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Synthesis of Methylene-Bridged Polyarenes

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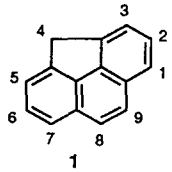
Abstract: Methylene-bridged polyarenes are a relatively rare class of polycyclic aromatic hydrocarbons whose chemistry is relatively unexplored. Although they are suspected carcinogenic environmental pollutants, few hydrocarbons of this class are known, and general synthetic approaches are lacking. Convenient syntheses of a series of methylene-bridged polyarenes are now described. These syntheses are based upon the prototype hydrocarbon cyclopenta[def]phenanthrene (**1**) which contains a pre-existing methylene bridge. Polyarenes prepared include 13*H*-dibenz[bc,l]aceanthrylene (**3**), 4*H*-cyclopenta[pqr]picene (**5**), 4*H*-benzo[b]cyclopenta-[mno]chrysene (**6**), 13*H*-indeno[2,1,7-qra]naphthacene (**7**), and 4*H*-cyclopenta[def]dibenz[a,c]anthracene (**8**), all of which were previously unknown. Attempts to prepare 4*H*-benzo[c]cyclopenta[mno]chrysene (**4**) by catalytic or chemical dehydrogenation of its hexahydro precursor failed. This is likely due to steric crowding in the *fjord* region of **4** coupled with resistance to deformation from planarity caused by the methylene bridge. Preliminary findings from mutagenesis assays support the hypothesis that the active mutagenic metabolites of methylene-bridged polyarenes are sulfate esters of alcohol metabolites in the bridge sites.

INTRODUCTION

The chemistry of methylene-bridged polyarenes is relatively unexplored.[1] The limited evidence available suggests that it may differ significantly from that of the parent alternant hydrocarbons. Thus, electrophilic substitution of the prototype methylene-bridged hydrocarbon cyclopenta[def]phenanthrene (**1**) takes place preferentially in the 1-position,[2-6] contrasting with that of phenanthrene which occurs mainly in the 9-position. High ratios of methyl-substituted and methylene-bridged polyarenes are found in crude petroleum,[7] and bridged polyarenes are produced in the combustion of organic matter at moderate temperatures by pyrolytic dehydrocyclization of polycyclic aromatic hydrocarbons that bear bay-region methyl groups.[7,8] It is also likely that significant levels of bridged polyarenes occur as environmental pollutants; however demonstration has been hindered by the lack of appropriate standards.



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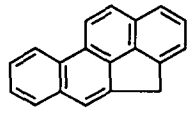

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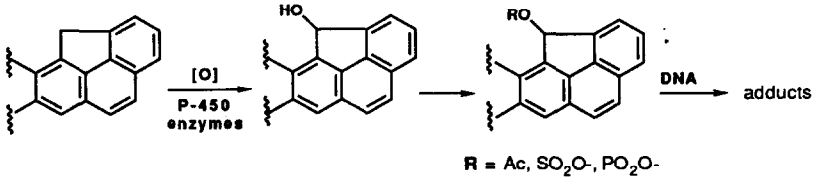
In view of the recently demonstrated carcinogenic potency of cyclopenta[def]chrysene (**2**),[9] it is of some importance to investigate the carcinogenic properties of the bridged polyarenes that occur environmentally. Investigations of the mechanism of carcinogenesis of alternant polyarenes that contain only fused six-membered

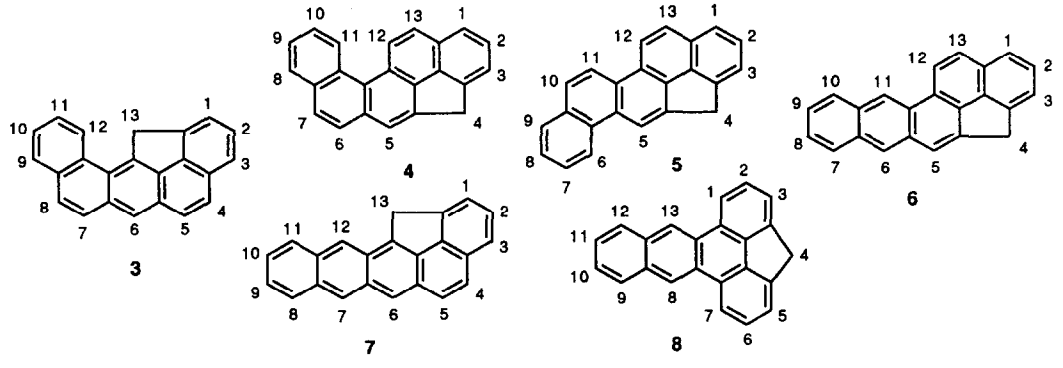
rings has led to identification of diol epoxide metabolites that bind covalently to nucleic acids as the active species responsible for their biological activities.[2,10] The methylene-bridged polyarenes are unique in that they may potentially undergo metabolic activation via an alternative mechanistic pathway involving enzymatic hydroxylation on the relatively acidic bridge positions followed by esterification to yield reactive sulfate, phosphate, or acetate esters (Scheme 1). These intermediates may be expected to react readily with DNA and other cellular macromolecules via SN_1 or SN_2 mechanisms.

Scheme 1



Investigations of the biological properties and mechanisms of carcinogenesis of the methylene-bridged polyarenes have been hampered by their relative synthetic inaccessibility. While syntheses of several methylene-bridged PAHs have been described,[11-13] general methods for their synthesis are lacking. In order to make non-alternant hydrocarbons of this class more readily available for research and to test the hypothesis in Scheme 1, we have explored novel, potentially more efficient synthetic approaches to methylene-bridged polyarenes.

In prior related studies, it was observed that attempted introduction of a methylene bridge into the benzo[a]pyrene and benzo[e]pyrene ring systems via cyclization of bay region carboxylic acid intermediates was accompanied by relatively facile decarboxylation,[11] leading to low yields of cyclized products. Therefore, we considered it desirable to develop an alternative route of ring assembly in which the methylene bridge is preformed in the starting compound. We now report on the synthesis of methylene-bridged polyarenes via routes based upon the prototype hydrocarbon cyclopent[def]phenanthrene (**1**). Syntheses of the methylene-bridged hydrocarbons 13*H*-dibenz[bc,l]aceanthrylene (**3**), 4*H*-benzo[c]cyclopenta[mno]chrysene (**4**), 4*H*-cyclopenta[pqr]picene (**5**), 4*H*-benzo[b]cyclopenta[mno]chrysene (**6**), 13*H*-indeno[2,1,7-qra]naphthacene (**7**), and 4*H*-cyclopenta[def]dibenz[a,c]anthracene (**8**) are described.[14]

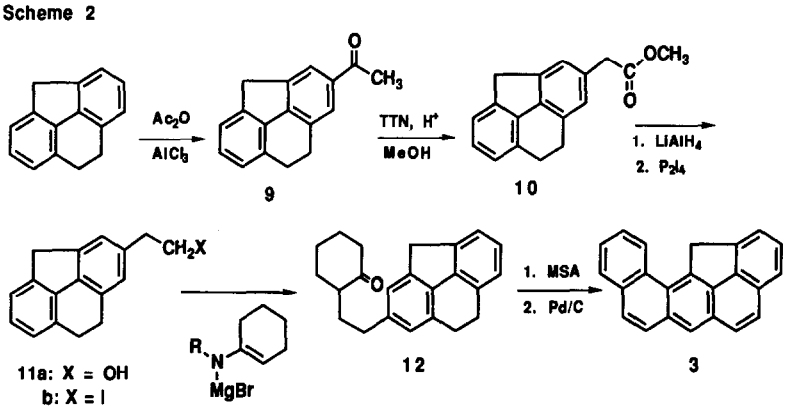


RESULTS

Initial efforts focused on use of the enamine alkylation method recently shown to provide an efficient synthetic route to alternant polyarenes.[15] This approach entails alkylation of enamines (or enamine salts) by benzylic halides (or β-haloethylaryl halides), followed by acid catalyzed cyclodehydration, and aromatization.

13*H*-Dibenz[bc,l]aceanthrylene (3). Synthesis of the bridged hydrocarbon **3** via a synthetic sequence involving alkylation of the bromomagnesium salt of N-cyclohexenylcyclohexanimine by 2-(2-haloethyl)-8,9-dihydrocyclopenta[def]phenanthrene (**11b**) is outlined in Scheme 2. Preparation of **11b** was accomplished readily in four steps from 8,9-dihydro-**1**. Although electrophilic substitution of **1** occurs preferentially in the 1-position, it was shown by Fieser and Cason[3] that substitution may be directed to the 2-position by prior hydrogenation of the 8,9-bond, effectively converting the aromatic portion of the molecule into a biphenyl derivative. Hydrogenation of **1**, previously carried out over a copper chromite catalyst at high pressure and elevated temperature,[3] was more conveniently effected by hydrogen addition over a 10% palladium/charcoal catalyst under mild conditions.[16] Acetylation of 8,9-dihydro-**1** gave 2-acetyl-8,9-dihydrocyclopenta[def]phenanthrene (**9**). Rearrangement of **9** took place smoothly on treatment with thallium trinitrate (TTN) and $HClO_4$ in methanol[17] to furnish the corresponding methyl acetate ester derivative **10**. Reduction of **10** with $LiAlH_4$ followed by treatment of the resulting alcohol with P_2I_4 provided **11b** in 62% overall yield.

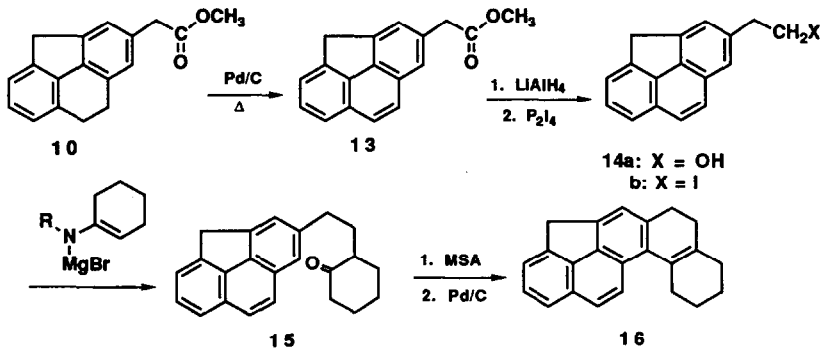
Scheme 2



Reaction of **11b** with the bromomagnesium salt of N-cyclohexenylcyclohexanimine followed by hydrolysis of the product afforded the alkylated ketone **12**. This intermediate on treatment with methanesulfonic acid at 0°C underwent cyclization regiospecifically to the 3-position of the cyclopenta[def]phenanthrene ring system to furnish a product which was dehydrogenated directly over a palladium-charcoal catalyst to yield 13*H*-dibenz[bc,l]aceanthrylene (**3**) in good overall yield. The structure of **3** was readily distinguished by its 500 MHz proton NMR spectrum from that of its isomer (**4**) which would have arisen from cyclization of **12** into the 1-position of the cyclopenta[def]phenanthrene ring system. Its NMR spectrum exhibited a low field doublet at δ 8.94 assigned to the sterically crowded bay region H_{12} proton, a singlet at δ 8.32 assigned to H_6, as well as a methylene peak at δ 4.94, and other peaks consistent with its structural assignment as **3** and not **4**.

4*H*-Benzo[c]cyclopenta[mno]chrysene (4). The synthetic approach to the isomeric methylene-bridged hydrocarbon **4** is based on the expectation that the direction of cyclization of **15** (Scheme 3), the fully aromatic derivative of **12**, is likely to be different than that of the latter, since it is a phenanthrene derivative for which cyclization to the 1-position has ample precedent.[3] Methyl (2-cyclopenta[def]phenanthryl)acetate (**13**) was most efficiently obtained by dehydrogenation of **10** over a Pd/C catalyst. The alternative route from **9** by catalytic dehydrogenation prior to rearrangement with TTN led to formation of a substantial amount of 2-ethylcyclopenta[def]phenanthrene as well as 2-acetylcyclopenta[def]phenanthrene in the dehydrogenation step. Apparently reduction of the carbonyl group by transfer hydrogenation is a facile process.

Scheme 3

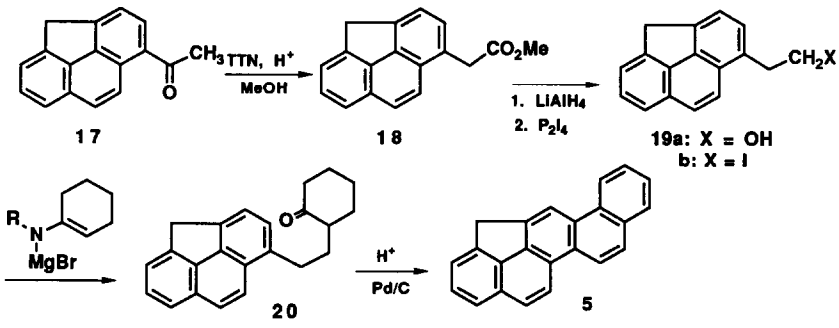


Reduction of **13** with $LiAlH_4$ followed by treatment of the resulting alcohol with P_2I_4 provided **14b** in 57% overall yield from **10**. Reaction of **14b** with the bromomagnesium salt of N-cyclohexylidenecyclohexylamine and hydrolysis of the product furnished the ketone **15**. Treatment of this intermediate with methanesulfonic acid at 0°C yielded a hydrocarbon product presumed to be **16** arising from cyclization into the 1-position of the cyclopenta[def]phenanthrene ring system. However, attempted aromatization of **16** over a Pd/C catalyst failed to afford the fully aromatic polyarene **4**. Other catalysts (e.g. Pd/C and sulfur, PtO_2, rhodium on alumina) and chemical dehydrogenation reagents, such as DDQ, were equally ineffective for this purpose. The resistance of **16** to dehydrogenation contrasts with the relatively facile aromatization of the partially saturated hydrocarbon precursor of **3**. This difference is partially a consequence of steric crowding in the fjord region of the aromatized product **4**. But this cannot be the sole determining factor, since the related hydrocarbons benzo[c]phenanthrene and benzo[c]chrysene, both of which contain a fjord region and are nonplanar, are obtainable via catalytic dehydrogenation of hydroaromatic precursors.[18,19] The greater resistance of **16** to aromatization is likely due to the considerable internal strain introduced into the ring system by the methylene bridge which increases the resistance of the molecule to deformation from planarity.

4*H*-Cyclopenta[pqr]picene (5). The synthesis of the methylene-bridged derivative of benzo[a]chrysene (**4**) is based on 1-acetylcyclopenta[def]phenanthrene (**17**) (Scheme 4). Acetylation of 4*H*-cyclopenta[def]phenanthrene with acetyl chloride and $AlCl_3$ reportedly affords principally the 1-acetyl isomer accompanied by the 3-, 2-, and 8-isomers in decreasing order of abundance in variable amounts dependent upon the solvent employed.[6,20] In order to develop a more regioselective acetylation method and avoid the tedious separation of

isomers, we investigated acetylation of **1** at low temperature. Acetylation at -78°C in CH_2Cl_2 afforded a mixture of the 1-acetyl isomer (88% by NMR) and the 3-acetyl isomer (12%) which could be readily separated by extraction with methanol. Treatment of **17** with TTN and $HClO_4$ in methanol[17] furnished the corresponding rearranged methyl acetate ester derivative **18**. Reduction of **18** with $LiAlH_4$ gave the corresponding alcohol **19a** which on treatment with P_2I_4 provided the related 2-iodoethyl compound **19b** in 69% overall yield from **17**. Reaction of **18b** with the bromomagnesium of salt of the enamine derivative of cyclohexanone gave the expected alkylated ketone derivative of 4*H*-cyclopenta[def]phenanthrene **20**. Acid-catalyzed cyclization and aromatization of **20** over a Pd/C catalyst furnished the fully aromatic bridged hydrocarbon **5**. The NMR spectrum of **5** was consistent with its assignment exhibiting a low field singlet at δ 8.99 assigned to the central H_5 proton, doublets at δ 8.87, 8.65, and 8.54 assigned to the additional bay region protons at H_6, H_{11}, and H_{12}, a methylene peak at δ 4.54, as well as other expected proton signals.

Scheme 4

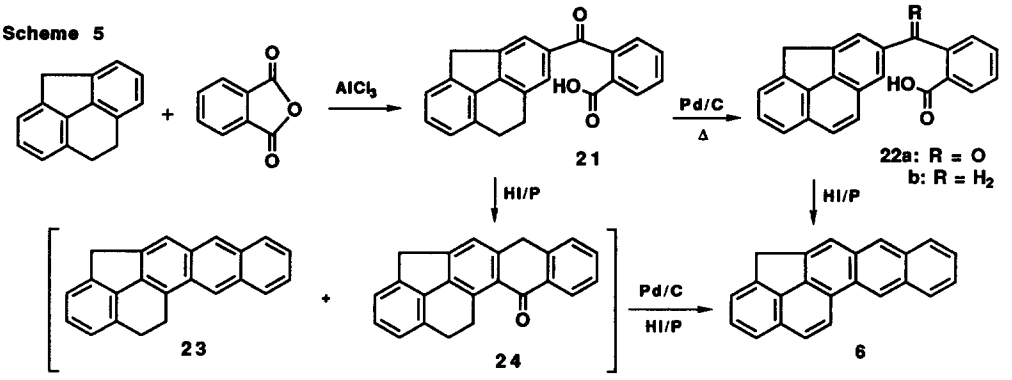


4*H*-Benzo[b]cyclopenta[mno]chrysene (6). For the synthesis of the methylene-bridged derivative of benzo[b]chrysene (**6**) a different approach was taken than for the preceding syntheses. Friedel-Crafts reaction of 8,9-dihydro-4*H*-cyclopenta[def]phenanthrene with phthalic anhydride and $AlCl_3$ took place selectively in the 2-position to give the keto-acid **21** (Scheme 5). It was anticipated on the basis of previous findings on the cyclization of the analogous 4*H*-cyclopenta[def]phenanthrene butyric acid derivatives[3] that dehydrogenation to the fully aromatic phenanthrene compound followed by reduction and acid catalyzed cyclization would lead to formation of **6**, whereas reduction and acid catalyzed cyclization of the dihydro compound followed by dehydrogenation would be expected to furnish 1,14-methanobenzo[a]naphthacene (**7**), arising from cyclization into the alternative ring position. However surprisingly, both routes led to formation of **6**. Thus, catalytic dehydrogenation of **21** over 10% Pd/C in refluxing triglyme furnished a 3:1 mixture of the expected keto-acid **22a** and the corresponding reduced acid **22b**. This mixture on treatment with HI and red phosphorus in refluxing acetic acid underwent reductive cyclization[21,22] and dehydrogenation to furnish **6**. The NMR spectrum of **6** was consistent with this assignment exhibiting a low field singlet at δ 9.10 and a doublet at δ 8.57 assigned to the bay region H_{11} and H_{12} protons, respectively, singlets at δ 8.45 and 7.90 assigned to the H_5 and H_6 protons, a methylene peak at δ 4.37, and other expected peaks.

Reductive cyclization of **21** with HI and red phosphorus in refluxing acetic acid for 20 h furnished a mixture of the cyclized product **23** accompanied by a lesser amount of the ketone intermediate **24**. Although reduction with HI/P was incomplete under these conditions, increased reaction time was found to be counter-

productive, resulting in overreduction of the desired product and formation of a high ratio of tarry products. The crude product mixture from HI/P reduction was heated with 10% Pd/C then treated again with HI/P to furnish **6**. Pure **6** was obtained in higher overall yield (63%) by this procedure than by the alternative route (47%).

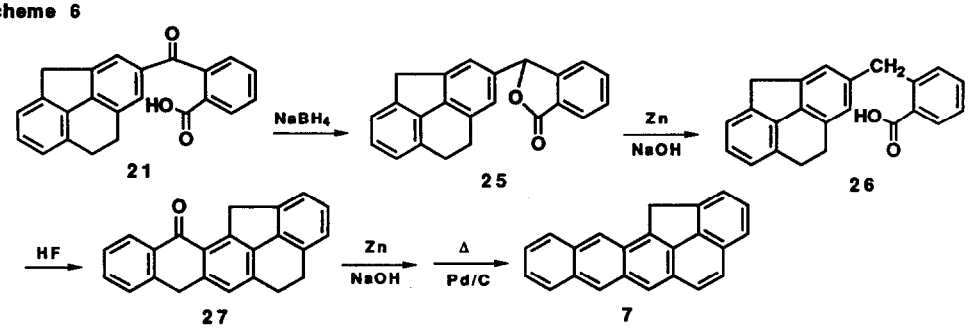
Scheme 5



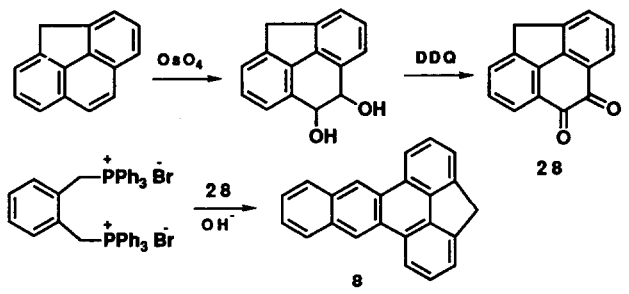
13*H*-Indeno[2,1,7-qra]naphthacene (7). The foregoing observations indicate that acid catalyzed cyclization of the keto acids **22a** and **22b** and the 8,9-dihydro analog of the latter take place preferentially to the 1-position of the 4*H*-cyclopent[def]phenanthrene ring system. However, the acid employed was HI, and HF was used by Fieser and Cason in the related syntheses of methylene-bridged derivatives of chrysene and benz-[a]anthracene wherein the direction of cyclization was observed to be dependent upon the state of saturation of the 8,9-dihydro ring positions.[3] Since there are numerous other examples of the dependency of the direction of cyclization upon the acid employed in the syntheses of PAHs,[23] we considered it worthwhile to investigate whether the direction of cyclization of the carboxylic acid in the present case could by altered to provide 1,14-methanobenzo[a]naphthacene (**7**) by the use of HF. Study of this reaction in greater detail, required a practical synthesis of the carboxylic acid derived from **21** by reduction of the carbonyl group. This acid (**26**) was readily obtained from **21** by two stage reduction first with $NaBH_4$ in ethanol and then by Zn/NaOH (Scheme 6). The reaction of **26** in liquid HF at room temperature for 24 h afforded smoothly the ketone product (**27**) arising from cyclization into the 3-position of the 4*H*-cyclopent[def]phenanthrene ring system. Reduction of **27** with zinc and alkali followed by dehydrogenation over palladium/charcoal provided **7** in good overall yield. The 500 MHz NMR spectrum of **7** was different from that of **6** and in good agreement with its structure, exhibiting a low field singlet at δ 8.39 assigned to H_{12} and two additional singlets at δ 7.71 and 7.69 assigned to H_6 and H_7, as well as a methylene singlet at at δ 4.62 and other peaks consistent with its assignment.

4*H*-Cyclopenta[def]dibenz[a,c]anthracene (8). The synthetic approach to this hydrocarbon (Scheme 7) was based upon the quinone derivative of cyclopenta[def]phenanthrene (**28**). This quinone was efficiently synthesized by reaction of **1** with osmium tetraoxide followed by oxidation of the resulting 8,9-cis-dihydrodiol product with DDQ. This method of synthesis affords **28** in higher overall yield than established alternative synthetic methods.[24] Wittig reaction of **28** with o-xylylene bis(triphenyphosphonium) bromide[25] furnished **8** directly in a single step in good overall yield.

Scheme 6



Scheme 7

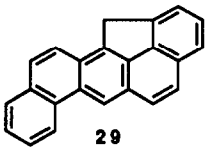


DISCUSSION

Convenient syntheses are described for a series of methylene-bridged hydrocarbons (**3-8**) representative of six different polycyclic aromatic ring systems. These hydrocarbons are all previously unknown compounds. The syntheses are based upon the prototype hydrocarbon 4*H*-cyclopenta[def]phenanthrene (**1**) and its readily accessible 8,9-dihydro or quinone derivatives. These methods may, in principle, be extended to the syntheses of a wide range of methylene-bridged hydrocarbon isomers having additional rings and to the synthesis of their substituted derivatives including their oxidized metabolites.

Prior to these investigations, it was anticipated that alkylation of an imine salt might not be useful as a synthetic route to polyarenes of this type due to the relatively high acidity of the hydrogens in the bridge. However, this proved not to be a serious problem. These reactions were carried out by the prior preparation of the bromomagnesium salt of the imine before the addition of the 4*H*-cyclopenta[def]phenanthrylethyl halide (e.g. **11b**) using a twofold excess of the imine salt. Under these conditions, the imine salt underwent relatively facile alkylation to afford good yields of the corresponding alkylated ketones (**12, 15, 20**). With the use of a lower ratio of the imine salt, yields were markedly diminished, indicating that reaction of the bromomagnesium salt with the bridge hydrogens does take place. However, this does not interfere seriously with formation of the desired product when a larger ratio of the reagent is employed.

Although syntheses of only two of the three possible methylene-bridged dibenzanthracene isomers (**3** and **8**) were carried out, the third isomer 13*H*-dibenz[bc,j]aceanthrylene (**29**) is potentially also accessible by appropriate modification of the same synthetic approach. This was not investigated, since **29** has been synthesized by an alternative route.[26]



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Studies of the electrophilic substitution patterns of the methylene-bridged polyarenes (bromination, acetylation, formylation) are currently in progress. Full details will be reported in due course.

Biological Studies. Preliminary findings from mutagenesis assays being conducted by Dr. H. Glatt, University of Mainz, Germany, indicate that several methylene-bridged polyarenes exhibit significant activity in the Ames assay with rat liver microsomal activation. The corresponding hydroxy derivatives substituted on the bridge position exhibit higher levels of activity without microsomal activation, and this activity is enhanced by the presence of sulfotransferase enzymes. These findings support the hypothesis (Scheme 1) that hydroxylation on the methylene bridge may play a key role in the mechanism of carcinogenesis of the methylene-bridged polyarenes. This represents a new mechanism of hydrocarbon carcinogenesis.

EXPERIMENTAL SECTION

Materials and Methods. 4*H*-Cyclopenta[def]phenanthrene was synthesized using a modification of the published procedure.[20,27] 8,9-Dihydro-4*H*-cyclopenta[def]phenanthrene was synthesized from the parent hydrocarbon by hydrogenation over a 5% Pd/C catalyst by the reported procedure.[28] N-Cyclohexylidenecyclohexylamine and its bromomagnesium salt were synthesized by the procedure of Stork and Dowd.[29] Tetrahydrofuran (THF) was redistilled from $LiAlH_4$ 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 unless stated otherwise. Integration was consistent with all structural assignments. The ultraviolet spectra were taken on a Perkin Elmer Lambda 5 spectrometer.

2-Acetyl-8,9-dihydro-4*H*-cyclopenta[def]phenanthrene (9). To a stirred solution of $AlCl_3$ (15 g, 112 mmol) and 5.7 mL (60 mmol) of Ac_2O in 90 mL of nitrobenzene at 0°C was added 8,9-dihydro-**1** (9.0 g, 47 mmol). The resulting solution was maintained at 5°C for 65 h, then 10 mL of 2N HCl was added. Nitrobenzene was removed by steam distillation, and the solution was extracted with chloroform, washed with water, dried over $MgSO_4$, and evaporated to dryness. The crude product was chromatographed on a column of Florisil eluted with CH_2Cl_2-hexane (3:7) to afford **9** as a pale yellow solid (10.4 g, 95%). Recrystallization from ethanol furnished pure **9** as white crystals: mp 102-103°C; NMR δ 7.94 (s, 1, H_1), 7.74 (s, 1, H_3), 7.33 (d, 1, H_5), 7.22 (t, 1, H_6), 7.11 (d, 1, H_7), 3.90 (s, 2, H_4), 3.16 (s, 4, $H_{8,9}$), 2.61 (s, 3, CH_3); IR (KBr) 2952, 1675 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.97; H, 6.05.

Methyl 2-(8,9-dihydro-4*H*-cyclopenta[def]phenanthryl)acetate (10). To a solution of **9** (2.0 g, 8.62 mmol) dissolved in 150 mL of MeOH were added 7 mL of perchloric acid and 4.0 g (9 mmol) of $TlNO_3.3H_2O$. The solution was stirred at rt for 15 h, then ether (100 mL) was added, and the solution was washed with H_2O and brine, dried, and evaporated to dryness. Chromatography of the crude product on a Florisil column furnished **10** (2.0 g, 88%) as a white solid on elution with CH_2Cl_2-hexane (7:3). Recrystalliz-

ation from ethanol gave pure **10**: mp 63.5-64.5°C; NMR δ 7.28 (d, 1, H_5), 7.22 (s, 1, H_1), 7.14 (t, 1, H_6), 7.06 (d, 1, H_7), 7.00 (s, 1, H_3), 3.85 (s, 2, H_4), 3.68 (s, 3, CH_3), 3.65 (s, 2, CH_2), 3.11 (s, 4, $H_{8,9}$); IR (KBr) 2870, 1732 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.68; H, 6.15.

2-[2-(8,9-Dihydro-4*H*-cyclopenta[def]phenanthryl)]ethanol (11a). To a solution of $LiAlH_4$ (1.5 g, 39.4 mmol) in 70 mL of dry ether was added dropwise a solution of **10** (4.0 g, 15.2 mmol) in 50 mL of dry ether. The resulting solution was heated at reflux for 2 h, then cooled to 0°C. The reaction was quenched with water, then ether (150 mL) was added, and the solution was washed with 2N HCl, H_2O, filtered through a short column of silica gel, and evaporated to dryness. Recrystallization from ethanol provided **11a** (3.27 g, 92%) as white crystals: mp 124.5-125.5 °C; NMR δ 7.29 (d, 1, H_5), 7.17 (s, 1, H_1), 7.14 (t, 1, H_6), 7.06 (d, 1, H_7), 6.95 (s, 1, H_3), 3.59 (t, 2, $\underline{CH_2}OH$), 3.41 (s, 2, H_4), 3.11 (s, 4, $H_{8,9}$), 2.89 (t, 2, CH_2). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.16; H, 6.79.

2-(2-Iodoethyl)-8,9-dihydro-4*H*-cyclopenta[def]phenanthrene (11b). A solution of **11a** (2.0 g, 8.5 mmol) and P_2I_4 (1.8 g, 3.2 mmol) in 80 mL of CS_2 was stirred at rt for 18 h. Then ether (100 mL) was added, and the solution was washed with water and filtered through a short column of silica gel to yield a yellow solid (2.33 g, 79%): mp 150-153°C. Recrystallization from ethanol furnished the analytical sample of **11b**: mp 157.5-158.5°C; NMR δ 7.29 (d, 1, H_5), 7.14 (t, 1, H_6), 7.13 (s, 1, H_1), 7.06 (d, 1, H_7), 6.91 (s, 1, H_3), 3.85 (s, 2, H_4), 3.34 (t, 2, CH_2), 3.19 (t, 2, CH_2), 3.11 (s, 4, $H_{8,9}$). Anal. Calcd for $C_{17}H_{15}I$: C, 58.98; H, 4.37. Found: C, 59.07; H, 4.38.

13*H*-Dibenz[bc,l]aceanthrylene (3). A solution of the bromomagnesium salt of N-cyclohexylidenecyclohexylamine was prepared by refluxing 6.5 mL of a solution of 2M EtMgBr (13.0 mmol) with the amine (2.10 g, 11.7 mmol) in 15 mL of dry THF for 3.5 h. The solution was cooled to rt, and a solution of **11b** (2.10 g, 6.10 mmol) in 10 mL of dry THF was added. This was heated at reflux for 1 h, then ether (150 mL) and water (25 mL) were added. The ether extract was dried and evaporated to dryness to afford 2.3 g of crude product which was chromatographed on silica gel. Elution with hexane-CH_2Cl_2 (1:1) gave **12** (1.54 g, 80%) as a white solid, melting at 126.0-127.0 °C. It was used directly in the next step. To a solution of **12** in 20 mL of CH_2Cl_2 at 0°C was added dropwise over 20 min a solution of CH_3SO_3H (35 mL) in 60 mL of CH_2Cl_2. When reaction was complete (TLC), the product was partitioned between ether and water, washed with water, 2N sodium carbonate, filtered through a short column of silica gel, and evaporated to dryness to give 1.5 g of a product which was heated with 450 mg of 10% Pd/C at 220 °C. The temperature was gradually raised to 250 °C over 30 min, kept at this temp. for 30 min, then raised to 285 °C, and kept at this temp. for 50 min. The mixture was cooled to rt, then 70 mL of chloroform was added, and refluxed for 10 min. The solution was filtered, and the residue washed with chloroform and evaporated to dryness to provide **3** (730 mg, 52%) as pale yellow needles: mp 228.0-229.0°C; NMR δ 8.94 (d, 1, H_{12}), 8.32 (s, 1, H_6), 7.64-7.98 (m, 10, Ar), 4.94 (s, 2, CH_2); UV λ_{max} (EtOH) 334 (ε 17700), 321 (18800), 301 (109000), 289 (67600), 278 (31400), 260 (33600), 226 (41300) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 95.04; H, 4.85.

2-Acetyl-4*H*-cyclopenta[def]phenanthrene. A solution of **9** (3.8 g, 16.2 mmol) and 10% Pd/C (3.0 g) in 150 mL of triglyme was heated at reflux for 4 h, then cooled, poured into water, and filtered. The product was dissolved in CH_2Cl_2 and transferred to a silica gel column. Elution with hexane-CH_2Cl_2 (8:2)

furnished initially 2-ethyl-4*H*-cyclopenta[def]phenanthrene (1.1g): mp 47.0-47.5 °C; NMR δ 7.56 (m, 3, Ar), 7.53-7.63 (m, 4, Ar), 4.29 (s, 2, CH_2), 2.92 (q, 2, CH_2), 1.37 (t, 3, CH_3). Further elution gave 2-acetyl-4*H*-cyclopenta[def]phenanthrene (2.1 g): mp 126.0-127.0°C (ethanol) (lit[6] mp 128.5-129.0°C); NMR δ 8.43 (s, 1, H_3), 8.26 (s, 1, H_1), 7.68-7.83 (m, 5, Ar), 4.34 (s, 2, CH_2), 2.77 (s, 3, CH_3). Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.41. Found: C, 88.00; H, 5.25.

Methyl 2-(4*H*-cyclopenta[def]phenanthryl)acetate (13). Reaction of **9** (3.5 g, 15.0 mmol) with $TlNO_3.3H_2O$ was carried out as described for **10**. The crude product (4.4 g) was dissolved in 150 mL of triglyme and 3 g of 10% Pd/C was added. The mixture was heated at reflux for 2 h, then poured into water and filtered. The solid was taken up in $CHCl_3$, filtered and evaporated to dryness. Recrystallization from MeOH afforded **13** (3.5 g, 89%): mp 63.0-64.0°C; NMR δ 7.57-7.79 (m, 7, Ar), 4.31 (s, 2, H_4), 3.89 (s, 2, CH_2), 3.70 (s, 3, CH_3). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.49; H, 5.41.

2-[2-(4*H*-Cyclopenta[def]phenanthryl)]ethanol (14a). The ester **13** (2.0 g, 7.6 mmol) was reduced with $LiAlH_4$ by the procedure employed for **11a** to give **14a** (1.7 g, 97%): mp 110.0-111.0°C; NMR δ 7.76 (m, 3, Ar), 7.64 (m, 2, Ar), 7.58 (t, 1, H_6), 7.55 (s, 1, Ar), 4.31 (s, 2, H_4), 3.97 (t, 2, CH_2), 3.15 (t, 2, CH_2), 1.44 (s, 1, OH). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.19; H, 6.05.

2-(2-Iodoethyl)-4*H*-cyclopenta[def]phenanthrene (14b). Reaction of the alcohol **14a** (3.10 g, 13.1 mmol) with P_2I_4 by the procedure for **11b** gave **15b** (3.07 g). Recrystallization from MeOH afforded pure **15b** (67%): mp 145.0-145.5 °C; NMR δ 7.74-7.80 (m, 3, Ar), 7.64 (d, 1, Ar), 7.60 (s, 1, Ar), 7.58 (d, 1, Ar), 7.49 (s, 1, Ar), 4.31 (s, 2, H_4), 3.45 (m, 4, CH_2). Anal. Calcd for $C_{17}H_{13}I$: C, 59.32; H, 3.81. Found: C, 59.22; H, 3.84.

Hexahydro-4*H*-benzo[c]cyclopenta[mno]chrysene (16). A solution of the salt of N-cyclohexylidenecyclohexylamine in 15 mL of THF was prepared from 2.10 g (11.7 mmol) from the amine by the usual method.[29] It was cooled to rt, a solution of **14b** (2.10 g, 6.1 mmol) in 10 mL of dry THF was added, and the solution was heated at reflux for 1 h. The product was partioned between ether (150 mL) and water (25 mL). The ether extract was dried, evaporated to dryness, and chromatographed on silica gel eluted with 1:1 hexane-CH_2Cl_2 to give the ketone **15** (1.80 g, 94%) as an oil which was used directly in the next step. To a solution of **15** in 35 mL of CH_2Cl_2 at 0°C was added dropwise over 30 min a solution of 35 mL of CH_3SO_3H in 60 mL of CH_2Cl_2. When reaction was complete as shown by disappearance of **15** by TLC, the product was partioned between ether and water and worked up conventionally to give **16** shown by NMR to be a mixture of isomers and partially disproportionated products. Attempts to dehydrogenate **16** were not successful.

1-Acetyl-4*H*-cyclopenta[def]phenanthrene (17). To a solution of $AlCl_3$ (12.0 g, 9.0 mmol) and Ac_2O (5,6 mL, 59 mmol) in 50 mL of dry CH_2Cl_2 was added dropwise a solution of **1** (7.00 g, 36.8 mmol) in 80 mL of dry CH_2Cl_2 at -78° C. The solution was stirred at this temperature for 2 h, then allowed to warm to -20 °C, and maintained at this temperature for 20 h. Ether was added and the solution was washed consecutively with 2N HCl, 2N Na_2CO_3 and water, then dried and evaporated to dryness to yield 8.6 g of a mixture of **17** (66 %) and the 3-acetyl isomer (12%) by NMR. Methanol (70 mL) was added and the solution was refluxed for 20 min, cooled, and filtered. This was repeated twice to give a total of 5.0 g of pure **17**. The filtrate was concen-

trated and the solid was recrystallized three times from MeOH to give an additional 0.48 g of **17** (total 5.48 g, 64%): mp 152.5-153.5 °C (lit[20] 152.0-153.5 °C); NMR δ 8.84 (d, 1, Ar), 8.15 (d, 1, Ar), 7.94 (d, 1, Ar), 7.81 (d, 1, Ar), 7.65 (m, 3, Ar), 4.32 (s, 2, H_4), 2.78 (s, 3, CH_3). Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.85; H, 5.23.

Methyl 1-(4*H*-cyclopenta[def]phenanthryl)acetate (18). Reaction of **17** with $TlNO_3.3H_2O$ as described for **10** followed by chromatographic purification on a column of silica gel eluted with hexane-CH_2Cl_2 (3:2) provided pure **18** (95%): mp 68.0 69.0 °C; NMR δ 7.90 (d, 1, Ar), 7.84 (d, 1, Ar), 7.79 (d, 1, Ar), 7.65 (d, 1, Ar), 7.61 (m, 2, Ar), 7.50 (d, 1, Ar), 4.30 (s, 2, H_4), 4.12 (s, 2, CH_2), 3.67 (s, 3, CH_3). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.33; H, 5.39.

2-[1-(4*H*-Cyclopenta[def]phenanthryl)]ethanol (19a). Reduction of **18** (4.0 g, 15.6 mmol) with $LiAlH_4$ by the procedure employed for **11a** gave **19a** (94%): mp 79.0-79.5°C; NMR δ 7.91 (d, 1, Ar), 7.81 (d, 1, Ar), 7.78 (d, 1, Ar), 7.56 (d, 1, Ar), 7.60 (m, 2, Ar), 7.45 (d, 1, Ar), 4.30 (s, 2, H_4), 4.01 (t, 2, CH_2), 3.38 (t, 2, CH_2), 1.47 (br s, 1, OH). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.19; H, 6.10.

1-(2-Iodoethyl)-4*H*-cyclopenta[def]phenanthrene (19b). Reaction of **19a** (3.00 g, 12.8 mmol) with P_2I_4 by the procedure for **11b** gave **19b** (3.10 g). Recrystallization from MeOH afforded pure **19b** (70%): mp 130.5-131.0 °C; NMR δ 7.86 (q, 2, Ar), 7.79 (d, 1, Ar), 7.66 (d, 1, Ar), 7.61 (m, 2, Ar), 7.44 (d, 1, Ar), 4.29 (s, 2, H_4), 3.68 (t, 2, CH_2), 3.49 (t, 2, CH_2). Anal. Calcd for $C_{17}H_{13}I$: C, 59.32; H, 3.81. Found: C, 59.48; H, 3.83.

4*H*-Cyclopenta[pqr]picene (5). The iodo compound **19b** (2.10 g) was used to prepare **5** (2.10 g) by the procedure used to prepare **3**. Recrystallization from benzene gave pure **5** (12%): mp 283.0-284.5 °C; NMR δ 8.99 (s, 1, H_5), 8.87 (d, 1, H_6; J = 8.22 Hz), 8.65 (d, 1, $H_{11 \text{ or } 12}$; J = 8.86 Hz), 8.54 (d, 1, $H_{12 \text{ or } 11}$; J = 8.86 Hz), 8.02 (d, 1, Ar), 7.98 (m, 2, Ar), 7.88 (d, 1, Ar), 7.61-7.71 (m, 4, Ar), 4.54 (s, 2, CH_2); UV λ_{max} (EtOH) 331 (ε 18500), 316 (15400), 284 (78100) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 94.89; H, 4.87.

2-Phthaloyl-8,9-dihydrocyclopenta[def]phenanthrene (21). To a solution of phthalic anhydride (2.00 g, 13.5 mmol) and $AlCl_3$ (4.5 g, 33.0 mmol) in 30 mL of nitrobenzene at 0 °C was added **1** (2.00 g, 10.4 mmol) and the solution was maintained at 5 °C for 60 h. After removal of nitrobenzene by steam distillation, the solid was filtered and recrystallized from 150 mL of acetone and 200 mL of water to afford **21** (3.20 g, 90 %): mp 227-228 °C (dec); NMR δ 8.02 (d, 1, Ar), 7.66 (s, 1, Ar), 7.59 (t, 1, Ar), 7.49 (t, 2, Ar), 7.31 (t, 2, Ar), 7.21 (t, 1, Ar), 7.07 (d, 1, Ar), 3.81 (s, 2, CH_2), 3.08 (m, 4, CH_2); IR (KBr) 2920 (br), 1700, 1660, 1585. Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 80.90; H, 4.81.

4*H*-Benzo[b]cyclopenta[mno]chrysene (6). The acid **21** (1.5 g, 4.4 mmol) and 10 mL of 50 % HI in 60 mL of acetic acid were heated at reflux for 20 h, then poured into water and filtered. The solid was dissolved in chloroform, filtered through a column of silica gel, dried, and evaporated to give a yellow solid which was taken up in 80 mL of triglyme. 1 g of 10 % Pd/C was added and the mixture was heated at reflux for

2 h, then poured into water, filtered, and dried. The solid product was dissolved in HOAc (30 mL), filtered, and 5 mL of 50 % HI was added and the mixture was refluxed overnight. Then 300 mg of red phosphorus was added and reflux was continued for another 20 h. The solution was poured into water, filtered, and dried to provide 900 mg of a solid which was dissolved in $CHCl_3$, and filtered through silica gel to give pure **6** (820 mg, 63 %): mp 254-255 °C (EtOH); the NMR spectrum matched that of an analyzed sample.

The acid **21** (4.00 g, 11.8 mmol) and 3.5 g of 10 % Pd/C in 130 mL of triglyme were heated at reflux for 4.5 h under N. The solution was cooled to rt, poured into water, and filtered. The solid was dissolved in 1 N NaOH and the solution was filtered, acidified to pH 1, refiltered, and dried to give 2.60 g of a 3:1 mixture of **22a** and **22b** (by NMR). This mixture was taken up in 120 mL of HOAc to which 2.0 g of red phosphorus and 20 mL of 50 % HI were added and heated at reflux for 20 h, then poured into water, and filtered. The solid was dissolved in CH_2Cl_2 and chromatographed through a short column of Florisil eluted with the same solvent. Evaporation to dryness followed by crystallization from $CHCl_3$ at -50 °C gave crude **6** (1.50 g, 41 %), mp 250-251 °C. Recrystallization from benzene gave the analytical sample of **6**: mp 254-255 °C; NMR δ 9.10 (s, 1, H_{11}), 8.57 (d, 1, H_{12}; J = 8.72 Hz), 8.49 (s, 1, H_6), 8.10 (d, 1, Ar), 8.02 (d, 1, Ar), 7.98 (d, 1, Ar; J = 8.64 Hz), 7.94 (s, 1, H_5), 7.82 (d, 1, Ar), 7.60 (m, 2, Ar), 7.50 (m, 2, Ar), 4.14 (s, 2, CH_2); UV λ_{max} (EtOH) 305 (ε 32900), 285 (13600) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 95.09; H, 4.87.

Lactone (25). A solution of the keto acid **21** (4.80 g, 14.1 mmol) and $NaBH_4$ (1.3 g, 35 mmol) in 120 mL of dry ethanol was stirred at rt for 20 h. After removal of solvent under vacuum, 1 N HCl was added and the solution was filtered and washed with water. The residue was taken up in $CHCl_3$, filtered again, dried, and evaporated to dryness. The solid was dissolved in 100 mL of benzene and refluxed overnight. Following removal of benzene under vacuum, 300 mL of ether was added and the solution was washed with aq. Na_2CO_3, water, dried, and filtered through a short column of silica gel to afford **25** (4.3 g, 94 %). Recrystallization from CH_2Cl_2-hexane (1:1) gave the analytical sample of **25**: mp 184-185 °C; NMR δ 7.94 (d, 1, Ar), 7.61 (t, 1, Ar), 7.52 (t, 1, Ar), 7.32 (d, 1, Ar), 7.29 (d, 1, Ar), 7.18 (s, 1, Ar), 7.16 (d, 1, Ar), 7.07 (d, 1, Ar), 6.96 (s, 1, Ar), 6.41 (s, 1, CH), 3.84 (s, 1, CH_2), 3.10 (q, 4, CH_2). Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 84.92; H, 4.91.

2-(2-Carboxybenzyl)-8,9-dihydrocyclopenta[def]phenanthrene (26). A mixture of **25** (5.20 g), zinc (40 g) and NaOH (17 g) in 250 mL of water and 15 mL of pyridine was refluxed for 20 h, cooled, and filtered. The filtrate was acidified to pH 1, filtered again, and the solid residue was washed with water. The solid was dissolved in hot $CHCl_3$, filtered, and evaporated to dryness to afford **26** (4.2 g, 80 %): mp 217.5-218.5 °C; NMR δ 8.01 (d, 1, Ar), 7.42 (t, 1, Ar), 7.23-7.28 (m, 3, Ar), 7.10 (s, 1, Ar), 7.10 (t, 1, Ar), 7.03 (d, 1, Ar), 6.89 (s, 1, Ar), 4.47 (s, 2, CH_2), 3.79 (s, 2, CH_2), 3.07 (t, 4, CH_2). Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.40; H, 5.59.

13*H*-Indeno-12-oxo-4,5,7,12-tetrahydro[2,1,7-qra]naphthacene (27). A solution of the acid **26** (2.00 g, 6.13 mmol) in 20 mL of HF was stirred at rt for 24 h. After evaporation of the HF, 2 N aq. Na_2CO_3 was added, and the mixture was stirred for 30 min. Chloroform (70 mL) was added, and the organic layer was washed with water, dried, and evaporated to dryness to yield **27** (1.73 g, 91 %): mp 215-218 °C

(benzene); NMR δ 8.33 (d, 1, Ar), 7.55 (t, 1, Ar), 7.43-7.54 (m, 2, Ar), 7.11 (d, 1, Ar), 4.44 (s, 2, CH_2), 4.43 (s, 2, CH_2), 3.19 (q, 4, CH_2). Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.24. Found: C, 89.47; H, 5.24.

13*H*-Indeno[2,1,7-qra]naphthacene (7). A mixture of **27** (350 mg, 1.14 mmol), Zn (3 g with 200 mg of $CuSO_4$), pyridine (1.5 mL), and NaOH (1.3 g) in 20 mL of water was heated at reflux for 16 h under N. The solution was cooled, 70 mL of $CHCl_3$ was added, and the resulting solution was filtered, washed with 2 N HCl and water, dried, and evaporated to dryness. The crude product (270 mg) was dissolved in 15 mL of triglyme and heated with 150 mg of 10 % Pd/C at reflux for 2 h under N. The solution was cooled to rt, water was added, and the solution was filtered to remove the catalyst and $CHCl_3$ was used to wash in the organic residue from the flask. The organic phase was dried, evaporated to dryness, taken up in a small volume of CH_2Cl_2 and passed through a short column of silical gel eluted with hexane-CH_2Cl_2 (7:3) to give **7** (150 mg, 46 %) as a pale yellow solid: mp 219-220 °C (benzene); NMR δ 8.72 (d, 2, Ar), 8.39 (s, 1, Ar), 8.04 (d, 1, Ar), 8.02 (d, 1, Ar), 7.73 (d, 1, Ar), 7.71 (s, 1, Ar), 7.69 (s, 1, Ar), 7.57 (d, 1, Ar), 7.45 (d, 1, Ar), 7.43 (m, 2, Ar), 4.62 (s, 2, CH_2); UV λ_{max} (EtOH) 428 (ε 9930), 321 (44600), 299 (80300), 261 (46300), 224 (34100) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 95.05; H, 4.91.

cis-8,9-Dihydrocyclopenta[def]phenanthren-8,9-diol. A solution of **1** (2.00 g, 10.5 mmol) and OsO_4 (3.0 g) in 40 mL of dry pyridine was stirred at rt for 3 days. To this was added 50 mL of 4% aqueous $NaHSO_3$, and the solution was stirred overnight, then filtered, washed with water, and dried to yield 2.03 g of product. The filtrate was extracted with $CHCl_3$, washed with water, and the organic layer was evaporated and crystallized from $CHCl_3$to afford an additional 150 mg of product (total yield 2.18 g, 92 %): mp 180.5-181.5 °C; NMR δ 7.32-7.47 (m, 4, Ar), 7.30 (7, 2, $H_{2,6}$), 5.10 (s, 2, H_4), 4.00 (d, 2, CHOH), 2.42 (br s, 1, OH), 1.58 (br s, 1, OH). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80,33; H, 5.40. Found: C, 80.21; H, 5.44.

Cyclopenta[def]phenanthren-8,9-dione (28). Method A. A solution of the cis-dihydrodiol (1.89 g, 8.44 mmol) and DDQ (9.0 g) in 120 mL of HOAc and 20 mL of H_2O was refluxed for 2 h and then cooled to rt. Chloroform (250 mL) was added, and the organic layer was separated, washed with 1N NaOH solution and water, and dried over $MgSO_4$. The solvent was evaporated and 20 mL of ether was added to the residue. This was refluxed for 20 min, cooled to rt and filtered to afford pure **28** (1.68 g, 95 %): mp 257.5-258.5 °C (lit[16] 260 °C): the NMR spectrum was in good agreement with that reported.[24] Method B. A solution of the diol (95 mg, 0.42 mmol) and DDQ (265 mg) in 3 mL of THF was stirred at rt for 25 min. Conventional workup and chromatography on a short column of silica gel afforded **28** (79 mg, 85 %): mp 257-258 °C.

4*H*-Cyclopenta[def]dibenz[a,c]anthracene (8). A solution of **28** (1.50 g, 6.81 mmol) and o-xylylene bis(triphenylphosphonium) bromide[25] (8.5 g, 10.8 mmol) in 100 mL of CH_2Cl_2 was stirred with an efficient mechanical stirrer and 35 mL of freshly prepared aq. 5 N LiOH solution was added. The resulting solution was stirred at rt for 3 days, then 150 mL of water was added, and the solution was extracted with 300 mL of CH_2Cl_2. The combined organic layer was evaporated to dryness, and the solid residue was transferred to a column of silica gel with a small volume of CH_2Cl_2, and the column was eluted with hexane-CH_2Cl_2 (4.1). After evaporation of the solvent, the solid product was washed with small volumes of ethanol and ether (vol. 150) several times to furnish **8** (1.08 g, 55 %) as pale yellow crystals: mp 213.0-213.5 °C; NMR δ 9.00 (s, 2, $H_{8,13}$), 8.37 (d, 2, $H_{1,7}$), 8.07 (m, 2, $H_{9,12}$, J = 7.5 Hz), 7.25-7.68 (m, 6, Ar), 4.25 (s, 2, H_4); UV λ_{max}

(EtOH) 343 (ε 4890), 299 (17000), 284 (78700), 274 (52000) nm. Anal. Calcd for $C_{23}H_{14}$: C, 95.14; H, 4.86. Found: C, 95.00; H, 4.81.

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