Synthesis of Hexabenzotriphenylene and Other Strained Polycyclic Aromatic Hydrocarbons by Palladium-Catalyzed Cyclotrimerization of Arynes
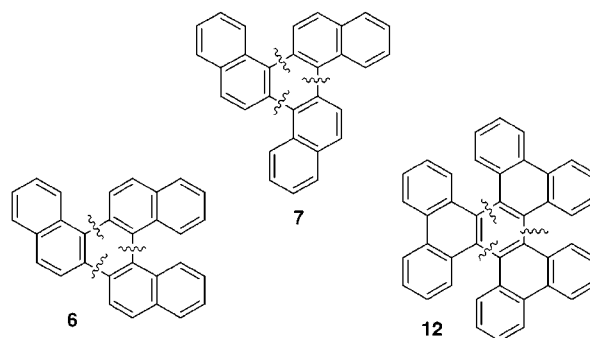
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ABSTRACT

To evaluate the potential of the recently developed palladium-catalyzed trimerization of arynes for the synthesis of strained polycyclic hydrocarbons, the trimerizations of 1,2-didehydronaphthalene (1) and 9,10-didehydrophenanthrene (2), generated from the corresponding *o*-trimethylsilylaryl triflates 5 and 11, respectively, were studied. The synthesis of tribenzo[*a,g,o*]triphenylene (6), tribenzo[*a,g,m*]triphenylene (7), and hexabenzo[*a,c,g,i,m,o*]triphenylene (12) is described.

The chemistry of overcrowded polycyclic aromatic hydrocarbons (PAHs) has become a field of increasing interest during the past decade. The synthesis of bowl-shaped PAHs that constitute significant fragments of fullerenes is particularly appealing,[1] but also important efforts have been directed to the construction of highly symmetric PAHs with different shapes, such as saddles or twists,[1,2] and to the synthesis of other structures that exhibit distortions from planarity, such as the helicenes.[3] In general, the syntheses of these kinds of compounds have in common the lack of general applicability, the use of harsh reaction conditions (e.g., FVP), and low

yields. In this Letter we report preliminary results on a novel, convenient approach to the synthesis of strained PAHs based on the palladium(0)-catalyzed cyclotrimerization of polycyclic arynes.

Recently we described the palladium-catalyzed cyclotrimerization of benzyne and substituted derivatives to afford triphenylenes.[4] We planned to apply this reaction to polycyclic arynes,[5] which would allow an easy access to complex polycyclic structures. Particularly, we became interested in the reaction of two arynes of increasing size and structural

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(2) (a) Pascal, R. A., Jr. *Pure Appl. Chem.* **1993**, *65*, 105–110. (b) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1531–1532.

(3) (a) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649–660. (b) Laarhoven, W. H.; Prinsen, W. J. C. In *Topics in Current Chemistry*, Vol. 125; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1984; pp 65–127. (c) Grimme, S.; Harren, J.; Sobanski, A.; Vögtle, F. *Eur. J. Org. Chem.* **1998**, 1491–1509.

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complexity: 1,2-didehydronaphthalene (**1**) and 9,10-dide-hydrophenanthrene (**2**) (Figure 1). The cyclotrimerization of
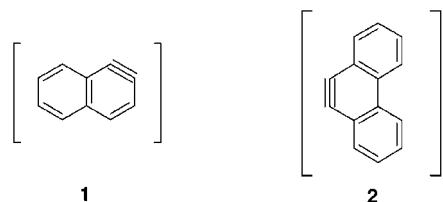

Figure 1.

1 would give us a first insight into the possibility of obtaining strained PAHs using our proposed strategy, and the cyclotrimerization of **2** would afford dibenzo[*f,j*]phenanthro[9,-10-*s*]picene (hexabenzo-[*a,c,g,i,m,o*]triphenylene, **12**), a molecule that has been recently characterized as a highly twisted, D_3-symmetric molecular propeller[6] and whose synthesis has been shown to be difficult so far.[6,7]

On the basis of our previously described methodology,[4,8] we selected the corresponding *o*-trimethylsilylaryl triflates as adequate aryne precursors for **1** and **2**. 1-Trimethylsilyl-naphthyl 2-trifluoromethanesulfonate (**5**) was prepared from commercially available 1-bromo-2-naphthol (**3**) as shown in Scheme 1. Treatment of **3** with hexamethyldisilazane (HMDS)
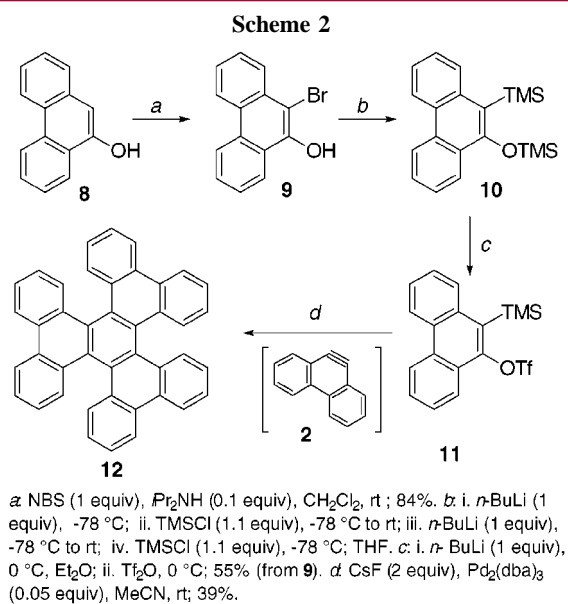

Scheme 1
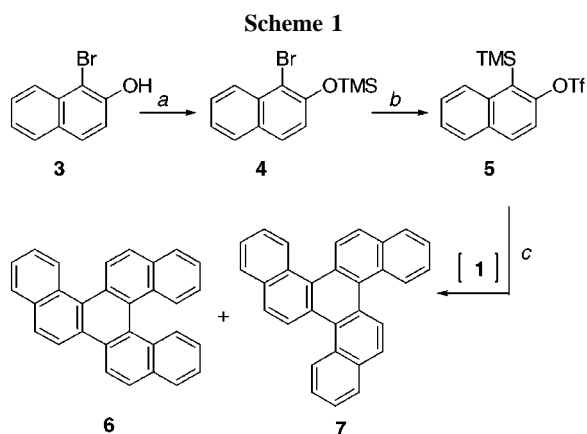
a: HMDS, 70 °C ; 100%. *b*: i. *n*-BuLi (1 equiv), THF, -78 °C to rt; ii. Tf₂O, Et₂O, -78 °C; 57%. *c*: CsF (2 equiv), Pd₂(dba)₃ (0.05 equiv), MeCN, rt; 60%.

at 70 °C gave trimethylsilyl ether **4** in quantitative yield, which was transformed into triflate **5** in one pot by sequential treatment with *n*-BuLi (1 equiv, −78 °C to room temperature) and Tf₂O. When **5** was subjected to the reaction conditions previously reported for the cyclotrimerization of

simple arynes[4] [CsF (2 equiv), Pd(PPh₃)₄ (0.1 equiv); CH₃-CN, room temperature], the expected trimers were not detected. Reasoning that the bulky and strongly coordinated ligand PPh₃ might prevent the reaction of this sterically demanding aryne, we switched to Pd₂(dba)₃ as a palladium source. When **5** was treated with CsF in the presence of 5 mol % of Pd₂(dba)₃, a mixture of trimers **6** and **7** was successfully obtained in 60% yield and 2.7:1 ratio,[9] with **6** being the major product. Both isomers are structurally interesting molecules: while tribenzo[*a,g,m*]triphenylene (benzo[*c*]naphtho[2,1-*p*]-chrysene, **7**) has recently attracted great attention as a potential precursor for the synthesis of hemifullerene,[10] tribenzo[*a,g,o*]triphenylene (naphtho[1,2-*s*]-picene, **6**) is a substituted pentahelicene. Furthermore, the isolation of **6** as a major product showed that sterically hindered, highly twisted polycyclic hydrocarbons could be efficiently obtained using this approach, opening the possibility of synthesizing **12**.

The preparation of 10-trimethylsilylphenanthryl 9-trifluo-romethanesulfonate (**11**) from commercially available 9-phenanthrol (**8**) is shown in Scheme 2. Selective *ortho*-

Scheme 2

a: NBS (1 equiv), *i*Pr₂NH (0.1 equiv), CH₂Cl₂, rt ; 84%. *b*: i. *n*-BuLi (1 equiv), -78 °C; ii. TMSCl (1.1 equiv), -78 °C to rt; iii. *n*-BuLi (1 equiv), -78 °C to rt; iv. TMSCl (1.1 equiv), -78 °C; THF. *c*: i. *n*- BuLi (1 equiv), 0 °C, Et₂O; ii. Tf₂O, 0 °C; 55% (from **9**). *d*: CsF (2 equiv), Pd₂(dba)₃ (0.05 equiv), MeCN, rt; 39%.

bromination was achieved in good yield by reaction of **8** with *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of diisopropylamine.[11] Sequential treatment of **9** with *n*-BuLi and TMSCl (twice) afforded in one pot trimethylsilyl ether **10**, which was highly unstable and therefore taken to the next step without further purification. Reaction of crude **10** with *n*-BuLi and quenching with Tf₂O

(5) General reviews on aryne chemistry: (a) Hoffmann, R. W.; *Dehy-drobenzene and Cycloalkynes*; Academic Press: New York, 1967. (b) Hart, H. In *The Chemistry of Functional Groups, Suppl. C2: The Chemistry of Triple-Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1994; pp 1017−1134.

(6) Barnett, L.; Ho, D. M.; Baldridge, K. K.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 727−733.

(7) (a) Hacker, N. P.; McOmie, F. W.; Meunier-Piret, J.; Van Meerssche, M *J. Chem. Soc., Perkin Trans. 1* **1982**, 19−23. Other authors reported the preparation of **1**, but no characterization was given: (b) Halleux, A. L., Br. Patent 852,981, 1960. (c) Barton, J. W.; Grinham, A. R. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 634−637.

(8) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827−5828.

afforded triflate **11** in 55% overall yield from **9**. Treatment of **11** with CsF in the presence of $Pd_2(dba)_3$ as catalyst afforded a single low-polarity product that was isolated and characterized[12] as hexabenzo[*a,c,g,i,m,o*]triphenylene (**12**) in a remarkable 39% yield. It is worth noting that the previously reported syntheses of **12** afforded the compound in yields as low as 5%[6] and 13%,[7a] starting from precursors which were difficult to prepare, and using severe reaction conditions (pyrolysis, 700 °C). It is evident that our procedure would be the method of choice for the preparation of large amounts of **12**.

(9) Ratio determined by ^{1}H NMR of the mixture. Samples of both isomers (**6** and **7**) were separated by flash chromatography and adequately characterized. Data for **6**: ^{1}H NMR (CDCl$_3$) δ 9.03−8.98 (m, 2 H), 8.64 (d, J = 8.9 Hz, 1 H), 8.59 (d, J = 8.9 Hz, 1 H), 8.35 (d, J = 8.5 Hz, 1 H), 8.30 (d, J = 8.7 Hz, 1 H), 8.12−7.95 (m, 6 H), 7.73−7.48 (m, 4 H), 7.36−7.28 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 133.7, 132.1, 132.0, 131.2, 130.6, 129.7, 129.6, 129.5, 129.2, 129.1, 128.7, 128.5, 128.1, 128.0, 127.9, 127.8, 127.6, 126.1, 125.94, 125.92, 125.86, 125.78, 125.5, 124.9, 124.8, 120.5, 120.4; MS, m/z (%) 378 (M$^+$, 63), 377 (68), 187 (100); HRMS for $C_{30}H_{18}$ calcd 378.1408, found 378.1408. Spectral data of **7** were in agreement with those reported in the literature (refs 10b,c).

(10) (a) Laarhoven, W. H.; von Broeckhoven, J. A. M. *Tetrahedron Lett.* **1970**, 73−76. (b) Winter, W.; Langjahr, V.; Meier, H.; Merkuschew, J.; Juriew, J. *Chem. Ber.* **1984**, *117*, 2452−2463. (c) Hagen, S.; Scott, L. T. *J. Org. Chem.* **1996**, *61*, 7198−7199 and references therein. (d) For a related substituted analogue, see: Mehta, G.; Raghava Sharma, G. V.; Krishna Kumar, M. A.; Vedavyasa, T. V.; Jemmis, E. D. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2529−2530.

(11) Fujisaki, S.; Eguchi, H.; Omura, A.; Okamoto, A.; Nishida, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1576−1579.

(12) The spectral data of our product were analogous to those reported by Pascal (ref 6) and Hacker (ref 7a). In addition, we were able to obtain a ^{13}C NMR spectra of **12**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.54 (dd, J = 8.2, 1.1 Hz, 6H), 8.15 (d, J = 8.2 Hz, 6H), 7.55 (dt, J = 7.6, 1.1 Hz, 6H), 7.22 (dt, J = 7.7, 1.2 Hz, 6H); ^{13}C NMR-DEPT (CD$_2$Cl$_4$, 125 MHz) δ 131.8 (C), 130.9 (CH), 130.3 (C), 128.5 (C), 125.8 (CH), 125.6 (CH), 123.3 (CH); MS, m/z (%) 528 (M$^+$, 29), 264 (16), 261 (66), 254 (100); HRMS for $C_{42}H_{24}$ calcd 528.1878, found 528.1869.