-9-BBD moieties].

(5) Although *trans*-**2** could result from the hydroboration of the *B*-propargyl isomer of **3** with **4**, we felt that a cis → trans isomerization pathway offered a more plausible explanation for these hydroboration products since it was already implicated in the formation of *trans*-**1**.

(6) The magnitude of this coupling constant is in complete agreement with those of other *cis*-vinylborane species. See: Soderquist, J. A.; Rane, A. M.; Matos, K.; Ramos, J. *Tetrahedron Lett.* **1995**, *36*, 6847.

Scheme 4



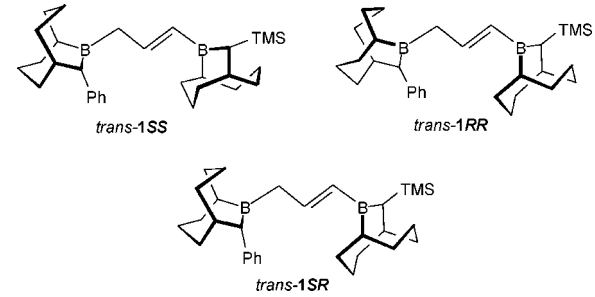
regioisomers *trans*-**1** and *trans*-**2** were in equilibrium and thus would react completely with an incoming ketone. Addition of acetophenone to an enantiomerically pure mixture of *trans*-**1*SS*** and *trans*-**2*SS*** resulted in the simultaneous and constant disappearance of the aforementioned α-vinylic hydrogen signals in the ^{1}H NMR spectrum [δ 5.96 (d, J = 17.1 Hz)] (Scheme 4). With this disappearance, two new hydrogen signals [δ 5.37 (d, J = 15.3 Hz) and 5.53 (m)] simultaneously grew in over a period of 3.5 h at 25 °C. These signals correspond to the formation of *trans*-**11*SS***. Also, inspection of the ^{11}B NMR spectrum of this product revealed two broad peaks at δ 56 and 83, which can be compared with the initial signals at δ 74 and 83 for the *trans*-**1**/*trans*-**2** mixture. These broad peaks are consistent with the presence of the borinic ester and trialkylborane components of **11**, respectively. *trans*-**11*SS*** was not the expected intermediate allylborane species. We rationalize the formation of **11** by means of a sterically driven suprafacial 1,3-borotropic rearrangement that occurs immediately after the ketone allylboration.

This rearrangement is triggered by highly unfavorable interactions between the 10-TMS-9-BBD moiety and the newly formed alkoxydialkylborane moiety. Even though this has not been observed for other 1,3-diborylpropenes,[1e] the formation of **11** from **10** is not unexpected given the propensity of the bulkier 10-TMS-9-BBD reagents to undergo 1,3-borotropic rearrangements, as we have previously reported.[7] The oxidation of *trans*-**11*SS*** (R_1 = Ph) produces exclusively (*S*)-(*E*)-2-butene-1,4-diol **13** in 99% ee, as determined by ^{13}C NMR analysis of its mono-Mosher ester derivative, further supporting the formation and stereochemistry of **11**. The single-crystal X-ray structure for **13** confirmed its *trans*-2-butene-1,4-diol configuration. Thus, the less sterically encumbered 10-Ph-9-BBD component of the *trans*-**1**/*trans*-**2** system has proven to efficiently allylate ketones. Since the 10-TMS-9-BBD moiety reacts extremely slowly with these substrates, *trans*-**1** rather than *trans*-**2** is the presumed

(7) (a) Canales, E.; González, A. Z.; Soderquist, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 397. (b) González, A. Z.; Soderquist, J. A. *Org. Lett.* **2007**, *9*, 1081. (c) Fang, G. Y.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 359.

Table 1. Sequential Asymmetric Double Allylboration with *trans*-**1** Employing Ketones Followed by Aldehydes

trans-**1**[a]	R_1 in **9**	R_2 in **12**	**16**[b]	yield (%)[c]	ee (%)[d]
SS	Ph	*p*-$MeOC_6H_4$	a***SSS***	68	99
RR	Ph	*p*-$MeOC_6H_4$	a***RRR***	65	99
SR	Ph	*p*-$MeOC_6H_4$	a***RRR***	68	99
SS	Ph	Ph	b***SSS***	57	99
SS	Ph	*i*-Bu	c***RSS***	63	98
SS	*i*-Pr	Ph	d***SSR***	71	98
SS	*p*-BrC_6H_4	Ph	e***SSS***	52	98
SS	*p*-$MeOC_6H_4$	*trans*-CH=CHMe	f***RSS***	71	99
SS	2-C_4H_3S	Ph	g***SSS***	58	99



[a] Regioisomeric mixtures of 1,3-diborylpropenes *trans*-**1** and *trans*-**2** (~60:40) were used in each case. The reactive species **1** in these studies are shown above. It should be noted that the computationally preferred boat−chair form of **1** is shown for each BBD ring system. [b] The *R* and *S* designations refer to positions 1, 2, and 3 in the 1,3-propanediol unit in **16**. [c] Isolated yields of analytically pure material. [d] Product ee was determined by ^{13}C NMR of the corresponding Mosher ester derivatives of **16**.

reacting species in this mixture. Accordingly, as *trans*-**1** reacts with the added ketone, the equilibrium between *trans*-**1** and *trans*-**2** is shifted toward the formation of *trans*-**1**, which continues to react, ultimately producing *trans*-**11*SS***.

By monitoring this process through ^{1}H NMR, we observed that the ~60:40 ratio of *trans*-**1**/*trans*-**2** was maintained throughout the addition of **9** to **1/2**. As expected, the addition of more than 1 equiv of acetophenone to *trans*-**1*SS*** and *trans*-**2*SS*** did not result in a second allylboration. However, addition of *p*-anisaldehyde to the intermediate *trans*-**11*SS*** (12 h, −78 °C) initiated the second allylation, this time using the 10-TMS-9-BBD moiety, yielding the expected borinic ester **15** (^{11}B NMR: δ 56). The oxidation of the mixture followed by silica gel column chromatography facilitated the isolation of 1,3-diol **16a**, a product that contains three contiguous stereogenic centers in near-perfect optical purity obtained through a single operation (Scheme 4 and Table 1, entry 1). As noted above, bimetallic reagents with a distinctly different allylating functionality have been fashioned for the synthesis of 1,4- and 1,5-diols, but the construction of 1,3-diols such as **16** through a double-allylation process is unprecedented.

Representative ketone/aldehyde combinations were examined in this sequential double-allylboration process. These results are presented in Table 1. The products **16** were isolated in good yields (52−71%) and excellent enantiomeric excess (>98%), as determined by ^{13}C NMR analysis of their corresponding mono-Mosher ester derivatives. The products were formed as single diastereomers in each case, as judged by a comparison of the ^{13}C NMR spectra of the crude **16** and the pure diol and supportive X-ray data for several systems. This is discussed in greater detail below. The new process proved to be equally selective for a variety of aliphatic, aromatic, and heteroaromatic ketones and aldehydes (see Table 1). Either enantiomeric form

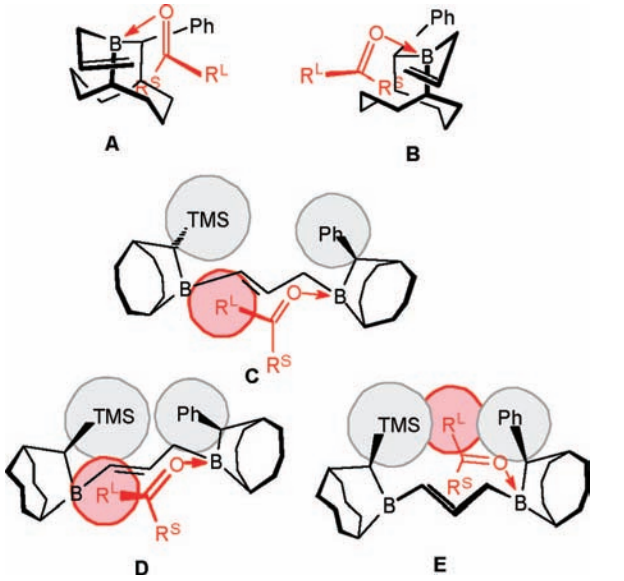


Figure 1. Models for the pre-transition-state complexes for the allylation of ketones with the BBD systems.

of **16** can be synthesized, depending on the choice of *trans*-**1*SS*** or *trans*-**1*RR*** employed.

Unexpectedly, the synthesis of **16a** *from trans*-**1SR** *produced the same enantiomeric form of this diol as obtained from trans*-**1RR** (see Table 1, entries 2 and 3). However, the reaction between *trans*-**1*SR*** and acetophenone takes 9 days (25 °C) to reach completion, which can be compared with 3.5 h with *trans*-**1*RR***. It was also observed that the synthesis of *rac*-**1** from *rac*-**3** and *rac*-**4** produces four stereo- and regioisomeric compounds (*trans*-**1*SS***, *trans*-**2*SS***, *trans*-**1*SR***, and *trans*-**2*SR***) and their respective enantiomers, as determined by ^{1}H NMR analysis of this product mixture. However, the sequential addition of a ketone and an aldehyde to this racemic mixture results in the formation of only one of the four possible diastereomeric products!

We have previously seen that the facial selectivity of our *B*-allyl BBD reagents is a direct consequence of the difference between the effective sizes of the atoms bonded to the boron in the pre-transition-state complex.[3a,b] Thus, the larger size of the sp^3 carbon atom in the allyl group compared with the oxygen atom of the ketone results in the preferred attack of the ketone cis to the 10-Ph group. This selectivity is represented in models **A** and **B**, where **A** is favored (Figure 1).[3b]

These models are very useful in explaining the origin of the selectivity observed for *trans*-**1*RR*** and its (*S*,*S*) counterpart, as is illustrated in **C**. An essentially perfect **A**-like selectivity, even higher than that achieved for these ketones with *B*-allyl-10-Ph-9-BBD itself, is observed for these reagents in all cases. This can be attributed to the 10-TMS-9-BBD moiety, whose 10-TMS group prefers a position away from the approaching ketone. This helps to block the alternative **B**-like approach of the ketone, further reinforcing the **A**-like selectivity. However, with *trans*-**1*RS*** and its enantiomer, molecular mechanics calculations suggest that a similar **A**-like approach of the ketone (i.e., **D**) is disfavored by TMS−ketone repulsions, which block this pathway to a competitive allylboration transition state. To avoid the TMS−ketone repulsions, the alternative **B**-like approaches of the ketone, illustrated by **E**, are preferred for (*R*,*S*) and (*S*,*R*) combinations. As expected, the added interactions introduced into the allylboration process by using these reagents as opposed

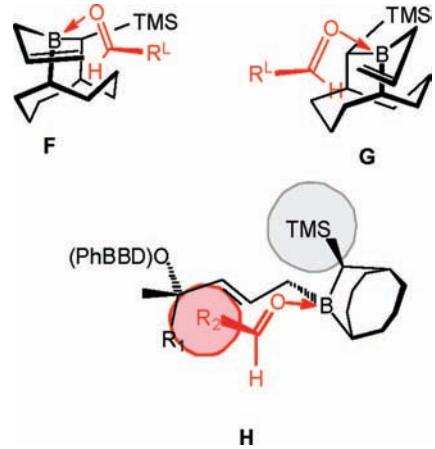


Figure 2. Models for the pre-transition-state complexes for the allylation of aldehydes with the BBD systems.

to their (*R*,*R*) or (*S*,*S*) counterparts result in a significantly slower allylation of PhCOMe with *trans*-**1*RS*** (9 days, 25 °C) than with *trans*-**1*RR*** (or **SS**) (3.5 h, 25 °C). Thus, the stereochemistry of the γ-(10-TMS-9-BBD) substituent in the allylic moiety plays the dominant role in determining the stereochemistry of **16**. To further illustrate this feature of the reagents **1**, the hydroboration of enantiomerically pure **3*S*** with *rac*-**4** was carried out, producing a mixture of *trans*-**1*RS*** and *trans*-**1*SS*** (with their respective regioisomers *trans*-**2**). After the sequential reactions of acetophenone (9 days, 25 °C) and *p*-anisaldehyde (12 h, −78 °C), **16a*SSS*** was obtained in 99% ee.

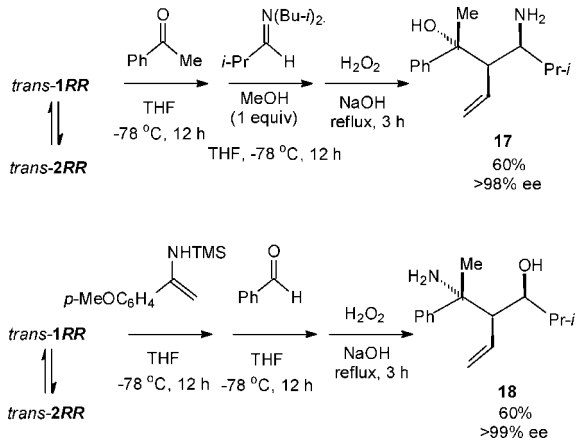
The relative stereochemistry of **16** was determined from the single-crystal X-ray structures of **16a** (both from *rac*-**1** and *trans*-**1*SR***), **16e**, and the hydrochloride salt of **18**. Through ^{13}C NMR analysis, all of the products **16**−**18** were observed as single diastereomers. We can account for the remarkable selectivity of this new process from the above observations for the stereochemistry of the addition of **1** to ketones, the pure trans stereochemistry of **11**, and the nearly perfect selectivity of the 10-TMS-9-BBD moiety in the allylation of aldehydes. This selectivity follows from the remarkable selectivity of the 10-TMS-9-BBD system in the allylboration of aldehydes.[3a] The reagent also exhibits very high selectivity even with chiral substrates. Attack of the aldehydic oxygen cis to the 10-TMS group (i.e., **F**) is highly favored over its trans counterpart (**G**) (Figure 2). For **11**, this results in a selectivity consistent with that illustrated by model **H**. The relative stereochemistry of the vinyl group in the stereotriad of **16** follows directly from the trans stereochemistry of the crotyl moiety in **11**. We obtain one observable diastereomeric diol **16** in essentially enantiomerically pure form from these processes.

The assignment of the absolute stereochemistry of **9a** was based upon a comparison of the specific rotation (95%) of the 1,4-diol **14** obtained from the catalytic hydrogenation of **13** prepared from both *trans*-**1*RR*** {$[\alpha]_D^{24} = +29.9°$ (c = 1.3, MeOH, 98% ee)} and *trans*-**1*SR*** {$[\alpha]_D^{24} = +29.5°$ (c = 1.1, MeOH, 98% ee)} with its literature value {for **14*R***, $[\alpha]_D^{24} = +21°$ (c = 0.74, $CHCl_3$, 99% ee)}.[8] The (*R*) configuration for **14** from both reagents is consistent with the proposed pre-transition-state models (Figure 1).

Synthesis of Amino Alcohols. Previous accounts from our laboratories have reported the ability of the 10-Ph- and 10-TMS-

(8) Date, M.; Tamai, Y.; Hattori, T.; Takayama, H.; Kamikubo, Y.; Miyano, S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 645.

Scheme 5



BBD reagents to selectively add to ketimines and aldimines, respectively.[3c,d] Thus, we decided to explore the asymmetric synthesis of amino alcohols by the sequential addition of an *N*-TMS enamine [precursor to the required (*Z*)-ketimine **19**][3d] and an aldehyde or, alternatively, a ketone and an *N*-H aldimine[3c] to *trans*-**1**. Fortunately, the process proceeds as planned to give the desired amino alcohols smoothly, providing highly stereoselective syntheses of **17** and **18** as single diastereomeric products, both in 60% yield and >98% ee (as determined by ^{13}C NMR analysis of their corresponding mono-Mosher amide derivatives) (Scheme 5). The single-crystal X-ray structure of **18** (as its HCl salt) reveals the relative stereochemistry of the product as depicted in Scheme 5. A close inspection of the ^{13}C NMR spectra of these compounds failed to reveal the presence of the formation of any diastereomeric products in any of these processes. This result is consistent with the selectivity observed in the synthesis of **16**.

We previously observed that the allylboration of *N*-TMS ketimines with *B*-allyl-10-Ph-9-BBD can be understood in terms of initial coordination of their enamine tautomers anti to the 10-Ph group (model **I**) followed by rearrangement to **J** (Figure 3). However, in the present case, the 10-TMS-9-BBD moiety evidently hinders this face in *trans*-**1*RR***, forcing the allylation of the ketimine to occur on the same side of the BBD as that observed for ketones, that is, syn to the 10-Ph substituent (**K**). This further supports the profound role played by the 10-TMS-9-BBD group in the first allylation step.

Conclusions

In this study, a novel chemoselective double-allylating reagent (*trans*-**1**) was successfully employed for the synthesis of 2-vinyl-1,3-diol stereotriads **16** (and amino alcohols **17** and **18**) with truly remarkable selectivities. Studies directed toward a better understanding this complex process focused initially upon the hydroboration of the allenylborane **3** with the 10-Ph-9-BBD reagent **4**, which gives a ~60:40 mixture of regioisomeric *trans*-1,3-diborylpropene adducts *trans*-**1** and *trans*-**2**. This led us to develop a working mechanism for the hydroboration of allenylboranes that involves the initial formation of a *cis*-1,3-diborylpropene adduct. This is followed by consecutive 1,3-

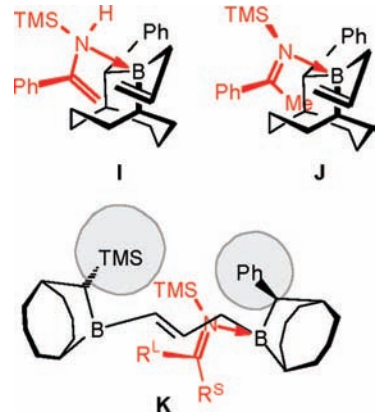


Figure 3. Models for the pre-transition-state complexes involved in the allylboration of ketimines with the 10-Ph-9-BBD reagents.

borotropic rearrangements, ultimately producing this mixture of more thermodynamically stable *trans*-1,3-diborylpropenes via a 1,1-diborylpropene intermediate. This mechanism was tested by inverting the BBD components through the hydroboration of **5** with **6**, which did indeed produce the same *trans*-**1**/*trans*-**2** mixture, albeit in a much slower process. Significantly, this permitted the kinetic hydroboration product *cis*-**2** to be observed prior to its isomerization to the *trans*-**1**/*trans*-**2** mixture. For the *cis*-1,3-diborylpropenes, the 10-Ph-9-BBD moiety was found to undergo 1,3-borotropic shifts much faster than its 10-TMS counterpart. The distinctive differences in the reactivities of the 10-Ph-9-BBD and 10-TMS-9-BBD systems permit the completely chemoselective allylboration of ketones or ketimines with only the 10-Ph-9-BBD component of **1**. Because of the highly congested nature of the reagent, the γ-10-TMS-9-BBD group plays a profound role in determining the stereochemical outcome of this allylboration. This is followed by a sterically driven 1,3-borotropic rearrangement to **11**, which does not react with ketones or ketimines. This intermediate functions as a molecular gate, shutting down the allylboration until an aldehyde or aldimine is added, triggering its allylboration. With essentially 100% selectivity, the *trans*-crotylborane **11** adds to these substrates to fix the remaining two stereocenters of the triad. Thus, the sequential addition of ketones/ketimines and aldehydes/aldimines to **1** results in the creation of three stereogenic centers in a single operation to access this novel class of highly functionalized small molecules.

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Supporting Information Available: Experimental procedures, analytical data, and selected spectra for **1**−**8**, **13**, **14**, **16**−**18**, and their derivatives as well as crystallographic data in CIF format for **16a**, **16e**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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