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Letter

Sodium-Promoted Borylation of Polycyclic Aromatic Hydrocarbons

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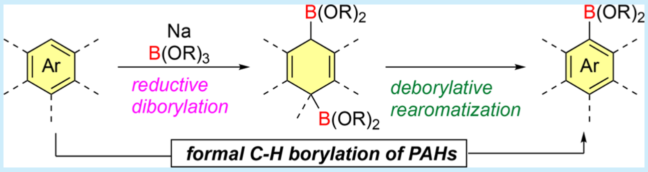
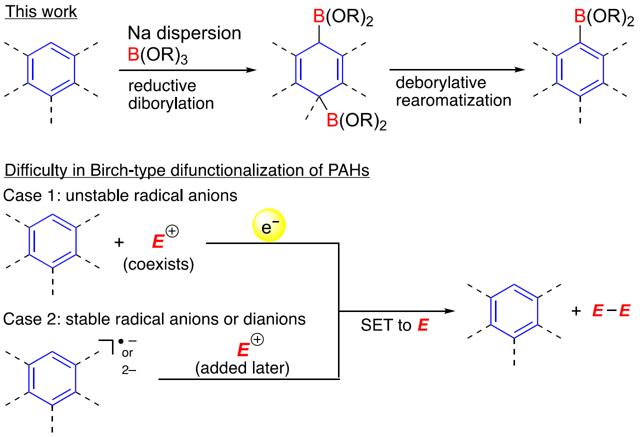
ABSTRACT: Sodium dispersion promotes the reductive borylation of polycyclic aromatic hydrocarbons (PAHs) with MeOBpin. Anthracenes and phenanthrenes are converted to the corresponding dearomatized diborylated products. The reductive diborylation of naphthalene-based small π-systems yields similar yet unstable products that are oxidized into formal C−H borylation products with unique regioselectivity. Pyrene is converted to 1-borylpyrene without the addition of 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 position[3] because one can apply a diverse range of transformations of arylboron compounds such as oxidation and Suzuki−Miyaura cross-coupling reaction to borylated PAHs. Because 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 borylation[4] or the metalation−borylation[5] that follows the electrophilic halogenation of PAHs.

The 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 it yields 1,4-cyclohexadienes by means of sodium metal in liquid ammonia.[6] We envisioned that the Birch-type reduction is applicable to the 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 thus-generated anionic species 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, whereas 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 a proton (Scheme 1).[10] First, 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 being readily reduced under Birch-type reductive conditions. Second, 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 dianions have a high potential to evoke single-electron transfer to the electrophile (Case 2). In considering the issues raised above, our reduction-resistant

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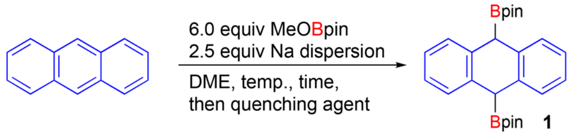
alkoxyborane perfectly meets the requirements for the Birch-type difunctionalization. We report here the reduction of PAHs with sodium dispersion in the presence of a trialkoxyborane and the behaviors of the initially formed diborylated dearomatized products.

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 1,2-dimethoxyethane (DME) at −40 °C for 2 h. The reaction was terminated with the addition of isopropyl alcohol to yield 9,10-diborylated dihydroanthracene **1** in 46% nuclear magnetic resonance (NMR) yield with high anti selectivity (entry 1). A major byproduct was found to be 9,10-dihydroanthracene, which indicated either that the borylation was inefficient or that the borylated intermediates, probably borates, in the reaction flask were unstable and could not undergo protodeborylation upon quenching the reaction. We found that the latter was the case and that a quenching agent played an important role: Instead of *i*PrOH, the addition of acetic acid and hydrochloric acid in ether afforded **1** in 74 and 81% yield, respectively (entries 2 and 3). The more stable conjugate bases, acetate and chloride, are not supposed to form reactive borate species efficiently. The diborylation at a lower temperature of −60 °C improved the anti selectivity up to 93:7 (entry 4).

Table 1. Reductive Diborylation of Anthracene



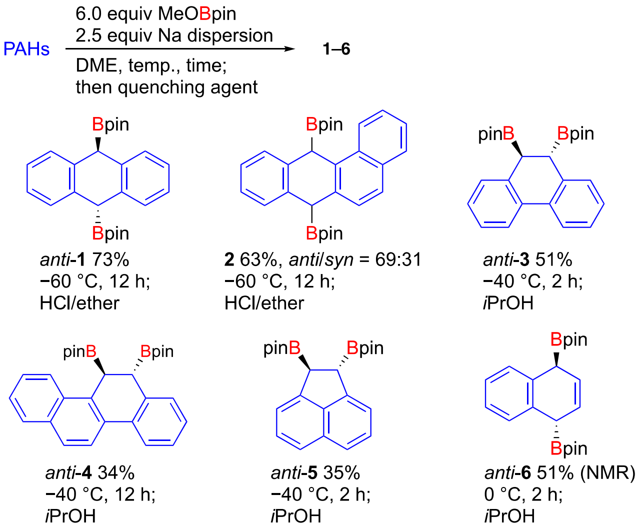
entry	temp., time	quenching agent	NMR yield (%)	anti/syn
1	−40 °C, 2 h	*i*PrOH	46[a]	89:11
2	−40 °C, 2 h	AcOH	74	76:24
3	−40 °C, 2 h	HCl/ether	81	74:26
4	−60 °C, 12 h	HCl/ether	82	93:7

[a] 9,10-Dihydroanthracene was obtained in 19% yield.

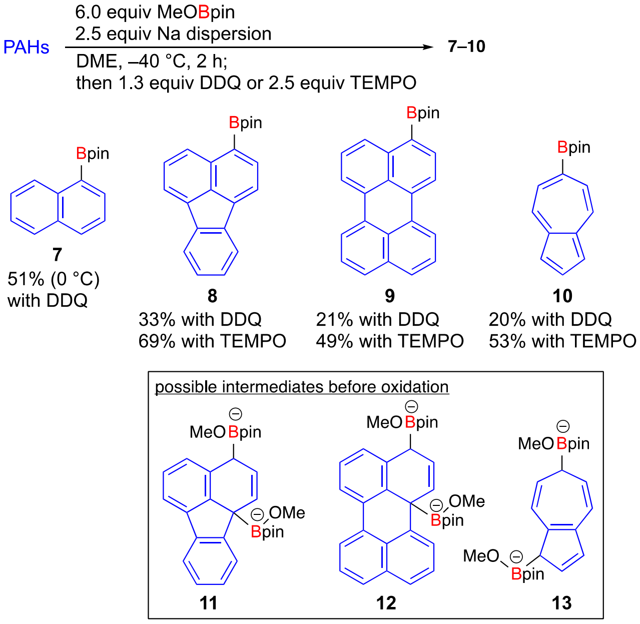
We then investigated the scope of this diborylation with respect to PAHs (Scheme 2). Chromatographic purification of the anti/syn mixture of **1** on silica gel resulted in the isolation of *anti*-**1** in 73% yield. Benz[*a*]anthracene was similarly converted to the diborylated product **2** as a mixture of diastereomers, where the predominance of the anti isomer was supposed by analogy to 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 the formation of their syn isomers. The stereochemistry of *anti*-**1** and *anti*-**3** was unambiguously assigned on the basis of X-ray diffraction (XRD) analysis.[11] It is worth noting that these diborylations took place at the positions to which the conventional Birch reduction adds the two hydrogens.[12]

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 workup 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 the selective oxidative monodeborylation to yield 1-borylnaphthalene **7** (Scheme 3). This sequence of reductive diborylation and oxidative monodeborylation is regarded as the formal C−H borylation of naphthalene.

Scheme 2. Reductive Diborylation of PAHs



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



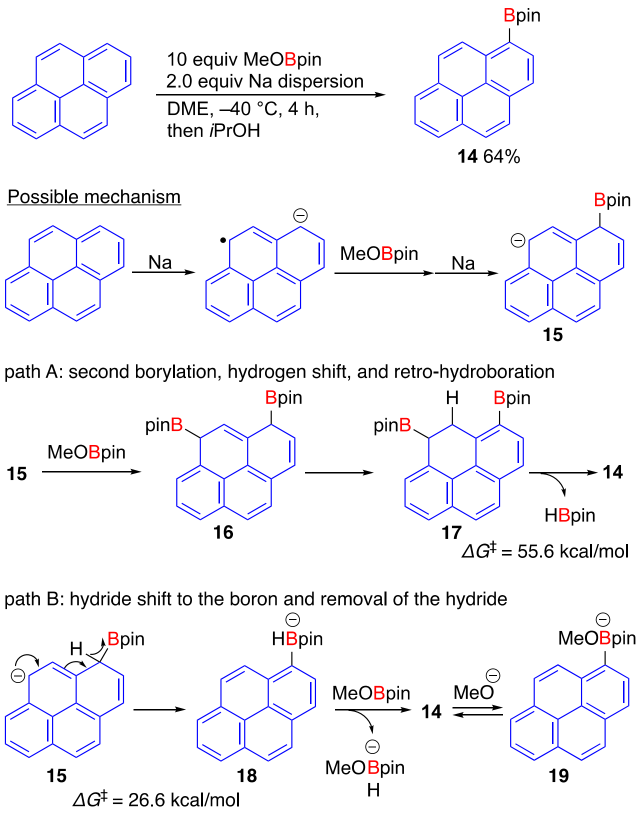
This transformation was applicable to fluoranthene and perylene that have a naphthalene motif to regioselectively give **8** and **9**, respectively. In these cases, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was found to be superior to DDQ as the oxidant in these cases. The products **7**−**9** are 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 two-position to yield 2-borylazulene,[14,15] and the electrophilic aromatic halogenation of azulene occurs at the most electron-rich one-position.[16] There are no reports on the direct functionalization of azulene at the six-position, whereas a very lengthy, six-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 reduction,[12] 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.

The treatment of pyrene under the standard conditions (entry 4 in Table 1) did not afford any conceivable diborylated products but afforded 1-borylpyrene **14** in 64% yield without exposure to DDQ or TEMPO (Scheme 4). To further explore the unexpectedly smooth formation of monoborylated **14**, we performed a 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 $[(RO)_4B]^-$ (3 ppm), the borylated pyrene was observed as its neutral form **14** (33 ppm) and its methoxyborate **19** (8 ppm, *vide infra*) even under an 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 $[MeOBH_3]^-$ according to the literature.[20] Thomas reported that the treatment of pinacolborane (HBpin) with sodium methoxide induces multiple hydride−alkoxide exchanges and results in the formation of $[MeOBH_3]^-$ and $[BH_4]^-$. We thus concluded that HBpin was formed together with **14** *in situ* before workup. The sharp quartet at −28 ppm is assignable to $[pyrenylBH_3]^-$ according to the literature.[21]

Scheme 4. Borylation of Pyrene



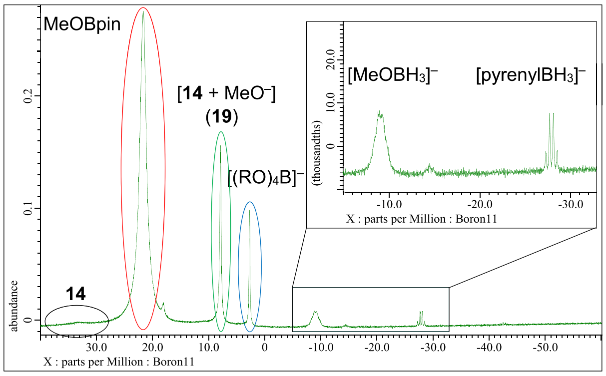


Figure 1. ^{11}B NMR spectrum of the reaction mixture.

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 Schemes 2 and 3: The second borylation of **15** affords **16**. The subsequent hydride shift followed by retro-hydroboration generates **14** with the concomitant formation of HBpin and with the recovery of aromaticity. We performed density functional theory (DFT) calculations[11] on the retro-hydroboration from **17** to **14** to reveal that the computed activation barrier is >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 a delocalized electron density. MeOBpin could not efficiently react with **15**, 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 that the shift is much more likely to occur.

We have examined the reaction of PAHs 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 workup 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.

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(3) Treatment of pyrene under the conditions for the reductive borylation affords 1-borylpyrene without the addition of an oxidant. This type of borylation is expected to occur in the reactions of larger PAHs. The borylation of types 2 and 3 offers a new approach to useful borylated PAHs, a protocol that is mechanistically different from the Ir-catalyzed direct C−H borylation and the stepwise borylation via halogenated PAHs. Further investigation into our synthetic strategy based on the combined use of alkali metal and reduction-resistant electrophiles is underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01355.

Experimental procedures and spectral data (PDF)

Accession Codes

CCDC 2078198−2078199 contain 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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