Stereoselective Synthesis of Putative Diol Epoxide Metabolites of 4*H*-Cyclopenta[*def*]chrysene[1]

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Syntheses of the *anti*-diol epoxide derivatives of the methylene-bridged polycyclic aromatic hydrocarbon 4*H*-cyclopenta[*def*]chrysene in both the bridge- and non-bridge-substituted rings (**2** and **3**) and the *syn*-diol epoxide derivative in the non-bridge-substituted ring (**14**) are described. These compounds are suspected to be active carcinogenic metabolites of the parent hydrocarbon. They are the first examples of the diol epoxide derivatives of a nonalternant methylene-bridged tumorigenic hydrocarbon to be synthesized. The bridge-substituted *anti*-diol epoxide derivative **2** is relatively stable, despite its relatively strained structure, and it possesses a unique "locked" structure which severely restricts conformational interconversion.

Introduction

Methylene-bridged polycyclic aromatic hydrocarbons (PAHs) are a relatively underinvestigated class of nonalternant polyarenes[2] that are produced in the combustion of organic matter at moderate temperatures.[3] They are present in relatively high abundance in crude petroleum[2] and are widespread environmental pollutants. Some members of this class, e.g. 4*H*-cyclopenta[*def*]-chrysene (**1**) exhibit mutagenic and tumorigenic properties.[4] In order to make methylene-bridged PAHs more readily available for chemical and biological investigations, we recently undertook to develop more efficient synthetic approaches[5] and to investigate patterns of electrophilic substitution of PAH molecules of this class.[6]

While the mechanism of metabolic activation of carcinogenic *alternant* PAHs, such as benzo[*a*]pyrene, has been intensively investigated and diol epoxide metabolites have been identified as the principal active species that bind covalently to DNA in vivo,[2,7] *nonalternant* PAHs have received relatively little attention[8] and virtually nothing is known concerning the mode of metabolic activation of the methylene-bridged PAHs. The likely pathways of activation (Figure 1) include, in addition to formation of diol epoxide metabolites in either bridge (**2**) or non-bridge (**3**) rings, an alternative pathway involving oxidation on the bridge positions to form alcohol intermediates (**4**) which undergo enzymatic conversion to reactive sulfate esters (**5**) which can give rise to carbonium ion intermediates capable of bonding covalently to nucleic acids.[5a] The feasibility of the diol epoxide mechanism is supported by the identification of a diol epoxide metabolite in the bridge-substituted ring as an active form of 1,11-methanocyclopenta[*a*]phenanthren-17-one (**6**).[9] Evidence for activation by oxidation on bridge sites is provided by recent findings that synthetic bridge alcohol derivatives of methylene-bridged PAHs, notably **4**, are activated to mutagens by sulfotransferase enzymes in the presence of 3′-phosphoadenosine-5′-phosphosulfate.[10] More detailed investigations of these potential mechanisms requires synthetic access to the key active metabolites. We reported recently an efficient method for the synthesis of the bridge alcohol and ketone derivatives of methylene-bridged PAHs, including **4**.[11] We now wish to report syntheses of the *anti*-diol epoxide

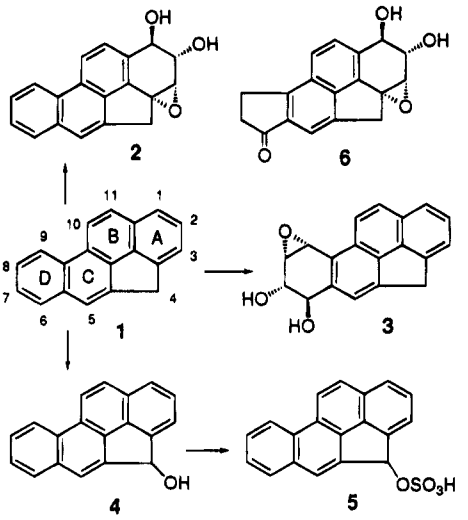

Figure 1. Potential pathways of metabolic activation of 4*H*-cyclopenta[*def*]chrysene (1). The diol epoxides **2** and **3** are the *anti*-isomers.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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(7) Harvey, R. G.; Geacintov, N. E. *Acc. Chem. Res.* **1988**, *21*, 66.

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(11) Harvey, R. G.; Abu-shqara, E., Yang, C. *J. Org. Chem.* **1992**, *57*, 6313.

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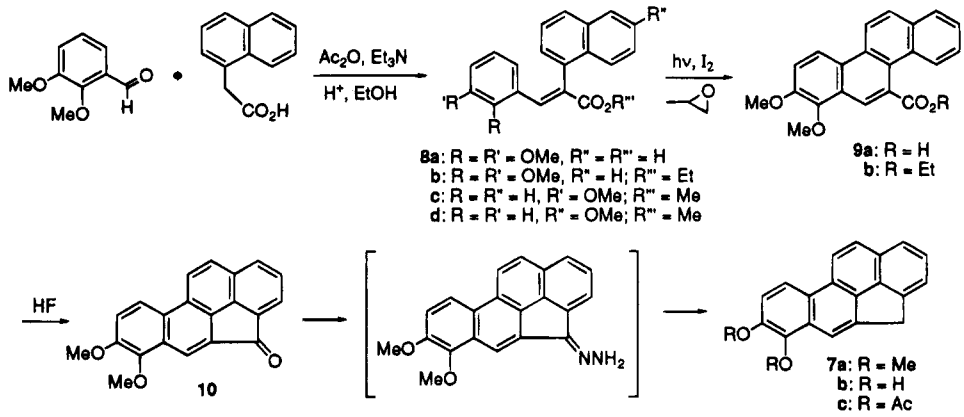
Scheme 1



derivatives of the methylene-bridged polycyclic aromatic hydrocarbon 4*H*-cyclopenta[*def*]chrysene in both the bridge- and non-bridge-substituted rings (designated herein as the A ring and D ring, respectively) and the *syn*-diol epoxide derivative of this hydrocarbon in the non-bridge-substituted ring.[12]

Results

Development of a new synthetic strategy, rather than modification of methods devised earlier for the synthesis of the diol epoxide metabolites of alternant polyarenes, such as chrysene and 5-methylchrysene,[13] was necessitated by the presence of the methylene bridge in the target molecules. The synthetic approach to the oxidized metabolites of 4*H*-cyclopenta[*def*]chrysene in the D-ring (i.e. **3**) is based on the key intermediate 6,7-dimethoxy-4*H*-cyclopenta[*def*]chrysene (**7a**) which contains the complete carbon skeleton as well as protected oxygen atoms for subsequent conversion to the dihydrodiol function (Scheme 1). An attractive potential synthetic route to **7a** is via photocyclization of an appropriately substituted benzylidene derivative of acenaphthene. However, synthesis of an unsubstituted analog of **7a** via an analogous route is reported to afford poor yields in both the preparation of the precursor and its photocyclization.[14] The low yield in the latter step was suggested to be due to the distance between the reactive centers and the strain in the reaction intermediate. For this reason, it was considered desirable to employ a less strained intermediate (**8a**) in the photocyclization step and introduce the five-membered ring by subsequent acid-catalyzed cyclization of a carboxylic ester substituent. This has precedent in the report that photoreactions of the monomethoxy derivatives **8c** and **8d** afford good yields (37–70%) of cyclized products.[15]

Condensation of 1-naphthylacetic acid with 2,3-dimethoxybenzaldehyde in the presence of acetic anhydride and triethylamine furnished smoothly the carboxylic acid **8a**. In order to avoid lactone formation under photolysis conditions,[16] the acid **8a** was converted to the ethyl ester derivative **8b**. Oxidative photocyclization of **8b** with I_2 and propylene oxide provided the chrysene ester derivative **9b** in 90% yield. Similar reaction in the absence of propylene oxide furnished **9b** in lower yield (~50%).[17] The second cyclization step was carried out in liquid HF at room temperature. Although decarboxylation is a relatively facile process for carboxylic acids in sterically crowded bay regions, no loss of the carboxylic ester function was detected under these mild conditions. However reaction was slow, with only ~40% completion after 3 days.[18] The low rate was rationalized as due to the poor solubility of the ester and/or the free acid in the HF medium. With the use of CH_2Cl_2 as cosolvent and a decreased volume of HF, reaction time could be cut from 3 days to 1 day. Under these conditions, the ketone product **10** was obtained in 94% yield. Attempts to directly reduce the carbonyl group of **10** by the Huang–Minlon modification of the Wolff–Kishner method were unsuccessful, affording only trace amounts of the desired reduction product **7a** along with more polar impurities. More satisfactory results were obtained by a two-step sequence in which condensation of the ketone **10** with anhydrous hydrazine in refluxing diethylene glycol for 3 h was carried out to generate a hydrazone intermediate which was decomposed by refluxing with 2% aqueous NaOH. The overall yield of **7a** was 85%.

Conversion of **7a** to the *trans*-6,7-dihydroxy-6,7-dihydro-4*H*-cyclopenta[*def*]chrysene (**11a**) was readily accomplished by deprotection of the methyl groups by treatment with BBr_3 followed by reduction of the hydroquinone product **7b** with $NaBH_4$ (Scheme 2). Purification of **7b** by recrystallization was unsatisfactory. Like other PAH catechols, **7b** was air-sensitive, changing color from white to reddish after a few days at room temperature, indicative of oxidation to the corresponding *o*-quinone. However, its structure was readily confirmed by diacetylation with acetic anhydride and pyridine to the stable diacetate **7c** which could be readily purified. Reduction of **7b** with $NaBH_4$ in EtOH was conducted with O_2 bubbling through the solution. It is likely that the mechanism of this process is more complex than a simple direct reduction (see Discussion).[19–22] Reductions of this

(12) In Figure 1 are shown the *anti*-diol epoxide isomers in both the bridge (**2**) or non-bridge (**3**) rings of 4*H*-cyclopenta[*def*]chrysene. These isomers are defined as the diastereomers which contain the epoxide oxygen atom and the benzylic hydroxyl group on opposite faces of the molecule. The *syn*-isomers, not shown, have these groups on same face of the molecule.

(13) Harvey, R. G.; Pataki, J.; Lee, H. *J. Org. Chem.* **1986**, *51*, 1407. Pataki, J.; Lee, H.; Harvey, R. G. *Carcinogenesis*. **1983**, *4*, 399.

(14) Nagel, D. L.; Kupper, R.; Antonson, K.; Wallcave, L. *J. Org. Chem.* **1977**, *42*, 3626.

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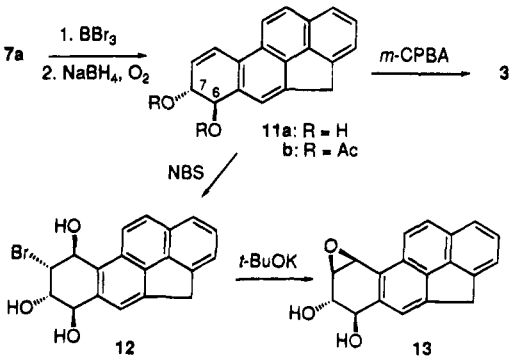
(16) Lee-Ruff, E.; Kruk, H.; Katz, M. *J. Org. Chem.* **1984**, *49*, 553.

(17) Propylene oxide is reported to enhance yields in photocyclization by scavenging the HI produced: Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

(18) Extent of reaction after 3 days was determined by ^1H NMR analysis of an aliquot.

Scheme 2

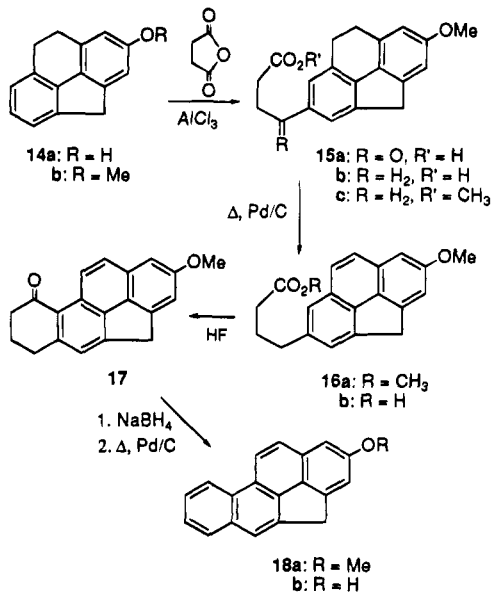


type are known to be highly *trans*-stereoselective.[19] The ^{1}H NMR spectra of **11a** and its diacetate (**11b**) were entirely consistent with assignment of **11a** as *trans*-6,7-dihydroxy-6,7-dihydro-4*H*-cyclopenta[*def*]chrysene. The value of the coupling constant $J_{6,7}$ = 11.3 Hz for **11a** indicates that like other nonsterically hindered dihydrodiols it exists predominantly as the diequatorial conformer.[19]

Conversion of **11a** to the corresponding *anti*- and *syn*-diol epoxide derivatives was carried out by standard methods (Scheme 2).[21,23] Epoxidation of **11a** with *m*-chloroperbenzoic acid provided the corresponding *anti*-diol epoxide, *trans*-6,7-dihydroxy-*anti*-8,9-epoxy-6,7,8,9-tetrahydro-4*H*-cyclopenta[*def*]chrysene (**3**), in good overall yield. Reaction of **11a** with *N*-bromosuccinimide in moist acetonitrile–THF gave the corresponding bromohydrin **12**. Treatment of **12** with *t*-BuOK furnished smoothly the corresponding *syn*-diol epoxide, *trans*-6,7-dihydroxy-*syn*-8,9-epoxy-6,7,8,9-tetrahydro-4*H*-cyclopenta[*def*]chrysene (**13**). The ^{1}H NMR spectra of **3** and **13** were in good agreement with their assignments. The coupling constants observed for the $H_{6,7}$ protons are consistent with the existence of both diol epoxide isomers predominantly in a conformation in which the hydroxy groups are oriented diequatorially, in agreement with previous findings for other similar compounds.[23]

Synthesis of the *anti*-diol epoxide isomer in the A-ring of 4*H*-cyclopenta[*def*]chrysene (**2**) was accomplished via a synthetic route based on the key intermediate 2-hydroxy-4*H*-cyclopenta[*def*]chrysene (**18b**). This phenol was itself prepared from 2-methoxy-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**14b**) which contains one less aromatic ring (Scheme 3). Synthesis of **14a** was previously described.[5a,24] Friedel–Crafts reaction of **14b** with succinic anhydride and $AlCl_3$ took place regiospecifically in the 6-position to furnish the keto-acid **15a**. This site of substitution is in accord with expectation based on prior findings that the 8,9-dihydro derivatives of 4*H*-cyclopenta[*def*]phenanthrene behave as biphenyl derivatives in electrophilic substitutions.[5a,b,24] Wolff–Kishner reduction of the keto group of **15a** with hydrazine and KOH took place smoothly to provide the reduced acid **15b**. It was necessary to dehydrogenate **15b** prior to acid-catalyzed cyclodehydration, since it was previously observed that

Scheme 3

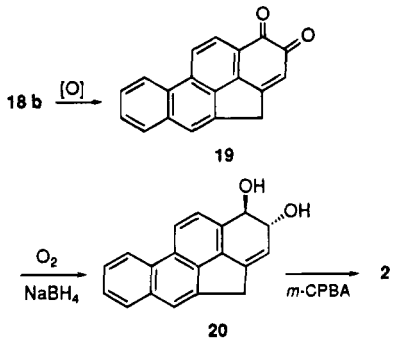


the unsubstituted analog of **15b** underwent preferential cyclization to the 5-position adjacent to the five-membered ring to furnish the undesired isomer,[5a,25] while cyclization of the fully aromatic compound took place regioselectively to the 7-position. Esterification of **15b** furnished the methyl ester **15c** which underwent dehydrogenation over a 10% Pd/C catalyst to provide the fully aromatic ester **16a**. Hydrolysis of **16a** followed by cyclodehydration of the free acid **16b** in liquid HF gave a single isomeric ketone product whose 500 MHz ^{1}H NMR spectrum permitted assignment as the desired ketone structure **17** arising from cyclization to the 7-position. This isomer was readily distinguished from the ketone formed by cyclization to the alternative ring position by the presence of a characteristic low field doublet at δ 9.18 for H_{10} due to the anisotropic effect of the carbonyl group in the sterically hindered bay region and a singlet at δ 7.49 for the H_5 aromatic proton adjacent to the five-membered ring, in addition to other expected peaks. Reduction of the keto group of **17** with $NaBH_4$ furnished the corresponding alcohol which on heating with 10% Pd/C underwent concurrent dehydration and dehydrogenation to yield 2-methoxy-4*H*-cyclopenta[*def*]chrysene (**18a**). Demethylation of **18a** with BBr_3 provided 2-hydroxy-4*H*-cyclopenta[*def*]chrysene (**18b**). Good yields were obtained in all steps for an overall yield of **18b** from **14b** of 31%.

Conversion of **18b** to the corresponding dihydrodiol was accomplished by oxidation with an aqueous solution of Fremy's salt in a two phase system with CH_2Cl_2 and the phase transfer agent Adogen 464 to furnish the related *o*-quinone derivative (**19**) (Scheme 4). Reduction of **19** with $NaBH_4$ in MeOH in the presence of O_2 yielded *trans*-1,2-dihydroxy-1,2-dihydro-4*H*-cyclopenta[*def*]chrysene (**20**). While the NMR data were consistent with this assignment, an unusual feature of the spectrum was the relatively low value of the coupling constant for the hydrogen atoms in the hydroxylated positions ($J_{1,2}$ = 6.0 Hz); the usual range of values for other structurally similar nonsterically hindered terminal ring dihydrodiols is 7.6–11 Hz.[19,25] This may indicate that the conforma-

(19) Reference 2, Chapter 13, pp 306–329.
(20) Platt, K. L.; Oesch, F. *Synthesis* **1982,** 459.
(21) Harvey, R. G. in *Polycyclic Hydrocarbons and Carcinogenesis*; Harvey, R. G., Ed., American Chemical Society Symposium Series, American Chemical Society: Washington, D. C., 1985; pp 35–62.
(22) Platt, K. L.; Oesch, F. *J. Org. Chem.* **1983,** *48,* 265.
(23) Reference 2, Chapter 14, pp 330–359. Harvey, R. G. *Synthesis* **1986,** 605.
(24) Minabe, M.; Yoshida, M.; Amimoto, T.; Nagata, T.; Kobori, M. *Bull. Chem. Soc. Jpn.* **1988,** *61,* 879.
(25) Harvey, R. G. in *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; Rabideau, P. W. Ed.; VCH Publishers: New York, 1989; pp 267–298.

Scheme 4



tional equilibrium is shifted in favor of a higher ratio of the diaxial conformer or that the substituted ring is distorted from the normal configuration by the rigidity imposed by the methylene bridge. Epoxidation of **20** with *m*-chloroperbenzoic acid gave the corresponding *anti*-diol epoxide, *trans*-1,2-dihydroxy-*anti*-3,4-epoxy-1,2,3,4-tetrahydro-4*H*-cyclopenta[*def*]chrysene (**2**), in good overall yield. Despite its apparently strained ring structure, this diol epoxide derivative appeared to be relatively stable, showing no evidence of spontaneous decomposition on storage as found for some other similar compounds, e.g. the *anti*-diol epoxide of 7,12-dimethylbenz[*a*]anthracene which decomposes within a few hours of its preparation.[26,27]

Discussion

Convenient syntheses are described for the diol epoxide derivatives in both terminal rings of 4*H*-cyclopenta[*def*]-chrysene (**1**). While syntheses of the diol epoxide metabolites of several alternant PAHs have been previously reported,[23] these are the first examples of diol epoxides of a methylene-bridged PAH.

The presence of the methylene group in 4*H*-cyclopenta-[*def*]chrysene necessitated new synthetic strategies. Synthesis of the oxidized metabolites in the D-ring was accomplished via a route involving oxidative photocyclization of an *o*-dimethoxy-substituted derivative **8b**. The presence of a single unsubstituted *ortho* position in this precursor predetermined that cyclization would occur regiospecifically to form a single isomer. This precursor had the additional advantage that the dimethoxy-substituted product could be converted in a later stage of the synthesis to the desired dihydrodiol intermediate in two steps, i.e. deprotection and reduction with $NaBH_4$, whereas the established synthetic route to molecules of this type via a monomethoxy-substituted intermediate[13] requires three steps, deprotection, oxidation to a quinone with Fremy's salt, and reduction with $NaBH_4$. Prior to the introduction of the dihydrodiol function, it was necessary to carry out a second cyclization step to introduce the five-membered cyclopentano ring. This was accomplished by cyclodehydration of the carboxylic ester **9b** in liquid HF. It is notable that reaction time could be decreased and the yield markedly enhanced by the use of CH_2Cl_2 as cosolvent. This modification may be useful in cyclodehydrations of other large PAH compounds which are poorly soluble in liquid HF. Conversion of 6,7-dimethoxy-4*H*-cyclopenta[*def*]chrysene (**7a**) to the desired dihydrodiol **11a** was effected efficiently by demethylation with BBr_3 to the hydroquinone **7b** followed directly by reduction of the air-sensitive **7b** with $NaBH_4$ with O_2 bubbling through the solution. Although the reduction of PAH hydroquinones to dihydrodiols was first reported more than a decade ago,[20] it has seen minimal application in synthesis.[22,28] The mechanism is believed to involve initial oxidation of **7b** to a quinone intermediate by molecular O_2 followed by *trans*-stereospecific reduction of the quinone to the dihydrodiol **11a**. The overall synthetic route to **11a** provides an efficient method for its synthesis from available compounds. The method is conveniently adaptable to the synthesis of **11a** and the corresponding *anti*- and *syn*-diol epoxides on preparative scale. The photocyclization step, which is often limiting in multistep syntheses because of the need to conduct reactions in extremely dilute solutions, is not a serious limitation in the present case, and good yields are obtained even with concentrated solutions.

The A-ring diol epoxide isomer of 4*H*-cyclopenta[*def*]-chrysene (**2**) is the first example of a diol epoxide in which a methylene-bridge is covalently linked to the saturated ring bearing an epoxide function. Although an analogous diol epoxide metabolite was postulated to be the active form of 1,11-methanocyclopenta[*a*]phenanthren-17-one (**6**),[9] its synthesis was not reported. The relative stability of **2**, despite its relatively strained structure, is somewhat surprising. On the other hand, diol epoxide isomers of fluoranthene and benzo[*j*]fluoranthene, which are also highly strained due to the presence of the epoxide ring at a ring juncture, are also stable.[29,30] Although the favored conformation of carcinogenic PAH diol epoxide metabolites in solution is diequatorial,[23,25] the energy barrier for conformational interconversion is low and it is uncertain whether this orientation is retained in subsequent reactions with nucleic acids. Since the structure of **2** is relatively rigid, investigation of its reactions with DNA may aid understanding of the role of conformation in the interaction of diol epoxides with nucleic acids.

Biological Studies. Recently completed tumorigenicity experiments confirm that both *anti*-diol epoxide derivatives of 4*H*-cyclopenta[*def*]phenanthrene (**2** and **3**) are potent tumorigens in newborn mice.[31] The A-ring diol epoxide **2** was the most active compound of the chrysene derivatives tested, showing greater activity than **3** which was more active than the *anti*-diol epoxide derivative of chrysene itself.

Experimental Section

Materials and Methods. 2-Hydroxy-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**14a**) was synthesized from 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene via acetylation[5a] fol-

(26) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1986**, *51*, 3502.

(27) Most diol epoxides are relatively reactive, hydrolizing readily in aqueous media and decomposing on exposure to mild acids or on heating.[19] Despite their sensitivity, they are sufficiently stable to conduct a wide range of biological studies.[2]

(28) Syntheses of dihydrodiol derivatives of chrysene and dibenzo-[*def,p*]chrysene (dibenzo[*a,l*]pyrene) via reduction of protected hydroquinones are described by Seidel, A.; Bochnitschek, W.; Glatt, H.; Hodgson, R. M.; Grover, P. L.; Oesch, F. in *Polynuclear Aromatic Hydrocarbons : Measurements, Means and Metabolism;* Cooke, M., Loening, K., Meritt, J., Eds.; Battelle Press: Columbus, OH, 1991; pp 801–817. Luch, A.; Glatt, H.; Platt, K. L.; Oesch, F.; Seidel, A. *Carcinogenesis* **1994**, *15*, 2507.

(29) Rastetter, W. H.; Nachbar, R. B., Jr.; Russo-Rodriguez, S.; Wattley, R. V.; Thilly, W. G.; Andon, B. M.; Jorgensen, W. L.; Ibrahim, M. *J. Org. Chem.* **1982**, *47*, 4873.

(30) He, Z.-M.; Rice, J. E.; LaVoie, E. J. *J. Org. Chem.* **1992**, *57*, 1784.

(31) Amin, S.; Desai, D.; Dai, W.; Harvey, R. G.; Hecht, S. S. *Carcinogenesis*, submitted.

lowed by Baeyer–Villeger oxidation and alkaline hydrolysis of the product by the method of Minabe et al.[24] 8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene was prepared from 4*H*-cyclopenta[*def*]phenanthrene by the published procedures.[5b,32,33] Fremy's salt [$(SO_3K)_2NO$] was prepared according to the literature method[34] and used fresh. *m*-Chloroperbenzoic acid (Aldrich) was purified by washing with pH 7.4 phosphate buffer and drying under reduced pressure. *N*-Bromosuccinimide was crystallized from water prior to use. Methyltrialkyl(C_8–C_{10})ammonium chloride (Adogen 464) was purchased from Aldrich. THF was distilled from sodium benzophenone ketyl. All of melting points are uncorrected. The UV spectra were measured on a Perkin-Elmer Lamda 5 spectrometer. ^{1}H NMR spectra were obtained on the University of Chicago 300- or 500-MHz ^{1}H NMR spectrometers in $CDCl_3$ with tetramethysilane as internal standard unless stated otherwise.

3-(2,3-Dimethoxyphenyl)-2-(1-naphthyl)propenoic Acid (8a). A solution of 1-naphthylacetic acid (16.8 g, 90 mmol) and 2,3-dimethoxybenzaldehyde (15.0 g, 90 mmol) in Ac_2O (100 mL) and Et_3N (50 mL) was stirred at 120 °C until TLC showed complete conversion of the starting acid (12 h). The solution was cooled to 0 °C, quenched with concentrated HCl, and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$. After removal of the solvent under vacuum, recrystallization from hexane–ethyl acetate–acetic acid gave **8a** (21.9g, 72%) as colorless crystals shown by NMR to be a mixture of *cis*- and *trans*-isomers: ^{1}H NMR δ 8.56 (s, 1), 7.89–7.30 (m, 7), 6.72 (d, 1, J = 9.1 Hz), 6.47 (t, 1, J = 8 Hz), 6.05 (d, 1, J = 8 Hz), 3.94 and 3.81 (2s, 6). MS, *m/e* 334 (M^+, 94), 303 (27), 288 (29), 257 (18). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.14; H, 5.31.

Ethyl 3-(2,3-Dimethoxyphenyl)-2-(1-naphthyl)propenoate (8b). The acid **8a** (21.9 g, 66 mmol) was converted to the ethyl ester by heating at reflux in EtOH (200 mL) with 2 mL of H_2SO_4 for 24 h. The ester was obtained as pale yellow crystals (23.5 g, 99%) as a mixture of *cis*- and *trans*-isomers: ^{1}H NMR δ 8.42 (s, 1), 7.77–7.23 (m, 7), 6.71 (d, 1, J = 8.0 Hz), 6.50 (t, 1, J = 8.0 Hz), 6.02 (d, 1, J = 8.0 Hz), 3.92 and 3.80 (2s, 6). MS, *m/e* 362 (M^+, 100), 331 (16), 316 (18), 303 (21). Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.17; H, 6.16.

7,8-Dimethoxy-5-carbethoxychrysene (9b). Argon was bubbled through a solution of the ester **8b** (2.5g, 6.9 mmol) and I_2 (1.74 g, 6.9 mmol) in benzene (450 mL) for 30 min. Then propylene oxide (10 mL) was added, and the solution was irradiated with a Hanovia 450 W medium-pressure mercury lamp through a Pyrex filter. The course of reaction was monitored by TLC, and irradiation was stopped when the TLC showed the reaction to be complete (15 h). The solvent was concentrated to 100 mL, washed with $Na_2S_2O_3$ (aq, 10%) and H_2O, and dried over $MgSO_4$. The crude product was triturated with ether to give the ester **9b** (2.23 g, 90%) as light yellow crystals, mp 183–184 °C: ^{1}H NMR δ 8.60 (d, 1, J = 9.1 Hz), 8.52 (s, 1), 8.47 (d, 1, J = 9.3 Hz), 8.22 (m, 1), 8.00 (d, 1), 7.98 (m, 1) 7.59–7.55 (m, 2), 7.48 (d, 1), 4.51 (q, 2, J = 7.2 Hz), 4.08 and 4.06 (2s, 6), 1.35 (t, 3, J = 7.2 Hz). MS, *m /e* 360 (M^+, 100), 345 (14), 331 (7), 317 (8). Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.44; H, 5.56.

6,7-Dimethoxy-4*H*-cyclopenta[*def*]chrysen-4-one (10). To a solution of the ester **9b** (2.3 g, 6.38 mmol) in CH_2Cl_2 (100 mL) was added HF (20 mL) in a gas-tight Teflon jar. The color of solution changed instantly from orange to purple. The solution was stirred for 24 h, and then the solvent was removed by evaporation in a well ventilated hood. The solid product was triturated with saturated aqueous $NaHCO_3$ and washed with H_2O and ether–hexane (1:9) to give the ketone **11** (1.9 g, 94%) as yellow crystals, mp 200–201 °C: ^{1}H NMR δ 8.64 (s, 1), 8.33 (d, 1, J = 9.0 Hz), 8.27 (d, 1, J = 8.9 Hz), 8.01 (d, 1, J = 8.1 Hz), 7.96 (d, 1), 7.90 (d, 1, J = 7.0 Hz), 7.63 (dd, 1), 7.42 (d, 1), 4.07 and 4.06 (2s, 6). MS, *m/e* 314 (M^+,100), 299 (28), 284 (29), 271 (23). Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.11; H, 4.55.

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6,7-Dimethoxy-4*H*-cyclopenta[*def*]chrysene (7a). Ketone **10** (0.5 g, 1.6 mmol) was dissolved in diethylene glycol (50 mL) at ~120 °C, and then the solution was cooled below 100 °C. Anhydrous NH_2NH_2 (149 μL, 4.8 mmol) was slowly added and the reaction mixture was heated at ~130 °C until TLC showed disappearance of **10** (5 h). The solution was cooled again below 100 °C, and aqueous NaOH (2%, 10 mL) was added. The reaction mixture was refluxed for another 7 h, cooled, and poured into an ice cold NH_4OH aqueous solution (1.0 L). Filtration of this aqueous suspension gave crude **7a** (0.41g, 85%) as a yellow solid, mp 179–180 °C: ^{1}H NMR δ 8.44 (d, 1, J = 8.7 Hz), 8.40 (d, 1, J = 9.0 Hz), 8.32 (s, 1), 7.97 (d, 1), 7.84 (dd, 1, J = 7.0 Hz, J = 2.0 Hz), 7.64 (d, 1, J = 7.0 Hz), 7.62 (t, 1), 7.42 (d, 1), 4.45 (s, 2), 4.06 and 4.05 (2s, 6). MS, *m/e* 300 (M^+, 100), 285 (41), 257 (35), 242 (36). Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.98; H, 5.40.

6,7-Dihydroxy-4*H*-cyclopenta[*def*]chrysene (7b). To a solution of crude **7a** (0.5 g, 1.6 mmol) in CH_2Cl_2 (100 mL) was added BBr_3 (2 mL, 12 mmol) at 0 °C. The resulting pale yellow suspension was warmed and stirred at room temperature until TLC showed reaction to be complete (1 h). Then the suspension was poured into ice cold aqueous NH_4OH (600 mL). After stirring for 1 h, the aqueous suspension was filtered to provide the crude catechol **7b** (0.41g, 90%) as a colorless solid (>98% pure): ^{1}H NMR δ 8.46 (d, 1, J = 8.7 Hz), 8.33 (s, 1), 8.20 (d, 1, J = 9.0 Hz), 8.02 (d, 1, J = 8.7 Hz), 7.86 (d, J = 8.1 Hz), 7.66 (m, 2), 7.30 (d, 1), 5.25 and 5.82 (2s, 2), 4.50 (s, 2). MS, *m/e* 272 (M^+, 100), 255 (9), 243 (12), 226 (26). HRMS, calcd for $C_{19}H_{12}O_2$: *m /e* 272.0837, found *m/e* 272.0837. The instability of the catechol made further purification impractical. However, its identity was readily confirmed by conversion to its stable diacetate **7c** by acetylation with Ac_2O and pyridine by the method used to prepare the dihydrodiol diacetate **11b**. Data on **7c**: mp 209–210 °C; ^{1}H NMR δ 8.58 (d, 1, J = 8.9 Hz), 8.45 (d, 1, J = 8.8 Hz), 8.01 (d, 1), 7.99 (dd, 1, J = 4.1 Hz), 7.87 (dd, 1, J = 5.2 Hz), 7.68 (s, 1), 7.67 (d, 1), 7.50 (d, 1), 4.46 (s, 2), 2.51 and 2.36 (2s, 6). MS, *m/e* 356 (M^+, 41), 314 (42), 272 (100), 243 (24). Anal. Calcd for $C_{23}H_{16}O_4$: C, 77.52; H, 4.53. Found: C, 77.40; H, 4.54.

***trans*-6,7-Dihydroxy-6,7-dihydro-4*H*-cyclopenta[*def*]chrysene (11a).** To a solution of **7b** (0.7 g, 2.57 mmol) in 600 mL of absolute EtOH was added $NaBH_4$ (2.5 g, 66 mmol) at room temperature. The reaction mixture was stirred in the dark for 72 h with O_2 slowly bubbling through the solution. The solvent was concentrated under vacuum without heating to ~50 mL and then poured into cold NH_4OH (saturated) and extracted with EtOAc. The organic layer was washed with H_2O and dried over Na_2SO_4. Trituration of the crude solid with ether gave the dihydrodiol **12a** (0.65 g, 92%) as a white solid, mp 221- 222 °C: ^{1}H NMR ($CDCl_3$–DMSO-d_6-D_2O, 5:1:1) δ 8.02 (s, 1), 7.89 (d, 1, J = 8.9 Hz), 7.77 (d, 1,), 7.74 (d, 1, J = 7.8 Hz), 7.63 (d, 1, J = 7.0 Hz), 7.56 (dd, 1), 7.12 (dd, 1, J = 1.7 Hz, J = 9.8 Hz), 6.15 (dd, 1, J = 9.8 Hz), 5.02 (d, 1, J = 11.3 Hz), 4.59 (dd, 1, J = 1.3 Hz), 4.29 (bs, 2); UV (ethanol) λ_{max} 269 (ϵ 36 450), 247 (34 300), 221 (55 070), 200 (21 500) nm. MS, *m/e* 274 (M^+, 1), 257 (19), 256 (100), 239 (10). Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.06; H, 5.20.

***trans*-6,7-Diacetoxy-6,7-dihydro-4*H*-cyclopenta[*def*]chrysene (11b).** A solution of **11a** (0.40 g, 1.49 mmol) in Ac_2O (25 mL) and pyridine (1 mL) was stirred at room temperature for 24 h. The reaction mixture was poured over crushed ice (300 mL), and the mixture was stirred until the ice melted. The solid product was collected by a filtration and purified by flash column chromatography on Florisil (benzene:ether, 1:1). The diacetate **11b** (0.45 g, 86%) was obtained as colorless crystals, mp 186–187 °C: ^{1}H NMR δ 7.96 (d, 1, J = 9.0 Hz), 7.84 (d, 1), 7.78 (d, J = 6.7 Hz), 7.67 (s, 1), 7.66 (d,1, J = 6.9 Hz), 7.61 (dd, 1), 7.44 (d, 1, J = 9.8 Hz), 6.34 (d, 1, J = 4.7 Hz), 6.21 (dd, 1), 5.57 (dd, 1, J = 4.5 Hz), 4.31 (s, 2), 2.10 (s, 3), 2.03 (s, 3). MS, *m/e* 298 (M^+ – AcOH, 26), 256 (100), 239 (13), 226 (22). Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 77.12; H, 5.19.

***trans*-6,7-Dihydroxy-*anti*-8,9-epoxy-6,7,8,9-tetrahydro-4*H*-cyclopenta[*def*]chrysene (3).** To a solution of dihydrodiol **11a** (50 mg, 0.18 mmol) in 120 mL of THF at 0 °C under

argon was added *m*-CPBA (500 mg, 2.9 mmol). The solution was stirred at 0 °C for 1 h. Stirring was continued at room temperature until TLC indicated disappearance of the starting material (2 h). The solution was concentrated to ~20 mL under vacuum without heating, and the residue was diluted with ice cold EtOAc (100 mL), washed with ice cold 10% NaOH (aqueous) and ice cold H_2O until neutral. The organic layer was dried over Na_2SO_4 (10 min). The entire workup should be done as rapidly as possible at low temperature in order to minimize decomposition of the diol epoxide. The crude product was triturated with ether to give the diol epoxide **3** (43 mg, 81%) as tiny yellow crystals which decomposed at 210 °C: ^{1}H NMR δ 8.22 (d, 1, J = 9.0 Hz), 8.00 (s, 1), 7.92 (d, 1, J = 9.0 Hz), 7.92 (d, 1, J = 7.8 Hz), 7.71 (d, 1, J = 7.1 Hz), 7.62 (d, 1), 4.86 (d, 1, J = 4.5 Hz), 4.53 (d, 1, J = 8.7 Hz), 4.34 (bs, 2), 3.81 (m, 2). MS, *m/e* 290 (M^+, 58), 272 (100), 256 (44), 243 (66). HRMS, calcd for $C_{19}H_{14}O_3$: *m/e* 290.0943 found *m/e* 290.0966.

8α-Bromo-6β,7α,9β-trihydroxy-6,7,8,9-tetrahydro-4*H*-cyclopenta[*def*]chrysene (12). To a solution of NBS (44 mg, 0.24 mmol) at 0 °C in CH_3CN–THF–H_2O (11 mL, 5:5:1) at 0 °C was added the dihydrodiol **11a** (65 mg, 0.24 mmol). The color of the solution changed from light yellow to light brown. The mixture was allowed to slowly warm up to room temperature while stirring for 10 min. Unreacted NBS was destroyed by addition of ice cold aqueous $Na_2S_2O_3$ (10%). The mixture was extracted with EtOAc:Et_2O (1:1, 3 × 50 mL) and dried over $MgSO_4$, and the solvent was removed on a rotovap equipped with a dry ice condenser without heating. The crude product was triturated with ether to furnish the bromohydrin **12** (77 mg, 86%) as a colorless solid which is decomposed at 120 °C: ^{1}H NMR (DMSO-d_6 : $CDCl_3$: D_2O, 1:8:1) δ 8.08 (d, 1, J = 9.1 Hz), 7.96 (s, 1), 7.84 (d, 1), 7.77 (d, 1, J = 7.8 Hz), 7.64 (d, 1, J = 6.9 Hz), 7.60 (dd, 1), 5.70 (d, 1, J = 2.6 Hz), 4.96 (d, 1, J = 7.7 Hz), 4.78 (dd, 1, J = 2.6 Hz), 4.33 (dd, 1), 4.32 (bs, 2). MS, m/e 370 (M^+, 30), 353 (75), 337 (34), 335 (15). Anal. Calcd for $C_{19}H_{15}O_3Br$: C, 61.47; N, 4.07. Found: C, 61.47; H, 4.12. HRMS, calcd for $C_{19}H_{15}O_3Br$: *m/e* 370.0208, found *m/e* 370.0204.

***trans*-6,7-Dihydroxy-*syn*-8,9-epoxy-6,7,8,9-tetrahydro-4*H*-cyclopenta[*def*]chrysene (13).** To a solution of the bromohydrin **12** (8 mg, 0.02 mmol) in THF (8 mL) was added a 0.08 M solution of *t*-BuOK in *t*-BuOH (3 mL, 0.24 mmol, prepared from an Aldrich 1 M solution of *t*-BuOK in *t*-BuOH) over a 20 min period at room temperature under argon. The reaction mixture was stirred at room temperature for 1 h. The mixture was poured into ice cold aqueous NH_4Cl (2% solution, 20 mL) and extracted with ice cold ether–EtOAc (1:1, 200 mL). The organic layer was washed with ice cold H_2O and dried over Na_2SO_4. Removal of the solvent under vacuum on a rotovap equipped with a dry ice condenser afforded the colorless diol epoxide **13** (5.3 mg, 85%) as a colorless solid which decomposed at 177 °C: ^{1}H NMR (DMSO-d_6) δ 8.28 (d, 1, J = 8.9 Hz), 7.97 (d, 1, J = 8.9 Hz), 7.88 (d, 1, J = 8.0 Hz), 7.76 (s, 1), 7.75 (d, 1, J = 6.9 Hz), 7.65 (dd, 1), 4.82 (d, 1, J = 3.7 Hz), 4.69 (d, 1, J = 3.0 Hz), 4.38 (bs, 2), 3.83 (m, 1). MS, *m/e* 290 (M^+, 52), 273 (80), 259 (21), 256 (36). HRMS, calcd for $C_{19}H_{14}O_3$: *m/e* 290.0943, found *m /e* 290.0944.

8,9-Dihydro-2-methoxy-4*H*-cyclopenta[*def*]-(6-phenanthrylcarbonyl)propanoic acid (15a). To a mixture of succinic anhydride (2.25 g, 22.5 mmol) and $AlCl_3$ (7.48 g, 56 mmol) in 100 mL of dry CH_2Cl_2 at 0 °C under argon was added **14b** (5 g, 22.5 mmol) over 10 min. The mixture was stirred at ambient temperature for 24 h and then cooled in an ice bath and hydrolyzed with cold dilute HCl. Following evaporation of the CH_2Cl_2 in vacuo, the crude keto acid was filtered, washed with dilute HCl and water, dried, and washed with hexane. Recrystallization from acetone provided pure **15a** (6.72 g, 93%) as pale yellow needles, mp 209–210 °C: ^{1}H NMR (DMSO-d_6) δ 7.96 (s, 1), 7.78 (s, 1), 7.02 (s, 1), 6.80 (s, 1), 3.91 (s, 2), 3.80 (s, 3), 3.25 (t, 2, J = 6.3 Hz), 3.09 (s, 4), 2.59 (t, 2, J = 6.3 Hz). Anal. Calcd for $C_{20}H_{18}O_4 \cdot H_2O$: C, 72.50; H, 5.74. Found: C, 72.79; H, 5.66.

8,9-Dihydro-2-methoxy-4*H*-cyclopenta[*def*]phenanthrene-6-butyric Acid (15b). A solution of **15a** (5.5 g, 18 mmol), hydrazine hydrate (11.3 mL), and KOH (5 g) in 150 mL of diethylene glycol was refluxed for 24 h and then cooled and acidified with HCl. The usual workup afforded the reduced acid **15b** (4.3 g, 78%), mp 126–128 °C (hexane–benzene): ^{1}H NMR δ 7.12 (s, 1), 6.91 (s, 2), 6.69 (s, 1), 3.83 (s, 3), 3.80 (s, 2), 3.07 (s, 4), 2.69 (t, 2, J = 7.4 Hz), 2.37 (t, 2, J = 7.4 Hz), 1.96 (quin, 2, J = 7.4 Hz). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.92; H, 6.49. Found: C, 77.64; H, 6.58.

Methyl 8,9-Dihydro-2-Methoxy-4*H*-cyclopenta[*def*]-phenanthrene-6-butyrate (15c). A solution of the acid **15b** (4.0 g, 13 mmol) and *p*-toluenesulfonic acid (200 mg) in 150 mL of MeOH was heated at reflux for 24 h. The usual workup followed by chromatography on silica gel furnished the methyl ester **15c** (3.55 g, 85%), mp 56–57 °C (hexane): ^{1}H NMR δ 7.12 (s, 1), 6.91 (s, 2), 6.70 (s, 1), 3.83 (s, 3), 3.81 (s, 2), 3.67 (s, 3), 3.08 (s, 4), 2.67 (t, 2, J = 7.3 Hz), 2.36 (t, 2, J = 7.3 Hz), 1.96 (quin, 2, J = 7.4 Hz). Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.30; H, 6.83.

Methyl 2-Methoxy-4*H*-cyclopenta[*def*]phenanthrene-6-butyrate (16a). A solution of **15c** (3.0 g, 9.3 mmol) in 60 mL of triglyme was heated with 1 g of a 10% Pd/C catalyst at reflux for 6 h. Conventional workup followed by chromatography on silica gel afforded **16a** (2.1 g, 70%) as colorless flakes, mp 86–87 °C (hexane): ^{1}H NMR δ 7.75 (d, 2, J = 2.4 Hz), 7.58 (s, 1), 7.49 (s, 1), 7.33 (s, 1), 7.23 (s, 1), 4.28 (s, 2), 2.97 (s, 3), 3.67 (s, 3), 2.92 (t, 2, J = 7.4 Hz), 2.39 (t, 2, J = 7.4 Hz), 2.08 (quin, 2, J = 7.4 Hz). Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.73; H, 6.28.

2-Methoxy-4*H*-cyclopenta[*def*]phenanthrene-6-butyric acid (16b). A solution of **16a** (2.0 g, 6.2 mmol), 2 g of KOH, 5 mL of water, and 50 mL of ethanol were heated at reflux for 1 h and then cooled and acidified with HCl. The usual workup gave **16b** (1.7 g, 89%) as white crystals, mp 166–167 °C (benzene): ^{1}H NMR δ 7.74 (d, 2, J = 2.8 Hz), 7.71 (s, 1), 7.58 (s, 1), 7.49 (s, 1), 7.22 (s, 1), 4.27 (s, 2), 3.97 (s, 3), 2.93 (t, 2, J = 7.4 Hz), 2.40 (t, 2, J = 7.4 Hz), 2.08 (quin, 2, J = 7.4 Hz). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.34; H, 5.90.

2-Methoxy-6,7,8,9-tetrahydro-4*H*-cyclopenta[*def*]chrysen-9-one (17). A solution of the acid **16b** (1.2 g, 3.9 mmol) in 50 mL of liquid HF was stirred for 24 h. The usual workup followed by chromatography on silica gel with CH_2Cl_2 as eluent furnished the pure ketone **17** (1.04 g, 92%) as white crystals, mp 184–185 °C: ^{1}H NMR δ 9.18 (d, 1, J = 9.1 Hz), 7.92 (d, 1, J = 9.1 Hz), 7.49 (s, 1), 7.32 (s, 1), 7.24 (s, 1), 4.22 (s, 2), 3.98 (s, 3), 3.22 (t, 2, J = 6 Hz), 2.80 (t, 2, J = 6 Hz), 2.25 (quin, 2, J = 6 Hz). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.23; H, 5.58.

2-Methoxy-4*H*-cyclopenta[*def*]chrysene (18a). A solution of **17** (900 mg, 3.12 mmol) in dry THF (5 mL) and ethanol (25 mL) under argon was cooled to 0 °C. $NaBH_4$ (1 g) was added over 10 min, and the mixture was stirred for 1 h then worked up conventionally. A solution of the alcohol product (830 mg) in 25 mL triglyme was heated at reflux with a 10% Pd/C catalyst for 5 h. The usual workup followed by chromatography on a silica gel column eluted with ether–hexane (1:5) gave **18a** (530 mg, 62%) as a white solid, mp 188–190 °C: ^{1}H NMR δ 8.63 (dd, 1, J = 7.9 Hz), 8.49 (d, 1, J = 8.8 Hz), 8.03 (dd, 1, J = 7.9 Hz, J = 1.2 Hz), 7.93 (d, 1, J = 8.8 Hz), 7.92 (s, 1), 7.59–7.70 (m, 2), 7.34 (s, 1), 7.26 (s, 1), 4.39 (s, 2), 3.99 (s, 3). Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.97; H, 5.27.

4*H*-Cyclopenta[*def*]chrysen-2-ol (18b). To a solution of **18a** (450 mg, 1.66 mmol) in 10 mL of CH_2Cl_2 at 0 °C under argon was added 5 mL of BBr_3, and the mixture was stirred at this temperature for 1 h and then poured into crushed ice. The product was extracted with 100 mL of CH_2Cl_2 and then washed with water, dried and evaporated to provide **18b** (380 mg, 89%) as a white solid, mp 218–220 °C: ^{1}H NMR δ 8.66 (d, 1, J = 8.0 Hz), 8.52 (d, 1, J = 8.8 Hz), 8.05 (d, 1, J = 7.9 Hz), 7.95 (s, 1), 7.89 (d, 1, J = 8.8 Hz), 7.60–7.70 (m, 2), 7.29 (s, 1), 7.25 (s, 1), 5.01 (s, 1, disappeared with D_2O), (s, 2). MS, *m/e* (relative abundance) 256 (M^+, 100%), 239 (30), 226 (55), 128 (35). Anal. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72. Found: C, 88.97; H, 4.77.

4*H*-Cyclopenta[*def*]chrysene-1,2-dione (19). To a solution of **18b** (300 mg, 1.2 mmol) in 60 mL of CH_2Cl_2 was added

4 drops of Adogen 464, 50 mL of 1/6 M KH_2PO_4, and 1.2 g of Fremy's salt. The mixture was stirred under argon for 1 h. Red crystals of the quinone precipitated from the reaction mixture. The solvent was evaporated under vacuum, and the red solid was filtered and triturated with ether and acetone to yield the quinone **19** (258 mg, 82%), mp 162–164 °C dec: ^{1}H NMR δ 8.53 (dd, 1, J = 8.8 Hz, J = 3.6 Hz), 8.41 (d, 1, J = 8.3 Hz), 8.09 (d, 1), 7.92 (dd, 1, J = 8.8 Hz, J = 4.0 Hz), 7.66–7.70 (m, 2), 7.63 (s, 1), 6.47 (s, 1), 4.22 (s, 2); UV (ethanol) λ_{max} 289 (ϵ 21 540), 255 (17 920), 215 (11 540) nm. MS, m/e (relative abundance) 270 (M^+, 100%), 243 (20), 107 (15), 128 (35); HRMS calcd for $C_{19}H_{10}O_2$ 270.0682, found 270.0682.

***trans*-1,2-Dihydroxy-1,2-dihydro-4*H*-cyclopenta[*def*]chrysene (20).** To a solution of **19** (200 mg, 0.74 mmol) in 50 mL of ethanol was added 600 mg of $NaBH_4$, and O_2 was bubbled through the solution for 48 h. The mixture was partitioned between EtOAc and water and worked up in the usual manner[12] to afford the crude dihydrodiol. Chromatography on silica gel gave pure **20** (162 mg, 80%) as a white solid, 195–197 °C: ^{1}H NMR δ 8.68 (d, 1, J = 7.2 Hz), 8.41 (d, 1, J = 8.2 Hz), 7.97 (dd, 1, J = 7.5 Hz, J = 1.6 Hz), 7.69 (d, 1), 7.64 (s, 1), 7.57–7.62 (m, 2), 5.90 (d, 1, J = 1.6 Hz), 5.50 (d, 1, J = 7.5 Hz, disappeared with D_2O), 5.19 (d, 1, J = 7.2 Hz, OH, disappeared with D_2O), 4.86 (t, 1, J = 5.9 Hz, changed to d, J = 6.0 Hz with D_2O), 4.52 (br s, 1), 3.99 (s, 2); UV (ethanol) λ_{max} 276 (ϵ 35 700), 245 (27 50), 220 (44 360), 197 (35 160) nm. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.21; H, 5.10. Found: C, 83.01; H, 5.21.

***trans*-1,2-Dihydroxy-*anti*-3,3a-epoxy-1,2,3,3a-tetrahydro-4*H*-cyclopenta[*def*]chrysene (2).** To a solution of **20** (30 mg, 0.11 mmol) in 3 mL of dry THF at 0 °C under argon was added *m*-CPBA (86 mg, 0.5 mmol), and the mixture was stirred for 30 min. The solution was diluted with ether (30 mL) and washed with ice-cold 2 N NaOH and with ice water and then dried over $NaSO_4$. The solvent was removed by evaporation under vacuum avoiding heating, and the residue was triturated with cold ether to afford **2** (22 mg, 70%) as a white solid, mp 143–146 °C dec: ^{1}H NMR (DMSO-d_6) δ 8.66 (dd, 1, J = 8.4 Hz, J = 1.4 Hz), 8.53 (d, 1, J = 8.3 Hz), 7.95 (dd, 1, J = 8.6 Hz, J = 1.9 Hz), 7.71 (d, 1), 7.68 (s, 1), 7.59–7.65 (m, 2), 5.76 (d, 1, J = 6.3 Hz, disappeared with D_2O), 5.63 (d, 1, J = 5.3 Hz, disappeared with D_2O), 4.65 (t, 1, J = 8.1 Hz, changed to d, J = 8.1 Hz with D_2O), 4.05 (s, 1), 3.80 (two overlapping d, J = 8.1 Hz, J= 18.9 Hz), 3.50 (d, 1, J = 18.9 Hz); UV (ethanol) λ_{max} 369 (ϵ 3500), 302 (6120), 257 (38 940), 215 (19 440) nm. MS, m/e (relative abundance) 290 (M^+, 52), 272 (45), 270 (70), 244 (71); HRMS calcd for $C_{19}H_{14}O_3$ 290.0943, found 290.0943.

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