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Diarylborinic Acid-Catalyzed Ring Opening of *cis*-4-Hydroxymethyl-1,2-Cyclopentene Oxides: Synthesis of 1,2,4-Trisubstituted Cyclopentanes

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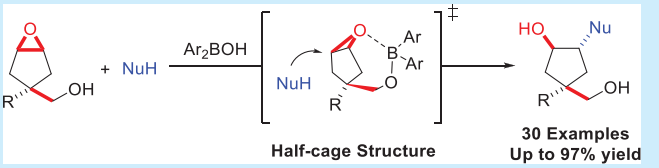
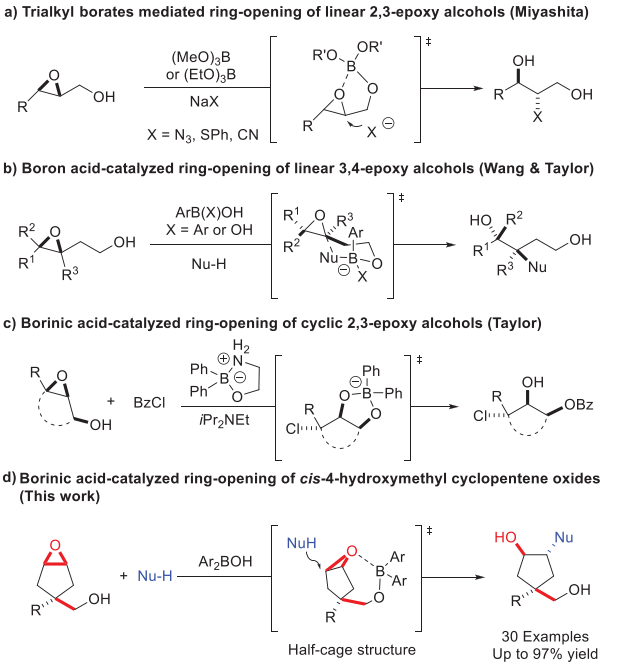
ABSTRACT: A diarylborinic acid-catalyzed ring opening of *cis*-4-hydroxymethyl-1,2-cyclopentene oxides was developed with *N*-nucleophiles including anilines, benzotriazole, and alkylamines, as well as *S*-nucleophiles, affording 1,2,4-trisubstituted cyclopentane compounds containing a quaternary carbon center. The mechanism study indicated that the "half-cage" structure formed by the epoxide substrate and the catalyst prevents the nucleophiles from attacking the inner side of the "half-cage", resulting in the desired ring-opening product.



The synthesis and application of functionalized small molecules in the construction of structurally diverse bioactive molecules and pharmaceuticals have attracted much attention in recent years.[1] As a member of small molecules, the functionalized cyclopentanes have been widely found in natural products and pharmaceuticals, such as simeprevir,[2] cyclohelminthol X,[3] and Pactamycin and its derivatives.[4] However, to obtain the polysubstituted functionalized cyclopentanes,[5] multistep synthesis or metal catalysts are usually required, especially those cyclopentanes containing quaternary carbon stereogenic centers. Therefore, developing a method for rapidly synthesizing these compounds from readily available materials is crucial.

The ring-opening reactions of epoxides by nucleophiles can produce two heteroatom functional groups in one step, which provides the possibility of affording polysubstituted cyclopentanes through ring-opening reactions of well-designed cyclopentene oxides. For ring-opening reactions of epoxides, metal Lewis acid catalysts or small organic molecule catalysts are well-developed, and excellent results have been achieved.[6] Organoboron compounds,[7] as another type of Lewis acid, have also been exploited and applied for this reaction, delivering different regioselective products. In 2003, trialkyl-borates-mediated ring-opening reactions of 2,3-epoxy alcohols have been exploited by Miyashita and co-workers, delivering the C2-selective products through endomode epoxide opening of intramolecular boron chelation (Scheme 1a).[8a] In 2018, Wang's group[8b] and Taylor's group[8c] independently discovered that boronic acid and borinic acid can accomplish the ring opening of acyclic 3,4-epoxy alcohols, affording the C3-selective ring-opening products (Scheme 1b). In such reactions, organoboron acid catalysts are proposed to catalyze the ring opening through a tethering mechanism where both the epoxide substrate and the nucleophile are activated by the

Scheme 1. Organoboron-Mediated/Catalyzed Ring Opening of Epoxides



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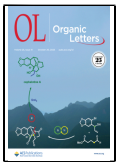


organoboron acid catalyst to form a cyclic transition state that controls the regioselectivity.[8] For the ring-opening reactions of cyclic epoxides, organoboron acid catalysts are also used. In 2015, Taylor's group reported borinic acid catalyzed ring-opening reactions of cyclic 2,3-epoxy alcohols,[8d] where the catalyst only activated the epoxide substrate toward sequential reactions with a nucleophile and an electrophile (Scheme 1c).

The catalytic modes of organoboron acid catalysts vary with epoxide substrates, which provide the multipossibility to access the desired products through a substrate-design strategy. In addition, asymmetric ring opening of readily available epoxides catalyzed by the chiral organoboron acid[9] have not been exploited yet. Considering the novel and variable activation modes of organoboron acids, we intend to explore the diarylborinic acid-catalyzed ring opening of *cis*-4-hydroxymethyl-1,2-cyclopentene oxides for facile synthesis of 1,2,4-trisubstituted cyclopentanes.

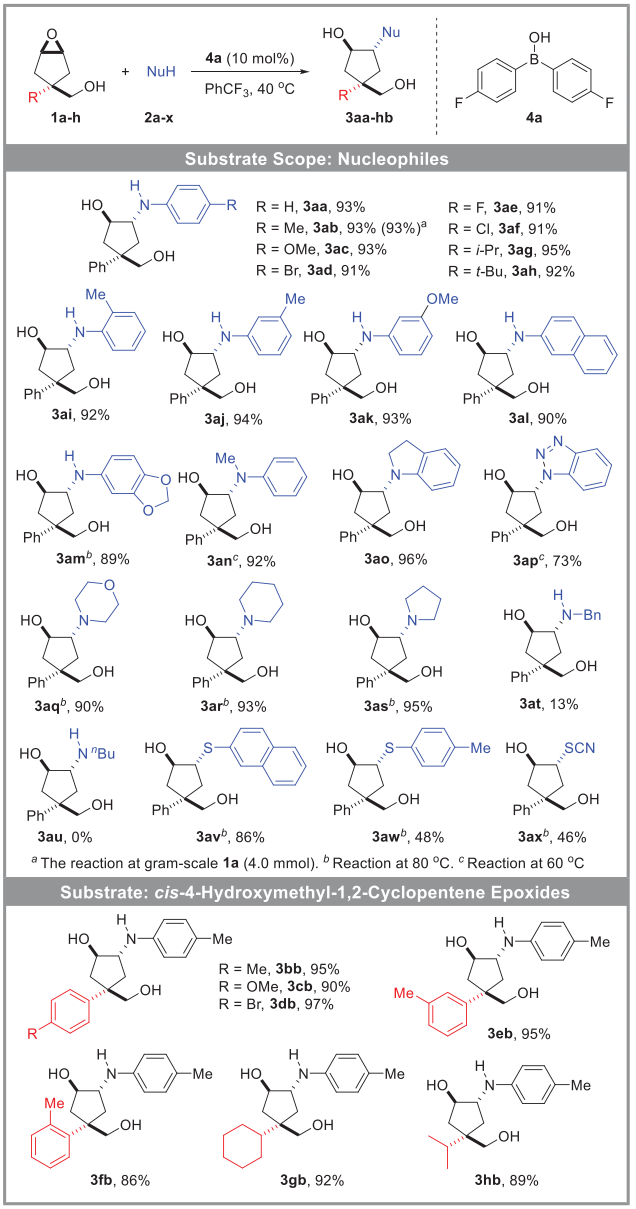
First, *cis*-4-hydroxymethyl-1,2-cyclopentene epoxides **1** was synthesized with an envelope configuration and a *cis*-epoxy group/hydroxymethyl group, forming a "half-cage" structure that facilitates nucleophilic attack from outside. Besides substrate configuration, the hydroxyl group and the oxygen atom of the epoxy moiety of compound **1** will reversibly bond with the organoboron acid catalyst, forming a temporary covalent bond and a coordination bond. This bonding will further block the attack of nucleophiles from the inner side of the "half-cage" (Scheme 1d). These factors increase the *cis* isomer product ratio in ring-opening reactions.

Initially, meso *cis*-4-hydroxymethyl-4-phenyl-1,2-cyclo-pentene oxide **1a** and aniline **2a** were selected as model substrates to optimize the reaction conditions. Using bis(4-fluorophenyl)-(hydroxy)borane **4a** as the catalyst and acetonitrile as the solvent, the single isomer of the product with 87% yield (see Table S1 in the Supporting Information) was obtained, whose configuration was confirmed to be *cis* (*OH* and CH_2OH) by X-ray crystallography (see Chapter S7 in the Supporting Information). Based on the screening results of reaction conditions (for a complete description of the reaction conditions, see Table S1), we used epoxide substrates (1.0 equiv), nucleophiles (2.0 equiv), borinic acid **4a** (10 mol %), and benzotrifluoride as the solvent in the following reactions.

The optimal conditions were used to evaluate the substrate scope (Scheme 2). The electronic properties and steric hindrance of various aromatic primary amines **2a**−**2m** were found to significantly affect the reaction. To obtain excellent yields, a longer reaction time is needed for anilines bearing electron-deficient substitutes and an *ortho*-substituent. The gram-scale reaction was also feasible, and 1.106 g of product **3ab** was obtained in 93% yield. The reaction also showed reactivity toward aromatic secondary amines **2n**−**2p** and several secondary cyclic alkylamines **2q**−**2s**, albeit with reduced reaction rates. Using relatively strong nucleophilic benzylamine **2t**, only a 13% yield was obtained, while no product was obtained with *n*-butylamine **2u**. *S*-Nucleophiles including arenethiols and ammonium thiocyanate could be used as well, giving various *β*-hydroxyl sulfides (products **3av**−**3ax**), which contain a characteristic motif in bioactive molecules.[10]

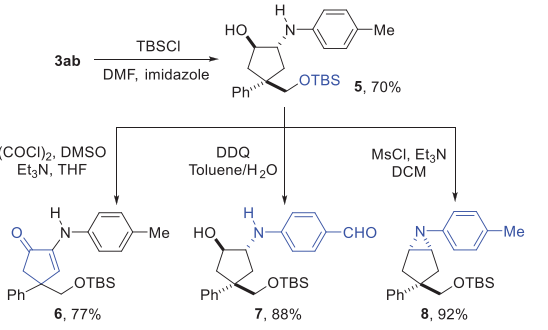
Substrate variations of *cis*-4-hydroxymethyl-1,2-cyclo-pentene oxide were explored (Scheme 2), and both electron-rich and electron-deficient substituents showed marginal impact on the reaction. Substrates with substituted phenyl groups (**1b**−**1f**) and cyclopentyl/isopropyl groups (**1g**, **1h**) reacted well, yielding the products in 86%−97% yields.

Scheme 2. Substrate Scope



Synthetic transformations were demonstrated to explore the synthetic utility of the above methodology (Scheme 3). Product **3ab** was converted to silyl ether **5** and then to *α*,*β*-

Scheme 3. Synthetic Utility



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unsaturated ketone product **6** *via* Swern oxidation. In addition, the oxidation of **5** with DDQ afforded product **7** in 88% yield. The aziridine **8** could be obtained by intramolecular cyclization.

To investigate the reaction mechanism, the importance of the hydroxyl group in epoxides **1** was studied (see Chapter S6.1.1 in the Supporting Information). Epoxide **1i**, lacking a hydroxymethyl group and unable to form the necessary "half-cage" structure, did not yield any product under standard conditions. Similarly, reactions of **1j** (hydroxy was protected) and **1k** (with ester group) produced only low yields of products **5** and **3kb** (20% and 34%, respectively). The reaction of the *anti*-epoxy alcohol **1l** (hydroxymethyl group *anti* to epoxy part) with aniline **2a** resulted in a lower yield of only 41%, compared to *cis*-epoxy alcohol **1a** (see Chapter 6.1.2 in the Supporting Information). We believe that the lower yield of using *anti*-epoxy alcohol is due to the opposite position of the epoxide and hydroxyl group, which prevents the activation of the epoxy part and the formation of a "half-cage" structure. The above results indicate that the formation of the "half-cage" structure is crucial for the reaction.

To support the formation of the "half-cage" structure, the interaction between the epoxide and the catalyst was investigated (see Chapter S6.2 in the Supporting Information for details). ^{1}H NMR spectroscopy revealed the formation of a new species during the reaction of **1a** and **4a** in *d*-chloroform (Figure S1 in the Supporting Information), as made evident by the appearance of new proton signals. The new compound formed during reaction exhibited lower-field proton signals for the hydroxymethyl group ($-CH_2OH$, 3.64 ppm) and the ethylene oxide part ($-CH(O)CH-$, 4.12 ppm) compared to free epoxide **1a** (3.49 and 3.65 ppm, respectively), indicating the strong interaction between **1a** and **4a** (Figures S1 and S2 in the Supporting Information). Furthermore, the chemical shifts of the two protons of $-CH_2-$ on the cyclopentyl were also affected due to their different spatial orientations; one shifted from 2.28 ppm to 2.67 ppm, and the other shifted from 2.62 ppm to 2.14 ppm. These results suggest the formation of a covalent bond and a coordinative bond between **1a** and **4a**, supporting the proposed "half-cage" structure.

The ^{11}B NMR spectroscopy of the mixture of **1a** and **4a** after 1 h in *d*-chloroform showed no new boron signals. The chemical shift of ~44.9 ppm (Figure S3 in the Supporting Information) indicates the B atom in the "half-cage" structure has the similar chemical surrounding as that of **4a** and a coordinative bond between epoxy part of **1a** and **4a** has little effects on the chemical shift of B atom.

For the ring opening of linear 3,4-epoxy alcohols with amine nucleophiles, Wang and Taylor proposed the cyclic transition state where the organoboron acid activated the epoxide substrate and the amine, forming a tetracoordinate anionic adduct.[8b,c] To check if the tetracoordinate anionic adduct is formed in our catalyst system, we reacted **1a** and **2a** with the stoichiometric catalyst **4a** in *d*-chloroform and measured boron spectra after 1 h. The results showed that, besides the main signal of the "half-cage" structure, a new boron signal was found at ~26.7 ppm (Figure 1c), which we believe comes from a new species and is supposed to be formed by **2a** competing with epoxy part to coordinate with **4a**. In the absence of **1a**, we also found a new boron signal of 28.7 ppm (Figure 1b). The boron spectrum of the catalyst **4a** was shown in Figure 1a. From these results, it seems that the tetracoordinate neutral boron complex of the "half-cage" structure was mainly formed

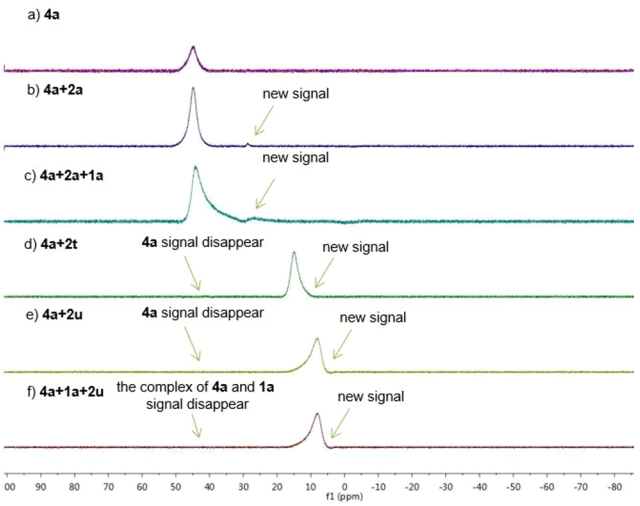

Figure 1. (a) ^{11}B NMR spectra of **4a**; (b) ^{11}B NMR spectrum of **4a** and **2a** at 40 °C for 1 h; (c) ^{11}B NMR spectrum of **4a**, **1a**, and **2a** at 40 °C for 1 h; (d) ^{11}B NMR spectrum of **4a** and **2t** at 40 °C for 1 h; (e) ^{11}B NMR spectrum of **4a** and **2u** at 40 °C for 1 h; and (f) ^{11}B NMR spectrum of **4a** and **1a** at 40 °C for 1 h and then **2u** was added for another 1 h.

in our reaction system and aniline **2a** may competitively, reversibly, and weakly coordinate to the "half-cage" structure.

Based on the above results, we speculated that strong nucleophiles can compete with the epoxy part to coordinate with borinic acid and disrupt the "half-cage" structure, which may lead to low reactivity. The reactions of **1a** with benzylamine **2t** or *n*-butylamine **2u** at 40 °C for 66 h afforded the products in 13%, and 0% yield, respectively, which support the disruption of the "half-cage" structure. ^{11}B NMR spectrum was measured when benzylamine **2t** was added to the *d*-chloroform solution of **4a**, a higher-field boron signal at 14.9 ppm emerged, and the signal of **4a** at 44.9 ppm disappeared (Figure 1d). **4a** and *n*-butylamine **2u** gave similar results, with a higher-field boron signal at 8.2 ppm due to the stronger nucleophilicity of **2u** (Figure 1e). In a competitive coordination experiment between epoxide **1a**, *n*-butylamine **2u**, and catalyst **4a**, ^{11}B NMR spectra show that a higher-field boron signal at 8.0 ppm was observed, while the boron signal of the "half-cage" structure formed by **4a** and **1a** at 44.9 ppm disappeared (Figure 1f). In the ^{1}H NMR spectra, the proton signals located at 4.12, 3.64, 2.67, and 2.14 ppm, which is belong to the hydroxymethyl group ($-CH_2OH$), the ethylene oxide part ($-CH(O)CH-$) and the cyclopentyl ($-CH_2-$) in the "half-cage" structure formed by coordination of **1a** and **4a** disappeared completely when **2u** was added to the mixture of **1a** and **4a** (Figure S4 in the Supporting Information). At the same time, the complete proton signal of free **1a** reappeared. All these results indicated that nucleophiles that are too strong such as primary alkylamines will coordinate with the boron catalyst and inhibit the formation of the "half-cage" structure, which is detrimental to the reaction.

Based on the above experiments, a possible catalytic cycle was proposed (Scheme 4). First, catalyst **4a** binds the epoxide **1a** to generate a "half-cage" intermediate **A**. At the same time, a very small amount of the intermediate **A′** is formed by **2a** competing with the epoxy part to coordinate with **4a**. Then, the ring-opening of **A** with **2a** *via* **B** gives **C**. The proton exchange from nitrogen to oxygen affords **D**, followed by

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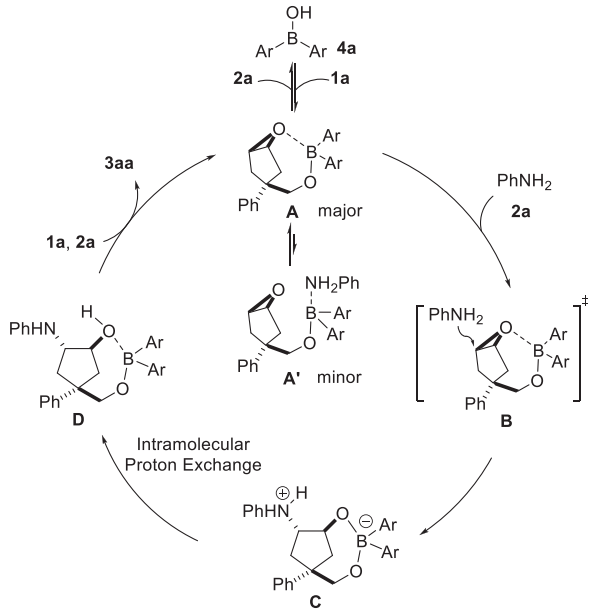
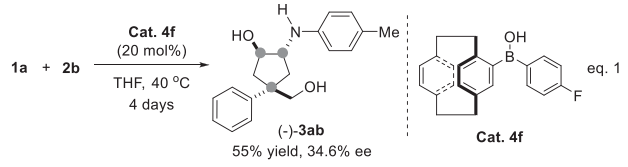
Scheme 4. Proposed Catalytic Cycle



release of product **3aa** and regenerates active species **A** in the presence of **1a** and **2a**.

After the success of achiral diarylborinic acid-catalyzed epoxide ring-opening reactions, chiral organoboron acid catalysts[9b,e] were used to prepare the chiral products, but only low enantioselectivity was achieved. (see Chapter S8.2 in the Supporting Information). To improve enantioselectivity, a new chiral borinic acid **4f** (eq 1) with planar chirality was synthesized, leading to a 55% yield and moderate 34.6% ee.



In conclusion, a facile strategy for synthesis of 1,2,4-trisubstituted cyclopentanes is developed through diarylborinic acid-catalyzed ring opening of *cis*-4-hydroxy-methyl-1,2-cyclopentene oxides. The catalytic system displayed good functional group tolerance, and different *N*-nucleophiles and *S*-nucleophiles are compatible. The mechanism study through ^{1}H NMR and ^{11}B NMR spectra supports a tetracoordinate neutral boron complex with a "half-cage" structure formed between the epoxide and the catalyst, which excludes the possibility of nucleophiles attacking from inside of the "half-cage", resulting in the desirable ring-opening product. In addition, some chiral borinic/boronic acid catalysts were synthesized and applied for this reaction. Unfortunately, only moderate enantioselectivity was achieved. Further research on the asymmetric version of this strategy and other asymmetric reaction types is currently underway.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.3c02886.

General information, optimization results, general procedures, characterization data, and spectra, X-ray data (PDF)

Accession Codes

CCDC 2180596 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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