A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

Title: Photochemical Intramolecular C-H Addition of Dimesityl-(hetero)arylboranes via a [1,6]-Sigmatropic Rearrangement

Authors: Naoki Ando, Aiko Fukazawa, Tomokatsu Kushida, Yoshihito Shiota, Shuhei Itoyama, Kazunari Yoshizawa, Yasunori Matsui, Yutaro Kuramoto,, Hiroshi Ikeda, and Shigehiro Yamaguchi

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201706929
Angew. Chem. 10.1002/ange.201706929

Link to VoR: http://dx.doi.org/10.1002/anie.201706929
http://dx.doi.org/10.1002/ange.201706929

WILEY-VCH

Photochemical Intramolecular C–H Addition of Dimesityl-(hetero)arylboranes via a [1,6]-Sigmatropic Rearrangement

Naoki Ando,[a] Aiko Fukazawa,[a] Tomokatsu Kushida,[a] Yoshihito Shiota,[b] Shuhei Itoyama,[b] Kazunari Yoshizawa,*[b] Yasunori Matsui,[c] Yutaro Kuramoto,[c] Hiroshi Ikeda,*[c] and Shigehiro Yamaguchi*[a,d]

Dedication ((optional))

Abstract: A new reaction mode for triarylboranes under photochemical conditions was discovered. Photoirradiation of dimesitylboryl-substituted (hetero)arenes produced spirocyclic boraindanes, where one of the C–H bonds in the *ortho*-methyl groups of the mesityl substituents was formally added in a *syn* fashion to a C–C double bond of the (hetero)aryl group. Quantum chemical calculations and laser flash photolysis measurements indicated that the reaction proceeds via a [1,6]-sigmatropic rearrangement. This behavior is reminiscent of the photochemical reaction mode of arylalkenylketones, demonstrating the isosteric relation between tricoordinate organoboron compounds and the corresponding pseudo-carbocationic species in terms of pericyclic reactions. Despite the disrupted π-conjugation, the resulting spirocyclic boraindanes exhibited a characteristic absorption band at relatively long wavelengths (370–400 nm).

Photochemical reactions of organic compounds containing boron have attracted continued attention due to the fundamental interest in their reactivity and their synthetic utility.[1] A crucial point for the understanding of the reactivity of organoboranes is the isosterism with their carbon congeners (Figure 1a,b). The similar photochemical behavior for anionic tetracoordinate boron compounds and neutral tetracoordinate carbon compounds has long been recognized. For instance, tetraorganoborates or base-coordinated triorganoboranes undergo a photoinduced di-π-borate rearrangement, which is the analogous reaction of the di-π-methane rearrangement of the corresponding carbon isosteres.[2–4] Wang and coworkers have recently applied this type of reaction to develop a photochromic system.[5] In contrast, photochemical reactions of neutral tricoordinate organoboranes have been limited to ligand-coupling reactions that involve B–C bond cleavage.[6–8] We have recently reported isosteric reactivity for a triorganoborane and its cationic carbon congener. Specifically, 9-dimesitylboryl-substituted dibenzoborepin **1** underwent an isomerization to a borata-allyl product **2** upon photoirradiation,[9] a reaction that can be regarded as a bora-Nazarov cyclization (Figure 1c). In order to evaluate the generality of this reaction mode, we examined various simplified substrates. However, we discovered that dimesitylboryl-substituted (hetero)arenes **3** undergo a different mode of photoisomerization, namely a formal intramolecular C–H bond addition that affords spirocyclic boraindane **4** (Figure 1d). This reaction likely involves a [1,6]-sigmatropic hydrogen rearrangement, which should result from a significant contribution of the vacant p-orbital of the boron atom. In light of the fact that the analogous reaction proceeds in arylalkenylketones,[10] this pericyclic reaction should be another example of the reaction modes of triorganoboranes that is characterized by the B/C^{+} isosterism. Herein, we disclose the details of this new photochemical reaction.

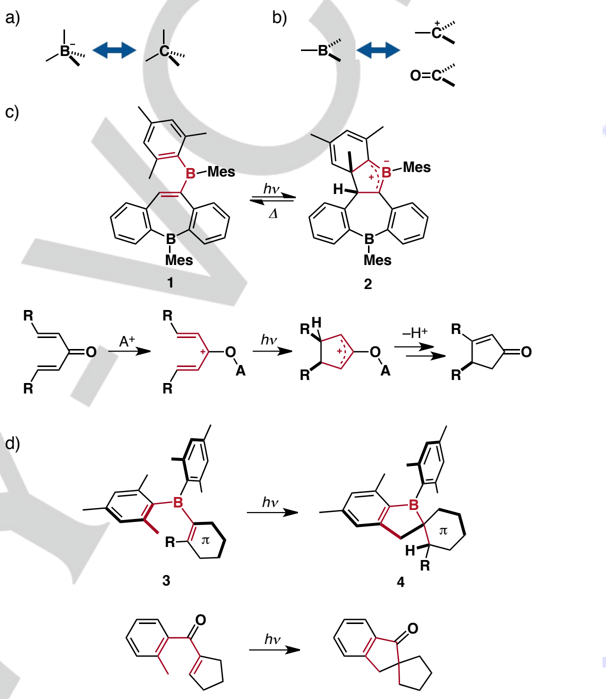


Figure 1. Isosterism in the photochemical reactions of organoboranes and their carbon congeners: isosteric relationships of (a) B^{-}/C and (b) B/C^{+}, as well as comparisons in (c) the Nazarov cyclization and (d) the formal intramolecular C-H addition reaction.

Initially, we conducted a photochemical reaction using 3-dimesitylboryl-2,5-dimethylthiophene (**3a**) as a starting material.

---

[a] N. Ando, Prof. Dr. A. Fukazawa, Dr. T. Kushida, and Prof. Dr. S. Yamaguchi
Department of Chemistry, Graduate School of Science, and Integrated Research Consortium on Chemical Sciences (IRCCS), Nagoya University
Furo, Chikusa, Nagoya 464-8602 (Japan)
Fax: (+81) 52-789-5947
E-mail: yamaguchi@chem.nagoya-u.ac.jp
[b] Prof. Dr. Y. Shiota, S. Itoyama, and Prof. Dr. K. Yoshizawa
Institute for Materials Chemistry and Engineering, Kyushu University
744 Motooka, Nishi-ku, Fukuoka 819-0395 (Japan)
[c] Dr. Y. Matsui, Y. Kuramoto, and Prof. Dr. H. Ikeda
Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531 (Japan)
[d] Prof. Dr. S. Yamaguchi
Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University
Furo, Chikusa, Nagoya 464-8602

Supporting information for this article is given via a link at the end of the document.

10.1002/anie.201706929

Upon irradiation of a dilute solution of **3a** (4.3×10^{-5} M) in THF with UV light (λ = 320 nm), the solution readily turned to pale yellow. This color change stands in sharp contrast to the deep blue color of the previously observed bora-Nazarov product **2**.[9] The color change was monitored by UV-vis absorption spectroscopy, which revealed that absorbance at λ_{max} = 322 nm for **3a** decreased and new broad bands emerged at λ_{max} = 269 and 375 nm with isosbestic points at λ = 284 and 354 nm (Figure 2). An NMR study of the reaction mixture demonstrated that **3a** was cleanly converted into a single product **4a** (Figure S1 in the Supporting Information). A synthesis on a preparative scale using a high-pressure mercury lamp furnished **4a** in 80% isolated yield. Although **4a** gradually decomposed in air, it was sufficiently stable to be purified by column chromatography on silica gel.

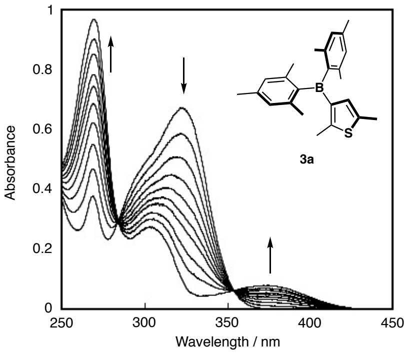


Figure 2. UV-vis absorption spectra of **3a** upon irradiation with UV light (λ = 320 nm) in THF (0–100 min).

The molecular structure of **4a** was unequivocally determined by single-crystal X-ray diffraction analysis (Figure 3), and the unit cell contains a pair of enantiomers. The molecular structure of **4a** is characterized by a spirocyclic boraindane framework with a chiral quaternary carbon atom, which arises from the formation of a new C–C bond between the *ortho*-methyl group of one of the mesityl substituents and the *ipso*-carbon atom of the thiophene moiety. The thiophene ring is transformed into a nonaromatic dihydrothiophene ring that exhibits substantially different C–C bond lengths [C19–C20: 1.543(2) Å; C21–C22: 1.332(2) Å] and an sp^3-hybridized C19 atom [angle sum C–C–C and C–C–S: 333.62°]. Thus, **4a** can be regarded as the product of a formal intramolecular C–H bond addition of the *ortho*-methyl C–H bond of a mesityl substituent to one of the C=C bonds of the thiophene ring. The C7–C20 and C19–H22 bonds adopt a *syn* configuration, demonstrating that the formal C–H bond addition proceeds in a highly stereoselective manner (*vide infra*). The boron atom in the five-membered ring retains a trigonal planar geometry [angle sum C–B–C: 359.55°].

The substrate scope of the reaction was investigated by employing a series of dimesitylboryl-substituted heteroarenes and related compounds (Table 1). The replacement of the dimethylthiophene moiety in **3a** with other five-membered heteroarenes, such as benzothiophene (**3b**), benzofuran (**3c**), and *N*-methylindole (**3d**), resulted in complete photocyclizations within an hour in hexane, and successfully furnished the corresponding spirocyclic boraindanes **4a**-**d** in good isolated yields (79–88%). The reaction of a phenanthrene precursor **3e** in benzene also produced **4e** in comparable yield, although a prolonged reaction time (6 h) was required for completion. In contrast, trimesitylborane was not susceptible to this reaction. These results demonstrate that low levels of aromaticity in the substrates are crucial for this reaction to proceed. In all these examples, the formal C–H addition products were obtained exclusively, and bora-Nazarov products were not observed. In addition, dimesitylboryl-substituted nonaromatic indene **3f** also afforded the cyclized product **4f**. This result implies that 5- or 6-membered ring structures in the substrates may be another important factor in order to dominantly promote the cyclization over the bora-Nazarov reaction, which is observed for the 7-membered borepin.

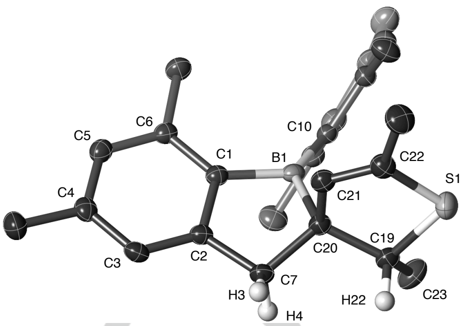
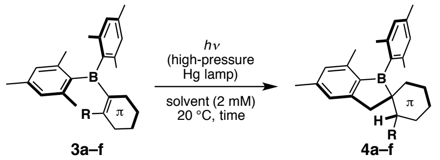


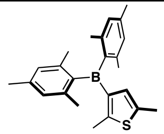
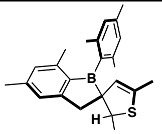
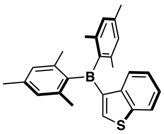
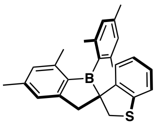
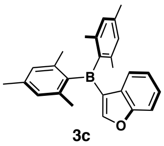
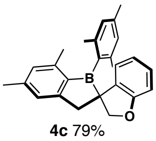
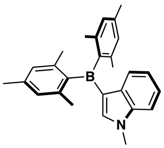
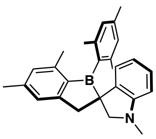
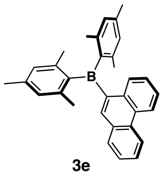
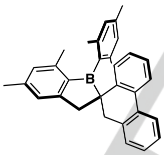
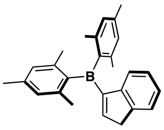
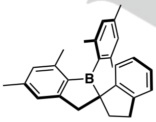
Figure 3. Molecular structure of **4a** (atomic displacement parameters set to 50% probability). Only one of the enantiomers is shown. Hydrogen atoms, except for H3, H4, and H22, are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C1 1.564(2), B1–C10 1.572(2), C1–C2 1.4124(19), C2–C3 1.390(2), C3–C4 1.394(2), C4–C5 1.400(2), C5–C6 1.394(2), C6–C1 1.4076(19), C2–C7 1.508(2), C7–C20 1.552(2), C19–C20 1.543(2), C20–C21 1.519(2), C21–C22 1.332(2), C1–B1–C10 123.21(13), C10–B1–C20 133.28(13), C1–B1–C20 103.06(12), S1–C19–C20 106.84(10), C20–C19–C23 116.17(13), C23–C19–S1 110.61(12).

This reaction likely proceeds via a [1,6]-sigmatropic rearrangement of the *ortho*-methyl hydrogen atom (Scheme 1). To elucidate the mechanism, DFT calculations on both the ground state (S_0) and the lowest (S_1) and second lowest excited singlet states (S_2) were conducted at the B3LYP/6-31G(d) level of theory. The geometry optimization of S_0 at the UB3LYP/6-31G(d) level of theory afforded two electronic structures for the transition state (TS) of the [1,6]H-shift, *i.e.*, an open-shell **TS(OS)** and a closed-shell singlet state **TS(CS)**, which lead to the H-shifted biradical ($\mathbf{5a}^{\bullet\bullet}$) and zwitterionic ($\mathbf{5a}^{+-}$) intermediates respectively, prior to the formation of the spirocyclic product **4a** (Figures 4a and S3). The energies of the geometries of these intermediates relative to the optimized geometry of **3a** in S_0 are +56.1 kcal mol^{-1} [**TS(OS)**], +68.0 kcal mol^{-1} [**TS(CS)**], +44.3 kcal mol^{-1} ($\mathbf{5a}^{\bullet\bullet}$), +53.8 kcal mol^{-1} ($\mathbf{5a}^{+-}$), and +12.5 kcal mol^{-1} (**4a**). The high activation energy of at least 56.1 kcal mol^{-1} indicates that the [1,6]H-shift unlikely occurs under thermal conditions. Intermediate $\mathbf{5a}^{\bullet\bullet}$, optimized for the open-shell form, is by 9.5 kcal mol^{-1} more stable than that for the closed-shell form ($\mathbf{5a}^{+-}$), indicating that the H-shifted intermediate **5a** contains a significant contribution of the resonance form $\mathbf{5a}^{\bullet\bullet}$ in S_0 compared to the zwitterionic form $\mathbf{5a}^{+-}$. For the transformation of

10.1002/anie.201706929

Table 1. Substrate scope for the photochemical cyclization of **3a–f**.[a]

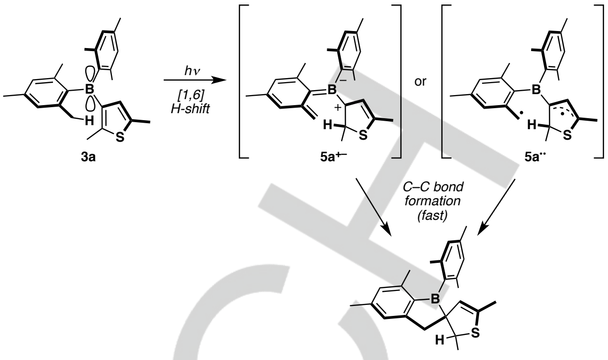


Entry	Substrate	Solvent, time	Product [%][b]
1	 **3a**	hexane, 1 h	 **4a** 80%
2	 **3b**	hexane, 1 h	 **4b** 82%
3	 **3c**	hexane, 1 h	 **4c** 79%
4	 **3d**	hexane, 1 h	 **4d** 88%
5	 **3e**	benzene, 6 h	 **4e** 70%
6	 **3f**	hexane, 1 h	 **4f** 81%

[a] The reactions were conducted on 2.0 mM solutions using the irradiation UV light from a high-pressure Hg lamp at 20 °C. [b] Isolated yield.

5a into **4a**, no transition state was found due to a shallow potential energy surface. These findings suggest the spontaneous formation of spirocyclic boraindane **4a** even in the ground state, once **5a** is produced.[11]

Along the reaction coordinate from **3a** to **5a**$^{\bullet\bullet}$ (S_0), the respective S_1 and S_2 energies were estimated by time-dependent density functional theory (TD-DFT) calculations. In the early reaction stage, near the Franck–Condon state for **3a**, S_1 and S_2 are energetically comparable. In contrast, the S_2 potential energy surface for the H-shift from **3a** to **TS** is significantly less favorable (*ca.* 30 kcal mol^{-1}), while that of S_1 is rather flat, exhibiting a slight increase in energy (*ca.* 10 kcal mol^{-1}). Moreover, S_1 and S_0 seem to form a weakly avoided crossing in the vicinity of **TS(CS)** due to the nonadiabatic coupling between the two states. Overall, the photoinduced cyclization



Scheme 1. A plausible reaction mechanism for the photoinduced formation of **4a**.

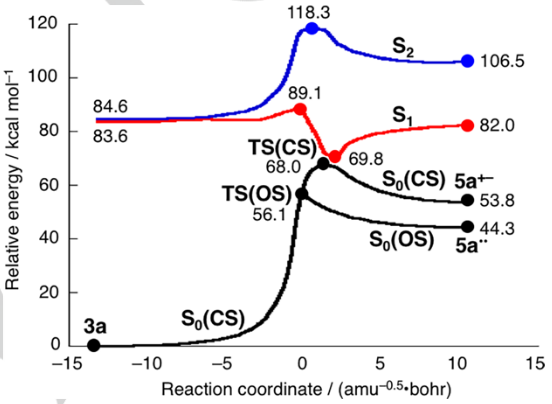


Figure 4. Energy profiles of S_0, S_1, and S_2 for the [1,6]H-shift of **3a**, calculated at the B3LYP/6-31G(d) level of theory. All energy values are relative to dimesitylborylthiophene **3a**. For the energy profiles of the transformation of **3a** into **5a**$^{\bullet\bullet}$ (S_0), the relative energies from **3a** to **TS(CS)** and **TS(OS)** to **5a**$^{\bullet\bullet}$ correspond to the closed-shell and open-shell singlet states, respectively.

likely proceeds via a [1,6]H-shift in the S_1, followed by a nonadiabatic transition from S_1 to S_0 to produce **5a**$^{+-}$, and a spontaneous C–C bond formation via either **5a**$^{+-}$ or **5a**$^{\bullet\bullet}$ in S_0 to afford the spirocyclic product **4a** (Scheme 1).

To gain experimental insight into the mechanism, we carried out nanosecond laser flash photolysis (LFP) studies. Upon LFP of a 1 mM solution of **3a** at 355 nm in dichloromethane or toluene at 235 K, no transient absorption band was observed. In contrast, a similar LFP of **3a** (0.2 mM) in acetonitrile afforded a broad and weak transient absorption band in the 600–900 nm region (Figure S5),[12] suggesting that the transient intermediate exhibits at least partially ionic character and can thus be stabilized in polar solvents. The transient intermediate decays with rate constants of k_{DECAY} = 0.86 (235 K), 1.06 (245 K), and 1.18 × 10^{7} s^{-1} (254 K), which were determined by analysis tracing of ΔOD at 720 nm (Figure S6). A kinetic analysis based on conventional transition-state theory provided the activation enthalpy ($\Delta H^{\ddagger}$ = 1.8 kcal mol^{-1}), activation entropy ($\Delta S^{\ddagger}$ = –18.7 cal K^{-1}), and the Gibbs energies of activation ($\Delta G^{\ddagger}$ = 7.4 kcal mol^{-1}) at 298 K (Figure S7). In particular, the small $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values imply that the observed transient intermediate should be highly reactive to undergo such a bond formation, which would significantly decrease its degrees of freedom. These results indicate that the transient intermediate observed by LFP is most likely H-shifted **5a**$^{+-}$, which contains a metastable borata-*ortho*-quinodimethane moiety. The observed ionic character of the transient intermediate is also consistent with the zwitterionic character of **5a**$^{+-}$. Considering that the transient intermediate could not be observed in toluene, the C–C bond formation from **5a** to **4a** is likely a very fast process under the reaction conditions. This is consistent with the fact that the spirocyclic products **4** were exclusively obtained as the *syn*-adducts.

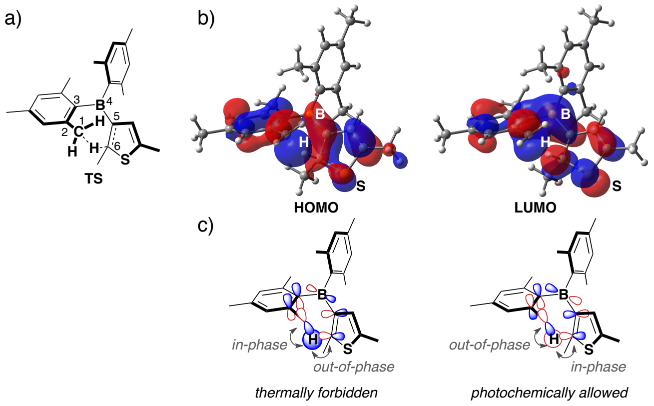


Figure 5. Frontier molecular orbitals analysis of the transition state for the [1,6]-sigmatropic rearrangement of **3a**: (a) structural formula of a transition state, (b) pictorial representation of the HOMO and LUMO for **TS(OS)**, and (c) the corresponding illustrations for the MO analysis.

In the mechanism of this cyclization, the initial [1,6]-sigmatropic rearrangement is highly intriguing. To elucidate the role of the boron atom on the orbital symmetry requirements of this sigmatropic reaction, we analyzed the frontier molecular orbitals of the transition state **TS(OS)** for **3a** (Figure 5).[13–15] In the propeller-like arrangement of the mesityl and thienyl groups on the boron center, only the antarafacial mode should be possible for this [1,6]-sigmatropic rearrangement. However, in the HOMO of **TS(OS)**, the p-orbital on C6 and the s-orbital on the migrating H atom are out-of-phase, indicating that the antarafacial [1,6]-sigmatropic hydrogen rearrangement in **3a** is thermally forbidden. In contrast, the corresponding orbitals in the LUMO are in-phase. These results are consistent with the experimental observations that **3a** undergoes the isomerization only under photochemical conditions. Notably, the vacant p-orbital of the boron atom contributes to the LUMO, inducing an effective delocalization of the molecular orbital over the boron-containing seven-membered cyclic structure.

It should be noted that the UV-vis absorption spectrum of spiroboraindane **4a** in THF exhibited an absorption band at longer maximum wavelength ($\lambda_{\max}$ = 375 nm) relative to 3-(dimesitylboryl)thiophene **3a** ($\lambda_{\max}$ = 322 nm), despite the disruption of the π-conjugation. Based on the results of the TD-DFT calculations (Figure S4), the longest-wavelength absorption band of **4a** can be assigned to an intramolecular charge-transfer transition from the HOMO, which is localized on the dihydrothiophene, to the LUMO, which is localized on the boraindane moiety. Importantly, the HOMO of **4a** consists of a σ-π interaction between the B–C and C–C bond σ-orbital in the boraindane moiety and the π-orbital of the dihydrothiophene moiety. This orbital interaction increases the energy of the HOMO, which is partially responsible for the bathochromically shifted absorption.

In summary, we have disclosed a photoinduced cyclization to produce unprecedented spirocyclic boraindanes as a new reaction mode for dimesityl(hetero)arylboranes. A combined experimental and theoretical study has supported the hypothesis that this reaction mode proceeds via a [1,6]-sigmatropic rearrangement, followed by an intramolecular C–C bond formation. This reaction is of particular interest as it is based on a significant contribution from the vacant p-orbital of the boron atom. This study indicates that the boron atom can function as an isostere of the carbocation in pericyclic reactions, which is one of the most fundamentally important reaction modes in organic chemistry. The obtained spirocyclic boraindanes represent a new class of boron-containing π-electron systems with characteristic absorption properties.

Acknowledgements

This work is partly supported by Grants-in-Aid for Scientific Research on Innovative Areas "Stimuli-responsive Chemical Species for the Creation of Functional Molecules" [JP24109007 and JP15H02163 (S.Y.), JP24109014 and JP15K13710 (K.Y.), as well as JP24109009 (H.I.)] from MEXT (Japan) and the MEXT Project of Integrated Research on Chemical Synthesis from Japan (A.F. and Y.S.).

Keywords: boron • photochemical reaction • sigmatropic rearrangement • pericyclic reaction • π-conjugation

[1] A. Pelter, R. T. Pardasani, P. Pardasani, *Tetrahedron*, **2000**, *56*, 7339.

[2] a) J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, D. G. Borden, *Chem. Commun. (London)* **1967**, 109; b) J. L. R. Williams, J. C Doty, P. J. Grisdale, R. Searle, T. H. Regan, G. P. Happ, D. P. Maier, *J. Am. Chem. Soc.* **1967**, *89*, 5153.

[3] a) J. J. Eisch, B. Shafii, A. L. Rheingold, *J. Am. Chem. Soc.* **1987**, *109*, 2526; b) J. J. Eisch, B. Shafii, J. D. Odom, A. L. Rheingold, *J. Am. Chem. Soc.* **1990**, *112*, 1847; c) J. J. Eisch, B. Shafii, M. P. Boleslawski *Pure Appl. Chem.* **1991**, *63*, 365.

[4] a) M. Kropp, K. Bhamidapaty, G. B. Schuster, *J. Am. Chem. Soc.* **1988**, *110*, 6252; b) J. D. Wilkey, G. B. Schuster, *J. Am. Chem. Soc.* **1988**, *110*, 7569; c) J. D. Wilkey, G. B. Schuster, *J. Am. Chem. Soc.* **1991**, *113*, 2149; d) M. A. Kropp, M. Baillargeon, K. M. Park, K. Bhamidapaty, G. B. Schuster, *J. Am. Chem. Soc.* **1991**, *113*, 2155; e) K. M. Park, G. B. Schuster, *J. Org. Chem.* **1992**, *57*, 2502.

[5] a) Y.-L. Rao, H. Amarne, S.-B. Zhao, T. M. McCormick, S. Martić, Y. Sun, R.-Y. Wang, S. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 12898; b) C. Baik, Z. M. Hudson, H. Amarne, S. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 14549; c) S. K. Murphy, C. Baik, J.-S. Lu, S. Wang, *Org. Lett.* **2010**, *12*, 5266; d) C. Baik, S. K. Murphy, S. Wang, *Angew. Chem.* **2010**, *122*, 8400; *Angew. Chem. Int. Ed.* **2010**, *49*, 8224; e) H. Amarne, C. Baik, S. K. Murphy, S. Wang, *Chem. Eur. J.* **2010**, *16*, 4750; f) Y.-L. Rao, H. Amarne, S. Wang, *Coord. Chem. Rev.* **2012**, *256*, 759; g) S. K. Mellerup, K. Yuan, C. Nguyen, Z.-H. Lu, S. Wang, *Chem. Eur. J.* **2016**, *22*, 12464–12472; h) Y.-L. Rao, C. Hörl, H. Braunschweig, S. Wang,

Angew. Chem. **2014**, *126*, 9232; *Angew. Chem. Int. Ed.* **2014**, *53*, 9086; i) D.-T. Yang, S. K. Mellerup, J.-B. Peng, X. Wang, Q.-S. Li, S. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 11513; j) S. K. Mellerup, C. Li, T. Peng, S. Wang, *Angew. Chem.* **2017**, *129*, 6189; *Angew. Chem. Int. Ed.* **2017**, *56*, 6093.

[6] J. L. R. Williams, P. J. Grisdale, J. C. Doty, *J. Am. Chem. Soc.* **1967**, *89*, 4538.

[7] V. V. Chung, K. Inagaki, M. Tokuda, M. Itoh, *Chem. Lett.* **1976**, 209.

[8] a) B. G. Ramsey, D. M. Anjo, *J. Am. Chem. Soc.* **1977**, *99*, 3182; b) G. C. Calhoun, G. B. Schuster, *J. Org. Chem.* **1984**, *49*, 1925; c) G. Bucher, *Liebigs Ann. Recueil* **1997**, 1415.

[9] A. Iida, S. Saito, T. Sasamori, S. Yamaguchi, *Angew. Chem.* **2013**, *125*, 3848; *Angew. Chem. Int. Ed.* **2013**, *52*, 3760.

[10] Photocyclizations of 1-cyclopentenyl ketones to afford the corresponding spirocyclic products have already been reported: a) A. B. Smith, III, W. C. Agosta, *J. Am. Chem. Soc.* **1973**, *95*, 1961; b) B. Pandey, U. R. Khire, N. R. Ayyangar, *J. Chem. Soc., Chem. Commun.* **1990**, 1791.

[11] The reaction profiles from **3a** to **TS** and from **TS** to **5a-OS** were calculated for the closed-shell and open-shell singlet states, respectively. For details, see the Supplementary Information.

[12] The LFP of **3a** in acetonitrile was conducted on 0.2 mM solution, as a 1 mM solution of **3a** could not be prepared due to its low solubility. The weak peak in the transient absorption spectrum may be attributed to the low concentration of **3a** in acetonitrile, and/or the small molar absorption coefficient of the transient species.

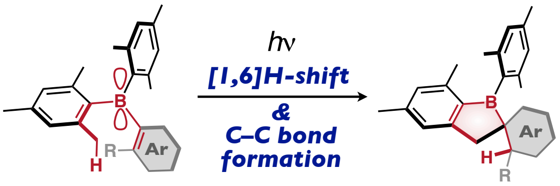
[13] a) R. Hoffmann, R. B. Woodward, *Acc. Chem. Res.* **1968**, *1*, 17; b) R. B. Woodward, R. Hoffmann, *Angew. Chem. Int. Ed.* **1969**, *8*, 781.

[14] N. J. Saettel, O. Wiest, *J. Org. Chem.* **2000**, *65*, 2331.

[15] Since the geometries of transition states in S_0, *i.e.*, **TS(OS)** and **TS(CS)**, and in S_1 are almost identical, the MOs of **TS(OS)** in S_0 were used for the current discussion. For details, see the Supporting Information.

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION



The photoinduced isomerization of dimesitylboryl-substituted (hetero)arenes to afford spirocyclic boraindanes is disclosed. This reaction proceeds via a [1,6]-sigmatropic rearrangement, followed by an intramolecular C–C coupling. The former process is characterized by the participation of the vacant p-orbital on boron, and thus constitutes a new reaction mode for triarylboranes. The obtained spirocyclic boraindanes showed characteristic absorption properties.

Naoki Ando, Aiko Fukazawa, Tomokatsu Kushida, Yoshihito Shiota, Shuhei Itoyama, Kazunari Yoshizawa, Yasunori Matsui, Yutaro Kuramoto, Hiroshi Ikeda,* and Shigehiro Yamaguchi**

Page No. – Page No.

Photochemical Intramolecular C–H Addition of Dimesityl-(hetero)arylboranes via a [1,6]-Sigmatropic Rearrangement