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A Forgotten Olefin: A Convenient One-pot Cascade Reaction Involving Suzuki–Miyaura and Mizoroki–Heck Couplings to Form (*E*)-1,2-Di(pyren-1-yl)ethylene

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The addition of 0.5 equiv of vinylboronic acid pinacol ester **I** to 1-bromopyrene derivative **3** in the presence of $[Pd(PPh_3)_4]$ and K_2CO_3 induced a cascade reaction involving Suzuki–Miyaura and Mizoroki–Heck couplings and afforded (*E*)-1,2-di(pyren-1-yl)ethylene derivative **1b**. An alternative synthesis of **1b** was carried out by an olefin metathesis. Formed **1b** showed absorption bands in the visible region and a low oxidation potential attributable to a narrow HOMO–LUMO gap.

Well-conjugated hydrocarbons (CHCs), including polyaromatic hydrocarbons (PAHs) and their analogs, have attracted much attention.[1,2] The design and synthesis of new CHCs poses a challenge to synthetic chemists. The obtained CHCs are expected to find use in advanced materials, such as light-emitting devices, molecule-based electronics, including field-effect transistors and lithium batteries,[3] and CHCs provide supramolecular synthons with attractive π–π interactions.[4] Breaking from the synthetic strategies commonly used to prepare PAHs, such as oxidative intramolecular couplings of oligophenylenes,[2] the authors focused on a classical simple methodology in which PAHs were connected to olefins, such as 1,2-diarylethenes (DArEs), in hope of obtaining new CHCs. Although thousands of DArEs have been reported thus far,[5] their aryl groups have been limited to, for example, benzenes, naphthalenes, anthracenes, metalloporphyrins,[6] and so on. Pyrene is one of the most commonly used PAHs, and its excited state properties are widely employed.[7] The corresponding DArE of pyrene, (*E*)-1,2-di(pyren-1-yl)ethylene (**1a**) (Chart 1), was reported for the first time in 1948.[8] Although the photochemistry of pyrenes is rich and a range of investigations have included DArEs, **1a** was unknown to chemists for a long time. To the best of our knowledge, only four papers describing **1a** have been reported and its substituted derivatives have not been previously described. Its instability and low solubility have prevented a detailed understanding of this molecule, and even its melting point remains poorly characterized or understood.[8–11] In this paper, we report an alternate synthesis of **1b**, that involves introduction of bulky soluble substituents that kinetically stabilize the molecule. Our initial attempts at using an olefin metathesis led to the identification of a one-pot cascade reaction involving Suzuki–Miyaura and Mizoroki–Heck couplings to afford **1b** directly. Spectroscopic, electrochemical, and theoretical studies revealed a significant decrease in the intramolecular HOMO–LUMO gap of **1b** relative to that of pyrene.

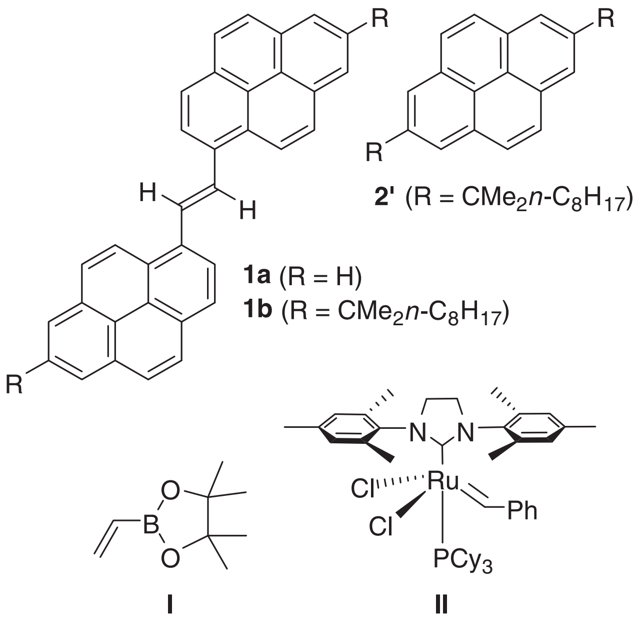
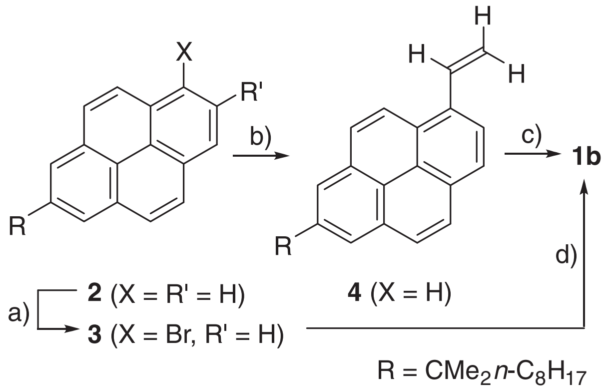


Chart 1. Unsubstituted and substituted dipyrenylethenes **1a** and **1b**, respectively, vinylboronic acid pinacol ester **I**, and Grubbs 2nd generation catalyst **II**.



Scheme 1. Synthesis of **1b**. Reagents and conditions: a) $Br_2/CH_2Cl_2/-70\,°C$ or $NBS/CH_2Cl_2/RT$, b) 2.2 equiv vinylboronic acid pinacol ester **I**/$[Pd(PPh_3)_4]$/DMF/70 °C, c) Grubbs 2nd generation catalyst **II**/CH_2Cl_2/RT, d) 0.5 equiv vinylboronic acid pinacol ester **I**/$[Pd(PPh_3)_4]$/DMF/75 °C → 120 °C.

The formation of an olefinic C=C bond is the key step in DArEs synthesis. Desulfurization of thioaldehyde,[8] the Wittig reaction,[9,11] and thermolysis of azine[10] have been applied to the preparation of **1a**. From the vantage point of contemporary synthetic chemistry, the authors adopted an olefin metathesis for this purpose (Scheme 1). Bromination of pyrene derivative **2** having a *tert*-alkyl group, which we reported recently,[12] was carried out by direct bromination with bromine. However, it was found that the reaction was extremely difficult to control, that is,

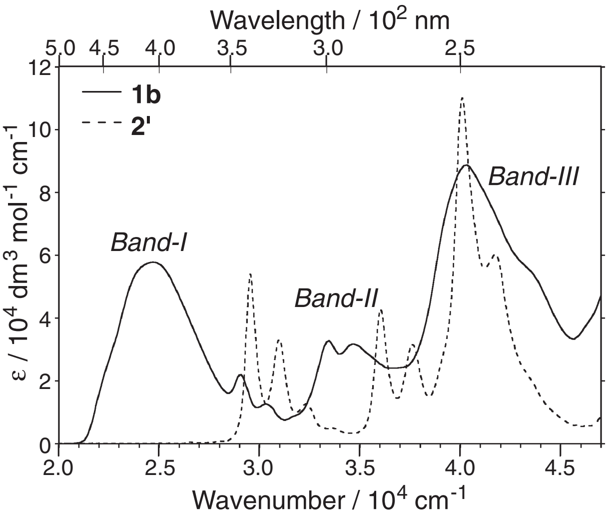


Figure 1. Absorption spectra of dipyrenylethene **1b** (solid line) and **2′** (dotted line) in hexane.

the reaction required that bromine be added as slowly as possible at low temperature. Conducting the reaction at temperatures above −40 °C and/or quickly adding bromine induced the formation of significant amounts of 1,3-dibromide. Replacement of bromine with NBS addressed this problem. Treatment of one equivalent of NBS at room temperature selectively afforded desired monobromopyrene **3** selectively. Introduction of a vinyl group to the pyrene was achieved by the Suzuki–Miyaura coupling in the presence of excess amounts of vinylboronic acid pinacol ester **I**. Heavy viscous oil **4** was obtained in an acceptable yield of 77% as unstable material toward heat and acid as usually observed for vinyl compounds such as styrene. The metathesis reaction was carried out using the Grubbs 2nd generation catalyst **II**. The reaction proceeded smoothly to give desired olefin **1b** in 57% yield as yellow needles (corrected yield of **1b** considering the recovered yield of **4**: 96%). It is worth noting that **1b** was stable toward typical operations, including column chromatography and recrystallization from boiling solvent, such as heptane (bp 98 °C), under ambient conditions. This stability sharply contrasted with the instability of **1a**, the parent molecule, which required special care and the avoidance of light and heat.[8–11] Presumably, the introduction of two bulky *tert*-alkyls kinetically stabilized the solid and concentrated solution states. Reflecting the bulkiness of the substituents, the ^{1}H NMR and absorption spectra of **1b** did not depend on the concentration or solvent, suggesting that the *tert*-alkyl groups prevented aggregation due to intermolecular interactions among the large π-systems of **1b**.

A careful workup of the synthesis of **4** revealed the formation of trace amounts of **1b**. Presumably, the initially formed Suzuki–Miyaura coupling product **4** then reacted with the organopalladium intermediate generated from remaining **3** via the Mizoroki–Heck reaction.[13] Therefore, treatment with 0.5 equiv of boronic acid ester **I** produced **4** in 50% theoretical yield. Then, **4** reacted with unreacted **3** to afford **1b** in one-pot. As expected, **1b** was obtained as the main product (38%).

All spectroscopic studies supported the formation of **1b** (see Supporting Information #1–#3, SI[16] It should be emphasized that a large lower field shift for the olefinic proton of **1b** was observed at 8.44 ppm in the ^{1}H NMR spectrum. This unusual behavior may be understood in terms of the deshielding effects of the two coplanar pyrenes in the *trans*-conformation.[14] The absorption spectrum of **1b** is shown in Figure 1 along with that of dialkylpyrene **2′**. A strong broad absorption was observed around 450–320 nm, *Band-I*, along with *Band-II* (310–280 nm) and *Band-III* (270–240 nm). Vibrational structures characteristic of pyrene were not observed in **1b**. This behavior could be explained in terms of the free rotation around the pyrene–ethene single bonds in its ground state.[15] As is clear in the figure, all bands of **1b** were shifted to lower energies suggesting a narrow intramolecular HOMO–LUMO gap. Density functional theory (DFT) and time-dependent DFT calculations revealed that 1) the energy levels of HOMO (ϕ_{112}) and LUMO (ϕ_{113}) were −4.94 and −1.99 eV, respectively, which were much higher and lower than those of pyrene; 2) *Band-I* was assigned to an allowed HOMO (ϕ_{112}) to LUMO (ϕ_{113}) transition, that is, $S_1 \leftarrow S_0$, with an oscillator strength of 1.33 in vacuum (*SI#3*). The lower oxidation potential of **1b**, estimated from electrochemical studies to be 0.44 and 0.83 V vs. Fc/Fc$^+$ in PhCN for **1b** and **2c**, respectively, was consistent with the results of the theoretical studies.

1,2-Di(pyren-1-yl)ethylene **1b** was synthesized and characterized with the goal of creating new CHCs. Along with the successful olefin metathesis, the authors serendipitously found a cascade reaction involving Suzuki–Miyaura and Mizoroki–Heck couplings. The yield was not high (38%); however, it was acceptable. Because this one-pot reaction avoids multistep syntheses and the handling of unstable vinyl intermediates, the reaction potentially provides a simple and convenient approach to the synthesis of DArEs from easily available bromoaryls. The excited state chemistry of **1b** and a systematic synthetic study of DArEs using the cascade reaction will be described elsewhere.

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