OL Organic Letters

Multiple Electrophilic C−H Borylation of Arenes Using Boron Triiodide

Susumu Oda, Kenta Ueura, Bungo Kawakami, and Takuji Hatakeyama*

Cite This: https://dx.doi.org/10.1021/acs.orglett.9b04483

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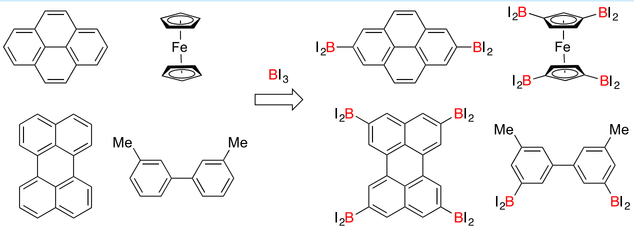
ABSTRACT: Electrophilic C−H borylation of arenes using boron triiodide has been developed. This reaction proceeded smoothly in the absence of additives, and the diiodoboryl group was installed at the most sterically accessible carbon, where the HOMO is localized to a certain extent. Moreover, regioselective multiple borylation of polycyclic aromatic compounds was achieved by using excess boron triiodide. The borylated intermediates were transformed into a variety of arylboron compounds such as arylboronates, boronic acids, and trifluoroborates.



Arylboron compounds not only have been used as useful synthetic intermediates,[1] but also have attracted considerable attention as functional materials.[2−5] For example, arylboronic acids participate in reversible Lewis pairing, boroxine formation, and esterification with diols to serve as catalysts,[2] medicines,[3] sensors,[4] and building blocks for covalent porous materials.[5] Over the past decade, transition metal-catalyzed direct C−H borylation has offered a straightforward approach for the synthesis of arylboronates.[6−8] However, these methods typically require precious-metal-based catalysts such as iridium-,[7a,b] rhodium-,[7c−e] and platinum-based catalysts,[7f−h] which are not suitable for industrial applications, while several non-noble transition metal-based catalysts have also been used for catalytic C−H borylation.[8]

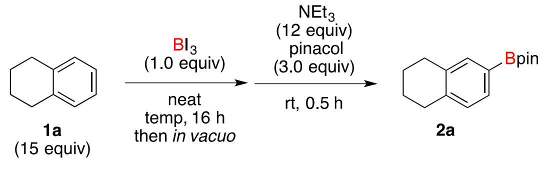
Electrophilic C−H borylation is a transition metal-free approach for the synthesis of arylboron compounds.[9−13] Since the pioneering contributions by Hurd, Muetterties, and Lappert et al.,[10] significant progress has been achieved by Vedejs and co-workers[11] and Ingleson and co-workers[12] toward establishing efficient arene borylation methods, which are complementary to the transition metal-catalyzed ones in terms of regioselectivity. However, these approaches require stoichiometric amounts of Lewis acids and do not allow for multiple borylations. Although several groups have reported electrophilic C−H borylation methodologies using catalytic activators[11b,12a,13h,l,o] or directing groups,[12i,13r] the development of additive-free borylation processes with a broad substrate scope is highly desirable. Recently, we reported the syntheses of BN-doped aromatic compounds, which showed high performance as luminescent materials for organic light-emitting diodes, via tandem electrophilic C−H borylation.[14] As part of our continued effort toward the development of novel methodologies for electrophilic C−H borylation, we found that boron triiodide (BI_3) is an effective reagent for the borylation of electron-rich triarylamines.[14b] Herein, we aim to demonstrate electrophilic C−H borylation of arenes by employing BI_3 in the absence of precious metal catalysts and additives. This simple system is applicable to the preparation of arylboronic acids, boronates, and trifluoroborates; construction of phenoxaborin and phenazaborin structures; and regioselective multiple borylation of polycyclic aromatic compounds,[15] which have not been achieved using electrophilic protocols.[9−13]

We began our study by investigating the electrophilic C−H borylation with tetralin **1a**, and Table 1 summarizes the optimization results. In the presence of 1.0 equiv of BI_3, **1a** was stirred at 120 °C for 16 h under neat conditions. After removal of the generated HI in vacuo, successive addition of triethylamine and pinacol provided the arylboronic acid pinacol ester **2a** in 78% yield (entry 1). Notably, selective borylation occurred at the 2-position and no regioisomer was obtained. After further screening of the reaction temperature, the yield was improved to be 94% by carrying out the reaction at 160 °C (entry 3). The reaction also proceeded with the use of a reduced amount of **1a** (5.0 equiv) and gave the product in 82% yield (entry 5).

As shown in Scheme 1, treatment of the borylated intermediate with water afforded the corresponding boronic acid **3** in 89% yield. The intermediate was also successfully converted to potassium trifluoroborate **4** in 86% yield by using potassium fluoride. Thus, this method enabled the facile transformation of the borylated intermediate to arylboronic acids and borates, which were not obtained by reported

Received: December 14, 2019

Table 1. Electrophilic C−H Borylation of Tetralin



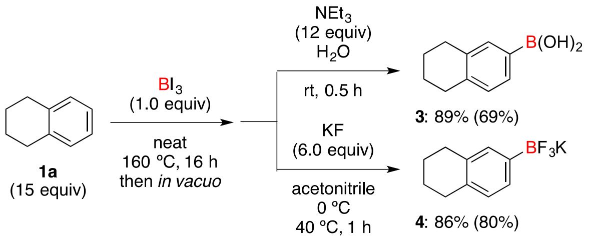
1a
(15 equiv)

2a

entry[a]	temp	yield[b]
1	120 °C	78%
2	140 °C	84%
3	160 °C	94% (84%)
4	180 °C	80%
5[c]	160 °C	82%

[a]Reaction conditions: tetralin (**1a**) (15 mmol), BI_3 (1.0 mmol) at 120−180 °C for 16 h under nitrogen atmosphere. [b]Yields were determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard, and isolated yields are shown in parentheses. [c]5.0 equiv of **1a** (5.0 mmol) was used.

Scheme 1. Synthesis of Boronic Acid and Trifluoroborate[a]



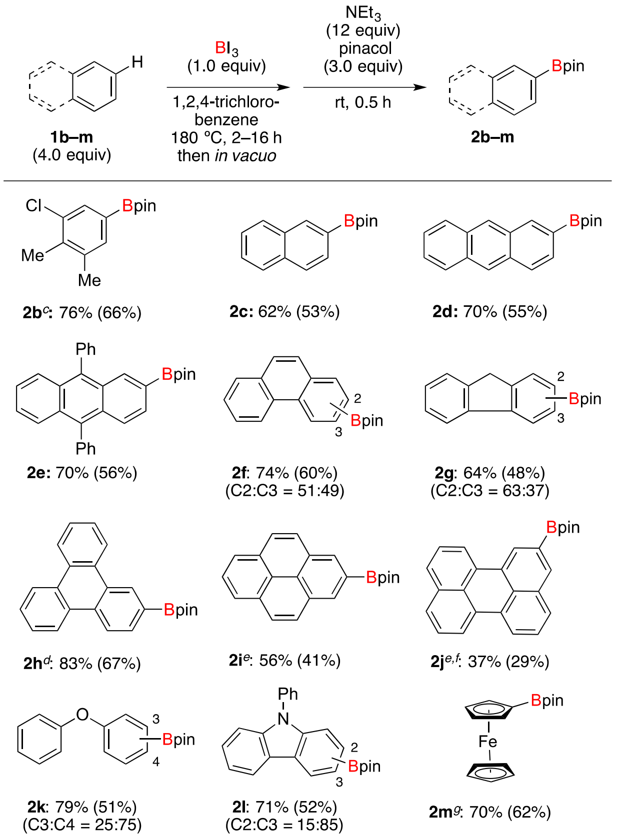
1a
(15 equiv)

3: 89% (69%)

4: 86% (80%)

[a]Yields were determined by ^1H NMR using dibromomethane as an internal standard, and isolated yields are shown in parentheses.

Scheme 2. Substrate Scope for Electrophilic C−H Borylation[ab]



1b–m
(4.0 equiv)

2b–m

2b[c]: 76% (66%)

2c: 62% (53%)

2d: 70% (55%)

2e: 70% (56%)

2f: 74% (60%)
(C2:C3 = 51:49)

2g: 64% (48%)
(C2:C3 = 63:37)

2h[d]: 83% (67%)

2i[e]: 56% (41%)

2j[e,f]: 37% (29%)

2k: 79% (51%)
(C3:C4 = 25:75)

2l: 71% (52%)
(C2:C3 = 15:85)

2m[g]: 70% (62%)

[a]Reaction conditions: arene (**1**) (0.8 mmol), BI_3 (0.2 mmol), 1,2,4-trichlorobenzene (1.6 mL) at 180 °C for 2−16 h under nitrogen atmosphere. [b]Yields were determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard, and isolated yields are shown in parentheses. [c]Reaction of arene (**1**) (15 mmol) with BI_3 (1.0 mmol) was conducted at 160 °C for 16 h under neat conditions. [d]Reaction was conducted at 160 °C for 8 h. [e]2.0 equiv of arene (**1**) was used. [f]Reaction was conducted at 200 °C for 8 h. [g]Reaction was conducted in 1,2-dichlorobenzene at 0 °C for 12 h.

methods, because the use of a stoichiometric amount of additives may hamper the transformation.[12e]

Having established conditions for the metal-free borylation, we evaluated the scope of the arene substrates, which are summarized in Scheme 2. First, 3-chloro-*o*-xylene **1b** was evaluated, and it underwent selective borylation at the 5-position to afford **2b** in 76% yield.[16] Unfortunately, the borylation of other chloro-substituted substrates such as chlorobenzene and 1,2-dichlorobenzene resulted in low yield due to its low reactivity and the reaction of 3-chloro-*o*-xylene only provided a satisfying yield so far. The borylation of naphthalene proceeded selectively at the 2-position and furnished **2c** in 62% yield.[17] Similarly, anthracene, triphenylene, pyrene, and perylene were also compatible with the reaction conditions and afforded the corresponding 2-borylated products (**2d**, **e**, **h**−**j**). The excess substrates mostly remained intact and were recovered.[18] In contrast, borylation of phenanthrene and fluorene resulted in a mixture of regioisomers, wherein the boron atoms were substituted at the 2- and 3-positions in 51:49 and 63:37 ratios, respectively (**2f**, **g**). Diphenyl ether and *N*-phenyl carbazole participated in C−H borylation and gave comparable yields with higher regioselectivity (**2k**, **l**). Notably, the borylation of ferrocene proceeded smoothly at 0 °C and furnished **2m** in 70% yield. In particular, the regioselectivity did not depend on the reaction time in all the cases.

To gain insight into the regioselectivity observed in this transformation, density functional theory (DFT) calculations for 3-chloro-*o*-xylene **1b**, diphenyl ether **1k**, 9,10-diphenylanthracene **1e**, and the corresponding borylated intermediates were performed at the B3LYP/6-31G(d) level of theory. Although the highest occupied molecular orbital (HOMO) of 3-chloro-*o*-xylene was localized on the carbon at the 6-position (indicated by the red circle), borylation took place at the 5-position (Figure 1). Given that **1b-5-BI**$_2$ is more stable than the other regioisomers by 5.1 kcal/mol, the observed regioselectivity cannot be explained by the electron density of HOMO but can be accounted for by considering the stability of the borylated product. However, in the case of diphenyl ether, **1k-3-BI**$_2$ and **1k-4-BI**$_2$ were formed in a 25:75 ratio. This value was inconsistent with the theoretically predicted ratio of 7:93, which was determined by their energy difference of 2.3 kcal/mol. These results indicated that this reaction is kinetically controlled due to the steric bulkiness of BI_3, which led to predominant borylation at the less hindered carbon. Furthermore, the DFT calculations for 9,10-diphenylanthracene showed that the HOMO is mainly localized on the anthracene skeleton and does not exist on the phenyl substituents. Although **1e-9b-BI**$_2$ is the most stable borylated intermediate and the *m*-carbon of the phenyl group is sterically less congested, the 2-borylated product was obtained selectively. This result suggested the borylation

https://dx.doi.org/10.1021/acs.orglett.9b04483
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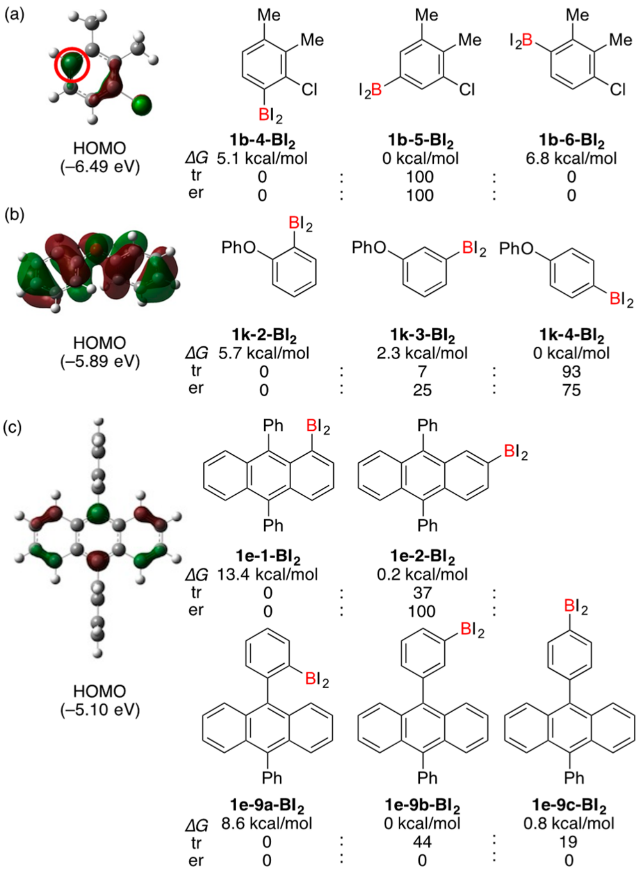
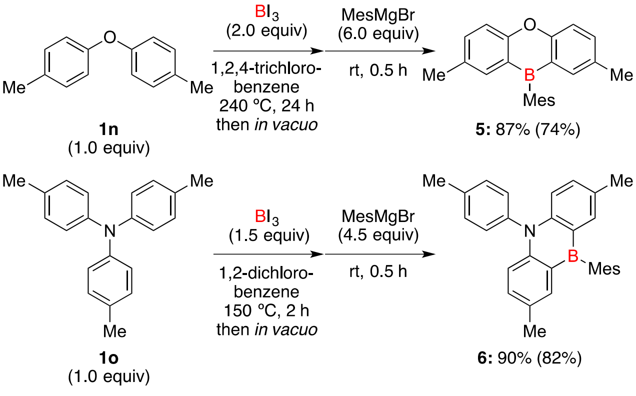


Figure 1. Kohn−Sham highest occupied molecular orbital and relative Gibbs free energies (Δ*G*) for borylated intermediates of (a) 3-chloro-*o*-xylene **1b**, (b) diphenyl ether **1k**, and (c) 9,10-diphenylanthracene **1e** calculated at the B3LYP/6-31G(d) level of theory. tr, theoretical ratio; er, experimental ratio. The theoretical ratio of regioisomers was determined using the equilibrium constant ($K = \exp(\Delta G/RT)$).

takes place at the most accessible carbon, where the HOMO is localized to a certain extent.

To demonstrate the utility of this method, phenoxaborin[19] and phenazaborin[20] analogues were synthesized (Scheme 3). Di-*p*-tolyl ether **1n** was reacted with BI_3 at 240 °C, followed by the addition of mesitylmagnesium bromide, which afforded phenoxaborin analogue **5** in 87% yield. In contrast to the case of the diphenyl ether, borylation took place selectively at the *ortho* position due to the presence of the methyl group at the position *para* to the oxygen, and the subsequent intramolecular reaction formed the phenoxaborin skeleton. Similarly, tri-*p*-tolylamine **1o** underwent regioselective borylation at the position *ortho* to the nitrogen, and the successive nucleophilic substitution with mesitylmagnesium bromide furnished phenazaborin analogue **6** in 90% yield.

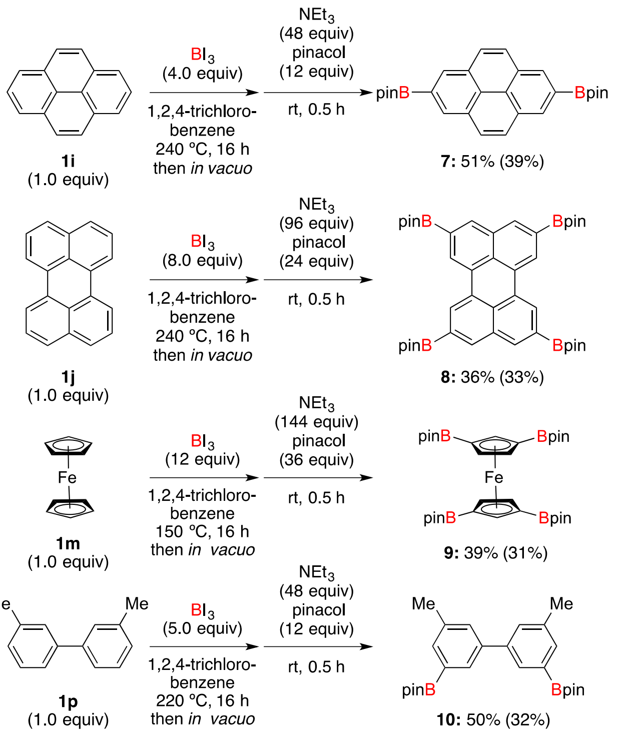
Scheme 3. Synthesis of Phenoxaborin and Phenazaborin Analogues[a]



[a] Yields were determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard, and isolated yields are shown in parentheses.

Notably, multiple borylation[15] of polycyclic aromatic compounds was successful with the use of excess BI_3 (Scheme 4). In the presence of 4.0 equiv of BI_3, double borylation occurred at the 2,7-position of pyrene and afforded **7** in 51% yield. Furthermore, the use of 8.0 equiv of BI_3 afforded 2,5,8,11-tetraborylated perylene **8** in 36% yield. Ferrocene and 3,3′-dimethylbiphenyl also underwent multiple borylations and furnished the corresponding tetra- and diborylated products **9** and **10** in 39% and 50% yield, respectively.

Scheme 4. Multiple Borylation of Pyrene, Perylene, Ferrocene, and 3,3′-Dimethylbiphenyl[a]



[a] Yields were determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard, and isolated yields are shown in parentheses.

In summary, we successfully developed a methodology for the electrophilic C−H borylation of arenes with boron triiodide, which enabled the direct synthesis of arylboronates, boronic acids, and borates. The DFT calculations suggested that this reaction is kinetically controlled to take place at the most sterically accessible carbon, where the HOMO is localized to a certain extent. Furthermore, we successfully synthesized phenoxaborin and phenazaborin analogues by the intermolecular and intramolecular electrophilic C−H borylation of di-*p*-tolyl ether and tri-*p*-tolylamine, respectively. The method was also extended to regioselective multiple borylation by simply using excess BI_3, producing multiborylated aromatic compounds, which can provide access to novel functional materials.[21]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04483.

Synthesis, analytical data, NMR spectra, DFT studies (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Takuji Hatakeyama − *Kwansei Gakuin University, Sanda, Japan;* orcid.org/0000-0002-7483-9525; Email: hatake@kwansei.ac.jp

Other Authors

Susumu Oda − *Kwansei Gakuin University, Sanda, Japan;* orcid.org/0000-0003-1088-1932
Kenta Ueura − *Kwansei Gakuin University, Sanda, Japan*
Bungo Kawakami − *Kwansei Gakuin University, Sanda, Japan*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.9b04483

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was supported by a Grant-in-Aid for Scientific Research (JP18H02051), Challenging Research (Exploratory, JP17K19164, 19K22191), and Grant-in-Aid for Early-Career Scientists (18K14228) from the Japan Society for the Promotion of Science (JSPS), Sumitomo Foundation, Kinoshita Memorial Enterprise, and Hyogo Science and Technology Association.

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