Synthesis of Benzo[g]chrysene, Benzo[g]chrysene 9,10-Oxide and Benzo[g]chrysene 1,2:9,10-Dioxide

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Benzo[g]chrysene has been synthesised and used in the preparation of the K-region arene oxide, benzo[g]chrysene 9,10-oxide. Attempts to synthesise the fjord region arene oxide, benzo[g]chrysene 1,2-oxide, were unsuccessful but a fjord region diarene oxide, benzo[g]chrysene 1,2:9,10-dioxide has been obtained.

Benzo[g]chrysene (**1**) is the simplest member of the polycyclic aromatic hydrocarbon (PAH) series to possess both bay and fjord regions. This carcinogenic[1,2] compound has been identified as one of the PAH components present in crude oil fractions.[3] Metabolism of PAHs in mammals occurs initially by the formation of arene oxides of which there are seven distinct types in benzo[g]chrysene. As part of a continuing study of the mechanism and stereochemistry of metabolism of PAHs,[4] the synthesis of arene oxides of benzo[g]chrysene (none of which have previously been synthesised) has been undertaken.

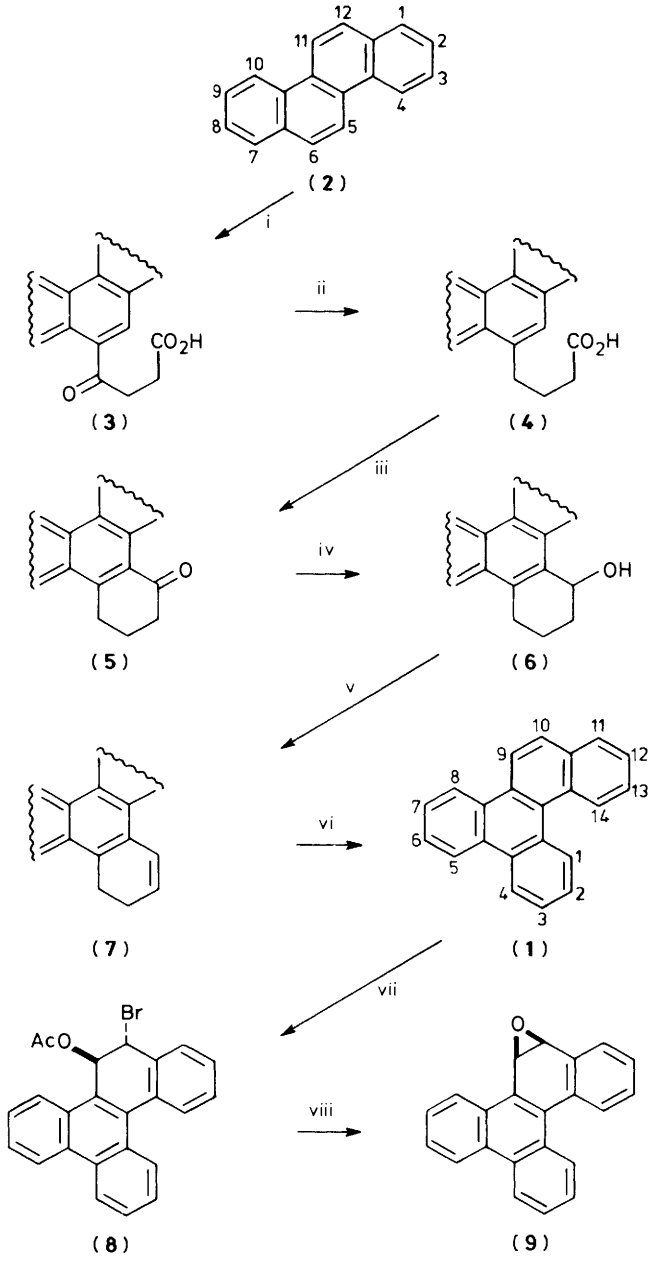
Benzo[g]chrysene (**1**) (also described as 1,2-benzochrysene, 1.2, 3.4-dibenzophenanthrene, and 1.2,3.4,5.6-tribenzonaphthalene in earlier literature[5]) has previously been synthesised by several methods.[6–10] In principle, synthesis of benzo[g]chrysene from the commercially available PAH chrysene (**2**) appears to be a useful synthetic method. In practice, previous attempts to synthesis benzo[g]chrysene (**1**) from (**2**) proved to be unsuccessful since the fjord-region alcohol (**6**), which was formed by the reaction sequence (**2**) ⟶ (**6**) (see Scheme 1), could not be dehydrated.[11] In view of previous observations from these laboratories on the ease of dehydration of similar tetrahydro alcohols (including bay region alcohols[12]) and the ability of substitution and dehydrobromination reactions to occur normally in the hindered fjord region,[4] the dehydration problem encountered by Cook and Graham has been re-examined.

Chrysene (**2**) was converted *via* 3-chrysen-6-ylcarbonylpropanoic acid (**3**) and 4-chrysen-6-ylbutanoic acid (**4**) into the ketone (**5**) in either comparable or better yields than previously reported using modifications of the literature methods.[11] Attempts to reduce the ketone (**5**) to 1,2,3,4-tetrahydrobenzo[g]chrysene using either Clemmensen[13] or Wolff-Kishner[11] reduction conditions yielded only the alcohol (**6**). This anomalous behaviour appears to be in accord with the present observations as ketone (**5**) was not reduced by sodium borohydride under normal conditions (ambient temperature). Prolonged treatment with $LiAlH_4$ at an elevated temperature [72 h in refluxing tetrahydrofuran (THF)] was required for complete reduction of the ketone (**5**). Despite the earlier report,[11] the dehydration of the alcohol (**6**) to yield the alkene (**7**) occurred in good yield (93%) under normal conditions (HCl, glacial acetic acid, 90 °C, 1.5 h). Thus, while the reduction reactions of ketones appear to be affected by steric congestion in the fjord region, bromination and dehydrobromination reactions (in the fjord region of benzo[c]phenanthrene[4]) and dehydration reactions appear to proceed normally. Dehydrogenation of 3,4-dihydrobenzo[g]chrysene (**7**) to form benzo[g]chrysene (**1**) proceeded in the expected manner using 2,3-dichloro-5,6-dicyano *p*-quinone (DDQ).

Synthesis of the K-region arene oxide (**9**) of benzo[g]chrysene involved the formation of a bromoacetate adduct by treatment of the parent PAH (**1**) with *N*-bromoacetamide. By analogy with the reaction of *N*-bromoacetamide with the K-region of other PAHs,[14] it was expected that compound (**8**) would be formed exclusively from opening of the cyclic bromonium intermediate. The n.m.r. spectrum of (**8**) was consistent with this expectation. Treatment of the bromoacetate (**8**) with sodium methoxide gave the K-region arene oxide, benzo[g]chrysene 9,10-oxide (**9**), as a crystalline product whose structure was confirmed by n.m.r. and mass spectral analysis and by rearrangement to a phenolic product upon treatment with trifluoroacetic acid.

There is at present no evidence from the isolated products to suggest that metabolism occurs at the fjord regions of PAHs (*e.g.* benzo[c]phenanthrene[4]) and thus fjord region arene oxides do not appear to have been synthesised by either enzymatic or non-enzymatic methods. The dihydrobenzo[g]chrysene (**7**) was used as a synthetic precursor in the attempted synthesis of the fjord region arene oxide, benzo[g]chrysene 1,2-oxide (Scheme 2). Using an equimolar quantity of *N*-bromoacetamide, reaction with compound (**7**) gave only the bromoacetate (**10**) indicating that addition at the 1,2-bond in the fjord region was faster than addition at the K-region (9,10-bond). Treatment of the bromoacetate (**10**) with *N*-bromosuccinimide yielded the insoluble succinimide by-product normally associated with a successful bromination. However, n.m.r. and t.l.c. analysis of the product indicated that a mixture of compounds was present, none of which appeared to be the desired dibromoacetate (**11**). This conclusion was confirmed by treatment of the product mixture with sodium methoxide. The fjord-region arene oxide (**12**) was not among the unidentified 'dehydrobromination' products. Similar results were obtained during successive attempts to synthesise compound (**12**) by this route. Thus, it appears that the dibromoacetate intermediate (**11**) may well have been formed initially but under the reaction conditions had decomposed totally to a mixture of products. No obvious reason for the failure to synthesise (**12**) by this method can be provided. The instability of compound (**11**) may however be related to the strain imposed upon the molecule by having a bromo acetate moiety in the fjord region.

Treatment of the alkene (**7**) with a 0.35 molar excess of *N*-bromoacetamide gave a mixture of the bromoacetate (**10**), 16% yield), the dibromo diacetate (**13**), (34% yield) and a trace of benzo[g]chrysene (**1**), (3%) which was separated by preparative t.l.c. The dibromodiacetate (**13**) was clearly formed by addition at the 9,10-bond of the bromoacetate (**10**) and is probably a mixture of two isomers [structure (**13**) in Scheme 2 shows only one isomer with bromine atoms in a *trans* relationship]. By contrast with compound (**10**), benzylic bromination of the dibromo diacetate mixture (**13**) occurred to yield an isomeric



Scheme 1. i, Succinic anhydride–$AlCl_3$–CH_2Cl_2; ii, N_2H_4–KOH–diethylene glycol; iii, PCl_5–$SnCl_4$–C_6H_6; iv, $LiAlH_4$–THF; v, AcOH–HCl; vi, DDQ–C_6H_6; vii, *N*-bromoacetamide, AcOH; viii, NaOMe–THF

mixture of compound (**14**) which was sufficiently stable to be characterised by n.m.r. analysis before being treated with sodium methoxide. The diarene oxide (**15**) was obtained as a crystalline product in 60% yield and was characterised both by n.m.r. analysis and by the formation of diphenols upon acidification. No evidence was obtained from the n.m.r. spectrum of (**15**) which would allow the relative *cis* or *trans* geometry to be distinguished or assigned. Both isomers are thus assumed to be present (only the *trans* isomer is shown in Scheme 2).

From an inspection of molecular models of compounds (**10**) and (**13**) it appears that the latter molecule exhibits greater conformational mobility and thus may be less strained. This may account for the greater stability of the tribromo diacetate (**14**) compared with dibromo acetate (**11**) and thus the successful synthesis of the fjord-region arene oxide, benzo[*g*]chrysene 1,2:9,10-dioxide (**15**).

The diarene oxides previously reported have all been di-K-region arene oxides of PAHs, *e.g.* pyrene,[15,16] benzo[*a*]pyrene[17] and dibenz[*a,h*] anthracene.[18] The synthesis of compound (**15**) indicates that alternative types of diarene oxides (*e.g.* K-region: non-K-region, K-region: bay region, and K-region: fjord region types) may be synthesised by the present method.

A diarene oxide metabolite of a PAH of similar type to compound (**15**) has not yet been reported. The recent detection[19] and synthesis[20,21] of a PAH metabolite having both epoxide groups on one ring (naphthalene 1,2:3,4-dioxide)[19] however suggests that diarene oxides having epoxide groups on different rings should not be excluded as potential products of metabolism.

Experimental

^1H n.m.r. spectra were obtained using a Bruker WH250 instrument with tetramethylsilane as internal reference. Mass spectral data were recorded at 70eV using an AEI-MS902 (updated by V.G. Instruments) instrument. Light petroleum refers to that fraction boiling in the range 40—60 °C.

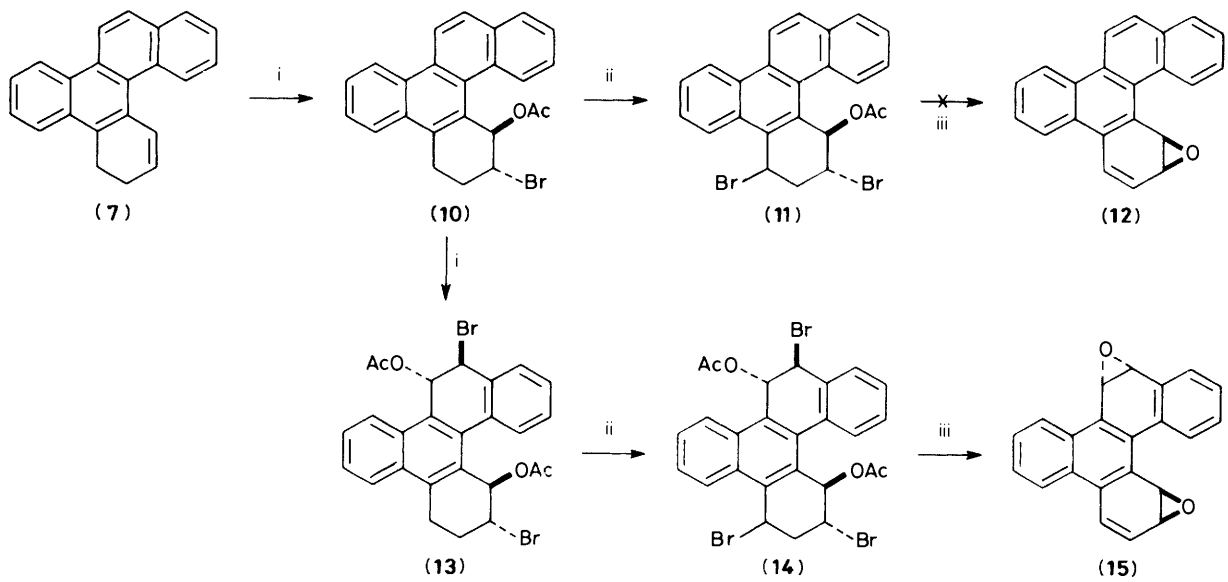
3-*Chrysen*-6-*ylcarbonylpropanoic Acid* (**3**).—The keto acid (**3**) was obtained by stirring a suspension of chrysene (11.4g, 50 mmol) and succinic anhydride (6.0 g, 50 mmol) in dry dichloromethane (200 cm^3) at 0 °C with $AlCl_3$ (16.0g, 120 mmol). After refluxing for 16 h, the keto acid (**3**) was obtained by the standard work-up procedure and finally purified by column chromatography on Florisil ($CHCl_3$ as eluant) to yield (**3**) as a crystalline solid (9.0 g, 55%), m.p. 194—195 °C (MeOH) (lit.,[13] m.p. 197—198 °C); δ_H [$(CH_3)_2SO$] 2.70 (2H, m, 2-H), 3.59 (2H, m, 3-H), and 7.72—9.06 (11 H, m, Ar).

4-*Chrysen*-6-*ylbutanoic Acid* (**4**).—The keto acid (**3**) (7.25 g, 20 mmol) was refluxed (1.5 h) in the presence of 99% hydrazine hydrate (7.25 g, 220 mmol) potassium hydroxide (5.2 g, 93 mmol) in diethylene glycol (125 cm^3). The reaction mixture was distilled until the temperature of the distillate reached 200 °C and the mixture was refluxed for a further period of 4 h. Acidification (50% HCl) and purification by column chromatography on Florisil (diethyl ether as eluant) gave the acid (**4**) as a crystalline product (6.7 g, 97%), m.p. 206—207 °C (Et_2O) (lit.,[13] 208—209 °C); δ_H($CDCl_3$) 2.23 (2 H, quint., *J* 7.3 Hz, 3-H), 2.55 (2 H, t, $J_{1,2}$ 7.2 Hz, 2-H), 3.34 (2 H, t, 7.6 Hz, 4-H), and 7.47—8.85 (11 H, m, Ar).

1-*Oxo*-1,2,3,4-*tetrahydrobenzo*[g]*chrysene* (**5**).—Cyclisation of the acid (**4**) (5.0 g, 16 mmol) in accordance with the literature method (PCl_5, $SnCl_4$, benzene) yielded the ketone (**5**) which was purified by column chromatography (Florisil, using light petroleum–diethyl ether as eluant); yield 3.0 g (64%), m.p. 220—221 °C (lit.,[13] m.p. 220—221 °C); δ_H($CDCl_3$) 2.46 (2 H, p, *J* 6.2 Hz, 3-H), 2.99 (2 H, t, *J* 6.8 Hz, 2-H), 3.37 (2 H, t, *J* 6.0 Hz, 4-H), and 7.45—8.75 (10 H, m, Ar).

1-*Hydroxy*-1,2,3,4-*tetrahydrobenzo*[g]*chrysene* (**6**).—A solution of ketone (**5**) (1.2 g, 4 mmol) in dry THF (10 cm^3) was added dropwise to the stirred suspension of $LiAlH_4$ (0.7 g) in dry THF (40 cm^3). The reaction mixture was refluxed for 72 h, the excess of $LiAlH_4$ was decomposed with water, and the product alcohol (**6**) was obtained upon drying and concentration of the filtrate. Recrystallisation from MeOH gave (**6**) (1.1 g, 91%), m.p. 174—175 °C (lit.,[13] m.p. 178—180 °C); δ_H($CDCl_3$) 1.70—2.50 (4 H, m, 2-H and 3-H), 3.4 (2 H, m, 4-H), 5.83 (1 H, m, 1-H), 7.58—8.76 (9 H, m, Ar), and 9.52 (1 H, d, Ar).

3,4-*Dihydrobenzo*[g]*chrysene* (**7**).—The alcohol (**6**) (0.8 g, 2.7



Scheme 2. i, *N*-Bromoacetamide–AcOH; ii, *N*-bromosuccinimide–CCl_4; iii, NaOMe–THF

mmol) in glacial acetic acid (30 cm^3) and conc. HCl (1 cm^3) was stirred for 1.5 h at 90 °C. Upon cooling the product was filtered off and purified by chromatography using Florisil and hexane as solvent. Recrystallisation from pentane gave compound (**7**) (0.7 g, 93%), m.p. 128—129 °C (Found: C, 94.1; H, 5.85. $C_{22}H_{16}$ requires C, 94.3; H, 5.7%), $\delta_H(CDCl_3)$ 2.60 (2 H, m, 3-H), 3.25 (2 H, t, *J* 8.4 Hz, 4-H), 6.32 (1 H, m, 2-H), 7.30 (1 H, d, $J_{1,2}$ 9.6 Hz, 1-H), and 7.54—8.78 (10 H, m, Ar).

Benzo[g]*chrysene* (**1**).—A mixture of 3,4-dihydrobenzo[*g*]-chrysene (**7**) (0.2 g, 0.71 mmol) and DDQ (0.2 g, 0.88 mmol) was refluxed in dry benzene (20 cm^3) for 1 h, cooled and filtered. The concentrated and dried filtrate was purified by chromatography (Florisil, eluted with hexane) to yield benzo[*g*]chrysene (**1**) (0.12 g, 60%), m.p. 114 °C (glacial acetic acid) (lit.,[5] m.p. 114.5—115.5 °C) (Found: C, 94.8; H, 5.1. Calc. for $C_{22}H_{14}$: C, 95.0; H, 5.0%), $\delta_H(CDCl_3)$ 7.57—7.75 (6 H, m, 2-H, 3-H, 7-H, 12-H and 13-H), 8.02 (2 H, m, 10-H and 11-H), 8.61—8.77 (4 H, m, 4-H, 5-H, 8-H, and 9-H), and 8.90—8.97 (2 H, m, 1-H and 14-H).

9-*Acetoxy*-10-*bromo*-9,10-*dihydrobenzo*[g]*chrysene* (**8**).—*N*-Bromoacetamide (0.029 g, 0.21 mmol) was added to a stirred solution of benzo[*g*]chrysene (**1**) (0.05 g, 0.2 mmol) and lithium acetate (0.1 g, 0.98 mmol) in glacial acetic acid (10 cm^3) and stirring was continued for 0.5 h. The reaction mixture was poured into water and the precipitated product was filtered off, washed with water and recrystallised from diethyl ether–pentane to yield the bromoacetate (**8**) (0.07 g, 84%), m.p. 140—143 °C (decomp.) (Found: C, 69.0; H, 4.1. $C_{24}H_{17}BrO_2$ requires C, 69.1; H, 4.1%), $\delta_H(CDCl_3)$ 2.09 (3 H, s, OAc), 5.48 (1 H, d, $J_{9,10}$ 2.6 Hz, 10-H), 6.9 (1 H, d, $J_{9,10}$ 2.6 Hz, 9-H), 7.38—7.75 (6 H, m, Ar), 7.97—8.01 (2 H, m, Ar), and 8.41—8.88 (4 H, m, Ar).

Benzo[g]*chrysene* 9,10-*Oxide* (**9**).—Powdered sodium methoxide (0.15 g) was added to a solution of the bromoacetate (**8**) (0.07 g) in dry THF at 0 °C and stirred for 16 h at 4 °C. The reaction mixture was concentrated, washed with water, and extracted using diethyl ether. The extract was washed with water and aqueous KOH (10% solution) dried (K_2CO_3 containing a trace of triethylamine) and concentrated to give the arene oxide (**9**) (0.03 g, 61%), m.p. 155—156 °C (decomp.) (Found: M^+, 294.10462. $C_{22}H_{14}O$ requires *M*, 294.10446), $\delta_H(CDCl_3)$ 4.90 (1 H, d, $J_{9,10}$ 4.2 Hz, 10-H) 5.41 (1 H, d $J_{9,10}$ 4.2 Hz, 9-H), 7.17 (1 H, d, Ar), 7.45—7.80 (6 H, m, Ar), and 8.48—8.91 (5 H, m, Ar).

Treatment of the arene oxide (**9**) with trifluoroacetic acid gave a phenolic product (Found: M^+, 294.10452. $C_{22}H_{14}O$ requires *M* 294.10446), $\delta_H(CDCl_3)$ 7.45—7.74 (6 H, m, Ar), 8.10—8.14 (2 H, m, Ar), and 8.41—8.91 (5 H, m, Ar). The spectral data did not allow an unequivocal distinction to be made between the 9- or 10-hydroxybenzo[*g*]chrysene isomers.

1-*Acetoxy*-2-*bromo*-1,2,3,4-*tetrahydrobenzo*[g]*chrysene* (**10**).—*N*-Bromoacetamide (0.138 g, 1.0 mmol) was added to a stirred solution of 3,4-dihydrobenzo[*g*]chrysene (**7**) (0.28 g, 1.0 mmol) and lithium acetate (0.2 g, 1.96 mmol) in a mixture of THF (5 cm^3)–glacial acetic acid (15 cm^3) and stirred for a further 0.5 h. The product bromoacetate (**10**) was purified by chromatography (Florisil, eluted with diethyl ether) and recrystallised from diethyl ether to give colourless needles (0.32 g, 76%), m.p. 236—238 °C (Found: C, 68.6; H, 4.6. $C_{24}H_{19}BrO_2$ requires C, 68.7; H, 4.5%), $\delta_H(CDCl_3)$ 1.99 (3 H, s, OAc), 2.54 (2 H, m, 3-H), 3.49 (2 H, m, 4-H), 4.9 (1 H, m, 2-H), 7.1 (1 H, d, $J_{1,2}$ 3.7 Hz, 1-H), and 7.51—8.69 (10 H, m, Ar).

1,9-*Diacetoxy*-2,10-*dibromo*-1,2,3,4,9,10-*hexahydrobenzo*[g]-*chrysene* (**13**).—Treatment of 3,4-dihydrobenzo[*g*]chrysene (**7**) (0.15 g, 0.54 mmol) with *N*-bromoacetamide (0.1 g, 0.75 mmol) under similar conditions to those used in the synthesis of the bromoacetate (**10**) gave three products which were separated by preparative t.l.c. [chloroform–light petroleum, 1:1].

The upper band (R_F 0.78) was identified as benzo[*g*]chrysene (**1**) (0.005 g, 3%). The bromoacetate (**10**) was recovered from the middle band (R_F 0.59, 0.035 g, 16%). The major component which had the lowest R_F value (0.33), was a crystalline solid (0.1 g, 34%), m.p. 144—145 °C whose microanalytical data (Found: C, 56.3; H, 4.2. $C_{26}H_{22}O_4Br_2$ requires C, 55.9; H, 3.9%) were consistent with its identification as the dibromodiacetate (**13**), $\delta_H(CDCl_3)$ 1.68 (3 H, s, 9-OAc), 1.91 (3 H, s, 1-OAc), 2.58 (2 H, m, 3-H), 3.50 (2 H, m, 4-H), 4.71 (1 H, m, 2-H), 5.39 (1 H, d, $J_{9,10}$ 2.8 Hz, 10-H), 6.79 (1 H, d, $J_{9,10}$) 2.8 Hz, 9-H), 7.29 (1 H, d, $J_{1,2}$ 3.7 Hz, 1-H), and 7.33—8.16 (8 H, m, Ar).

1,9-*Diacetoxy*-2,4,10-*tribromo*-1,2,3,4,9,10-*hexahydrobenzo*-[g]*chrysene* (**14**).—A solution of the dibromo diacetate (**13**) (0.15 g, 0.27 mmol), *N*-bromosuccinimide (0.08 g, 0.44

mmol) and α,α-azoisobutyronitrile (0.005 g) in carbon tetrachloride (25 cm^3) was irradiated with a heating lamp and refluxed under N_2 for 0.5 h. The precipitated succinimide was removed by filtration and the filtrate was dried and concentrated to give the tribromo diacetate product (**14**) (0.15 g, 88%). Owing to its instability, compound (**14**) was identified only by n.m.r. spectroscopy $\delta_H(CDCl_3)$ 1.71 (3 H, s, 9-OAc), 1.91 (3 H, s, 1-OAc), 1.61 (2 H, m, 3-H), 4.8 (1 H, m, 2-H), 5.4 (1 H, d, *J* 2.8 Hz, 10-H), 6.10 (1 H, m, 4-H), 6.79 (1 H, d, *J* 2.8 Hz, 9-$H^{9,10}$), 7.3—8.8 (9 H, m, 1-H and Ar).

Similar treatment of the bromoacetate (**10**, 0.29 g, 0.69 mmol) with *N*-bromosuccinimide (0.16 g, 0.9 mmol) yielded succinimide as a by-product. The crude product obtained (0.3 g) showed little evidence of the required dibromoacetate (**11**) by n.m.r. analysis. T.l.c. analysis of the crude product mixture (silica gel, eluted with light petroleum–chloroform, 6:4) indicated the presence of at least five components in the mixture. Identical results were obtained during two further unsuccessful attempts to synthesise the dibromoacetate (**11**) by this route.

Benzo[g]*chrysene* 1,2:9,10-*Dioxide* (**15**).—Using a similar procedure to that outlined in the synthesis of benzo[*g*]chrysene 9,10-oxide (**9**), the tribromo diacetate (0.15 g, 0.24 mmol) was transformed into benzo[*g*]chrysene 1,2:9,10-dioxide (**15**) (0.05 g, 60%), m.p. 90—95 °C (decomp.) (Found: M^+, 310.09934 $C_{22}H_{14}O_2$ requires *M*, 310.09937); $\delta_H(CDCl_3)$ 4.2 (1 H, m, 2-H), 4.86 (1 H, d, $J_{9,10}$ 4.2 Hz, 10-H), 4.88 (1 H, d, $J_{1,2}$ 4.2 Hz, 1-H), 5.4 (1 H, d, $J_{9,10}$ 4.2 Hz, 9-H), 6.6 (1 H, dd, $J_{2,3}$ 3.8 Hz, $J_{3,4}$ 10.1 Hz, 3-H), 7.58 (1 H, d, $J_{3,4}$ 10.1 Hz, 4-H), and 7.3—8.9 (8 H, m, Ar).

Aromatization of the diarene oxide (**15**) occurred upon addition of a drop of trifluoroacetic acid. The products were identified as diphenols by mass spectrometry (Found: M^+, 310.09934. $C_{22}H_{14}O_2$ requires *M*, 310.09937) and n.m.r. analysis $\delta_H(CDCl_3)$ 5.8 (2 H, br s, OH), 7.61—7.66 (4 H, m, Ar), and 8.36—8.83 (8 H, m, Ar).

When the crude product obtained by attempted benzylic bromination of the bromoacetate (**10**) was also treated with sodium methoxide under identical conditions, the expected arene oxide (**12**) was not among the products (n.m.r. analysis).

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