

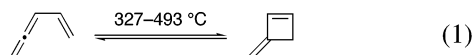
## Dramatic Effects of Boryl Substituents on Thermal Ring-Closing Reaction of Vinylallenes

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Electrocyclic ring-opening and -closing reactions between cyclobutene derivatives and conjugated dienes have been a source of continuing interest.<sup>1</sup> Both thermodynamic and kinetic properties of the reactions change according to the structural variation with additional unsaturation. Cyclobutene undergoes a thermal ring-opening reaction in gas phase at temperatures ranging from 130 to 175 °C, producing 1,3-butadiene, which is thermodynamically more stable than cyclobutene.<sup>2</sup> On the other hand, 1,2,4-pentatriene-(vinylallene) and methylenecyclobutene possess comparable thermodynamic stabilities such that thermal treatment produces an equilibrium mixture of them (eq 1).<sup>3,4</sup>

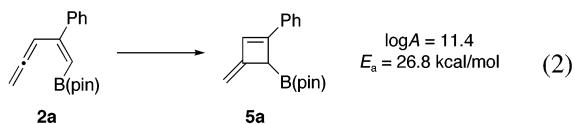


On the basis of theoretical calculation, de Lera et al. suggested that introduction of a methyl group at the vinylic terminus of a vinylallene renders the ring-closed methylenecyclobutene the thermodynamically favored form.<sup>4b</sup> We have described the remarkable effects that silyl substituents have on the electrocyclization of vinylallenes.<sup>5,6</sup> A silyl substituent at the vinylic terminus stabilizes the ring-closed product and, in particular, lowers the temperature required for the ring closure to 110 °C. Recently, Sato et al. reported that a titanium-substituted vinylallene formed as a reaction intermediate underwent a unidirectional ring-closing reaction even at 0 °C.<sup>7,8</sup> Herein, we report the dramatic effects that a boron substituent exerts on electrocyclization of vinylallenes together with the electronic interpretation.

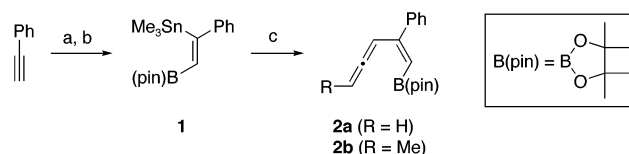
5-Borylpenta-1,2,4-trienes were chosen as the reaction substrates. *Cis*- and *trans*-isomers **2** and **4** were synthesized as shown in Schemes 1 and 2, respectively. The palladium-catalyzed stannaboration<sup>9</sup> of phenylacetylene with stannylborane afforded the *cis*-adduct **1** stereoselectively. Subsequent palladium-catalyzed coupling at the vinyltin moiety of **1** with propargyl bromide produced the *cis*-isomer **2a**. Vinylallene **2b** was synthesized in an analogous manner.

*trans*-Isomer **4** was prepared from 1-(trimethylsilyl)penta-1,4-diyne, which was subjected to the palladium-catalyzed stannaboration. Only the terminal acetylenic moiety reacted with the stannylborane to give adduct **3**. The phenyl group was introduced by the cross-coupling reaction of **3** with iodobenzene. Desilylation and isomerization under basic conditions afforded the *trans*-isomer **4**.<sup>10</sup>

Heating the *cis*-isomer **2a** in xylene at 140 °C affected the electrocyclic ring-closing reaction in 3 h, providing the ring-closed product **5a** in 96% isolated yield (eq 2). The kinetics of the

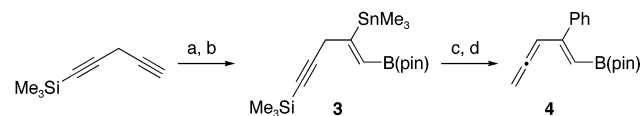


### Scheme 1. Synthesis of *cis*-Boryl-Substituted Vinylallenes **2a** and **2b**<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a)  $\text{Me}_3\text{Sn}-\text{B}(\text{NEt}_2)_2$ ,  $\text{Pd}(\text{PPh}_3)_4$ , benzene, 60 °C. (b) Pinacol, room temperature (90%, two steps). (c) Propargyl bromide,  $\text{PhCH}_2\text{PdCl}(\text{PPh}_3)_2$ ,  $\text{CuI}$ , DMF, room temperature–35 °C (**2a** 45%); 3-chloro-1-butyne,  $\text{PhCH}_2\text{PdCl}(\text{PPh}_3)_2$ ,  $\text{CuI}$ , DMF, room temperature–35 °C (**2b** 11%).

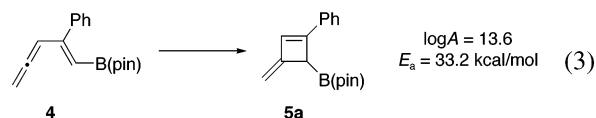
### Scheme 2. Synthesis of *trans*-Boryl-Substituted Vinylallene **4**<sup>a</sup>



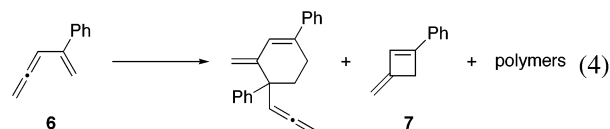
<sup>a</sup> Reagents and conditions: (a)  $\text{Me}_3\text{Sn}-\text{B}(\text{NEt}_2)_2$ ,  $\text{Pd}(\text{PPh}_3)_4$ , toluene, room temperature. (b) Pinacol, room temperature (52%, two steps). (c) Iodobenzene,  $\text{PhCH}_2\text{PdCl}(\text{PPh}_3)_2$ ,  $\text{CuI}$ , DMF, 90 °C (24%). (d)  $\text{NaOH}$ ,  $\text{MeOH}$  (16%).

electrocyclization of **2a** were investigated. A dilute solution of **2a** was heated over the temperature range 90–120 °C in a sealed NMR tube, and the conversion to product was determined by <sup>1</sup>H NMR. The reaction was shown to be first order in **2a**, and the rate was described by the Arrhenius equation  $k = 10^{11.4} \exp(-26.8/RT) \text{ s}^{-1}$ .

The *trans*-isomer **4** also underwent ring-closure, leading to **5a** unidirectionally (eq 3). However, the reaction was much slower than that of **2a**. An Arrhenius plot provided activation parameters  $k = 10^{13.6} \exp(-33.2/RT) \text{ s}^{-1}$ . It is of note that the activation energy for **4** is 6.4 kcal/mol greater than that of the *cis*-isomer **2a**.

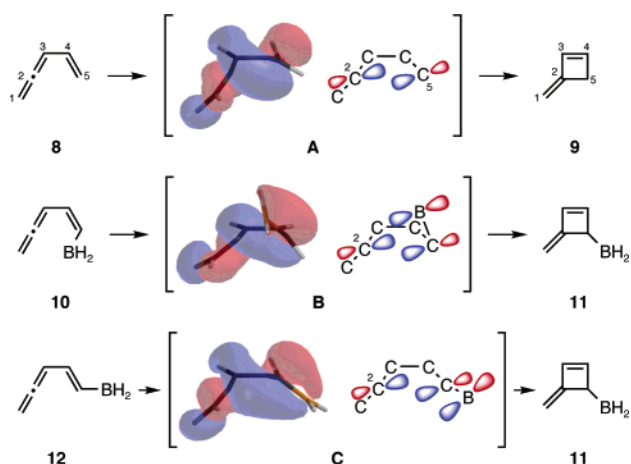


For comparison, the thermal reactivity of vinylallene **6** lacking a boryl group was examined (eq 4). Self-dimerization of **6** by [4 + 2] cycloaddition occurred while being stored neat even at –30 °C. Only the [4 + 2] cycloaddition was observed in a xylene solution up to 90 °C. When heated at 140 °C for 8 h, the electrocyclic ring-closed product **7** was formed in ca. 20% yield (estimated by <sup>1</sup>H NMR) together with intractable polymeric compounds.<sup>11</sup>



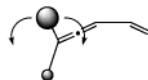
Thus, introduction of a boron substituent caused a dramatic change in the reactivity of vinylallene. It markedly facilitated the

Scheme 3

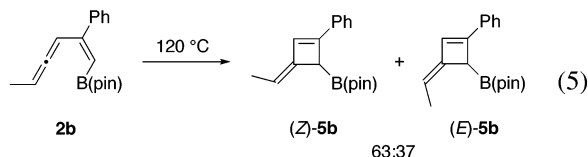


electrocyclic ring-closing reaction. Furthermore, a large difference between the activation energies for the *cis*- and *trans*-stereoisomers was observed. These results can be understood by assuming electronic participation of the vacant p orbital of the boryl substituent, in accord with the prediction made by Houk for the ring-opening reaction of 3-borylcyclobutene.<sup>12</sup> The vacant p orbital interacts with the frontier orbitals of the transition states as an electron acceptor. Scheme 3 shows the second highest occupied molecular orbitals (SHOMOs) of the transition states **A** from vinylallene **8** to methylenecyclobutene **9**, **B** from *cis*-borylvinylallene **10** to borylmethylenecyclobutene **11**, and **C** from *trans*-borylvinylallene **12** to **11**.<sup>13</sup> A significant part of the SHOMO of **A** is concentrated along the  $\sigma$ -bond axis developing between C2 and C5, which is still distorted as exemplified by the schematic depiction.<sup>14</sup> With the SHOMOs of **B** and **C**, there is extensive mixing of the distorted  $\sigma$ -orbital with the vacant p orbital of boron. This mixing leads to a stabilizing two-electron interaction and thus results in stabilization of the transition states. Furthermore, the mixing of the distorted  $\sigma$ -bond with the boron p orbital is greater at **B** than that at **C**, because the boron p orbital of **B** is in much closer proximity to the orbital sketched on the remote C2. Therefore, the reaction of the *cis*-isomer is more accelerated than that of the *trans*-isomer.

If the allene terminus is unsymmetrically substituted, torquoselection would be transferred to the stereochemistry of the ring-closed product.<sup>4a</sup>

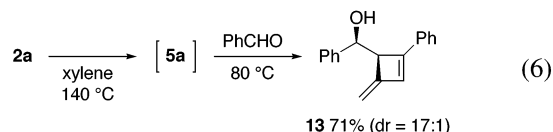


The ring-closing reaction of vinylallene **2b** having one methyl group at the allene terminus furnished a mixture of (*Z*)- and (*E*)-isomers



(63:37 at 120 °C) (eq 5). The low selectivity observed suggests that the terminal methyl group has a limited effect on the torquoselectivity.

The products of the ring closure reaction have a doubly-allylic boron substituent, which is a competent partner in allylation chemistry. When **2a** was heated at 140 °C in xylene (5 h) and then at 80 °C with benzaldehyde (48 h), sequential ring-closing reaction and allylation took place, yielding homoallylic alcohol **13** with high diastereoselectivity (eq 6). The allylation occurs exclusively at the endocyclic position of **5a** to avoid the formation of an antiaromatic cyclobutadiene. Although the relative configuration was not determined, we predict, on the basis of a six-membered cyclic chairlike transition state, the major isomer as shown in eq 6.



In summary, we have shown that boryl substituents have pronounced effects on the ring-closing reaction of vinylallenes. These effects can be accounted for by considering electronic participation of the vacant boron p orbital.

**Supporting Information Available:** Experimental details and selected spectral data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Frontier molecular orbitals were generated with restricted Hartree–Fock calculations with the 6-31G(d) basis set using Spartan.
- (14) The transition state HOMO is essentially the bonding  $\pi$ -orbital of the C1–C2 double bond.

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