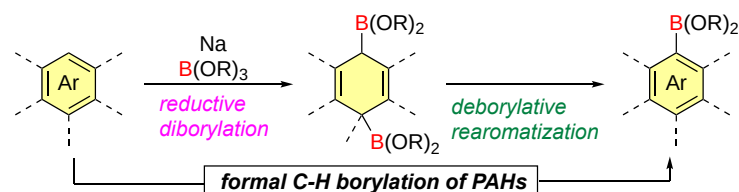


Sodium-promoted Borylation of Polycyclic Aromatic Hydrocarbons

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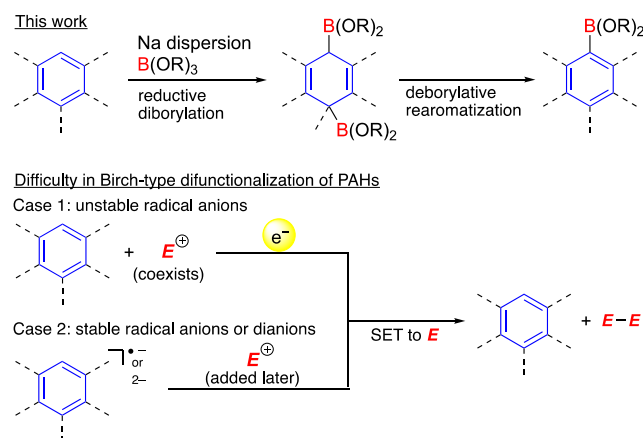
ABSTRACT: Sodium dispersion promotes reductive borylation of polycyclic aromatic hydrocarbons with MeOBpin. Anthracenes and phenanthrenes are converted to the corresponding dearomatized diborylated products. The reductive diborylation of naphthalene-based small π systems yields similar yet unstable products, which are oxidized into formal C-H borylation products with unique regioselectivity. Pyrene is converted to 1-borylpyrene without adding an oxidant. The latter two reactions represent a new route to useful borylated PAHs that rivals C-X borylation and catalytic C-H borylation.

Polycyclic aromatic hydrocarbons (PAHs) represent an important class of aromatic compounds that find numerous applications in material sciences.¹ Peripheral functionalizations of PAHs are therefore very important to extend their π -conjugations and to endow PAH-based molecules with intriguing properties. For the functionalization, electrophilic aromatic substitutions have been used as classical and reliable methods.² Recently, iridium-catalyzed C-H borylation has occupied an alternative central position³ because one can apply a diverse range of transformations of arylboron compounds such as oxidation and Suzuki-Miyaura cross-coupling reaction to borylated PAHs. As the importance of borylated PAHs has been increasing, there should be a potential high demand for new methods that rival the Ir-catalyzed C-H borylation and Pd-catalyzed Miyaura-Ishiyama borylation⁴ or metalation-borylation⁵ that follows electrophilic halogenation of PAHs.

Reduction of unsaturated hydrocarbons with alkali metal provides an interesting series of irreplaceable transformations in organic synthesis. The Birch reduction of aromatic rings is a representative and yields 1,4-cyclohexadienes by means of sodium metal in liquid ammonia.⁶ We envisioned that the Birch-type reduction is applicable to borylation of PAHs as illustrated in Scheme 1. We have been interested in the combined use of sodium dispersion for efficient reduction^{7,8} and reduction-resistant electrophiles for efficient trapping of the resulting unstable anionic species.⁹ Given that the reduction of a PAH with sodium dispersion proceeds in the presence of a reduction-resistant alkoxyborane, the anionic species thus generated would be trapped with the boron-based electrophile to yield a borylated dearomatized product. The initial product is expected to be a diborylated one of synthetic use on its own,

while it can undergo deborylative rearomatization to yield a monoborylated PAH.

Scheme 1. Reductive Borylation of PAHs



In the arena of Birch-type reductive transformations of aromatic compounds, it is very difficult to trap the resulting anionic species with electrophiles other than proton (Scheme 1).¹⁰ Firstly, the initially formed radical anions of arenes are generally very unstable and hence require immediate trapping with an electrophile (Case 1). However, coexisting electrophiles are generally prone to be readily reduced under Birch-type reductive conditions. Secondly, even though some of the radical anions of PAHs are reasonably stable to allow us to add an electrophile after their generation, the electron-rich radical anions and/or dianions have a high potential to evoke single electron transfer to the electrophile (Case 2). In considering the issues raised above, our reduction-resistant alkoxyborane perfectly meets the

requirements for the Birch-type difunctionalization. We report here reduction of PAHs with sodium dispersion in the presence of a trialkoxyborane and the behaviors of the initially formed diborylated dearomatized products.

We started our investigation by using anthracene as a model substrate (Table 1). A mixture of anthracene and methoxypinacolborane (MeOBpin, 6.0 equiv) was treated with sodium dispersion (2.5 equiv) in DME at $-40\text{ }^{\circ}\text{C}$ for 2 h. The reaction was terminated with an addition of isopropyl alcohol to yield 9,10-diborylated dihydroanthracene **1** in 46% NMR yield with high *anti* selectivity (entry 1). A major byproduct was found to be 9,10-dihydroanthracene, which indicate either that the borylation is inefficient or that borylated intermediates, probably borates, in the reaction flask are unstable to undergo protodeborylation upon quenching the reaction. We found that the latter is the case and that a quenching agent plays an important role: Instead of *i*PrOH, additions of acetic acid and of hydrochloric acid in ether afforded **1** in 74% and 81% yields, respectively (entries 2 and 3). The more stable conjugate bases, acetate and chloride, are supposed not to form reactive borate species efficiently. The diborylation at a lower temperature of $-60\text{ }^{\circ}\text{C}$ improved the *anti* selectivity up to 93:7 (entry 4).

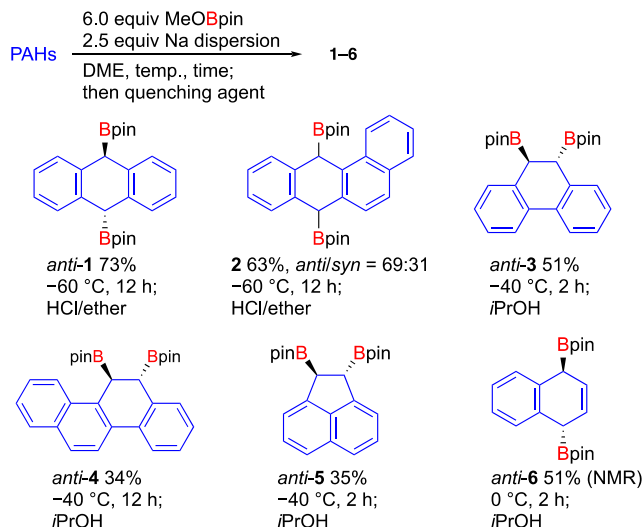
Table 1. Reductive Diborylation of Anthracene

entry	temp., time	quenching agent	NMR yield /%	<i>anti</i> / <i>syn</i>
1	$-40\text{ }^{\circ}\text{C}$, 2 h	<i>i</i> PrOH	46 ^a	89:11
2	$-40\text{ }^{\circ}\text{C}$, 2 h	AcOH	74	76:24
3	$-40\text{ }^{\circ}\text{C}$, 2 h	HCl/ether	81	74:26
4	$-60\text{ }^{\circ}\text{C}$, 12 h	HCl/ether	82	93:7

^a9,10-dihydroanthracene was obtained in 19% yield.

We then investigated the scope of this diborylation with respect to PAHs (Scheme 2). Chromatographic purification of the *anti*/*syn* mixture of **1** on silica gel resulted in isolation of *anti*-**1** in 73% yield. Benz[*a*]anthracene was similarly converted to the diborylated product **2** as a mixture of diastereomers, where the predominance of the *anti* isomer is supposed by analogy with the preferable formation of *anti*-**1**. Phenanthrene, chrysene, and acenaphthylene were diborylated at the most reactive double bonds to yield *anti*-**3**, **4**, and **5**, respectively, without formation of their *syn* isomers. The stereochemistry of *anti*-**1** and *anti*-**3** was unambiguously assigned on the basis of XRD analysis.¹¹ It is worth noting that these diborylation took place at the positions to which the conventional Birch reduction adds the two hydrogens.¹²

Scheme 2. Reductive Diborylation of PAHs



Naphthalene was diborylated to yield *anti*-**6** in moderate yield according to NMR analysis. However, we failed to isolate *anti*-**6** because of its instability during work-up and purification (Scheme 2). Instead of quenching the reaction with an acid to obtain diborylated *anti*-**6**, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was added as an oxidant to the reaction mixture. The addition successfully resulted in oxidative monodeborylation selectively to yield 1-borylnaphthalene **7** (Scheme 3). This sequence of reductive diborylation and oxidative monodeborylation is regarded as formal C–H borylation of naphthalene.

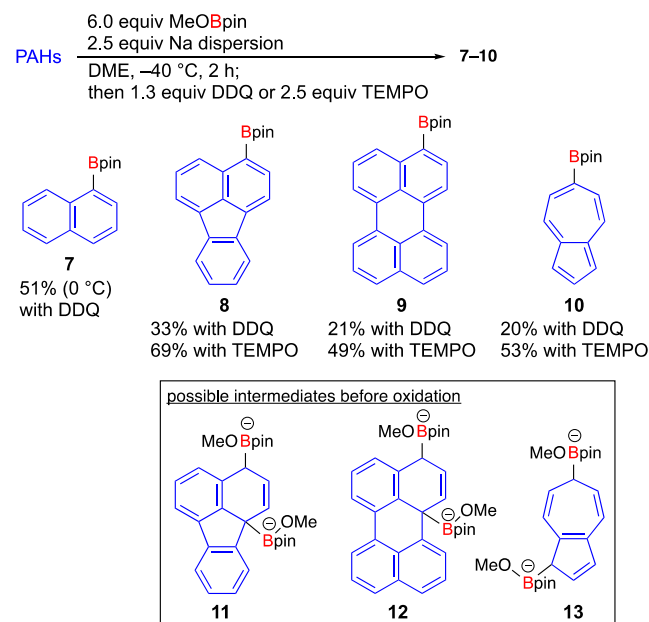
This transformation was applicable to fluoranthene and perylene that have a naphthalene motif to regioselectively give **8** and **9**, respectively. In these cases, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was found to be superior to DDQ as the oxidant in these cases. The products **7–9** are inaccessible through the conventional Ir-catalyzed C–H borylation and are typically synthesized via the corresponding halogenated PAHs.¹³

More interestingly, the formal C–H borylation is applicable to azulene, a constitutional isomer of naphthalene, to yield 6-borylazulene **10** with exclusive regioselectivity. Notably, the Ir-catalyzed borylation of azulene usually occurs at the least hindered 2 position to yield 2-borylazulene^{14,15} and the electrophilic aromatic halogenation of azulene occurs at the most electron-rich 1 position.¹⁶ There are no reports on the direct functionalization of azulene at the 6 position, while a very lengthy, 6-step synthesis of **10** from 2-chlorotropone was reported.^{17,18} Our formal C–H borylation of azulene will find applications in the chemistry of azulene-based functional molecules.¹⁹

The regioselectivity of the monoborylation in Scheme 3 would depend on the following two factors: 1) the regioselectivity of the initial diborylation, which obeys that of the conventional Birch reduction¹² and 2) the regioselectivity of the oxidative deborylation. Although the exact reaction mechanism for the oxidative deborylation is unclear, the deborylation is likely to involve the more crowded, more electron-rich, and thus less stable boryl group in each intermediate **11** or **12**. The situation is more complex in the case of azulene derivative **13**. We speculate that the oxidation

event takes place at the more conformationally constrained cyclopentadienylboryl group.

Scheme 3. Reductive Diborylation and Oxidation to Yield C-H-Borylated PAHs



Treatment of pyrene under the standard conditions (entry 4 in Table 1) did not afford any conceivable diborylated products but 1-borylpyrene **14** in 64% yield without exposure to DDQ or TEMPO (Scheme 4). Wondering the unexpectedly smooth formation of monoborylated **14**, we performed mechanistic study by monitoring the reaction of pyrene by ^{11}B NMR spectroscopy (Figure 1). Along with the expected signals for the remaining MeOBpin (22 ppm) and its borate $[(\text{RO})_4\text{B}]^-$ (3 ppm), the borylated pyrene was observed as its neutral form **14** (33 ppm) and its methoxyborate **19** (8 ppm, *vide infra*) even under inert atmosphere. More importantly, two unexpected signals appeared at -9 ppm as a broad quartet and at -28 ppm as a sharp quartet, respectively. The broad quartet was assigned to be methoxyborohydride $[\text{MeOBH}_3]^-$ according to the literature.²⁰ Thomas reported that treatment of pinacolborane (HBpin) with sodium methoxide induces multiple hydride-alkoxide exchanges and results in the formation of $[\text{MeOBH}_3]^-$ and $[\text{BH}_4]^-$. We thus conclude that HBpin was formed together with **14** in situ before work-up. The sharp quartet at -28 ppm is assignable to $[\text{pyrenylBH}_3]^-$ according to the literature.²¹

On the basis of these experiments, Scheme 4 shows a possible reaction mechanism for the borylation of pyrene. The first one electron reduction generates the radical anion of pyrene, which reacts with MeOBpin followed by another one electron reduction to yield monoborylated anion **15**. From **15**, we are tempted to propose two pathways. Path A includes a process similar to the reactions in Scheme 3 and 4: the second borylation of **15** affords **16**. The subsequent hydride shift followed by retro-hydroboration to generate **14** with concomitant formation of HBpin and with recovery of aromaticity. We performed DFT calculations¹¹ on the retro-hydroboration from **17** to **14** to reveal the computed

activation barrier is more than 50 kcal/mol. We hence deny the possibility of path A. Path B does not include the second borylation: The anion **15** has a highly conjugated π -system and delocalized electron density. MeOBpin could not react with **15** efficiently, and, instead, a 1,2-hydride shift from the borylated carbon to the boron center would occur to yield aromatized borate **18**. The shifted hydride would be removed by the action of Lewis acidic MeOBpin to eventually provide **14**, which is in equilibrium with its methoxy borate **19**. The activation energy of the 1,2-hydride shift was calculated to be 26.6 kcal/mol, which indicates the shift is much more likely to occur.

Scheme 4. Borylation of Pyrene

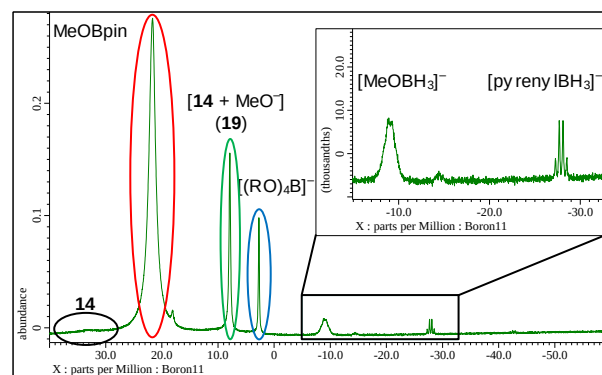
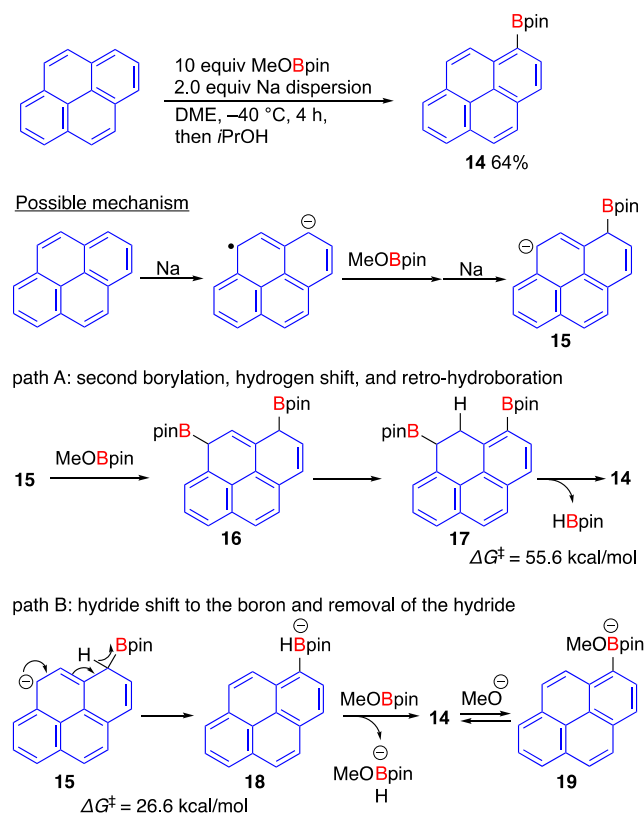


Figure 1. ^{11}B NMR spectrum of the reaction mixture

We have examined the reaction of polycyclic aromatic hydrocarbons with MeOBpin promoted by sodium and have found three different types of borylation. 1) Anthracene and

phenanthrene derivatives: The corresponding dearomatized diborylated products were obtained as stable primary products. The remaining aromatic systems would endow the diborylated products with sufficient stability even after the dearomatization. 2) Naphthalene-based smaller π systems: The initial dearomatized diborylated products are unstable to handle because of the significant loss of aromaticity and are subjected to oxidation before work-up to afford formal C-H borylation products regioselectively. The products represent isomers that are not accessible via the Ir-catalyzed C-H borylation. This method provides by far the most concise approach to synthetically useful 6-borylazulene. 3) Treatment of pyrene under the conditions for the reductive borylation affords 1-borylpyrene without adding an oxidant. This type of borylation is expected to occur in the reactions of larger PAHs. The borylation of type 2) and 3) offers a new approach to useful borylated PAHs, being a protocol that is mechanistically different from the Ir-catalyzed direct C-H borylation and the stepwise borylation via halogenated PAHs. Further investigation on our synthetic strategy based on the combined use of alkali metal and reductive-resistant electrophiles is underway in our laboratory.

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Supporting Information

Experimental procedures and spectral data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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