Chromosorb W. Preparative GC separations were carried out with a Varian Aerograph 90P (TC detector) equipped with either a $^1/_2$ in. × 20 ft column packed with 10% carbowax 20M on Chromosorb W or a $^3/_8$ in. × 20 ft column packed with 10% SE-30 on Chromosorb W. Distillations were usually performed with a Buchi Kugelrohr apparatus and the temperatures given are pot temperatures. Tetrahydrofuran, diglyme, benzene, and toluene were distilled over sodium benzophenone ketyl. Tetrakis(triphenylphosphine)palladium was prepared from palladium dichloride.[28] Phenylsilane and phenyltrideuteriosilane were prepared by reduction of trichlorophenylsilane with $LiAlH_4$ and $LiAlD_4$, respectively, in dry ether.[29]

Substrates. Compounds **3**, **4**, **7**, **12**, and **13** were purchased from Aldrich and **14** from Light & Co. Ltd. Compound **5** was prepared as reported.[30] Compounds **2**, **8**,[31] **9**,[32] **10**,[33] and **15** were prepared by dropwise addition of bromine (0.1 mol) into a solution of the parent ketone (0.1 mol) in glacial acetic acid (50 mL) at room temperature, followed by extraction with ether, washing with aqueous sodium carbonate, removal of the solvent, and finally vacuum distillation. All products were found to be pure by GC and NMR. Compounds **6**[34] and **11**[35] were prepared by dropwise addition of bromine (0.1 mol) into a vigorously stirred mixture of the parent ketone (0.1 mol) in water (50 mL) at room temperature, followed by ether extraction and distillation.

General Procedure for Dehalogenation with Pd(0) Catalyst. The α-halo ketone (0.10–0.83 mmol) was dissolved in THF (5 mL) along with diphenylsilane (1.0–3 equiv) and, in some cases, K_2CO_3 (1–2 equiv). $Pd(PPh_3)_4$ (3.5–10 mol %) was added and the mixture was stirred at room temperature (inert atmosphere was not required). The composition of reaction mixture was monitored by GC using internal standards. More details are given in Table I.

General Procedure for Dehalogenation with Mo(0) Catalyst. The α-halo carbonyl substrate (0.2–0.6 mmol) was dissolved in THF (0.5–1.0 mL) and mixed with $Mo(CO)_6$ (4–11 mol %), triphenylphosphine (17–33 mol %), phenylsilane (120–280 mol %), and sodium bicarbonate (80–250 mol %). The mixture was refluxed or heated to the desired temperature (when other solvent was used). Progress of the reaction progress was monitored by GC and/or NMR, using internal standards. More details are given in Tables II and III.

Preparative Procedures. Reduction of 4-Bromononan-5-one. A mixture comprised of 4-bromononan-5-one (1.62 g, 6.87 mmol), $Mo(CO)_6$ (0.09 g, 0.34 mmol), phenylsilane (1.08 g, 10 mmol), triphenylphosphine (0.35 g, 1.33 mmol), and $NaHCO_3$ (0.83 g, 9.83 mmol) in 7 mL of THF was refluxed for 80 min (completion of the reaction was evident by GC). The mixture was cooled to room temperature, water (0.15 mL) was added, and the solvent was removed under reduced pressure. Distillation of the residue afforded pure (GC, NMR) 5-nonanone (0.98 g, 96% yield).

Reduction of α-Bromocamphor. A mixture of α-bromocamphor (2.24 g, 9.69 mmol), $Mo(CO)_6$ (0.14 g, 0.53 mmol), phenylsilane (1.30 g, 12 mmol), and $NaHCO_3$ (0.88 g, 10.46 mmol) in 6 mL of THF was refluxed for 1.5 h (completion of the reaction was evident by GC). The solution was worked up as described above, affording pure camphor (GC, NMR) (1.19 g, 81% yield).

Acknowledgment. We thank the fellowship program of the Consejo Nacional de Investigaciones Cientificas y Tecnicas de la Republica Argentina for their generous financial support.

Registry No. **1**, 13939-06-5; **2**, 42330-10-9; **2** (debromo deriv), 123-19-3; **3**, 70-11-1; **3** (debromo deriv), 98-86-2; **4**, 99-73-0; **4** (debromo deriv), 99-90-1; **5**, 19967-55-6; **5** (debromo deriv), 563-80-4; **6**, 822-85-5; **6** (debromo deriv), 108-94-1; **7**, 1925-58-2; **7** (debromo deriv), 76-22-2; **8**, 1073-25-2; **8** (debromo deriv), 497-38-1; **9**, 3212-63-3; **9** (debromo deriv), 565-80-0; **10**, 2648-71-7; **11**, 10409-47-9; **11** (debromo deriv), 583-60-8; **12**, 533-68-6; **12** (debromo deriv), 105-54-4; **13**, 532-27-4; **14**, 107-59-5; **14** (debromo deriv), 123-86-4; **15**, 42330-11-0; **15** (debromo deriv), 502-56-7; Ph_2SiH_2, 775-12-2; $Pd(PPh_3)_4$, 14221-01-3; Et_3SiH, 617-86-7; $PhSiH_3$, 694-53-1; $Pd(OAc)_2$, 3375-31-3.

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Fjord Region 3,4-Diol 1,2-Epoxides and Other Derivatives in the 1,2,3,4- and 5,6,7,8-Benzo Rings of the Carcinogen Benzo[*g*]chrysene

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Dihydrodiol and diol epoxide derivatives of the carcinogen benzo[*g*]chrysene (BgCh) have been prepared to probe structural factors involved in the carcinogenesis and mutagenesis of polycyclic aromatic hydrocarbons. Preparation of 1,2-dihydrobenzo[*g*]chrysen-4(3*H*)-one (**6**) and 7,8-dihydrobenzo[*g*]chrysen-5(6*H*)-one (**11**), ketones suitable for further elaboration to potential metabolites of benzo[*g*]chrysene in the 1,2,3,4- and 5,6,7,8-benzo rings, respectively, was achieved through two cyclization steps. Photochemical closure of 2-(1- or 2-naphthyl)styrene derivatives **4** and **9** afforded chrysene and benzo[*c*]phenanthrene ring systems with a butyric ester/acid side chain poised for a second ring closure (acid-catalyzed) to the desired ketones. Preparation of pure BgCh 3,4-diol 1,2-epoxides **23** and **24** from the dihydrodiol diester **14** by conversion to separable trans bromohydrins, cyclization to the epoxides, and hydrolysis of the acetates was found to be more successful than preparation from the dihydrodiol **15**.

In the mid-1970s, evidence linking diol epoxide derivatives of polycyclic aromatic hydrocarbons (PAHs) to the carcinogenicity of PAHs began to emerge.[1,2] Since then, syntheses of these molecules and their dihydrodiol pre-

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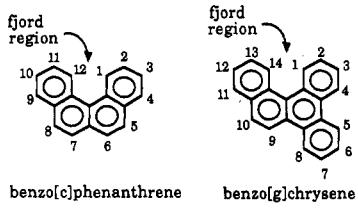
Chart I. Structural Formulas for Benzo[*c*]phenanthrene and Benzo[*g*]chrysene



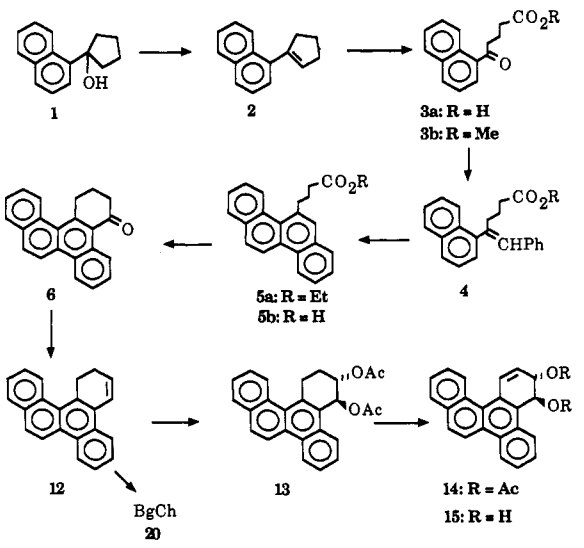
cursors[3] have contributed significantly to studies of the metabolism,[4] mutagenicity, and tumorigenicity of PAHs. It is now generally accepted that diol epoxides are the ultimate mutagenic and carcinogenic forms of alternant PAHs. Among the structural factors that affect these biological activities, the presence of the epoxide moiety in a "bay region" has been found to be a requirement for high activity.[5] Within the group of bay region diol epoxides, reactivity, conformation, and absolute stereochemistry have been shown to contribute to mutagenicity and carcinogenicity.[5]

In recent years, primarily through the study of benzo[*c*]phenanthrene (BcPh)[6] and 5-methylchrysene[7] diol epoxides, evidence has also been obtained that those bay region diol epoxides with additional steric bulk in the proximity of the epoxide moiety exhibit enhanced mutagenicity and carcinogenicity, despite low solvolytic reactivity. In order to further probe the structural factors affecting the activity of bay region diol epoxides, we have initiated syntheses of benzo[*g*]chrysene (BgCh) diol epoxides, and other derivatives, for use in biological studies.

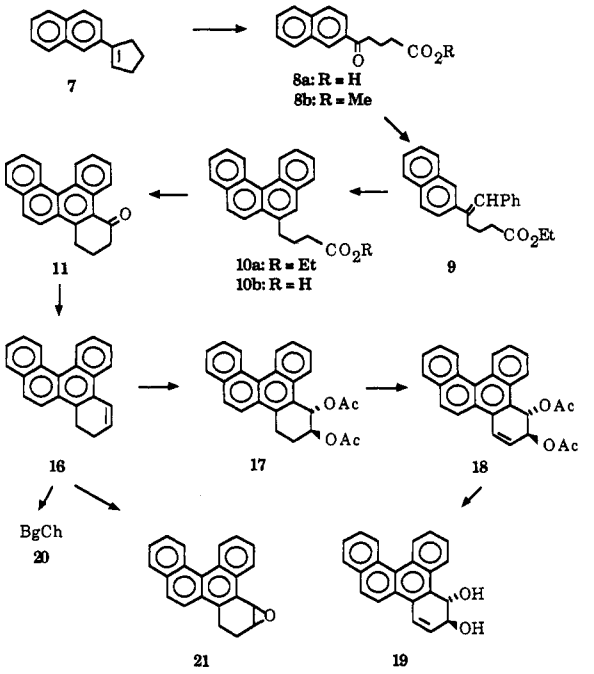
BgCh is a potent carcinogen,[8] in contrast to BcPh, which is only weakly active, due to limited metabolism to its diol epoxide derivatives.[9] BcPh is symmetrical, and consequently has only one set of bay region diol epoxide (termed "fjord" region diol epoxides for this specific geometry) stereoisomers (Chart I). However, the additional benzo ring in BgCh leads to two sets of fjord region diol epoxides: BgCh 3,4-diol 1,2-epoxides and BgCh 11,12-diol 13,14-epoxides (Chart I). The BgCh 3,4-diol 1,2-epoxides present unique, opposing structural factors. The epoxide moiety occupies a fjord position associated with very high mutagenicity and tumorigenicity, but the conformation of the hydroxyl groups is expected to be pseudodiaxial, and this conformational effect has significantly attenuated mutagenicity and tumorigenicity of all bay region diol epoxides so far studied.[5] The BgCh 11,12-diol 13,14-epoxides have a tetrahydrobenzo ring environment similar to that of the BcPh fjord region diol epoxides and are expected to exhibit the pseudodiequatorial hydroxyl group conformations of the BcPh fjord region diol epoxides.

In this work, we report syntheses of the BgCh 3,4-diol 1,2-epoxides and their precursors, as well as derivatives in the 5,6,7,8-benzo ring of BgCh. Syntheses of the BgCh 11,12-diol 13,14-epoxides will be reported separately.

Scheme I



Scheme II



Results and Discussion

Synthesis of Tetrahydro Ketones. The dihydrodiols and diol epoxides were prepared in several steps from the appropriate tetrahydro ketones 6 (Scheme I) and 11 (Scheme II). The pentacyclic ring systems for the tetrahydro ketones were constructed through two key steps: photocyclization of 2-(1- or 2-naphthyl)styrene derivatives,

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which led to the four-ring aromatic systems, and acid-catalyzed cyclization of a butyryl ester, which produced the fifth ring bearing the ketone. Efficient syntheses were achieved by incorporating the ester side chain into the styrene derivatives prior to photocyclization.

1,2-Dihydrobenzo[*g*]chrysen-4(3*H*)-one. Prior to development of the photochemical route, the alternative approach of succinoylation of chrysene, followed by reduction of the keto group and acid-catalyzed cyclization, was attempted. Beyer[10] reported that chrysene was succinoylated at C-5 when nitrobenzene was used as solvent. However, the NMR spectrum of the succinoylation product was inconsistent with substitution at C-5, since integration gave five protons below δ 8.4 and six protons between δ 7.5 and 8.4, rather than the expected values of four and seven, respectively.

The photochemical route is patterned after a synthesis of 5-methylchrysene.[11] In the present case, a butyric ester side chain as in **4** (Scheme I) was needed, rather than a methyl group. To prepare **4**, keto ester **3b** was needed. Initially, **3b** was prepared by acylation of naphthalene with methyl 4-(chloroformyl)butyrate at 0 °C, which, according to a literature report,[12] yields C-1 substitution. Although the major product was found to be substituted at C-1 (46%), contamination by the C-2 product (13%) made it desirable to pursue an alternative route. 1-Bromonaphthalene was converted to the Grignard reagent, which was condensed with cyclopentanone. Dehydration of the crude alcohol **1** with *p*-TsOH in PhH gave alkene **2** in 74% overall yield. Satisfactory conversion (25–56%) of **2** to 4-(1-naphthoyl)butyric acid (**3a**) in large-scale reactions (up to 23 g of alkene) was achieved with $KMnO_4$ and 18-crown-6 in THF. Other conditions (CrO_3/HOAc; $KMnO_4$/18-crown-6/PhH; $KMnO_4/H_2O$/acetone; $KMnO_4/NaIO_4$) often gave acceptable yields in small-scale reactions, but poor yields in large-scale reactions. The keto acid was converted to the methyl ester **3b** with MeOH/HCl. Reaction of the keto ester for 3 days at reflux in EtOH with the Wittig reagent obtained from benzyltriphenylphosphonium chloride and NaOEt gave **4** in 86% yield. Product **4** was estimated to be a 2:1 mixture of *Z* and *E* isomers on the basis of the relative areas of the singlets at δ 6.62 (assigned to *Z* and δ 6.75 (assigned to *E*). Photolysis was effected without further purification of **4**, since the *E* isomer was expected to isomerize to the *Z* isomer under the conditions of photocyclization.[13] Photolysis of 1.5–1.6-g samples of **4** for 3–4 days at 300 nm in alkene-free cyclohexane containing I_2, and through which dry air was bubbled, led to a 53% yield of ethyl 4-(5-chrysenyl)butyrate **5a**. The aromatic proton absorptions in the NMR spectrum of **5a** were very similar to those reported for 5-methylchrysene.[14] As expected, integration showed three protons from δ 8.6 to 8.9 corresponding to the bay region protons and eight protons between δ 7.6 and 8.0 in the aromatic region. Compound **5a** was not rigorously purified, but was hydrolyzed in 76% yield to the carboxylic acid **5b**, which was easily purified by crystallization from MeOH. Rigorous purification at this stage was important, since isolation and purification of the ketone produced by cyclization in the subsequent step was otherwise hampered by the presence of impurities. Cyclization of **5b** at 55–70 °C in $MeSO_3H$ led to a high (85%) yield of ketone **6**. The NMR spectrum of **6** shows a significant downfield shift (to δ 9.25) for the proton at C-5, which is deshielded by the carbonyl group at C-4. A similar downfield shift (to δ 9.24) is observed for the analogous proton in 3,4-dihydrotriphenylen-1(2*H*)-one, which was available for spectral comparison.

7,8-Dihydrobenzo[*g*]chrysen-5(6*H*)-one. A photochemical route was also used to gain access to derivatives in the 5,6,7,8-tetrahydrobenzo ring of BgCh (Scheme II). 2-Bromonaphthalene was converted to the Grignard reagent with Mg in THF. Condensation with cyclopentanone gave an intermediate alcohol, which was not purified, but was converted directly to alkene **7** with *p*-TsOH in PhH. The overall yield of alkene was 86%. Alkene **7** was oxidized to 4-(2-naphthoyl)butyric acid **8a** with $KMnO_4$ in PhH containing 18-crown-6 ether. In order to achieve reproducible, good yields (50–60%) in large-scale oxidations (>1 g), addition of glass beads and the use of overhead stirring were found to be important. Crude **8a** was converted to the methyl ester **8b** in 68% yield, with MeOH/HCl. This product was identical with the minor product obtained in the Friedel–Crafts reaction of naphthalene with 4-(chloroformyl)butyrate. Conversion to alkene **9** was achieved in 89% yield via Wittig reaction. Compound **9** was a mixture containing about 56% *E* isomers and 44% *Z* isomers, as judged by integration of the olefinic peaks at δ 6.90 (assigned to *E* isomer) and δ 6.56 (assigned to the Z isomer) in the NMR spectrum. Photolysis of **9** in alkene-free cyclohexane containing I_2 gave ester **10a** as an oil. The ester was converted to the carboxylic acid **10b** with aqueous KOH. The overall yield of **10b** from **9** was 73%. In principle, **9** could photocyclize either to a BcPh derivative (by ring closure at the α-position of the naphthalene moiety) or to a BA derivative (by ring closure at the vacant β-position of naphthalene). Closure to the BcPh derivative was expected, since previous studies have shown BA derivatives to result only when high concentrations of I_2 were used.[13] In the present case, the NMR spectra of **10a** and **10b** were able to easily establish that a BcPh rather than a BA derivative had been produced, since downfield singlets at ca. δ 8.2 and 9.0 expected for the meso hydrogens in BA were absent, and the absorptions in **10a** and **10b** closely paralleled those recently reported for BcPh.[15] Ring closure to the ketone **11** was effected in high yield (86%) with $MeSO_3H$ at 60 °C. In addition to the fjord-region proton absorptions (H-1 and H-14) at δ 8.86 and 8.96, the aromatic hydrogen at C-4 also appeared at low field (δ 9.24), due to deshielding by the carbonyl group.

***trans*-3,4-Dihydroxy-3,4-dihydrobenzo[*g*]chrysene.** Conversion of tetrahydro ketone **6** to 3,4-dihydroxy-3,4-dihydrobenzo[*g*]chrysene (BgCh 3,4-dihydrodiol, **15**) was effected as shown in Scheme I. The ketone was reduced to the alcohol with $NaBH_4$ in MeOH. Dehydration of the crude alcohol with *p*-TsOH in benzene gave alkene **12** in 85% yield, based on the ketone. Oxidation of **12** with DDQ/PhH gave BgCh (**20**), thereby establishing that the correct carbon skeleton was in hand. Reaction of **12** with $AgOAc/I_2$/PhH gave the trans diacetate **13** in 80–90% yield. Conversion of **13** to dihydrodiol diacetate **14** was not routine. Bromination of **13** with NBS led to a mixture of products, which could include the desired bromodiacetate(s), resulting from benzylic bromination, as well as dihydrodiol diacetate **14** and a 1,2-dibrominated product. It appears that the initial bromodiacetate slowly eliminates HBr at the temperature of the reaction (60 °C) to give **14**, which is vicinally dibrominated. Depending on the length

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Table I. ^{1}H NMR Spectral Data for BgCh Dihydrodiols and Dihydrodiol Diacetates

BgCh derivative	benzylic CHOH(Ac)	nonbenzylic CHOH(Ac)	benzylic vinyl	nonbenzylic vinyl	OAc(OH)
14	6.90 (H_4)	5.49 (H_3)	7.66 (H_1)	6.47 (H_2)	2.03, 2.08
$J_{1,2}$ = 9.7, $J_{2,3}$ = 6.0, $J_{3,4}$ = 1.7. Aromatic H's: δ 8.48–8.80 (m, 3 H), 8.01–8.13 (m, 3 H), 7.63–7.73 (m, 4 H)					
18	6.90 (H_5)	5.47 (H_6)	7.72 (H_8)	6.54 (H_7)	1.98, 2.07
$J_{5,6}$ = 1.8, $J_{6,7}$ = 5.4, $J_{7,8}$ = 9.7. Aromatic H's: δ 8.97–9.04 (m, 2 H), 8.19–8.26 (m, 2 H), 7.96–8.08 (m, 2 H), 7.60–7.70 (m, 4 H)					
15	5.60 (H_4)	4.69 (H_3)	7.59 (H_1)	6.51 (H_2)	1.70, 1.89
$J_{1,2}$ = 9.7, $J_{2,3}$ = 5.9, $J_{3,4}$ = 1.8, $J_{3,OH}$ = $J_{4,OH}$ = 7.3. Aromatic H's: δ 8.53–8.77 (m, 3 H), 8.47 (m, 1 H), 8.03 (m, 2 H), 7.63–7.73 (m, 4 H)					
19	5.61 (H_5)	4.59 (H_6)	7.63 (H_8)	6.60 (H_7)	1.88
$J_{5,6}$ = 1.1, $J_{6,7}$ = 5.7, $J_{7,8}$ = 9.8, $J_{5,OH}$ = 6.9, $J_{6,OH}$ = 7.2. Aromatic H's: δ 8.97–9.04 (m, 2 H), 8.50 (d, 1 H), 7.98–8.24 (m, 3 H), 7.66–7.75 (m, 4 H)					

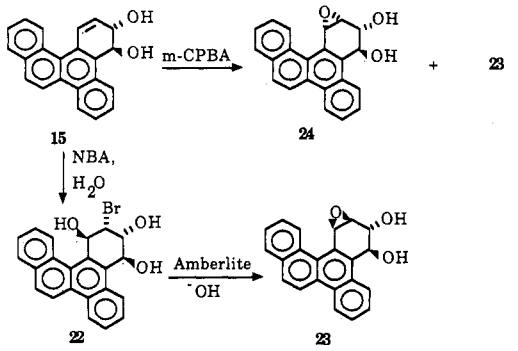
of the reaction time, the composition of the mixture varies. Attempts to isolate **14** from these mixtures by chromatography led to low yields of **14**. However, it was found that both the mono- and dibrominated intermediates could be effectively converted to **14** with DBN. The best yields for conversion to **14** (83% from **13**) were obtained when DBN was added directly to the reaction mixture containing the products from the NBS reaction, and the reaction mixture was stirred for 24 h at room temperature. No evidence for bromination of the aromatic ring in **14** could be found either by mass spectrometry or by careful analysis of the 300-MHz ^{1}H NMR spectrum. The acetate groups were cleaved with NH_3/MeOH at room temperature which led to dihydrodiol **15** in 82% yield.

***trans*-5,6-Dihydroxy-5,6-dihydrobenzo[*g*]chrysene.** Conversion of tetrahydro ketone **11** to *trans*-5,6-dihydroxy-5,6-dihydrobenz[*g*]chrysene (BgCh 5,6-dihydrodiol, **19**) was effected as shown in Scheme II. Reduction of **11** with $NaBH_4$ in MeOH, followed by dehydration of the intermediate alcohol with *p*-TsOH in benzene, gave alkene **16** in 80% overall yield. Reaction of the alkene with DDQ at room temperature led to formation of BgCh. This further established that the correct ring skeleton had been produced in the reaction sequence. Conversion to the tetrahydrodiol diacetate **17** was effected by Prevost reaction with $AgOAc/I_2$ in PhH, in 80% yield. Bromination was effected with NBS in CCl_4 containing $NaHCO_3$, at 55 °C, and glassware was treated prior to use with dilute NH_4OH and distilled H_2O to avoid acidity. In this case, as for dihydrodiol diacetate **14**, yields were consistent and good when precautions to avoid acidity were taken. When such measures were not taken, yields were sometimes very low, and considerable side product thought to consist largely of phenolic acetate (from loss of acetic acid) was formed. The crude bromodiacetate mixture was dehydrobrominated with DBN in dry THF. This led to isolation of **18** in 51% overall yield from **17**. Conversion to BgCh 5,6-dihydrodiol was effected with NH_3/MeOH. Purification of crude **19** by chromatography on silica gel appeared to result in loss of material, and a 30% yield of dihydrodiol was obtained.

Alkene **16** was also converted to epoxide **21**, as shown in Scheme II. This was accomplished by conversion to the bromohydrin with *N*-bromoacetamide (NBA) in THF/H_2O, followed by cyclization to **21** with Amberlite resin in the hydroxide form. This two-step procedure was more effective than direct epoxidation with *m*-chloroperoxybenzoic acid, (*m*-CPBA), which led to a mixture containing side products, from which it was difficult to obtain pure **21**.

NMR spectral data for dihydrodiol diacetates **14** and **18** and for dihydrodiols **15** and **19** are shown in Table I. The spectra for the two pairs of compounds are very similar. The low values (1.1–1.8 Hz) for the coupling constants ($J_{3,4}$, $J_{5,6}$) between the benzylic and nonbenzylic carbinol hydrogens and the analogous hydrogens attached to the acetate-bearing carbons indicate a conformation that strongly favors pseudodiaxial OH's and OAc's. The benzylic vinyl hydrogens were shifted to low field (δ 7.59–7.72) in all cases due to deshielding by the proximal benzo ring.

Scheme III



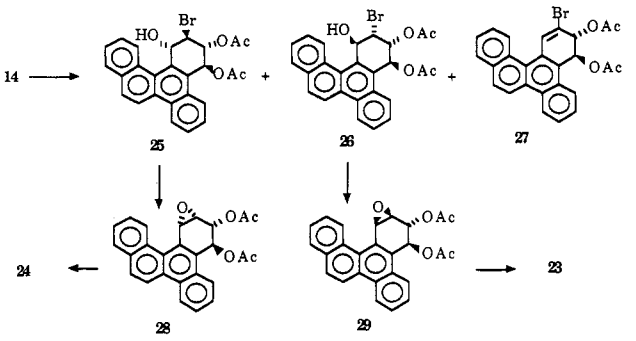
Synthesis of BgCh 3,4-Diol 1,2-Epoxides. Initially, conversion of BgCh 3,4-dihydrodiol **15** to diol epoxide derivatives was effected as shown in Scheme III. The fjord region diol epoxide with the epoxide oxygen cis to the benzylic hydroxyl group (diol epoxide-1, **23**) was prepared in two steps. The bromotriol was formed from the dihydrodiol by reaction with NBA in aqueous THF. Chromatography of the crude product on silica gel gave the bromotriol in 26% yield. The bromotriol was converted to **23** in 79% yield with Amberlite in the hydroxide form. The production of a single epoxide, in high yield, argues in favor of the stereochemistry assigned to the bromotriol, as well as for the stereochemistry assigned to the epoxide. In previous cases, where bromotriol with trans relationships for all vicinal groups was formed by anti addition to the opposite stereotopic faces of the double bond, both possible epoxides were formed upon cyclization of the bromotriol with base.[16] In this case, no BgCh 1,4-diol 2,3-epoxide was observed. Also, as discussed below, the NMR spectrum of the diol epoxide was consistent with the assigned structure. Reaction of BgCh 3,4-dihydrodiol with *m*-CPBA resulted in formation of the *trans*-diol as major product under carefully controlled conditions. The most selective conversion was achieved with a 10-fold excess of *m*-CPBA in THF at 10–15 °C for 4 h. Under these conditions, a four- to fivefold excess of **24** over **23** was observed. At higher temperatures, significant formation of byproducts thought to be adducts of *m*-chlorobenzoic acid with the diol epoxides was observed, and the ratio of **24** to **23** was less favorable (ca. 2:1). At 0–15 °C, byproduct formation occurred, but was minor. At temperatures below 0 °C, the reaction was very slow. Attempts to improve the ratio of products by using CH_3CN as solvent resulted in a 2:1 ratio of **24** to **23** at 0 °C. Reactions in CH_2Cl_2 at room temperature, with or without added base ($NaHCO_3$), resulted in total conversion to byproducts. The diol epoxide mixture was freed of contaminants by HPLC on silica gel, by using 40% THF in hexane. Considerable loss of ma-

(16) Yagi, H.; Thakker, D. R.; Lehr, R. E.; Jerina, D. M. *J. Org. Chem.* **1979**, *44*, 3429–3442.

Table II. ^{1}H NMR Spectral Data for BgCh Dihydrodiol and Dihydrodiol Diacetate Epoxides

compd	H-1	H-2	H-3	H-4	H-14	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$
23	5.15	4.06	4.91	5.65	<9.0	4.0	2.6	2.7	1.7
24	4.51	4.45	4.75	5.66	9.27	4.0	6.0	3.1	
29	4.93	3.89	5.80	6.97	<9.0	3.9	2.0	2.0	2.0
28	4.48	4.43	5.34	6.90	9.26	3.8	5.6	2.8	

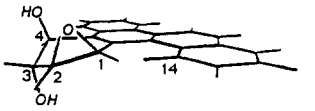
Scheme IV



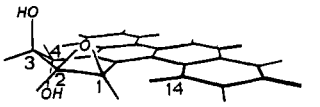
terial occurred unless the column was cooled by an external coil of chilled water. After chromatography, the diol epoxide mixture was 84% **24** and 16% **23**, as judged by NMR integration. The diol epoxides were isolated in 50% overall yield, based on starting dihydrodiol. Separation of the diol epoxides from each other was not achieved.

In order to achieve preparation of **24**, uncontaminated by **23**, the approach outlined in Scheme IV was adopted. Treatment of *trans*-dihydrodiol diacetate **14** with NBA in THF/H_2O led to a mixture of bromohydrins **25** (32%) and **26** (13%), as well as the bromo alkene **27** (23%). The bromohydrins could be readily separated by column chromatography on silica gel without apparent loss of material. Cyclization with Amberlite (hydroxide form) in THF led to high yields (>95%) of the epoxides **28** and **29**. Hydrolysis with NH_3/MeOH at 0 °C (2 h) and 15 °C (2 h) led to clean conversion to the diol epoxides, which were isolated in greater than 90% yield.

NMR spectral values for the diol epoxides and epoxy diacetates are cited in Table II. There are several notable features in the NMR spectra. First, in all cases, the $J_{3,4}$ values are small (2.7–3.1 Hz), which indicates that the hydroxyl and acetoxyl groups strongly prefer pseudodiaxial (and the hydrogen atoms pseudodiequatorial) conformations due to steric hindrance from the benzo ring near the C-4 hydroxyl/acetoxyl group (Figure 1). In contrast, in the BcPh fjord region diol epoxides, where there is no corresponding benzo ring, the hydroxyl groups strongly prefer the pseudodiequatorial conformation, as shown by the large couplings ($J_{3,4}$ = 9.0 and 8.0 Hz) between the pseudodiaxial hydrogen atoms.[17] Second, long-range coupling ($J_{2,4}$ = 1.7 and 2.0 Hz) is observed for **23** and **29**, respectively, which provides strong support for their assignment as the epoxide-1 isomers. Inspection of models indicates that the requisite geometry for *W* coupling between H-2 and H-4 is present only in the diaxial conformation of **23** and **29**. *W* coupling has been observed between the corresponding protons in the diol epoxide-1 isomers of benzo[*e*]pyrene (J = 2.5 Hz) and triphenylene (J = 1.7 Hz), which also have strongly preferred pseudodiaxial conformations for the hydroxyl groups.[16] Third, the much larger $J_{2,3}$ for **24** (6.0 Hz) and **28** (5.6 Hz) compared to **23** (2.6 Hz) and **29** (2.0 Hz) is also consistent with the assigned structures. In the former cases, H-2 and H-3



BgCh 3,4-diol-1,2-epoxide-1



BgCh 3,4-diol-1,2-epoxide-2

Figure 1. Pseudodiaxial hydroxyl conformations for benzo[*g*]-chrysene diol epoxides-1 and -2.

are eclipsed in the pseudodiaxial conformation, whereas in the latter cases the dihedral angle is about 50°. Finally, significant chemical shift differences for the H-1 and H-14 absorptions support the structural assignments. For H-1, the absorption is at significantly lower field for isomer-1 relative to isomer-2 for both the diol epoxides ($\Delta\delta$ = 0.45) and the epoxy diacetates ($\Delta\delta$ = 0.64). Inspection of models indicates that this results from greater edge deshielding of H-1 in **23** and **29** than in **24** and **28** due to its being closer to the fjord region benzo ring. For H-14, the absorption is at significantly lower field (δ 0.4–0.5) for the epoxide-2 isomers relative to the epoxide-1 isomers. This likely results from deshielding by the oxirane oxygen, which is closer to H-14 in the pseudodiaxial conformation of **24** and **28** than in the corresponding conformation of **23** and **29**. Substantial, although somewhat smaller ($\Delta\delta$ = 0.39 at C-1 and 0.45 at C-12) chemical shift differences have also been observed for the corresponding protons in the BcPh fjord region diol epoxides. For BcPh, however, H-1 is shifted downfield in the trans isomer, and H-12 (corresponding to H-14 in BgCh) is shifted downfield in the cis isomer, exactly opposite to the effect observed for the BgCh fjord region diol epoxides. This reversal results from the preferred pseudodiaxial hydroxyl conformation for the BgCh fjord region diol epoxides, as opposed to the preferred pseudodiequatorial hydroxyl conformation for the BcPh fjord region diol epoxides. As a consequence, the orientation of the oxirane ring relative to the fjord region benzo ring is the same for a BcPh fjord region diol epoxide-1 as for a BgCh fjord region diol epoxide-2, and vice versa.

Experimental Section

Melting points were obtained on a Kofler melting point apparatus and are uncorrected. Nominal mass spectra were recorded on a Hewlett-Packard 5985 quadrupole mass spectrometer. Spectra were recorded at 70 eV, unless noted otherwise. High-resolution mass spectra were recorded on a Kratos MS25 RF mass spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer in $CDCl_3$. Chemical shifts are reported in δ and coupling constants are reported in hertz. Ultraviolet spectra were recorded on a Perkin-Elmer Lambda 3 spectrophotometer. HPLC was accomplished on a Beckman Model 330 liquid chromatograph with an Altex Ultrasphere-Si 10 mm × 25 cm column. Preparative photolysis was accomplished with a Rayonet RS preparative photochemical reactor and 300-nm lamps. Cyclohexane and hexane for photolysis experiments were treated with concentrated H_2SO_4, washed with H_2O, and distilled from $CaSO_4$. EtOH for

(17) Sayer, J. M.; Yagi, H.; Croisy-Delcey, M.; Jerina, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 4970–4972.

Wittig reactions was obtained by distillation of absolute EtOH from Mg/I_2. THF was freshly distilled from CaH_2. Anhydrous PhH was obtained by distillation from Na. Air used in photochemical reactions was dried by passing through KOH pellets, followed by $CaSO_4$. For workup procedures, Na_2SO_4 was used as a drying agent, and solvents were evaporated under reduced pressure (rotovap). Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

1-(1-Naphthyl)cyclopentanol (1). To a dry flask containing 5.67 g (0.233 mol) of Mg and equipped with N_2 inlet, reflux condenser, addition funnel, and mechanical stirrer were added anhydrous Et_2O (25 mL), 1-bromonaphthalene (2 g), and a crystal of I_2. After heating at reflux had initiated the reaction, stirring was begun, and 48 g of 1-bromonaphthalene (50 g total, 0.242 mol) and 75 mL of anhydrous Et_2O were added over a 2-h period. The mixture was refluxed until the Mg was almost entirely consumed. Dry PhH (75 mL) was then added, the mixture was cooled in an ice bath, and cyclopentanone (19.8 g, 0.236 mol) was added dropwise. The mixture was stirred at room temperature for 1–2 h, after which 20% NH_4Cl was added dropwise. The mixture was washed with H_2O (2 × 100 mL) and brine, and the organic phase was collected. After evaporation of solvents, the residue was purified by flash chromatography with PhH as the solvent. This gave **1** (24 g, 49%) as a white solid: mp 74.5–75.5 °C (lit.[18] mp 75.5–76 °C); NMR δ 8.66 (d, $J_{7',8'}$ = 7.7, 1 $H_{8'}$), 7.87 (d, J = 7.1, 1 H), 7.78 (d, J = 8.1, 1 H), 7.60 (d, J = 7.3, 1 H), 7.3–7.6 (m, 3 H), 1.8–2.4 (m, 9 H).

1-(1-Naphthyl)cyclopentene (2). Alcohol **1** (10.1 g) and *p*-TsOH (15 mg) in benzene (100 mL) were heated to reflux for 2 h. The mixture was cooled to room temperature and then extracted with H_2O (2 × 100 mL). The organic phase was dried, filtered, and evaporated to give a quantitative yield of **2**.

Overall higher yields (74%) of **2**, as a colorless oil, were obtained by dehydrating crude alcohol **1** as above and purifying the crude alkene by Kugelrohr distillation at 150–170 °C and 1–2 Torr: NMR δ 8.29 (m, 1 $H_{8'}$), 7.9 (m, 2 H), 7.4–7.6 (m, 4 H), 6.06 (m, 1 H_2), 2.93 (m, 2 H), 2.75 (m, 2 H), 2.21 (m, 2 H).

4-(1-Naphthoyl)butyric Acid (3a). To THF (1 L) in a 2-L round-bottom flask equipped with a magnetic stirrer were added **2** (12.0 g, 0.062 mol), 18-crown-6 ether (1.0 g, 0.004 mol), and $KMnO_4$ (20.5 g, 0.130 mol). The mixture was stirred at room temperature 3 h. Although TLC on silica gel with PhH indicated the presence of alkene, the reaction was terminated to avoid the overoxidation observed in longer runs. Sodium bisulfite (14 g) and 6 N HCl (200 mL) were added portionwise and alternately until the mixture was clear. The THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2. The organic phase was extracted with 0.5 N NaOH (2 × 150 mL). The basic extracts were acidified (concentrated HCl) and extracted with CH_2Cl_2. The organic phase was washed with brine, dried, filtered, and evaporated to give the crude acid. Repetition of the above procedure with 11.3 g of **2**, followed by combination of the crude products led to 7.2 g of keto acid **3a**. Kugelrohr distillation of the neutral residue led to recovery of 15.2 g of **2**. The yield of **3a** based upon reacted **2** was 70%.

Methyl 4-(1-Naphthoyl)butyrate (3b). Crude keto acid **3a** was refluxed in anhydrous MeOH (100 mL) containing concentrated HCl (1 mL) for 3 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The organic phase was washed with H_2O and aqueous $NaHCO_3$, dried, filtered, and evaporated. The residue was purified by flash chromatography with PhH. Keto ester **3b** was isolated in 32–45% yield as an oil: NMR δ 8.58 (d, J = 8.8, 1 H), 7.98 (d, J = 8.3, 1 H), 7.87 (d, J_{app} = 7.3, 2 H), 7.4–7.6 (m, 3 H), 3.68 (s, 3 H), 3.13 (t, J = 7.3, 2 H), 2.48 (t, J = 7.1, 2 H), 2.14 (m, 2 H); mass spectrum (12 eV), m/e (relative intensity) 256 (22), 238 (5), 155 (100). Compound **3b** was also prepared according to a literature method.[12] Naphthalene (15.6 g, 0.122 mol) was dissolved in CH_2Cl_2 (100 mL), and the mixture was cooled in an ice bath. $AlCl_3$ (32.7 g, 0.246 mol) was added, and the reaction mixture was stirred for 10 min. Methyl 4-(chloroformyl)butyrate (20.0 g, 0.122 mol) in 25 mL CH_2Cl_2 was added dropwise, with continued cooling of the reaction mixture. The mixture was stirred overnight at room temperature. H_2O was added dropwise with cooling, and the organic phase was extracted with H_2O (100 mL), 0.5 N NaOH, dilute HCl, and H_2O, dried, and evaporated. The residue was purified by Kugelrohr distillation at 0.5 Torr. A first fraction distilled at 150–180 °C and was discarded. A second fraction distilling at 210–220 °C (18.4 g) was collected. Absolute EtOH (100 mL) was added to the fraction, followed by sufficient petroleum ether to induce cloudiness. Upon cooling of the mixture overnight at −20 °C, a solid formed and was collected by filtration. This was methyl 4-(2-naphthoyl)butyrate (**8b**) which was identical with **8b** prepared by an alternate route (vide infra). Removal of solvents from the filtrate gave **3b** (14.3 g, 46%) as a light yellow oil.

Ethyl 5-(1-Naphthyl)-6-phenyl-5-hexenoate (4). NaOEt, prepared from 1.7 g (0.073 mol) of Na in 88 mL of dry EtOH, was added dropwise to a solution of 28.3 g (0.073 mol) of benzyltriphenylphosphonium chloride in 80 mL of dry EtOH. Stirring was continued for 1 h after addition was complete. Keto ester **3b** (14.34 g, 0.056 mol) in 50 mL of EtOH was then added, and the mixture was refluxed for 72 h, with exclusion of moisture. EtOH was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The organic phase was washed with H_2O, dried, filtered, and evaporated. PhH was added to dissolve the residue, followed by petroleum ether, which precipitated Ph_3PO. The precipitate was collected and washed with PhH/petroleum ether, and the combined filtrates were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel first with petroleum ether and then with benzene as the solvent. Removal of solvents gave **4** (16.6 g, 86%), which was a 2:1 mixture of *Z* and *E* isomers, as judged by integration of the peaks at δ 6.62 and 6.75, respectively: mass spectrum, m/e (relative intensity) 344 (12), 229 (40), 165 (100).

Ethyl 4-(5-Chrysenyl)butyrate (5a). Ester **4** (1.55 g, 0.00472 mol) and I_2 (80 mg) were dissolved in 1.5 L of freshly distilled cyclohexane in a Pyrex photolysis flask fitted with a gas inlet bubbler, reflux condenser, and magnetic stir bar. The solution was aerated with dry air and lamps of 300 nm wavelength maximum were used in a Rayonet RS Preparative photochemical reactor. NMR analysis indicated that reaction was 90% complete after 3 days, as judged by comparison of the areas under the peaks at δ 2.82 and 3.63, and the reaction was halted. The cyclohexane was evaporated, and the residue was dissolved in CH_2Cl_2 and partially purified by flash chromatography on silica gel, first with petroleum ether and then with 10% ether in petroleum ether. This gave 1.1 g of crude product, approximately 80% pure as judged by NMR, which was hydrolyzed to the acid without further purification. Large quantities of **5a** were obtained by repeating photolyses on a 1.5–1.7-g scale, which was more successful than single, large-scale photolysis.

4-(5-Chrysenyl)butyric Acid (5b). A mixture of butyric ester **5a** (6.37 g, 0.019 mol), KOH (10 g, 0.178 mol), and H_2O (180 mL) was refluxed for 3.5 h. The mixture was cooled to room temperature, and then it was extracted with ether (2 × 100 mL). The aqueous layer was acidified with HCl and then extracted with CH_2Cl_2. The organic layer was dried, filtered, and evaporated to give an oil, which was crystallized from ether. The solid was collected by filtration and washed with cold ether to give 3.45 g (59%) of **5b**: mp 161–165 °C; NMR δ 8.6–8.8 (m, 3 H), 7.8–8.0 (m, 4 H), 7.4–7.7 (m, 4 H), 3.65 (m, 2 H_4), 2.52 (t, $J_{2,3}$ = 7.2, 2 H_2), 2.29 (m, 2 H_3); mass spectrum, m/e (relative intensity) 314 (70), 253 (38), 241 (100), 239 (76).

1,2-Dihydrobenzo[*g*]chrysen-4(3*H*)-one (6). Butyric acid **5b** (3.45 g) in 30 mL of $MeSO_3H$ was heated at 55 °C for 2.5 h, with exclusion of moisture. The mixture was cooled to room temperature and then poured onto ice. The mixture was extracted with CH_2Cl_2 (3 × 70 mL), and the combined organic extracts were washed with H_2O (100 mL), dried, filtered, and evaporated. The residue was dissolved in PhH, and the solution was filtered through a short column of silica gel. Additional benzene (250 mL) was used to remove all of the ketone from the column. Evaporation of the solvent gave 2.76 g (85%) of ketone **6**. If a deep yellow color remains at this point, it may be removed by washing the solid with cold Et_2O to give a cream-colored solid; mp 159–161.5 °C; NMR δ 9.22–9.26 (m, 1 H_5), 8.52–8.74 (m, 3 H), 7.98–8.05 (m, 2 H), 7.61–7.72 (m, 4 H), 3.72 (t, J_{app} = 5.6, 2 H_1), 2.88 (t, J_{app} = 6.7, 2 H_3), 1.96 (m, 2 H_2); mass spectrum, m/e

(18) Bachmann, W.; Kloetzel, M. *J. Am. Chem. Soc.* **1938**, *60*, 2204.

(relative intensity) 296 (66), 268 (14), 239 (100).

1-(2-Naphthyl)cyclopentene (7). Mg turnings (1.61 g, 0.0661 mol) were crushed and placed in a flame-dried three-neck round-bottomed flask equipped with a mechanical stirrer, a reflux condenser with a drying tube, and an addition funnel. The reaction was initiated by adding ca. 10% of the halide in a minimal volume of THF and heating with a heating mantle to sustain a reflux. The balance of the 2-bromonaphthalene (13.86 g total, 0.0669 mol) in dry THF (50 mL) was then added dropwise. Stirring was continued for 2 h at reflux. The mixture was cooled to room temperature and cyclopentanone (5.62 g, 0.0669 mol) in 30 mL of dry THF was added dropwise with stirring. The exothermic reaction was moderated by external cooling with an ice bath. The mixture was then stirred overnight at room temperature. Aqueous HCl was added, and the aqueous phase was extracted three times with ether (400 mL total). The ether layer was washed with brine, dried, filtered, and evaporated to give the alcohol 1-(2-naphthyl)cyclopentanol.

The crude alcohol, in 100 mL of PhH containing a few crystals of *p*-TsOH, was dehydrated by heating at reflux for 2 h. The reaction mixture was washed with H_2O and brine, and the organic phase was dried and evaporated. The crude product was purified by flash chromatography on silica gel, with petroleum ether as the developing solvent. This gave 11.16 g of alkene **7** (86%): NMR δ 7.69–7.88 (m, 4 H), 7.42–7.51 (m, 3 H), 6.34 (t, $J_{2,3}$ = 2.2, 1 H_2), 2.86 (m, 2 H), 2.61 (m, 2 H), 2.09 (m, 2 H_4).

4-(2-Naphthoyl)butyric Acid (8a). To a 500-mL three-necked flask equipped with an overhead mechanical stirrer were added alkene **7** (1.13 g, 0.00582 mole, 18-crown-6 ether (0.112 g, 0.00042 mol), and PhH (300 mL). Glass beads were then added in sufficient quantity to grind the solid reactants without binding the stirrer, followed by $KMnO_4$ (1.84 g, 0.0116 mol). Stirring was continued for 4 h at room temperature, followed by alternating addition of sodium bisulfite and 6 N HCl until unreacted $KMnO_4$ and MnO_2 were destroyed. When the solution became colorless, the layers were separated. The organic layer was saved, and the aqueous layer was extracted with CH_2Cl_2. The organic extracts were combined and extracted with 0.5 N NaOH until the aqueous layer became colorless and the extract was basic. The basic extracts were combined and acidified with aqueous HCl. The resulting aqueous phase was extracted with CH_2Cl_2, and the organic phase was washed with brine, dried, filtered, and evaporated to give 0.784 g of **8a** (56%), which was used without further purification: NMR δ 8.49 (s, 1 $H_{1'}$), 7.86–8.05 (m, 4 H), 7.58 (m, 2 H), 3.23 (t, J = 7.1, 2 H), 2.56 (t, J = 7.1, 2 H), 2.16 (m, 2 H).

Methyl 4-(2-Naphthoyl)butyrate (8b). Crude keto acid **8a** (2.66 g, 0.011 mol), MeOH (100 mL), and concentrated HCl (10 drops) were heated at reflux for 2 h. The MeOH was then removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. This solution was washed with H_2O, 5% $NaHCO_3$, and H_2O, dried, filtered, and evaporated. The residue was recrystallized from EtOH/petroleum ether to give 1.92 g of **8b** (68%), mp 86–88 °C.

Ethyl 5-(2-Naphthyl)-6-phenyl-5-hexenoate (9). In the manner described for **4**, except that a 16-h reflux period was sufficient, NaOEt prepared from Na (0.11 g, 0.0048 mol), benzyltriphenylphosphonium chloride (1.88 g, 0.0048 mol), and keto ester **8b** (0.701 g, 0.0027 mol) in dry EtOH (30-mL total volume), were reacted to give a crude product, which was purified by flash chromatography (twice) on silica gel, with PhH as eluting solvent. After evaporation of the PhH, 0.839 g (89%) of **9** was obtained, as a 56 (*E*):44 (*Z*) mixture: NMR δ 6.90 (s, 1 H, assigned to the *E* isomer), 6.56 (s, 1 H, assigned to the *Z* isomer); mass spectrum, *m/e* (relative intensity) 344 (67), 299 (12), 255 (38), 165 (100).

Ethyl 4-(6-Benzo[*c*]phenanthrenyl)butyrate (10a). In the manner described for **5a**, alkene **9** (0.830 g, 0.0024 mol), distilled cyclohexane (1 L), and I_2 (50 mg) were photolyzed for 40 h to give crude product, which was filtered through a short column of silica gel with 5% EtOAc in PhH. Evaporation of the solvent afforded 0.88 g of crude ester **10a**. The NMR spectrum showed a downfield multiplet at 9.01–9.10 (2 H) characteristic of H-1 and H-12 of benzo[*c*]phenanthrene.

4-(6-Benzo[*c*]phenanthrenyl)butyric Acid (10b). Crude ester **10a** (2.51 g, 0.0073 mol), H_2O (60 mL), and KOH (4 g, 0.071 mol) were heated at reflux for 1.5 h. Additional H_2O was added, and the mixture was extracted with ether. The aqueous phase was acidified with HCl and extracted with CH_2Cl_2. The CH_2Cl_2 phase was dried, filtered, and evaporated. The residue was crystallized from ether/petroleum ether to give 1.592 g of **10b** (73%): mp 120–122 °C; NMR δ 9.01–9.10 (m, $H_{1'}$ and $H_{12'}$), 8.10 (d, J = 8.9, 1 H), 8.02 (dd, J = 7.6, 1.9, 1 H), 7.96 (d, J = 9.0, 1 H), 7.94 (d, J = 8.8, 1 H), 7.74 (s, $H_{5'}$), 7.57–7.69 (m, 4 H), 3.27 (t, J = 7.7, 2 H), 2.55 (t, J = 7.2, 2 H), 2.20 (m, 2 H); mass spectrum, *m/e* (relative intensity) 314 (93), 241 (100).

7,8-Dihydrobenzo[*g*]chrysen-5(6*H*)-one (11). A mixture of 1.50 g of acid **10b** and 30 mL of $MeSO_3H$ were heated at 60 °C for 1.5 h, with exclusion of moisture. The mixture was cooled to room temperature and poured onto crushed ice (100 g). Additional H_2O (100 mL) was added, and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried, filtered, and evaporated, and the residue was purified by flash chromatography with benzene as the developing solvent. After removal of benzene, the residue was triturated with Et_2O to give 1.216 g (86%) of **11** as a light cream-colored solid: mp 138–140 °C; NMR δ 9.21 (d, $J_{3,4}$ = 7.8, H_4), 8.96 (m, 1 H), 8.86 (d, J = 7.92, 1 H), 8.11 (d, J = 8.9, 1 H), 8.02 (m, 1 H), 7.96 (d, J = 8.9, 1 H), 7.58–7.67 (m, 4 H), 3.48 (t, J_{app} = 6.1, 2 H_8), 2.87 (t, J_{app} = 6.8, 2 H_6), 2.35 (m, 2 H_7); mass spectrum, *m/e* (relative intensity) 296 (100), 268 (54), 239 (86).

1,2-Dihydrobenzo[*g*]chrysene (12). Ketone **6** (4.32 g, 0.0146 mol) was suspended in THF (40 mL) and MeOH (150 mL). The mixture was stirred magnetically and cooled in an ice bath, and then $NaBH_4$ (2.808 g, 0.0739 mol) was added in portions over 15–20 min. The ice bath was removed, and the mixture was stirred 1 additional h. A white precipitate formed and was collected by filtration and dissolved in CH_2Cl_2 (800–1000 mL). The CH_2Cl_2 phase was washed with H_2O, dried, filtered, and evaporated to give 3.585 g of crude 4-hydroxy-1,2,3,4-tetrahydrobenzo[*g*]-chrysene, mp 195–198 °C. The NMR spectrum showed H-4 at δ 5.77; mass spectrum, *m/e* (relative intensity) 298 (71), 280 (51), 241 (44), 239 (69), 120 (100).

The crude alcohol was suspended in a solution of a few crystals of *p*-TsOH in PhH (250 mL), and the mixture was stirred for 16 h at room temperature, with protection from light. The mixture was extracted with H_2O (2 × 100 mL), and the organic layer was dried, filtered, and evaporated. The residue was purified by flash chromatography with petroleum ether as the developing solvent to give 2.97 g of **12** (88% based on the alcohol), mp 140.5–143 °C. Additional **12** (0.528 g) was obtained by *p*-TsOH/PhH dehydration of the residue from the filtrate obtained in the preparation of 4-hydroxy-1,2,3,4-tetrahydrobenzo[*g*]chrysene. The overall yield of **12** (3.49 g) was 85% based on ketone **6**: UV spectrum in 95% EtOH 222 (2.66×10^4), 241 (3.86×10^4), 260 (3.57×10^4), 268 (4.01×10^4), 273 (4.08×10^4), 383 (sh, 2.96×10^4), 327 (sh, 1.08×10^4), 337 (1.54×10^4), 352 (1.46×10^4), 377 (1.5×10^3).

***trans*-3,4-Diacetoxy-1,2,3,4-tetrahydrobenzo[*g*]chrysene (13).** AgOAc (1.55 g, 0.00929 mol) and I_2 (1.18 g, 0.00464 mol) were added to dry PhH (75 mL). The mixture was stirred at room temperature for 20–30 min with protection from light and moisture, by which time the initial red color had disappeared. Alkene **12** (1.00 g, 0.00357 mol) was added, and the mixture was stirred at room temperature for 1 h. The mixture was then refluxed for 3 h and filtered hot. The filtrate was concentrated and then purified by flash chromatography on silica gel, with PhH as the initial solvent to remove nonpolar materials, followed by 5% EtOAc in PhH to remove **13**. Evaporation of solvents gave **13** as an aerosol (1.285 g, 90%). Crystallization from $CHCl_3$/petroleum ether gave **13**: mp 128.5–131 °C; NMR δ 8.60–8.77 (m, 3 H), 7.9–8.0 (m, 3 H), 7.6–7.7 (m, 4 H), 6.84 (d, $J_{3,4}$ = 3.1, 1 H_4), 5.48 (m, 1 H_3), 3.6–3.9 (m, 2 H_1), 2.19 (s, 3 H), 2.0–2.17 (m, 5 H); mass spectrum, *m/e* (relative intensity) 398 (11), 338 (22), 326 (11), 296 (99), 278 (50), 252 (53), 239 (100).

***trans*-3,4-Diacetoxy-3,4-dihydrobenzo[*g*]chrysene (14).** All glassware and the stirring bar were treated with dilute NH_4OH and dried prior to use. Tetrahydro diacetate **13** (180 mg, 0.452 mol), NBS (166 mg, 0.932 mmol), Na_2CO_3 (2 g), and a few milligrams of AIBN were added to CCl_4 (55 mL, freshly distilled from K_2CO_3). N_2 was bubbled through the mixture for 15 min, and then the mixture was heated at 62 °C for 4 h, with exclusion of moisture. Analysis of an aliquot by NMR spectroscopy indicated that **13** had been consumed. The mixture was cooled in an ice bath for 20 min and then DBN (2 mL) was added. The mixture was stirred at 0–5 °C for 1 h and at room temperature for 24 h.

EtOAc (250 mL) was added, and the organic phase was washed with H_2O (2 × 100 mL), 0.01 M HCl (2 × 100 mL), 1% NH_4OH (100 mL), and brine (2 × 100 mL), dried, filtered, and evaporated to give 170 mg of crude **14**, which was purified by flash chromatography on silica gel, with 5% EtOAc in PhH, to give 150 mg (83%) of pure dihydrodiol diacetate **14**: mp 154–156 °C; NMR, see Table I; mass spectrum, *m/e* (relative intensity) 396 (5); 336 (20); 294 (100).

***trans*-3,4-Dihydroxy-3,4-dihydrobenzo[*g*]chrysene (15).** Dihydrodiol diester **14** (253 mg) was added to MeOH (100 mL), which was cooled to 0 °C and saturated with NH_3. The reaction flask was capped with a balloon, and the mixture was stirred at room temperature for 16 h. The MeOH was removed under reduced pressure at room temperature, and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 phase was washed with H_2O, dried, filtered, and evaporated. The residue was purified by flash chromatography, with the silica gel wetted with PhH prior to loading of **15** as a solution in CH_2Cl_2. Initially, 5% EtOAc in PhH was used as a developing solvent to remove less polar materials, and then 50% EtOAc in petroleum ether was used to elute **15**. Removal of solvents gave 163 mg **15** (82%): mp 149–151 °C; NMR, see Table I; mass spectrum, *m/e* (relative intensity) 312 (48), 294 (34), 266 (100), 265 (76), 252 (42); UV spectrum in 95% EtOH (λ_{max}, ϵ_{max}) 223 (2.67×10^4), 268 (3.83×10^4), 278 (3.63×10^4), 290 (2.44×10^4), 313 (6.6×10^3), 327 (8.8×10^3), 343 (8.8×10^3). Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.50; H, 5.49.

7,8-Dihydrobenzo[*g*]chrysene (16). Tetrahydro ketone **11** (1.166 g, 0.00394 mol) was dissolved in THF (10 mL) and MeOH (60 mL). $NaBH_4$ (0.837 g, 0.022 mol) was added in portions, and the mixture was cooled with an ice bath to minimize foaming. The reaction flask was capped with a balloon, and the mixture was stirred at room temperature for 1 h. H_2O (20 mL) was added, followed by enough dilute HCl to make the mixture acidic. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase was dried, filtered, and evaporated to give a light yellow solid, which was triturated with petroleum ether and dried to give 1.066 g (91%) of 5-hydroxy-5,6,7,8-tetrahydrobenzo[*g*]chrysene: mp 158–162 °C; NMR δ 8.98 (d, J = 7.9, 2 H), 8.50 (d, J = 8.0, 1 H), 8.09 (d, J = 8.9, 1 H), 8.00 (dd, J = 6.8, 2.2, 1 H), 7.93 (d, J = 8.9, 1 H), 7.62 (m, 4 H), 5.61 (br s, 1 H), 3.40 (m, 1 H), 3.12 (m, 1 H), 2.02–2.33 (m, 5 H); mass spectrum, *m/e* (relative intensity) 298 (100), 280 (41). The alcohol (1.0035 g) was dissolved in benzene (100 mL), and a few crystals of *p*-TsOH were added. The reaction mixture was heated at 50 °C for 1 h, with exclusion of moisture. The mixture was cooled to room temperature and extracted with H_2O. The benzene phase was dried, filtered, and evaporated. The residue was purified by flash chromatography on silica gel, with petroleum ether as developing solvent. Removal of solvent gave 0.855 g of **16** (91%) as a light green oil that would not solidify, even at −20 °C: NMR δ 9.02 (m, 2 H), 8.30 (dd, J = 7.0, 2.5, 1 H), 8.13 (d, J = 9.0, 1 H), 8.00 (dd, J = 7.7, 1.8, 1 H), 7.92 (d, J = 8.9, 1 H), 7.57–7.90 (m, 4 H), 7.37 (d, $J_{5,6}$ = 9.9, 1 H_5), 6.41 (m, $J_{5,6}$ = 9.9, $J_{6,7}$ = 4.8, 1 H_6), 3.34 (t, J_{app} = 8.8, 2 H_8), 2.54 (m, 2 H_7); mass spectrum, *m/e* (relative intensity) 280 (100), 265 (5.3); UV spectrum in MeOH (λ_{max}, ϵ_{max}) 278 (5.54×10^4), 287 (5.19×10^4), 299 (4.74×10^4), 318 (1.11×10^4), 334 (1.26×10^4), 351 (1.26×10^4).

***trans*-5,6-Diacetoxy-5,6,7,8-tetrahydrobenzo[*g*]chrysene (17).** AgOAc (0.496 g, 0.00297 mol) and I_2 (0.377 g) were stirred in dry PhH (15 mL) for 15–30 min, alkene **16** (0.320 g, 0.0011 mol) was added, and the mixture was stirred at room temperature for 1 h. The mixture was then refluxed for 20 h and filtered hot. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel with PhH to elute nonpolar compounds and then 5% EtOAc in PhH to elute **17**. Evaporation of the solvents gave 0.364 g of **17** (80%) as a clear aerosol. Crystallization from EtOAc/petroleum ether at −20 °C gave **17** as a white powder: mp 171–175 °C; NMR δ 9.01 (m, 2 H), 8.11 (d, J = 9.0, 1 H), 7.95–8.05 (m, 3 H), 7.63–7.69 (m, 4 H), 6.69 (d, $J_{5,6}$ = 3.3, 1 H_5), 5.41 (m, 1 H_6), 3.28–3.43 (m, 2 H_8), 2.17–2.44 (m, 2 H_7), 2.12 (s, 3 H), 2.01 (s, 3 H); mass spectrum, *m/e* (relative intensity) 398 (11), 338 (36), 296 (100).

***trans*-5,6-Diacetoxy-5,6-dihydrobenzo[*g*]chrysene (18).** Due to the apparent high sensitivity of compounds in this sequence to acid, all glassware was washed with dilute NH_4OH and H_2O and then dried prior to use. $NaHCO_3$ (0.5 g), **17** (119 mg, 0.299 mmol), and NBS (69 mg, 0.388 mmol) were added to 30 mL of CCl_4, and the mixture was heated to 55 °C for 2.5 h, with exclusion of moisture. The mixture was extracted with H_2O, and the organic phase was dried, filtered, and evaporated. The crude residue, which had peaks in the mass spectrum at *m/e* 478 and 476, indicative of monobromination, was dissolved in dry THF (25 mL), and 200 drops of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were added. The mixture was flushed with Ar and placed in a freezer at −20 °C for 16 h and at 0 °C for 2 h. EtOAc (20 mL) was added, and the organic layer was washed with H_2O (2 × 20 mL), 1 N HCl (2 × 30 mL), 5% $NaHCO_3$ (20 mL), and H_2O (20 mL). The organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography with dry column grade silica gel, with 0.7% EtOAc in PhH as the solvent. Evaporation of the solvent gave 60 mg (51%) of **18** as a white solid: mp 133–136 °C;, NMR, see Table I; mass spectrum, *m/e* (relative intensity) 396 (4), 336 (24), 294 (100), 263 (54). Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.74; H, 5.19.

***trans*-5,6-Dihydroxy-5,6-dihydrobenzo[*g*]chrysene (19).** Dihydrodiol diacetate **18** (17 mg) was dissolved in MeOH (10 mL). The mixture was cooled to 0 °C and saturated with NH_3. The reaction flask was capped with a balloon and stirred overnight at room temperature. The MeOH was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed with H_2O and brine, dried, filtered, and evaporated. The residue was purified by column chromatography on silica gel, with 30% EtOAc in PhH as the developing solvent. After evaporation of solvents and treatment of the residue with benzene/petroleum ether, 11.9 mg (89%) of **19** was obtained as a white solid: mp 77–80 °C; NMR, see Table I (the second OH absorption is evidently hidden under the H_2O peak); mass spectrum, *m/e* (relative intensity) 312 (0.8), 294 (100); UV spectrum in 95% EtOH (λ_{max}, ϵ_{max}) 219 (5.22×10^4), 246 (6.29×10^4), 251 (sh, 5.60×10^4), 286 (6.79×10^4), 294 (7.16×10^4), 310 (sh, 2.25×10^4), 323 (sh, 1.38×10^4), 343 (8.4×10^3), 370 (8.7×10^2).

Benzo[*g*]chrysene (20). Benzo[*g*]chrysene was prepared by oxidation of both 1,2-dihydrobenzo[*g*]chrysene (**12**) and 7,8-dihydrobenzo[*g*]chrysene (**16**) with 1.1 molar equiv of DDQ in PhH at room temperature. In both cases, the reaction mixture was filtered after overnight with stirring, the benzene was removed, and the residue was purified by chromatography on silica gel, with petroleum ether as the developing solvent. This gave benzo[*g*]chrysene (189 mg from 258 mg of **16**, 74%, and 187 mg from 200 mg of **12** 94%): mp 112–114 °C (lit.[19] mp 114.5–115 °C); NMR spectral values identical with those reported in the literature.

5,6-Epoxy-5,6,7,8-tetrahydrobenzo[*g*]chrysene (21). To a solution of freshly distilled THF (9 mL) and H_2O (3 mL) was added 67.2 mg (0.240 mmol) of 7,8-dihydrobenzo[*g*]chrysene (**16**), followed by *N*-bromoacetamide (36.7 mg, 0.264 mmol) and 1 drop of concentrated HCl. The mixture was stirred at room temperature for 45 min, then EtOAc (10 mL) was added, and the organic layer was washed with H_2O (3 × 10 mL). The reaction mixture was purified by flash chromatography on silica gel, with PhH as the solvent. After removal of solvents, *trans*-6-bromo-5-hydroxy-5,6,7,8-tetrahydrobenzo[*g*]chrysene was obtained as a white solid: mp 72–74.5 °C; NMR δ 9.00 (d, J = 6.7, 2 H), 8.41 (d, J = 8.0, 1 H), 8.09 (d, J = 9.0, 1 H), 8.02 (m, 1 H), 7.96 (d, J = 9.0, 1 H), 7.60–7.72 (m, 4 H), 5.72 (dd, J = 5.5, 3, 1 H), 4.76 (m, 1 H), 3.40–3.48 (m, 2 H), 2.66–2.71 (m, 1 H), 2.42–2.49 (m, 2 H); mass spectrum (12 eV), *m/e* (relative intensity) 378 (52), 376 (54), 360 (100), 358 (100), 279 (75), 278 (95). Anal. Calcd for $C_{22}H_{17}BrO$: C, 70.04; H, 4.54; Br, 21.18. Found: C, 69.93; H, 4.80; Br, 20.99.

The bromohydrin (50.8 mg) was dissolved in dry THF (6 mL) in a 10-mL flask containing sufficient Amberlite IRA-400 ($^-$OH) resin so that the THF barely covered the resin. The mixture was stirred magnetically for 3 h, with exclusion of moisture and then was filtered. The Amberlite resin was washed with an additional 10 mL of THF, and the combined THF washings were evaporated to give 34.8 mg of **21** as a white solid: mp 46–48 °C; NMR δ 9.00–9.05 (m, 2 H), 8.52 (d, J = 8.7, 1 H), 8.09 (d, J = 8.9, 1 H),

(19) Clar, E. *Polycyclic Hydrocarbons*; Academic: New York, 1964; p 266.

8.00–8.03 (m, 1 H), 7.92 (d, J = 9.0, 1 H), 7.61–7.72 (m, 4 H), 4.83 (d, J = 4.5, 1 H), 3.96 (m, 1 H), 3.47–3.55 (m, 1 H), 2.96–3.00 (m, 1 H), 2.65–2.72 (m, 1 H), 1.98–2.05 (m, 1 H); mass spectrum (12 eV), m/e (relative intensity) 296 (100), 268 (26), 254 (22); high-resolution mass spectrum calcd for $C_{22}H_{16}O$ 296.1206, found 296.1220; UV spectrum in 95% EtOH (λ_{max}, ϵ_{max}) 217 (3.74×10^4), 225 (2.24×10^4), 276 (4.25×10^4), 283 (4.66×10^4), 302 (sh, 1.03×10^4), 316 (8.7×10^3), 326 (sh, 5.4×10^3).

(±)-3α,4β-Dihydroxy-1β,2β-epoxy-1,2,3,4-tetrahydrobenzo[g]chrysene (BgCh 3,4-diol 1,2-epoxide-1) (23). (a) Via Bromotriol. Dihydrodiol **15** (31.4 mg, 0.101 mmol) and NBA (13.9 mg, 0.101 mmol) were dissolved in freshly distilled THF (6 mL) and H_2O (2 mL). The mixture was cooled to 0 °C and 1 drop of 6 N HCl was added. The reaction mixture was stirred for 1 h and then poured into EtOAc (10 mL). The organic phase was extracted with H_2O (2 × 8 mL) and brine (8 mL), dried, filtered, and evaporated. The residue was purified by dry column chromatography on silica gel, first with PhH, then with 30% EtOAc, and with 50% EtOAc in PhH as the eluting solvents. After removal of the solvents, 10.5 mg (26%) of (±)-2α-bromo-1β,3α,4β-trihydroxy-1,2,3,4-tetrahydrobenzo[g]chrysene (**22**) was obtained as an off-white solid: mp 87–90 °C; NMR δ 8.99 (m, 1 H), 8.76 (m, 1 H), 8.66 (d, J = 9.2, 1 H), 8.42 (m, 1 H), 8.01 (m, 2 H), 7.35–7.75 (m, 4 H), 6.26 (dd, J = 5.7, 5.4, 1 H), 5.69 (dd, J = 4.2, 3.7, 1 H), 4.84 (m, 2 H), 3.30 (d, J = 5.7, 1 H), 2.61 (d, J = 6.4, 1 H), 2.57 (d, J = 4.2, 1 H); mass spectrum (12 eV), m/e 374, 372 (no molecular ion was observed).

Amberlite IRA-400 ($^-$OH) (0.75 g) and sufficient dry THF to just cover the resin were placed in a 25-mL round-bottom flask. Bromo triol **22** (10.0 mg) was dissolved in a minimal volume of dry THF and added to the flask. The mixture was stirred for 3 h at room temperature with exclusion of moisture and then filtered. Evaporation of the THF gave 6.3 mg (79%) of diol epoxide **23**: mp 134–137 °C; NMR, see Table II, additional resonances not cited there are δ 8.64–8.77 (m, 3 H), 8.37–8.41 (m, 1 H), 8.05 (m, 2 H), 7.64–7.77 (m, 4 H), 2.85 (d, J = 11.9, OH_4), 1.38 (d, J = 8.7, OH_3); high-resolution mass spectrum calcd for $C_{22}H_{16}O_3$ 328.1099, found 328.1093; UV spectrum in 95% EtOH (λ_{max}, ϵ_{max}) 217 (2.19×10^4), 267 (5.25×10^4), 302 (6.1×10^3), 315 (7.6×10^3), 327 (7.4×10^3).

(b) From Bromohydrin 26 Obtained from Dihydrodiol Diacetate 14. Dihydrodiol diacetate **14** (94.6 mg, 0.2388 mmol) was added to a solution of freshly distilled THF (40 mL) and H_2O (20 mL). The mixture was cooled to 5 °C and NBA (40 mg, 0.289 mmol) was added, followed by 2 drops of concentrated HCl. The mixture was stirred at 0–5 °C for 20 h. EtOAc (250 mL) was added, and the organic phase was washed with brine until the aqueous extracts were neutral. The organic phase was dried, filtered, and evaporated. The residue was purified by flash chromatography on silica gel, with PhH (400 mL), 2% EtOAc/PhH (400 mL), and 3% EtOAc/PhH as the eluting solvents. Compounds **27** (20.6 mg, 23%), **25** (37.4 mg, 32%), and **26** (15 mg, 13%) were eluted successively, in addition to aromatized products (<3%), which were eluted first. For (±)-3α,4β-diacetoxy-2β-bromo-1α-hydroxy-1,2,3,4-tetrahydrobenzo[g]chrysene (**25**), the following physical data were obtained: mp 136–140 °C; R_f 0.36 (5% EtOAc/benzene, silica gel); NMR δ 8.86 (d, J = 8.03, 1 H), 8.75 (d, J = 7.9, 1 H), 8.65 (d, J = 9.2, 1 H), 7.99–8.01 (m, 2 H), 7.84 (d, J = 7.6, 1 H), 7.6–7.8 (m, 4 H), 6.91 (d, J = 4.5, 1 H), 6.25 (dd, J = 6.9, 6.1, 1 H), 5.88 (dd, J = 4.5, 9.4, 1 H), 4.29 (dd, J = 6.9, 9.4, 1 H), 3.05 (d, J = 6.1, 1 OH), 2.24 (s, 3 H), 2.05 (s, 3 H); mass spectrum, m/e (relative intensity) 494 (1.3), 492 (2.2), 416 (13), 374 (88), 294 (100); high-resolution mass spectrum calcd for $C_{26}H_{21}O_5Br$ 494.0546 and 492.0566, observed 494.0551 and 492.0572. For (±)-3α,4β-diacetoxy-2α-bromo-1β-hydroxy-1,2,3,4-tetrahydrobenzo[g]chrysene (**26**), the following physical data were obtained: mp 182–186 °C; R_f 0.23 (5% EtOAc/PhH); NMR δ 9.47 (d, J = 8.6, 1 H), 8.81 (d, J = 7.7, 1 H), 8.68 (d, J = 8.9, 1 H), 8.25 (d, J = 9.4, 1 H), 8.0–8.05 (m, 2 H), 7.65–7.78 (m, 4 H), 6.52 (dd, J = 5.9, 4.0, 1 H), 6.20 (d, J = 5.9, 1 H), 5.91 (dd, J = 8.9, 4.8, 1 H), 5.45 (d, J = 8.9, 1 OH), 4.88 (dd, J = 4.8, 4.0, 1 H), 2.26 (s, 3 H), 2.10 (s, 3 H); mass spectrum, m/e (relative intensity) 494 (10.1), 492 (8.1), 466 (4.9), 432 (2.6), 416 (3.5), 372 (26), 311 (100), 294 (30); high-resolution mass spectrum calcd for $C_{26}H_{21}O_5Br$ 494.0546 and 492.0566, observed 494.0551 and 492.0572. For *trans*-3,4-diacetoxy-2-bromo-3,4-dihydrobenzo[g]chrysene (**27**), the following physical data were obtained: mp 198–202 °C (recrystallization from EtOAc); R_f 0.51 (5% EtOAc/PhH); NMR δ 8.76 (d, J = 8.3, 1 H), 8.66 (d, J = 9.1, 1 H), 8.45 (d, J = 7.4, 1 H), 8.02–8.15 (m, 3 H), 7.99 (s, 1 H), 7.65–7.73 (m, 4 H), 6.85 (d, J = 2.4, 1 H_4), 5.87 (d, J = 2.4, 1 H_3), 2.13 (s, 3 H), 2.05 (s, 3 H); mass spectrum, m/e (relative intensity) 476 (0.4), 474 (0.3), 374 (32), 372 (32), 294 (17), 276 (9.7), 263 (18).

To a 100-mL round-bottomed flask containing Amberlite IRA 400 ($^-$OH) (10 g), barely covered with dry THF was added bromohydrin **26** (25.2 mg) dissolved in dry THF (2 mL). The mixture was stirred under N_2 at room temperature for 16 h and then was filtered. The filtered resin was washed with dry THF (3 × 15 mL), and the THF filtrates were combined and evaporated to give 20.1 mg (96%), of pure (±)-3α,4β-diacetoxy-1β,2β-epoxy-1,2,3,4-tetrahydrobenzo[g]chrysene (**29**), mp 218–222 °C.

A solution of diacetate epoxide **29** (24.3 mg) in MeOH (20 mL) was cooled to 0 °C. NH_3 was bubbled through the solution for 1 h, and the solution was stirred at 0 °C for an additional 2 h and at 10 °C for 2 h. The MeOH was evaporated, and the residue was dissolved in EtOAc (80 mL). The EtOAc phase was washed with brine (2 × 30 mL), dried, filtered, and evaporated to give BgCh 3,4-diol 1,2-epoxide-1 **23**; (18.2 mg, 94%): mp 133–136 °C; NMR spectrum identical with that of **23** produced by method (a) (vide supra).

(±)-3α,4β-Dihydroxy-1α,2α-epoxy-1,2,3,4-tetrahydrobenzo[g]chrysene (Benzo[g]chrysene 3,4-diol 1,2-epoxide-2) (24). (a) From *m*-CPBA Treatment of Dihydrodiol 15. Dihydrodiol **15** (13.3 mg, 0.043 mmol) was dissolved in dry THF (1.0 mL). The solution was cooled to 10 °C and *m*-CPBA (73.3 mg, 0.426 mmol) was added. The solution was stirred for 1 h, with exclusion of moisture, Et_2O (5 mL) was added, and the organic phase was washed with H_2O (5 mL), 2% NaOH (2 × 5 mL), and H_2O (5 mL), dried, filtered, and evaporated. The residue was dissolved in 300 μL of dry THF, and 25-μL aliquots were injected on an Altex Ultrasphere-Si 10 mm × 25 cm column, which was cooled by a coil of circulating cold water. A flow rate of 4 mL/min of 40% THF in hexane was used to elute the diol epoxides. Removal of solvent gave 7.0 mg of an 84:16 mixture of diol epoxides **23** and **24** (major): NMR, see Table II. Other absorptions not cited in Table II are δ 8.70–8.86 (m, 2 H), 8.38–8.43 (m, 1 H), 8.05 (m, 2 H), 7.77 (m, 4 H), 2.86 (d, J = 8.3, OH_3), 1.90 (d, J = 4.4, OH_4); high-resolution mass spectrum calcd for $C_{22}H_{16}O_3$ 328.1099, found 328.1083.

(b) From Bromohydrin 25 from Dihydrodiol Diacetate 14. To a 100-mL round-bottomed flask containing Amberlite 400 ($^-$OH) (12 g), barely covered with dry THF, was added bromohydrin **25** (56 mg, 0.114 mmol; for preparation of **25**, see section b under preparation of BgCh diol epoxide-1, **23**) dissolved in dry THF (2 mL). The mixture was stirred, under N_2, for 24 h at room temperature and then was filtered. The filtered resin was washed with dry THF (3 × 15 mL). The THF filtrates were combined and evaporated, leaving 44.4 mg (95%), of pure (±)-3α,4β-diacetoxy-1α,2α-epoxy-1,2,3,4-tetrahydrobenzo[g]chrysene (**28**), mp 144–148 °C.

The above diacetate epoxide, **28** (44.4 mg) was dissolved in MeOH (50 mL), which was cooled to 0 °C. NH_3 was bubbled through the solution for 1 h, and the mixture was stirred an additional 3 h at 0 °C and 40 min at 10 °C. The MeOH was evaporated, and the residue was dissolved in EtOAc (100 mL). The EtOAc solution was washed with brine (2 × 50 mL), dried, and evaporated, leaving 32.3 mg (91%) of BgCh 3,4-diol 1,2-epoxide-2 (**24**): mp 165–168 °C after trituration with ether/petroleum ether; NMR spectrum identical with that of **24** obtained by *m*-CPBA treatment of dihydrodiol **15**; UV spectrum of **24** in 95% EtOH (λ_{max}, ϵ_{max}) 216 (2.93×10^4), 265 (7.76×10^4), 297 (9.1×10^3), 313 (1.12×10^3), 326 (7.8×10^3).