Synthesis of Methylene-Bridged Polycyclic Aromatic Hydrocarbons

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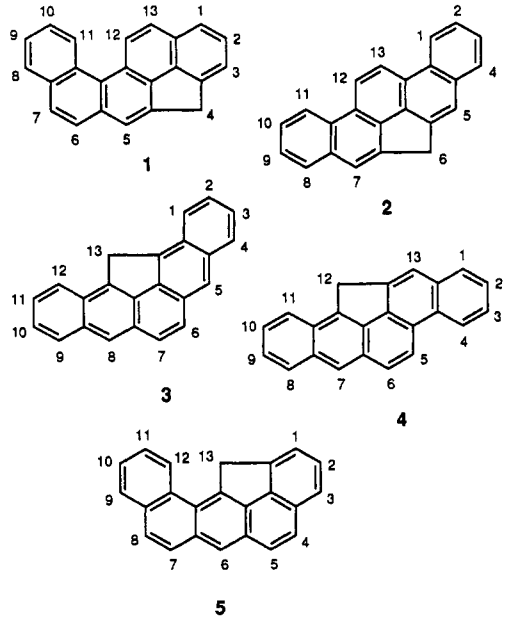
Methylene-bridged polycyclic hydrocarbons are present in relatively high ratios in crude petroleum[1] and they are important environmental pollutants produced in the combustion of organic matter at moderate temperatures.[2] 4*H*-Cyclopenta[*def*]chrysene, a typical hydrocarbon of this class, is found in cigarette smoke and has recently been shown to be tumorigenic.[3] However, surprisingly little is known concerning the chemistry or biological properties of most methylene-bridged polyarenes.[4,5] This is primarily a consequence of their relative inaccessibility through synthesis.

We recently reported the synthesis of several methylene-bridged polycyclic hydrocarbons.[6-8] However, attempts to prepare 4*H*-benzo[*c*]cyclopenta[*mno*]chrysene (**1**) from its hexahydro precursor by various chemical or catalytic methods of dehydrogenation failed. We now report successful synthesis of **1** via a photochemical route as well as synthesis of the previously unknown bridged polyarenes 6*H*-cyclopenta[*ghi*]picene (**2**), 13*H*-cyclopenta[*rst*]pentaphene (**3**), and 12*H*-benzo[*b*]cyclopenta[*def*]chrysene (**4**), and a new synthesis of 13*H*-dibenz[*bc,l*]aceanthrylene (**5**).[9]

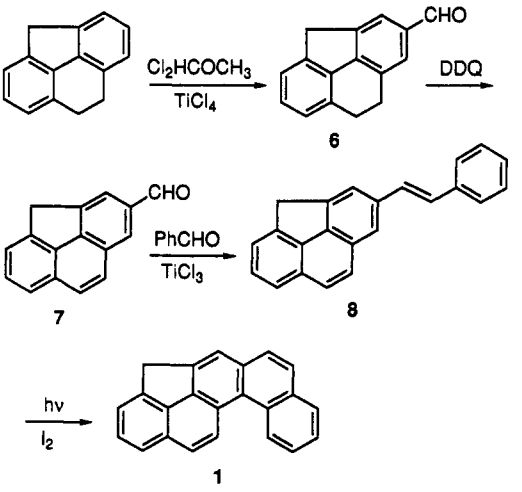


1 **2** **3** **4** **5**

Results

In view of the previously observed resistance to dehydrogenation of the 6,7,8,9,10,11-hexahydro derivative of **1**, we sought an alternative synthetic route for which dehydrogenation would not be the final step. The method adopted is based on the prototype methylene-bridged hydrocarbon 4*H*-cyclopenta[*def*]phenanthrene (Scheme I).[10] Although electrophilic substitution of this hydrocarbon takes place regioselectively in the 1-position, it may be directed to the 2-position through initial hydrogenation of the 8,9-positions with the K-region specific catalyst Pd/C.[11,12] Reaction of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene with dichloromethyl methyl ether and $TiCl_4$ furnished smoothly the 2-formyl derivative (**6**) which was dehydrogenated with DDQ to give 4*H*-cyclopenta[*def*]phenanthrene-2-carboxaldehyde (**7**). McMurray coupling of **7** with benzaldehyde in the presence of $TiCl_3$ provided the olefin **8**. Synthesis of **8** was also accomplished via the Wittig reaction of **7** with benzyltriphenylphosphonium chloride.

Scheme I



Conversion of **8** to 4*H*-benzo[*c*]cyclopenta[*mno*]chrysene (**1**) was accomplished directly in a single step by oxidative photocyclization in the presence of I_2 and propylene oxide.[13,14] Photoreaction takes place regiospecifically in only one of the two available sites consistent with the anticipated greater reactivity of the 1-position of the 4*H*-cyclopenta[*def*]phenanthrene ring system. The structural assignment of **1** was consistent with its NMR spectrum which showed a pair of characteristic low-field doublets at δ 9.44 and 9.29 for the sterically crowded *fjord* region protons H_{11} and H_{12} as well as a singlet at δ 4.52 for the bridge methylene protons.

A modification of this synthetic approach was used to also synthesize 13*H*-dibenz[*bc,l*]aceanthrylene (**5**) (Scheme

(1) Blumer, M. *Sci. Am.* **1976**, *234*, 35.
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(3) Rice, J.; Jordan, K.; Little, P.; Hussain, N. *Carcinogenesis* **1988**, *9*, 2275.
(4) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons; Chemistry and Carcinogenicity*; Cambridge University Press: Cambridge, 1991.
(5) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964.
(6) Yang, C.; Harvey, R. G. *Tetrahedron* **1992**, *48*, 3735.
(7) Young, R. J.; Harvey, R. G. *Tetrahedron Lett.* **1989**, *30*, 6603.
(8) Yang, C.; Harvey, R. G. In *Polycyclic Aromatic Compounds: Synthesis, Properties, Analytical Measurements, Occurrence and Biological Effects*; Garrigues, P., LaMotte, M., Eds.; Gordon & Breach: Switzerland, 1993; pp 151–157.
(9) The names and numbering of the methylene-bridged polyarenes are based on official IUPAC nomenclature rules. These hydrocarbons may be named less formally as methano derivatives of the parent ring system, e.g. 13*H*-dibenz[*bc,l*]aceanthrylene becomes 1,14-methanodibenz[*a,j*]anthracene.
(10) Yang, C.; Harvey, R. G. *Polycyclic Aromat. Compds.* **1992**, *2*, 229.
(11) Minabe, M.; Yamamoto, Y.; Yoshida, M.; Nakada, K.; Suzuki, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 725.
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(13) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1.
(14) Propylene oxide was recently shown to enhance the yields in oxidative photocyclizations by removing the HI which is responsible for photoreduction of double bonds; Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

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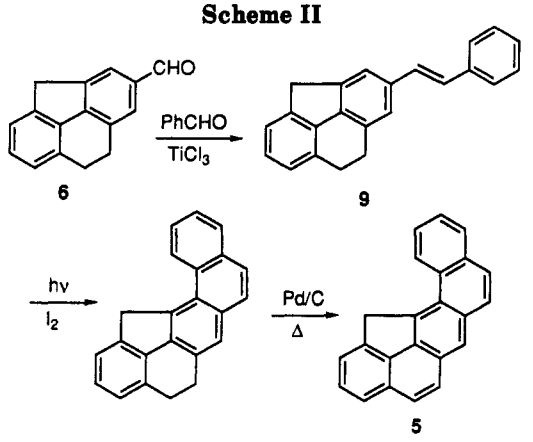
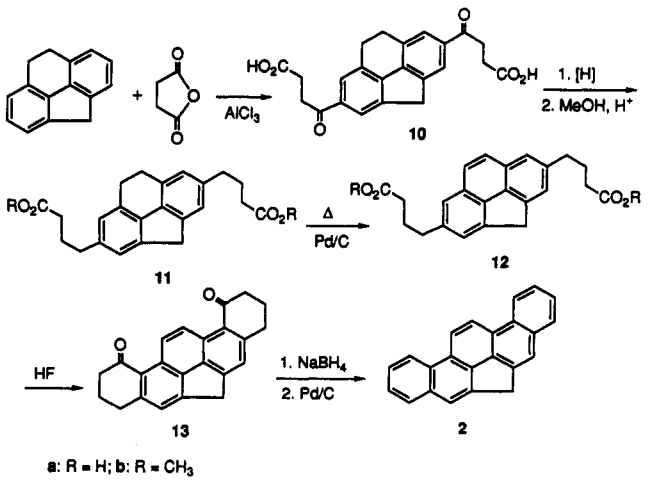
Scheme II



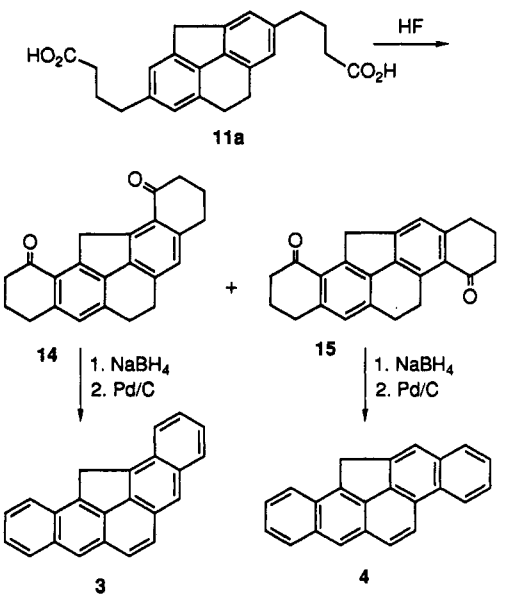
Scheme III



II). It was reasoned that the direction of cyclization observed for **8** might be changed in its 8,9-dihydro derivative to favor formation of the alternative 13*H*-dibenz[*bc*,*l*]aceanthrylene ring system. Reaction of the aldehyde **6** with benzaldehyde and $TiCl_3$ furnished the 8,9-dihydro stilbene derivative **9**. Oxidative photocyclization under the same conditions used for the preparation of **1** afforded a mixture of products containing dihydro-**5**. Dehydrogenation of the mixture over Pd/C provided **5**, readily distinguished from **1** by its high resolution NMR spectrum which was identical with that reported earlier for authentic **5**.[6]

In order to extend these studies to additional polycyclic ring systems, we investigated the double Friedel–Crafts succinoylation of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (Scheme III). This reaction afforded smoothly the diketo dibasic acid **10**. Wolff–Kishner reduction followed by esterification with methanol and methanesulfonic acid furnished the reduced diester **11b**. Dehydrogenation of the central ring over a Pd/C catalyst in refluxing triglyme gave the aromatized diester **12b**. Basic hydrolysis of the diester gave the free diacid **12a** which was cyclized in liquid HF. It was anticipated that double cyclization should take place in the direction to favor electrophilic substitution in the more reactive 1,7-positions of the 4*H*-cyclopenta[*def*]phenanthrene ring system. In agreement with this expectation, there was obtained the diketone **13** as the sole isomeric product. The structural assignment of this highly symmetrical structure was consistent with the relative simplicity of its NMR spectrum. In particular, the aromatic protons appeared as a low field singlet at δ 9.22 assigned to the central $H_{12,13}$ protons flanked by the bay region carbonyl groups and a higher field singlet at δ 7.46 assigned to the $H_{5,7}$ protons adjacent to the methylene bridges. Other peaks in the NMR spectrum were also consistent with this assignment. Conversion of **13** to 6*H*-cyclopenta[*ghi*]picene (**2**) was accomplished by initial reduction with $NaBH_4$ to the corresponding diol followed by heating in refluxing triglyme over a Pd/C catalyst. The ^1H NMR spectrum of **2** resembled that of picene,[15] but with differences consistent with the 6,7-dialkylated picene structure, exhibiting a characteristic doublet at δ 8.69 and a singlet at δ 8.64 assigned to the two pairs of bay region protons, $H_{1,11}$ and $H_{12,13}$, respectively. In further confirmation of the structural assignment of **2**, its UV spectrum closely matched that of picene[15] with an ~10-nm shift to longer wavelength.

Scheme IV



Cyclization of the diacid **11a** with a saturated central bond was investigated as a potential synthetic route to additional hexacyclic methylene-bridged isomers (Scheme IV). Cyclization of **11a** in liquid HF afforded a mixture of two diketone products (in ~3:1 ratio) separable by chromatography on silic gel. The major and minor isomers were assigned the structures **14** and **15**, respectively. The NMR spectrum of **14** showed a high degree of symmetry as anticipated for this structure. In particular, the methylene protons of the five-membered ring of **14** appeared as a singlet at δ 4.57 consistent with their location between two carbonyl functions; in contrast, the methylene protons of **11b** are found at δ 3.80. In further agreement with this assignment, the $H_{6,7}$ methylene protons of **14** appeared as an apparent singlet at δ 3.14, indicating absence of an adjacent carbonyl function. The NMR spectrum of the minor isomer **15** showed greater complexity. The most distinctive features were the shift of the signal for the methylene protons of the five-membered ring to higher field (δ 4.22), consistent with their location adjacent to a single carbonyl function, and the appearance of the $H_{5,6}$ methylene protons as two separate triplets, one at δ 3.13 for H_6 without an adjacent carbonyl group and one at δ 3.66 for H_5 with an adjacent carbonyl group.

(15) Karcher, W. *Spectral Atlas of Polycyclic Aromatic Compounds*; Kluwer Academic Publishers: Dordrecht, 1988; Vol. 2.

Reduction of 14 with $NaBH_4$ converted it to the corresponding diol. This underwent dehydration and dehydrogenation by heating in refluxing triglyme over a Pd/C catalyst to yield 13*H*-cyclopenta[*rst*]pentaphene (3). Similar reduction and dehydrogenation of 15 transformed it to 12*H*-benzo[*b*]cyclopenta[*def*]chrysene (4). These structural assignments were in good agreement with the NMR and UV spectral data.

Experimental Section

Materials and Methods. 4*H*-cyclopenta[*def*]phenanthrene was synthesized by the published procedure.[10] 8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene was prepared by hydrogenation of the parent hydrocarbon over a 5% Pd/C catalyst under mild conditions.[11,12] Dimethoxyethane (DME) was dried over molecular sieves 3A prior to use. The proton NMR spectra were obtained on the University of Chicago 300- or 500-MHz NMR spectrometers in $CDCl_3$ with tetramethylsilane as internal standard. Integration was consistent with all assignments. Ultraviolet spectra were taken on a Perkin-Elmer Lambda 5 spectrometer.

8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene-2-carboxaldehyde (6). To a stirred solution of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (800 mg, 4.2 mmol) in 10 mL of CH_2Cl_2 at 0 °C was added 5 mL of 1 M $TiCl_4$ followed by 0.5 mL of dichloromethyl methyl ether. The mixture was stirred at 0 °C for 1 h and then allowed to warm to room temperature for an additional 2 h before quenching by the addition of dilute HCl. The product was extracted with CH_2Cl_2, and the combined extracts were washed with 2 H HCl and water and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by chromatography on a silica gel column. Elution with hexane–ether (3:1) afforded 6 (510 mg, 56%) as a yellow solid: mp 81.5–82.5 °C; NMR δ 9.99 (s, 1, CHO), 7.87 (s, 1, H_3), 7.68 (s, 1, H_1), 7.39 (d, 1, H_5; J = 6.5 Hz), 7.27 (t, 1, H_6; J = 7.5 Hz), 7.16 (d, 1, H_7; J = 7.4 Hz), 3.96 (s, 2, CH_2), 3.20 (s, 4, $H_{8,9}$). Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.30; H, 5.54.

4*H*-Cyclopenta[*def*]phenanthrene-2-carboxaldehyde (7). A solution of the aldehyde 6 (130 mg, 0.60 mmol) and DDQ (350 mg, 1.54 mmol) in 7 mL of dry benzene was heated at reflux for 3 h. The solution was cooled to ambient temperature and ether was added, and the organic layer was washed with 10% NaOH and water and dried over $CaCl_2$. After removal of the solvent, the residue was dissolved in a small volume of benzene and passed through a short Florisil column. Elution with benzene furnished 7 (110 mg, 84%) as a pale yellow solid: mp 110.5–111.5 °C; NMR δ 10.26 (s, 1, CHO), 8.35 (s, 1, H_3), 8.23 (s, 1, H_1), 7.93 (s, 2, $H_{8,9}$), 7.87 (m, 1, Ar), 7.75 (m, 2, Ar), 4.41 (s, 2, CH_2). Anal. Calcd for $C_{16}H_{10}O$: C, 88.05; H, 4.62. Found: C, 88.19; H, 4.68.

1-[2-(4*H*-Cyclopenta[*def*]phenanthryl)]-2-phenylethylene (8). Reaction of the aldehyde 6 with benzaldehyde was carried out by the procedure described below for the preparation of 9 to yield 8 (75 mg, 60%) predominantly as the trans isomer. This olefin was also prepared by the Wittig reaction of 6 (560 mg, 2.5 mmol) with benzyltriphenylphosphonium chloride (1.1 g, 2.8 mmol). To this mixture in 45 mL of CH_2Cl_2 was added 3.5 mL of 50% NaOH, and the solution was stirred vigorously for 20 min. The organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated to dryness. The residue was taken up in a small volume of CH_2Cl_2 and filtered through a short column of silica gel eluted with hexane–CH_2Cl_2 (4:1) to provide 8 (695 mg, 95%) as a mixture of *cis–trans* isomers; crystallization from ethanol furnished *trans*-8 (280 mg): mp 165–166 °C; NMR δ 7.97 (s, 1, Ar), 7.91 (s, 1, Ar), 7.82 (s, 2, Ar), 7.80 (d, 1, Ar), 7.69 (d, 1, Ar), 7.64 (d, 1, Ar), 7.59 (d, 1, Ar), 7.69 (d, 1, Ar), 7.28–7.46 (m, 5, Ar and vinyl), 4.35 (s, 2, CH_2). Anal. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.36; H, 5.58.

1-[2-(8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthryl)]-2-phenylethylene (9). A mixture of lithium (0.20 g) and $TiCl_3$ (1.4 g) in 30 mL of dry DME was refluxed under argon for 2 h and cooled to rt. To this was added a solution of the aldehyde 7 (500 mg, 2.27 mmol) and benzaldehyde (0.6 mL) in 10 mL of DME, and the mixture was heated at reflux for 16 h. Benzene was added and the solution was filtered, washed with water, dried, and evaporated to dryness. The residue was taken up in CH_2Cl_2 and purified by chromatography on a column of silica gel eluted with hexane–CH_2Cl_2 (10:1) to give 9 (500 mg, 83%) as a pale yellow solid: mp 163–165 °C; NMR δ 7.54 (m, 3, Ar), 7.35 (m, 4, Ar), 7.14–7.26 (m, 5, Ar and vinyl), 3.92 (s, 2, CH_2), 3.16 (s, 4, $H_{8,9}$). Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.73; H, 6.23.

4*H*-Benzo[*c*]cyclopenta[*mno*]chrysene (1). A solution of 8 (60 mg, 0.21 mmol) in 450 mL of benzene was irradiated in the presence of I_2 (54 mg) and excess propylene oxide (4 mL) for 5 h. After removal of solvent by evaporation, the residue was dissolved in a small amount of benzene and passed through a short column of silica gel. Elution with benzene gave 1 (37 mg, 62%) as a pale yellow solid: mp 182–183 °C; NMR δ 9.44 (d, 1, H_{11}, J = 8.5 Hz), 9.29 (d, 1, H_{12}; J = 9.1 Hz), 7.68–8.14 (m, 10, Ar), 4.52 (s, 2, CH_2); UV λ_{max} (EtOH) 318 (ε 9955), 307 (23180), 279 (70910), 207 (32730). Anal. Calcd for $C_{23}H_{14}$: C, 95.15; H, 4.86. Found: C, 94.91; H, 4.90.

13*H*-Dibenzo[*bc,l*]aceanthrylene (5). A solution of 9 (100 mg, 0.37 mmol) in 450 mL of benzene was irradiated in the presence of I_2 (94 mg, 0.37 mmol) and excess propylene oxide (4 mL) for 5 h. The product mixture obtained following similar workup as in the preceeding example was heated with 10% Pd/C (70 mg) at 300 °C for 1 h. The residue was taken up in $CHCl_3$, filtered, and chromatographed on silica gel. Elution with hexane–benzene (1:1) gave 5 (15 mg, 15%): mp 218–219 °C (lit.[6] mp 228–229 °C); the NMR spectrum matched that of an authentic sample.

Succinoylation of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene. To a solution of succinic anhydride (7.5 g, 75 mmol) and $AlCl_3$ (15 g, 0.11 mmol) in 200 mL of CH_2Cl_2 at 0 °C was added 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (6.2 g, 32 mmol), and the mixture was stirred at 5 °C for 16 h. Reaction was quenched by careful addition of 250 mL of 2 N HCl. The reaction mixture was heated with stirring, allowing the solvent to evaporate. The solid product was filtered off and washed with ether–hexane (1:1) to give 11.6 g of the crude diketo diacid 10. This was reduced directly to the diacid 11a by addition to a solution of KOH (23.0 g) and hydrazine (50 mL) in 300 mL of diglycol and heated at reflux for 18 h. The reaction mixture was cooled, poured into water, and acidified to pH 1 with 6 N HCl, and the solid was filtered and dried under vacuum. The crude diacid was converted to the corresponding methyl ester by stirring overnight with 300 mL of MeOH containing 3 mL of methanesulfonic acid. Conventional workup followed by chromatography on a silica gel furnished on elution with hexane–CH_2Cl_2 the diester 11b (8.6 g, 68%) as a white solid: mp 54.0–54.5 °C; NMR δ 7.10 (s, 2, $H_{3,5}$), 6.88 (s, 2, $H_{1,7}$), 3.80 (s, 2, H_4), 3.65 (s, 6, OMe), 3.07 (s, 4, $H_{8,9}$), 2.67 (s, 4, CH_2; J = 7.5 Hz), 2.34 (t, 4, CH_2; J = 7.5 Hz), 1.96 (m, 4, CH_2; J = 7.5 Hz). Anal. Calcd for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.38; H, 7.21.

Dehydrogenation of 11b to 12b. A mixture of the diester 11b (5.0 g, 12.8 mmol) and 10% Pd/C (4.0 g) in 100 mL of triglyme was refluxed overnight and then poured onto ice and filtered. The solid was dissolved in $CHCl_3$, washed with 2 N Na_2CO_3 and water, and dried over $MgSO_4$. Evaporation of the solvent under vacuum gave 12b (4.6 g, 93%) as a pale yellow solid; mp 70.0–72.0 °C; NMR δ 7.70 (s, 2, $H_{8,9}$), 7.55 (s, 2, $H_{1,7}$), 7.47 (s, 2, $H_{3,5}$), 4.26 (s, 2, H_4), 3.64 (s, 6, CH_3), 2.92 (t, 4, CH_2; J = 7.5 Hz), 2.37 (t, 4, CH_2; J = 7.5 Hz), 2.08 (m, 4, CH_2; J = 7.5 Hz). Anal. Calcd for $C_{25}H_{28}O_4$: C, 76.90; H, 6.71. Found: C, 76.81; H, 6.71.

Cyclodehydration of the Diacid 12a. A solution of the diester 12b (4.5 g, 11.5 mmol) in 100 mL of 1 N KOH in ethanol was heated at reflux for 5 h, then poured into water, acidified to pH 1 with 6 N HCl, filtered, and dried to give the crude diacid 12a. This was dissolved in liquid HF (150 mL) and stirred overnight in a well-ventilated hood. Following the usual workup, the crude product was purified by chromatography on a column of silica gel. Elution with CH_2Cl_2–acetone (19:1) provided the diketone 13 (2.85 g, 76%). An analytical sample had mp 288–291 °C dec (CH_2Cl_2): NMR δ 9.22 (s, 2, $H_{12,13}$), 7.46 (s, 2, $H_{5,7}$), 4.24 (s, 2, H_6), 3.21 (t, 4, CH_2; J = 6.0 Hz), 2.78 (t, 4, CH_2; J = 6.5 Hz), 2.22 (m, 4, CH_2). Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.54; H, 5.60.

6*H*-Cyclopenta[*ghi*]picene (2). A mixture of the diketone **13** (740 mg, 2.3 mmol) and excess $NaBH_4$ (1.30 g) in 35 mL of ethanol was stirred overnight. Reaction was quenched by the careful addition of 30 mL of 2 N HCl. The product was filtered, washed with 2 N HCl and water, and dried. The crude alcohol product (710 mg) was combined with 650 mg of 10% Pd/C suspended in 20 mL of triglyme, and the mixture was heated at reflux for 18 h. Water was added and the product was filtered, dissolved in $CHCl_3$, filtered through a short column of silica gel, and evaporated to dryness to give **2** (490 mg, 74%) as a pale yellow solid. Recrystallization from benzene afforded 425 mg of pure **2** as white needles; mp 266–267 °C; NMR δ 8.69 (d, 2, $H_{1,11}$; J = 7.9 Hz), 8.64 (s, 2, $H_{12,13}$) 8.01 (d, 2, $H_{4,8}$; J = 7.8 Hz), 7.89 (s, 2, $H_{5,7}$), 7.68 (t, 2, $H_{2,10}$; J = 7.6 Hz), 7.65 (t, 2, $H_{3,9}$; J = 7.5 Hz), 4.51 (s, 2, CH_2); UV λ_{max} (EtOH) 332 (ϵ 21 000), 303 (24 400), 283 (89 300), 252 (54 400), 227 (22 900), 191 (23 800) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 94.98; H, 4.60.

Cyclodehydration of the Diacid 11a. A solution of the diester **11b** (5.2 g, 13.3 mmol) in 130 mL of 1 N KOH in ethanol was heated at reflux for 4 h, poured into water, and acidified with 6 N HCl, and the solid product was filtered and dried. The crude diacid was dissolved in liquid HF (130 mL) and stirred in a well-ventilated hood for 15 h. HF was removed by evaporation, the residue was dissolved in $CHCl_3$, and the solution was washed with 2 N Na_2CO_3. The organic layer was dried and evaporated to dryness. Chromatography of the reside on a column of silica gel eluted with CH_2Cl_2–acetone (10:1) gave the diketones **14** (2.85 g) and **15** (870 mg), total yield 86%. **14**: mp 261–264 °C dec; NMR δ 7.01 (s, 2, $H_{5,8}$), 4.57 (s, 2, H_{13}), 3.14 (s, 4, $H_{6,7}$), 3.01 (t, 4, CH_2; J = 5.9 Hz), 2.67 (t, 4, CH_2; J = 6.5 Hz), 2.14 (m, 2, CH_2; J = 6.2 Hz). Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.97; H, 6.12. **15**: mp 254–256 °C; NMR δ 7.26 (s, 1, H_{13}), 7.01 (s, 1, H_7), 4.22 (s, 2, H_{12}), 3.66 (t, 4, H_5; J = 7.8 Hz), 3.13 (t, 2, H_6; J = 7.0 Hz), 3.02 (m, 4, CH_2), 2.66 (m, 4, CH_2), 2.11 (m, 4, CH_2). Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.92; H, 6.20.

13*H*-Cyclopenta[*rst*]pentaphene (3). Conversion of **14** (800 mg, 2.4 mmol) to **3** was carried out by the procedure employed for the preparation of **2**. Recrystallization of the crude product (350 mg) from benzene afforded pure **3** (245 mg, 35%) as pale yellow crystals: mp 207–208 °C; NMR δ 8.22 (d, 2, $H_{1,12}$; J = 8.8 Hz), 8.19 (s, 2, $H_{5,8}$), 8.12 (d, 2, $H_{4,9}$ J = 8.2 Hz), 7.70 (s, 2, $H_{6,7}$), 7.60 (t, 2, $H_{3,10}$; J = 7.6 Hz), 7.53 (t, 2, $H_{2,11}$; J = 7.5 Hz), 4.78 (s, 2, CH_2); UV λ_{max} (EtOH) 362 (ϵ 24 000), 343 (25 000), 330 (34 700), 314 (45 000), 258 (87 400), 226 (60 700), 195 (25 900) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 94.98; H, 4.87.

12*H*-Benzo[*b*]cyclopenta[*def*]chrysene (4). Preparation of **4** from **15** (370 mg) was carried out using the procedure employed for the preparation of **2**. Pure **4** (190 mg, 58%): mp 243.5–244.5 °C; NMR δ 8.62 (d, 1, H_4; J = 8.0 Hz), 8.45 (d, 1, H_5; J = 9.0 Hz), 8.38 (s, 1, H_7), 8.18 (m, 2, Ar; J = 8.7 Hz), 8.05 (m, 3, Ar), 7.66 (t, 1, Ar), 7.59 (m, 2, Ar), 7.52 (m, 1, Ar), 4.73 (s, 2, CH_2); UV λ_{max} (EtOH) 395 (ϵ 8750), 373 (9890), 353 (7200), 334 (5560), 288 (99 400), 244 (40 100), 200 (24 500), 192 (20 600) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 94.96; H, 4.91.

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