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A Convenient Synthesis of Benzo[*c*]naphtho[2,1-*p*]chrysene

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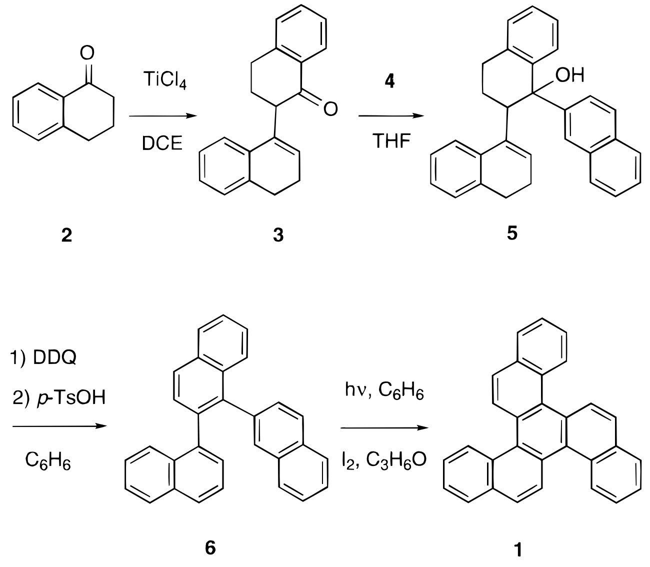
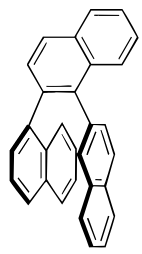
The polycyclic aromatic hydrocarbon (PAH) benzo[*c*]naphtho[2,1-*p*]chrysene[1] (**1**) has recently attracted renewed attention as a potential precursor for the synthesis of bowl-shaped fullerene substructures.[2] The published synthetic approaches to **1**, however, are lengthy and entail one or more photocyclizations of stilbene-type compounds that suffer from competing [2 + 2]cycloaddition reactions at normal concentrations and are thereby rendered quite inefficient.[2bc,3,4] We report here a convenient four-step synthesis of **1** that can be performed on a multigram scale starting from the commercially available α-tetralone (**2**) and 2-bromonaphthalene.

By a method similar to that of Eisenbraun et al.,[5c] the aldol condensation of **2** with TiCl$_4$ in refluxing 1,2-dichloroethane (DCE) gives the dimeric ketone **3** in 71% yield (Scheme 1).[5a−c] In contrast to the condensation of 6-methoxy-α-tetralone with TiCl$_4$,[6] no products arising from the connection of three molecules of **2** were observed even at these elevated temperatures. The reaction of **3** with 2-naphthyl lithium (**4**) in THF at −70 °C produces the desired tertiary alcohol **5** (70%), which can be aromatized to 1,2′:1′,2″-ternaphthalene (**6**) in high yield (94%) by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in refluxing benzene.[7]

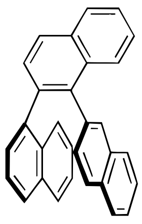
By ^{1}H-NMR spectroscopy, **6** was shown to consist of a nearly 1:1 mixture of two conformers at room temperature (**6a** and **6b**)[8] with significant barriers to rotation around the aryl−aryl bonds hindering their interconversion. Since the ^{1}H-NMR spectrum is badly overlapping, and thereby poorly suited for variable temperature NMR studies, the free enthalpy of activation for signal coalescence ($\Delta G_c^\ddagger = 20.0 \pm 0.2$ kcal/mol) was determined by ^{13}C-NMR spectroscopy (125.7 MHz, DMSO-d$_6$), an average value being taken from the coalescence of three different signals.[9] No attempt was made to separate **6a** and **6b**, since a rotational barrier of 20 kcal/mol is insufficient to prevent complete reequilibration of the individual conformers within a few minutes at room temperature.[10]

Scheme 1





6 a



6 b

Photocyclization of **6** in benzene by the method of Katz et al.,[11] with iodine and propylene oxide, results in the formation of **1** (96%). Benzo[*b*]naphtho[2,1-*p*]chrysene (**7**), the other possible product of photocyclization, could not be detected. The high site selectivity of this photochemical reaction is in accord with the calculated sums of the free valencies in the S_1 state (F_{rs}*) for the carbon centers that are to be linked (F_r*, F_s*). As required,[4c,12] F_{rs}* is greater than 1.0 for the formation of **1** and lower than 1.0 for the unobserved formation of **7** (Scheme 2).

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[1] The name benzo[*c*]naphtho[2,1-*p*]chrysene is in accord with the nomenclature for PAH recommended by the IUPAC and applied by *Chemical Abstracts*. The more common name in the chemical literature for compound **1** is tribenzo[*c*,*i*,*o*]triphenylene.

[2] (a) Faust, R.; Vollhardt, K. P. C. 7th International Symposium of Novel Aromatics, Victoria, B.C., Canada, 1992; Poster 61. (b) Mehta, G.; Raghava Sharma, G. V.; Krishna Kumar, M. A.; Vedavyasa, T. V.; Jemmis, E. D. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2529. (c) Erickson, M. S.; Milliken, J. *Polycyclic Arom. Compd.* **1996**, *8*, 1. (d) The successful conversion of **1** to benz[5,6]-*as*-indaceno[3,2,1,8,7-*mnopqr*]indeno[4,3,2,1-*cdef*]chrysene has been presented: Hagen, S.; Bratcher, M. S.; Scott, L. T.; Zimmermann, G. 210th ACS National Meeting, New Orleans, 1996; Organic Division poster 52.

[3] Laarhoven, W. H.; van Broekhoven, J. A. M. *Tetrahedron Lett.* **1970**, *1*, 73.

[4] (a) Juriew, J.; Skorochodowa, T.; Merkuschew, J.; Winter, W.; Meier, H. *Angew. Chem.* **1981**, *93*, 285; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 269. (b) Winter, W.; Langjahr, U.; Meier, H.; Merkuschew, J.; Juriew, J. *Chem. Ber.* **1984**, *117*, 2452. (c) Meier, H. *Angew. Chem.* **1992**, *104*, 1425; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399.

[5] For prior synthesis of **3** see: (a) Orchin, M.; Reggel, L.; Friedel, R. A. *J. Am. Chem. Soc.* **1949**, *71*, 2743. (b) Burnham, J. W.; Melton, R. G.; Eisenbraun, E. J.; Keen, G. W.; Hamming, M. C. *J. Org. Chem.* **1973**, *38*, 2783. (c) Holba, A. G.; Premasager, V., Barot, R. C., Eisenbraun, E. J. *Tetrahedron Lett.* **1984**, *26*, 571.

[6] Pyrko, A. N. *Zh. Org. Khim.* **1992**, *28*, 215.

[7] This work was originally inspired by the publication of Burnham *et al.*[5b] In the present case, however, their approach did not result in **1** but gave instead its constitutional isomer naphtho[2,1-*s*]picene and the PAH phenanthro[1,2,3,4-*ghi*]perylene. These findings are still under investigation and will be published elsewhere.

[8] The calculated differences in the heats of formation of **6a** and **6b** are 0.019 kcal/mol (PM3) and 0.042 kcal/mol (AM1).

[9] Signals at $\delta = 138.46$ ppm ($\Delta\nu = 18.9$ Hz, $T_c = 117 \pm 2$ °C), $\delta = 136.23$ ppm ($\Delta\nu = 23.5$ Hz, $T_c = 120 \pm 2$ °C), $\delta = 135.41$ ppm ($\Delta\nu = 33.7$ Hz, $T_c = 120 \pm 2$ °C); δ given for fast exchange at 160 °C; $\Delta\nu$ given for slow exchange at 25 °C.

[10] (a) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003. (b) Ibuki, E.; Ozasa, S.; Fujioka, Y.; Mizutani, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 845.

[11] Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

[12] (a) Scholz, M.; Dietz, F.; Muehlstaedt, M. *Z. Chem.* **1967**, *7*, 329. (b) Scholz, M.; Dietz, F.; Muehlstaedt, M. *Tetrahedron Lett.* **1967**, 665. (c) Laarhoven, W. H.; Cuppen, T. H. J. M.; Nivard, R. J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 687.

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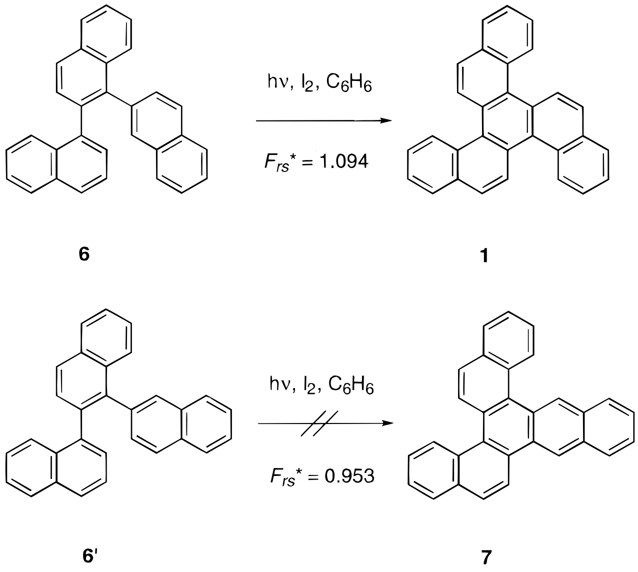
Scheme 2



The fact that only extraction or recrystallization is necessary to obtain analytically pure samples in each of the four steps emphasizes the convenience of this synthesis.

Experimental Section

General Procedures. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded in $CDCl_3$ with $CDCl_3$ ($\delta = 7.26$ and 77.23 ppm, respectively) or TMS ($\delta = 0.00$ ppm) as internal standard unless otherwise noted. Melting points are uncorrected.

3,3′,4,4′-Tetrahydro-[1,2′-binaphthalen]-1′(2′*H*)-one (3). To a stirred solution of α-tetralone (**2**, 10.0 g, 68.5 mmol) in 50 mL of 1,2-dichloroethane at 25 °C under N_2 was added 5.00 mL of $TiCl_4$ (45.5 mmol) all at once. The dark brownish reaction mixture was heated under reflux for 30 min, cooled, and poured into ice-cooled 2 M HCl. The organic phase was washed with 1 M HCl and water, dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the crude product was extracted with hot pentane yielding 6.675 g (71%) of pale yellow crystals of **3** (mp 130.5−132 °C (lit.[5a] mp 132.5−134.2 °C); IR, UV, ^{1}H-NMR, and MS were in agreement with those reported in the literature[5b,c]). ^{13}C-NMR: δ 199.08, 144.12, 136.97, 135.32, 133.83, 133.48, 133.01, 128.84, 127.86, 127.62, 127.18, 126.83, 126.76, 126.33, 123.17, 50.83, 28.77, 28.30, 28.15, 23.20.

3,4,3′,4′-Tetrahydro-[1,2′:1′,2″-ternaphthalen]-1′(2′*H*)-ol (5). To a stirred solution of 2-bromonaphthalene (5.657 g, 27.3 mmol) in 400 mL of THF at −70 °C were added 12.3 mL of 2.5 M *n*-butyllithium in hexane (31 mmol) under N_2. After the yellow solution had been stirred for 1 h (glass stirrer), a solution of ketone **3** (5.821 g, 21.2 mmol) in 100 mL of THF was added dropwise. The reaction mixture was stirred for another 1 h at −70 °C, allowed to warm to room temperature over a period of 2 h, stirred for 1 h more, and then quenched with NH_4Cl solution. After the addition of 100 mL of diethyl ether, the organic phase was washed with water, dried with $MgSO_4$, and filtered. After evaporation of the solvent under reduced pressure, the residue was dissolved in boiling *n*-hexane and allowed to crystallize overnight, yielding colorless crystals of **5** (5.973 g, 70%, mp = 136.5−136.8 °C). IR (KBr): ν 3427 cm^{-1} (OH). ^{1}H-NMR: δ 7.63−7.56 (m, 3H), 7.51 (d, $J = 8.5$ Hz, 1H), 7.35−7.31 (m, 2H), 7.26−7.21 (m, 2H), 7.17 (d, $J = 8.6$ Hz, 1H), 7.11−7.09 (m, 2H), 6.81 (d, $J = 7.0$ Hz, 1H), 6.74-6.68 (m, 2H), 6.62−6.59 (m, 1H), 6.14 (m, 1H), 3.68 (d, $J = 10.4$, 1H), 3.17 (s, 1H), 3.13−3.03 (m, 2H), 2.62−2.58 (m, 2H), 2.33−2.24 (m, 2H), 2.17−2.08 (m, 1H), 2.00−1.93 (m, 1H). ^{13}C-NMR: $\delta = 145.42$, 142.25, 137.58, 137.31, 136.33, 134.78, 132.63, 132.39, 130.46, 128.72, 128.08, 127.68, 127.36 (2 C), 127.20, 127.07, 126.65, 126.19, 125.77 (2 C), 125.71, 125.65, 125.57, 122.38, 76.31, 47.55, 29.92, 28.91, 25.32, 23.47. HRMS: $C_{30}H_{26}O$ calcd 402.1984, found 402.1987. Anal. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.37; H, 6.39.

1,2′:1′,2″-Ternaphthalene (6). To a stirred solution of alcohol **5** (6.25 g, 15.5 mmol) in 600 mL of benzene was added DDQ (13.6 g, 60 mmol) in one portion, and the solution was heated under reflux with stirring for 1.5 h. Then 100 mg of *p*-TsOH was added, and the reaction mixture was stirred for another 2 h under reflux. After the mixture was cooled to room temperature, the organic phase was extracted with 5% NaOH solution until the aqueous phase remained colorless, washed with saturated NH_4Cl solution and water, dried with $MgSO_4$, and filtered. Evaporation of the solvent under reduced pressure, treatment with refluxing methanol, and filtration yielded 5.30 g (90%) of colorless crystals of **6** (mixture of isomers, mp = 161.5−162.5 °C). From the filtrate was crystallized additionally 0.27 g (4.5%) of **6**. UV (CH_3CN): λ_{max}(log ϵ) 220 nm (5.135), 272 (4.342, sh), 284 (4.390). ^{1}H-NMR (25 °C, two conformers): δ 7.97−7.93 (m, 4H), 7.81 (s, 1H), 7.74−7.67 (m, 8H), 7.62−7.48 (m, 8H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.39−7.28 (m, 12H), 7.23−7.12 (m, 5H), 7.01 (d, $J = 8.4$ Hz, 1H). ^{13}C-NMR (125.7 MHz, DMSO-d_6, 160 °C, δ 39.51 ppm as internal standard): δ 138.46, 137.73, 136.23, 135.41, 132.33, 132.18, 131.90, 131.74, 131.32, 131.11, further signals at 129.2−123.0 (no complete coalescence). MS (70 eV): m/z (rel int) 381 (32), 380 (100), 379 (31), 377 (14), 376 (13), 253 (13), 252 (20). HRMS: $C_{30}H_{20}$ calcd 380.1565, found 380.1560. Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.77; H, 5.27.

Benzo[*c*]naphtho[2,1-*p*]chrysene (1). A stirred solution of hydrocarbon **6** (4.74 g, 12.5 mmol), iodine (3.30 g, 13 mmol), and propylene oxide (40 mL, 570 mmol) in 550 mL of benzene in a quartz flask purged with N_2 was irradiated with a 450 W medium-pressure mercury UV-lamp for 21 h. After evaporation of the solvent under reduced pressure and recrystallization of the crude product from benzene/hexane, the mother liquor was irradiated for another 3 h and worked up in the same manner, yielding a total of 4.52 g (96%) of **1** (mp = 231−232 °C (lit.[3] mp 233−234 °C); MS, UV, ^{1}H-NMR, and ^{13}C-NMR were in agreement with those reported in the literature[2c,3,4b]).

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