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Synthesis of Dibenz[*a*,*h*]anthracenes by Pd-Catalyzed Intramolecular Double-cyclization of (*Z*,*Z*)-*p*-Styrylstilbenes

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Dibenz[*a*,*h*]anthracene (**1a**) and its dimethoxy derivatives **1b** and **1c** were synthesized by the Pd-catalyzed intramolecular double-cyclization of the corresponding (*Z*,*Z*)-*p*-styrylstilbene derivatives **2**–**5**, which were readily prepared by the Wittig reaction. The optical properties of the dibenz[*a*,*h*]anthracenes **1a**–**1c** are also presented.

Fused polycyclic aromatic compounds have been attracting a great deal of interest in view of the application of organic materials for electronic devices such as organic field effect transistors (OFETs) and light-emitting diodes (OLEDs).[1] Among them, linearly fused systems, such as pentacene (Chart 1) and its derivatives, have been intensively studied for their application to organic materials for electronic devices.[2] Picene, which is an isostructural analogue of pentacene, contains a condensed zigzag form with five benzene rings. An FET with a thin film of picene shows a high μ value more than 1 $cm^2 V^{-1} s^{-1}$ and the FET properties are clearly improved, not only the μ value but also the on–off ratio under air/O_2 conditions.[3a] Furthermore, alkali-metal, potassium or rubidium, doped picene exhibits superconductivity below 18 K.[3b] Compared to pentacene and picene, little is known for the application of dibenz[*a*,*h*]anthracene (**1a**), which has angularly fused systems consisting five benzene rings, to organic materials.[4,5] Moreover, examples of the synthetic methods of dibenz[*a*,*h*]anthracene and its derivatives are still rare; (i) cyclization of naphthyl lactone derivative followed by sequential transformation,[6] (ii) photoinduced cyclization of substituted 1,4-distyrylbenzenes,[7] (iii) ring-closing olefin metathesis of 2,2′,5′,2″-tetravinyl-[1,1′;4′,1″]terphenyl by Schrock and Grubbs catalysts,[8] (iv) ruthenium-catalyzed cyclization of diethynylterphenyl,[9] (v) tandem radical cyclization of (*Z*,*Z*)-1,4-bis(2-iodostyryl)benzene derivatives,[10] and (vi) ruthenium-catalyzed C–H arylation of aromatic ketones.[5] In addition, there are several drawbacks for these methods, such as lengthy sequences for their preparation, using expensive and unstable transition metals, and limitation of the substrates.

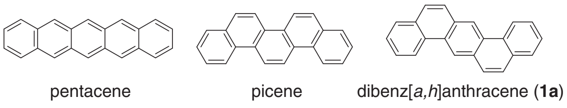
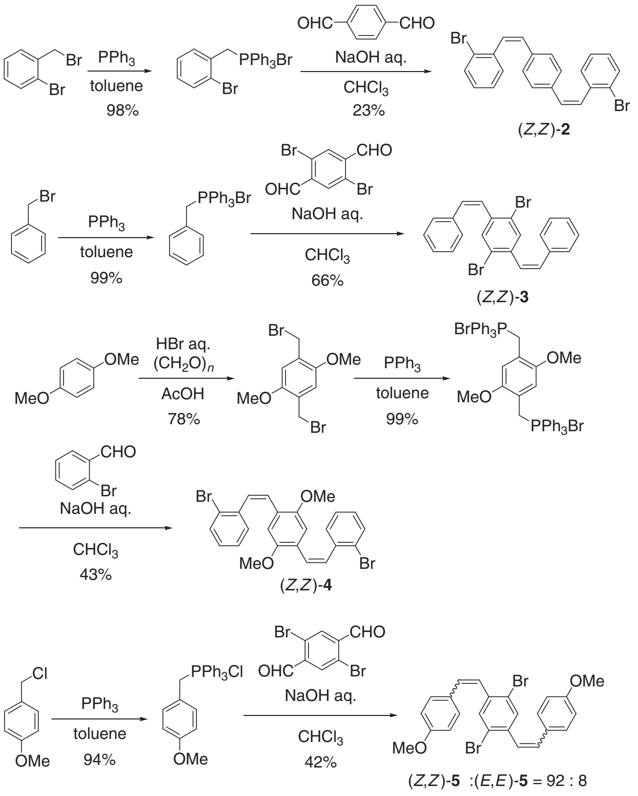


Chart 1.

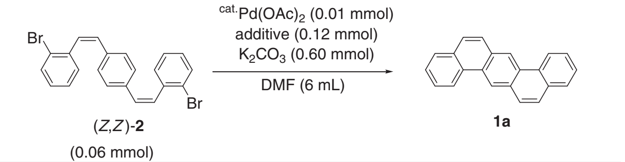
Pd-Catalyzed C–H arylation is a powerful method for the construction of polycyclic aromatic carbons.[11] Indeed, various types of polycyclic aromatic carbons, including highly conjugated polyarenes, polycyclic heteroarenes, and helicenes, have been prepared by Pd-catalyzed intramolecular C–H arylation.[12] However, there is no example of the application of Pd-catalyzed C–H arylation in the synthesis of dibenz[*a*,*h*]anthracenes. We now report the synthesis of dibenz[*a*,*h*]anthracenes **1** by the Pd-catalyzed intramolecular double-cyclization of the corresponding (*Z*,*Z*)-*p*-styrylstilbene derivatives **2**–**5** and investigation of the optical properties of **1**.



Scheme 1. Synthesis of *p*-styrylstilbenes **2**–**5**.

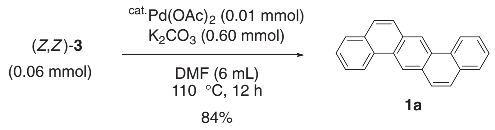
The synthesis of *p*-styrylstilbenes **2**–**5** as precursors of dibenz[*a*,*h*]anthracenes **1** is shown in Scheme 1.[13] The reaction of *o*-bromobenzyltriphenylphosphonium bromide and terephthalaldehyde followed by the purification by silica gel chromatography and recrystallization from $CHCl_3$ gave the dibromostyrylstilbene (*Z*,*Z*)-**2**. Likewise, (*Z*,*Z*)-**3** was synthesized from benzyltriphenylphosphonium bromide and 2,5-dibromoterephthalaldehyde. 1,4-Bis(bromomethyl)-2,5-dimethoxybenzene, which was prepared by the reaction of 1,4-dimethoxybenzene, HBr aq., and paraformaldehyde, was allowed to react with triphenylphosphine to give the corresponding phosphonium compound. The Wittig reaction of the above phosphonium compound with *o*-bromobenzaldehyde afforded (*Z*,*Z*)-**4** after reprecipitation from a mixed solvent of $CHCl_3$ and hexane. The Wittig reaction of *p*-methoxybenzyltriphenylphosphonium chlo-

Table 1. Pd-Catalyzed intramolecular cyclization of (*Z*,*Z*)-*p*-styrylstilbene **2**



Entry	Additive	Time /h	Temp /°C	Recovery of **2**/%[a]	Yield of **1a**/%[a]
1	LiBr, TBAB	12	80	56	—
2	LiBr, TBAB	6	110	—	41
3	LiI, TBAB	6	110	12	34
4	—	12	110	2	81 (79)
5[b]	—	12	110	75	—

[a] Determined by ^{1}H NMR with internal standard. The number in parenthesis shows the isolated yield. [b] (*E*,*E*)-Isomer **2** was used.



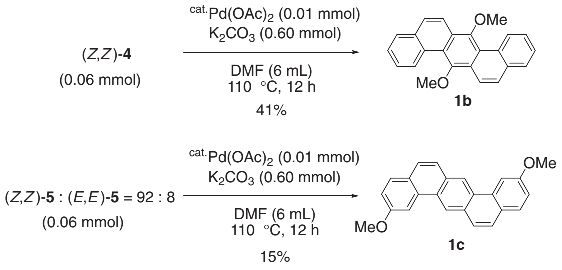
Scheme 2. Synthesis of dibenz[*a*,*h*]anthracene (**1a**) by Pd-catalyzed intramolecular cyclization.

ride and 2,5-dibromoterephthalaldehyde gave the isomeric mixture of styrylstilbene **5** in the ratio of (*Z*,*Z*):(*E*,*Z*):(*E*,*E*) = 49:15:36. Repeated recrystallization from toluene gave a 92:8 mixture of (*Z*,*Z*)- and (*E*,*E*)-**5** in 42% combined yield.

First, the reaction of (*Z*,*Z*)-**2** (0.06 mmol) in the presence of a catalytic amount of Pd(OAc)$_2$ (0.01 mmol), K$_2$CO$_3$ (0.60 mmol), LiBr (0.12 mmol), and tetrabutylammonium bromide (TBAB) (0.12 mmol) at 110 °C gave **1a** in moderate yield (Entry 2 in Table 1). At a lower reaction temperature (80 °C), the reaction did not proceed and the isomeric mixtures of **2** were recovered together with uncharacterized polymeric materials (Entry 1). With the addition of LiI instead of LiBr, the yield of **1a** slightly decreased (Entry 3). It is interesting to note that the reaction smoothly proceeded without additives, TBAB and LiBr, to give dibenz[*a*,*h*]anthracene (**1a**) in high yield (Entry 4). When the reaction using (*E*,*E*)-**2** instead of (*Z*,*Z*)-**2** was carried out under the same conditions as Entry 4, the cyclization did not proceed and the isomeric mixtures of **2** were recovered (Entry 5). In all cases, the formation of [5]helicene was not observed.[14]

Next, the Pd-catalyzed intramolecular cyclization of (*Z*,*Z*)-**3** was examined under the optimized conditions as Entry 4 in Table 1 (Scheme 2). Dibenz[*a*,*h*]anthracene (**1a**) was formed in good yield (84%). The treatment of (*Z*,*Z*)-**4** and (*Z*,*Z*)-**5**, which contained a small amount of (*E*,*E*)-**5**, under the same conditions gave 7,14-dimethoxydibenz[*a*,*h*]anthracene (**1b**)[15] and 2,9-dimethoxydibenz[*a*,*h*]anthracene (**1c**),[16] respectively (Scheme 3).

The UV–vis and FL spectroscopy of dibenz[*a*,*h*]anthracenes **1a**–**1c** were measured in CH$_2$Cl$_2$ (Figure 1) and the results of the photophysical properties of **1a**–**1c** are shown in Table 2. The UV–vis spectrum of **1a** shows the characteristic absorption bands, such as the α-, β-, and para-bands, of aromatic



Scheme 3. Synthesis of 7,14- and 2,9-dimethoxydibenz[*a*,*h*]anthracenes (**1b** and **1c**) by Pd-catalyzed intramolecular cyclization.

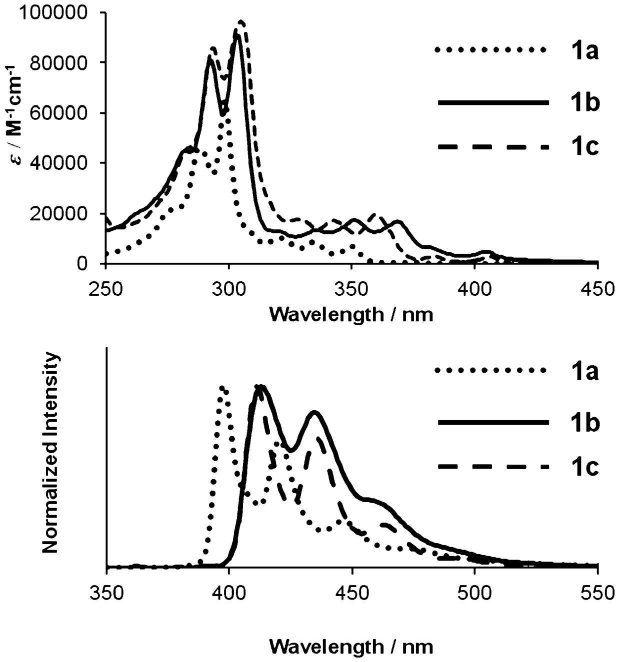


Figure 1. UV–vis absorption (top) and fluorescence (bottom) spectra of dibenz[*a*,*h*]anthracenes **1a**–**1c** in CH$_2$Cl$_2$.

Table 2. Optical properties of dibenz[*a*,*h*]anthracenes **1a**–**1c** in CH$_2$Cl$_2$[a]

	Absorption λ_{abs}/nm (ε/M^{-1} cm^{-1})	Fluorescence λ_{em}/nm	Fluorescence Φ[b]
1a	288 (46100), 298 (65200), 321 (10300), 334 (8500), 350 (7100), 373 (500), 395 (500)	398, 420, 446	0.035
1b	293 (81000), 303 (91100), 336 (13300), 351 (17300), 369 (16700), 404 (4700)	413, 435, 464	0.118
1c	305 (96500), 329 (17600), 343 (17200), 360 (19500), 384 (2900), 406 (2900)	411, 435, 463	0.083

[a] **1a** ($c = 3.59 \times 10^{-5}$ M), **1b** ($c = 2.96 \times 10^{-5}$ M), **1c** ($c = 2.96 \times 10^{-5}$ M). [b] Absolute quantum yield measured using an integrating sphere.

hydrocarbons (see also Figure S1 in SI[20]).[17] The absorption maxima of **1a** is bathochromically shifted by about 15 nm in comparison to picene.[18] The FL spectrum of **1a** exhibits a significant vibrational fine structure due to its rigid planarity. In the case of **1b** and **1c**, their absorption maxima are slightly red-shifted and the fluorescence quantum yields of them increased compared to that of **1a**.

In conclusion, we succeeded in the synthesis of dibenz[*a*,*h*]anthracene (**1a**) and the 7,14- and 2,9-dimethoxydibenz[*a*,*h*]anthracenes (**1b** and **1c**) by the Pd-catalyzed intramolecular double-cyclization of (*Z*,*Z*)-*p*-styrylstilbene derivatives **2**–**5**.[19] The optical spectra of dibenz[*a*,*h*]anthracenes **1a**–**1c** exhibited typical features of polycyclic aromatic hydrocarbons and were significantly influenced by the positions of the substituted methoxy groups.

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20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.