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An Efficient Synthesis of the Sterically Strained Hydrocarbon Tetrabenzo[*de,hi,mn,qr*]naphthacene

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Tetrabenzo[de,hi,mn,qr]naphthacene[1] (**3**) is a sterically crowded molecule that is anticipated to be distorted from planarity due to the steric interaction of the *fjord* region protons.[2] Although several synthetic approaches to **3** have been described, they entail relatively large numbers of steps and afford relatively low overall yields.[3-5] We now report an efficient synthesis of **3** involving double Wagner–Meerwein rearrangement of the carbonium ion arising from **1**.

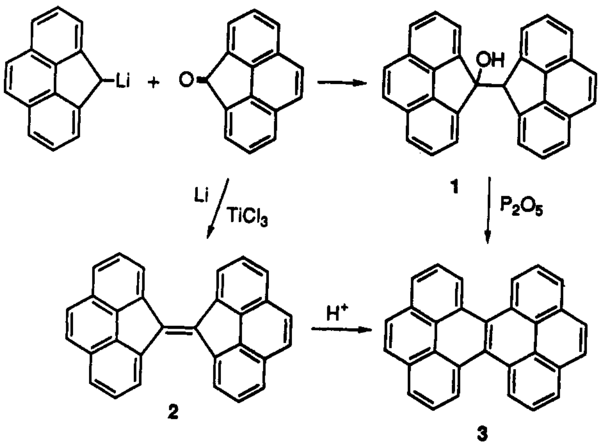
This synthetic approach is based on the prior observation that oxidation of 4*H*-cyclopenta[*def*]phenanthrene with *n*-butyllithium and oxygen gave as a major product the dimeric alcohol **1**.[6] This alcohol was presumed to arise from reaction of the anion of 4*H*-cyclopenta[*def*]phenanthrene with 4*H*-cyclopenta[*def*]phenanthren-4-one (Scheme I). This reaction is now shown to afford **1** in 90% yield, confirming the feasibility of this reaction pathway. Treatment of **1** with P_2O_5 in refluxing xylene directly provided **3** (70%). Alternatively, reductive coupling of 4*H*-cyclopenta[*def*]phenanthren-4-one with the low-valent titanium reagent[7] generated from reaction of lithium with $TiCl_3$ furnished 4,4′-bi-4*H*-cyclopenta[*def*]-phenanthrylidene (**2**). Reaction of **2** with polyphosphoric acid in refluxing xylene also led to formation of the rearranged product **3**.

In principle, this synthetic methodology is applicable to the preparation of other large sterically crowded nonplanar polycyclic hydrocarbon ring systems, a topic of considerable current research interest.[8]

Experimental Section

Materials and Methods. 4*H*-Cyclopenta[*def*]phenanthrene and its 4-keto derivative were prepared by previously published procedures.[6,9] Proton NMR spectra were obtained on 300- or 500-MHz spectrometers in $CDCl_3$ with tetramethylsilane as internal standard.

Scheme I



4-Hydroxy-4,4′-bi-4*H*-cyclopenta[*def*]phenanthryl (1). To a solution of 4*H*-cyclopenta[*def*]phenanthrene (840 mg) in 10 mL of dry THF cooled in a dry ice bath was added 2.0 mL of 2.5 M butyllithium. This solution was stirred at this temperature for 45 min, and then a solution of the 4-keto derivative of this hydrocarbon (612 mg, 3 mmol) in 6 mL of dry THF was added dropwise over 5 min. The temperature of the red-colored solution was allowed to rise, and stirring was continued overnight. The reaction was quenched with water, and the product was extracted with ether–THF (1:1). The combined organic phase was washed with 2 N HCl and water, dried over $CaCl_2$, and evaporated to dryness. The crude product was purified by chromatography on a column of silica gel. Elution with hexane–CH_2Cl_2 (3:7) gave **1** (1.07 g, 90%) as white crystals, mp 144–145.5 °C (lit.[6] 134–135 °C); the NMR spectrum matched that reported.[6]

Tetrabenzo[*de,hi,mn,qr*]naphthacene (3). Method 1. A mixture of **1** (200 mg, 0.53 mmol) and P_2O_5 (700 mg) in 10 mL of xylene was heated at reflux for 40 min until the red color disappeared and then cooled to ambient temperature. The reaction mixture was filtered through a short column of Florisil eluted with benzene to afford **3** (135 mg, 70%) as pale yellow needles: mp 306–308 °C (benzene) (lit.[3] mp 305–307 °C); NMR δ 9.21 (d, 4, $H_{1,8,9,16}$; $J = 7.8$ Hz), 8.23 (d, 4, $H_{3,6,11,14}$; $J = 7.2$ Hz), 8.14 (s, 4, $H_{4,5,12,13}$), 8.05 (t, 4, $H_{2,7,10,15}$; $J = 7.8$ Hz). Similar experiments conducted at lower temperature gave a mixture of the olefin **2** and **3**.

Method 2. A mixture of **2** (100 mg, 0.27 mmol) and polyphosphoric acid (1 mL) in 5 mL of xylene was refluxed under argon for 2 h, cooled, and decomposed with ice. $CHCl_3$ was added and the product worked up conventionally. The crude product was crystallized from benzene to afford **3** (55 mg, 55%) identical in its properties with that prepared by method 1.

4,4′-Bi-4*H*-cyclopenta[*def*]phenanthrylidene (2). A slurry of Li (164 mg, 23.6 mmol) and $TiCl_3$ (1.20 g, 7.8 mmol) in 20 mL of dry DME was refluxed under argon for 1 h and then cooled to 0 °C, and a solution of 4*H*-cyclopenta[*def*]phenanthren-4-one (500 mg, 2.5 mmol) in 10 mL of DME was added. Refluxing was continued for 4 h, the reaction monitored by TLC, and then the mixture filtered, and the solid residue was washed with benzene. The combined filtrate was washed with 2 N HCl and water, dried over Na_2SO_4, and evaporated to dryness. The crude product was dissolved in a small amount of benzene and chromatographed on a column of Florisil. Elution with benzene provided **2** (402 mg, 86%) as red crystals: mp 265–267 °C (lit.[10] mp 264–266 °C); NMR δ 8.72 (d, 4, $J = 7.4$ Hz), 7.84 (s and d, 8), 7.65 (t, 4, J – 7.6 Hz).

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[1] The name tetrabenzo[*de,hi,mn,qr*]naphthacene accords with current rules of polycyclic hydrocarbon nomenclature recommended by IUPAC and employed by Chemical Abstracts. The alternative names pyreno(1′,2′:1,2)pyrene and pyreno[4,5-4′,5′]pyrene are found in the older literature.

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