Synthesis of Diarene Oxides of Benz[*a*]anthracene, Chrysene and Benzo[*c*]phenanthrene

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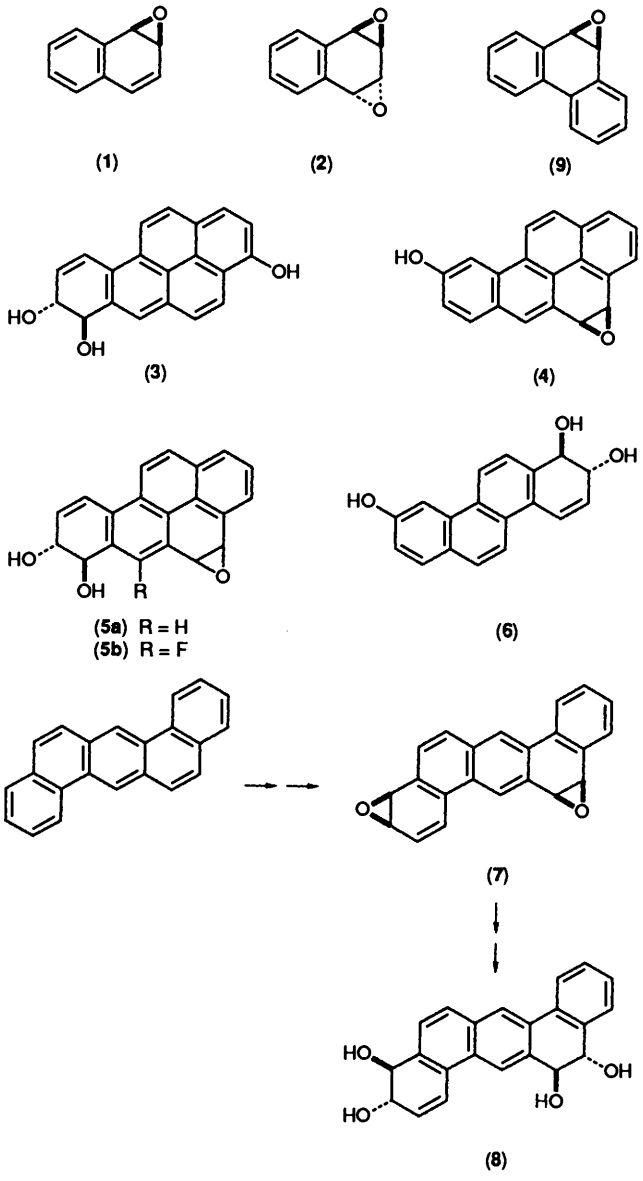
A three-step synthetic route to the diarene oxides 5,6;10,11-diepoxy-5,6,10,11-tetrahydrobenz[*a*]anthracene **18**, 5,6;8,9-diepoxy-5,6,8,9-tetrahydrobenz[*a*]anthracene **22**, 3,4;5,6-diepoxy-3,4,5,6-tetrahydrochrysene **26** and 3,4;7,8-diepoxy-3,4,7,8-tetrahydrobenzo[*c*]-phenanthrene **30**, from the corresponding *trans*-bromo acetate precursors **15**, **19**, **23**, and **27** has been developed. Acid-catalysed isomerization studies to isomeric mixtures of phenols have been carried out.

Polycyclic aromatic hydrocarbons (PAHs) are partial combustion products of fossil fuels which occur widely in the environment. Many members of the PAH series have been identified as carcinogens and a comprehensive study of structure–reactivity relationships within this series has been carried out. It is now generally accepted that PAHs require metabolic activation before they become carcinogenic or mutagenic.[1] Monooxygenases catalyse the incorporation of one atom of dioxygen into the substrate molecule forming an arene oxide which can then undergo further reactions.[2] Since arene oxides do not appear to be the ultimate carcinogenic metabolites, attention has switched to the investigation of other derived metabolites such as *trans*-dihydro diols and the derived epoxides (diol epoxides).[3] Evidence has been found to support the theory that diol epoxides having the oxirane ring in a bay-region are important metabolites exhibiting increased carcinogenic activity.[4] Despite the success of the bay-region theory it cannot fully account for the mutagenic/carcinogenic activity of some PAHs which are devoid of a bay-region. As part of the quest for other metabolites which may also be responsible for the mutagenic/carcinogenic activity of PAHs, much effort has recently been devoted to the detection of newer types of polyoxygenated metabolites.[5,6] Thus, for example, triols and triol epoxides have been detected from the metabolism of chrysene.[6]

Two epoxidation steps have been found on the *same* aromatic ring during animal liver metabolism of naphthalene *via* naphthalene 1,2-oxide **1** to yield *trans*-naphthalene 1,2;3,4-dioxide **2**.[7] Two epoxidation steps on *different* aromatic rings are probably involved in the metabolism of benzo[*a*]pyrene to yield the phenolic *trans*-diol **3**,[8] the phenolic arene oxide **4**,[9] the *trans*-diol arene oxides **5a** and **5b**,[10] and biotransformation of chrysene **11** to yield the phenolic *trans*-diol **6**.[8]

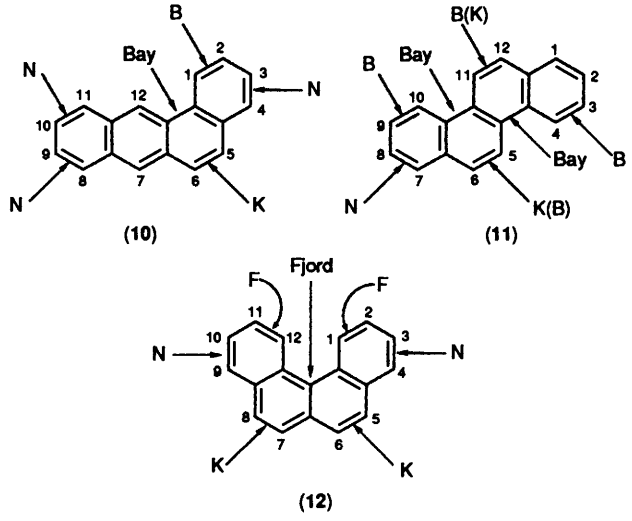
The intermediacy of diarene oxides in the formation of the latter phenol and diol metabolites has not been established. Diarene oxide **7** has, however, been proposed as a metabolic precursor of the tetraol **8** during metabolism of dibenz[*a*,*h*]-anthracene.[11] This appears to be the first report[11] of diarene oxide involvement in the metabolism of PAHs.

The nomenclature used in this report, *i.e.* 'arene oxide', 'arene dioxide', and 'diarene oxide' is that previously used in the literature.[12–14] Thus, the term 'arene oxide' refers to the monoepoxide formed when a formal double bond in a benzene ring has been epoxidized, *e.g.* the mono arene oxide of phenanthrene **9**. *trans*-Naphthalene 1,2;3,4-dioxide **2** is an



example of an 'arene dioxide' where two epoxides are present on the same benzene ring. The term 'diarene oxide' denotes that two distinct mono arene oxides (formed by epoxidation of a double bond in two different rings) are present in one molecule, *e.g.* **7**.

Diarene oxides have previously only been synthesised by the cyclisation of tetraaldehydes with tris(dimethylamino)-phosphine (Mark's reagent).[15] In the latter method the overall yields were poor (1–29%), and this route was applicable only to di-K-region epoxides. Since other categories of diarene oxides [*e.g.* the K-region/non-K-region diarene oxide **7**] may be formed during metabolism, the present study (reported in preliminary form[13]) was undertaken to provide a general synthetic route to diarene oxides possessing only one K-region



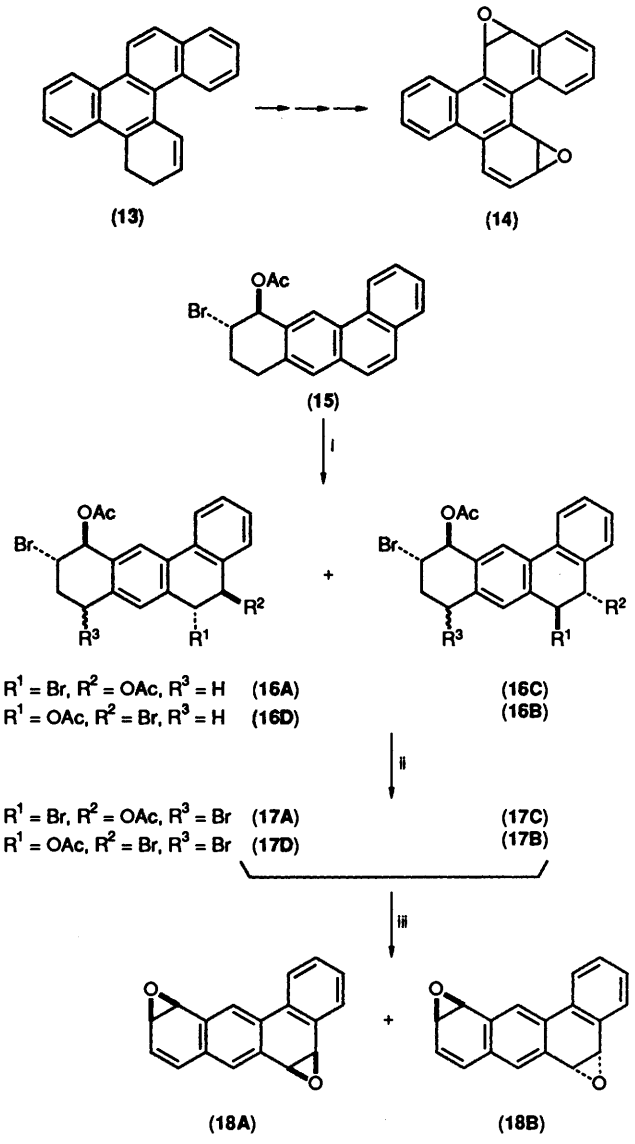
N = Non-K-region, K = K-region, B = Bay-region, F = Fjord-region.

epoxide. The appropriate K-, non-K-, bay- and fjord-regions are indicated for the PAHs benz[*a*]anthracene **10**, chrysene **11** and benzo[*c*]phenanthrene **12**. These PAH systems were used in the present study since appropriate bromoacetate precursors were available from previously reported studies from these laboratories.

Chrysene **11**, although considered to be non-carcinogenic, is a weak tumour initiator,[16] while benz[*a*]anthracene (B[*a*]A, **10**) and benzo[*c*]phenanthrene (B[*c*]Ph, **12**) are both relatively weak carcinogens.[16,17] All three hydrocarbons have either K-/non-K- or K-/bay-regions while in addition B[*c*]Ph **12** also possesses a fjord-region between C-1 and C-12 and as a result is non-planar due to steric congestion about this region. While oxidative metabolism occurs mainly at the 5,6- and 8,9-positions of B[*a*]A (**10**), it has also been shown to occur at the 10,11-positions.[1,18] A similar regioselectivity for metabolism at the 3,4- and 5,6-positions of chrysene[16] **11** and the 3,4- and 5,6-positions of B[*c*]Ph (**12**)[19] was observed. With the evidence from these studies it was reasonable to assume that the corresponding diarene oxides might also be potential metabolites.

The serendipitous formation of the K-/fjord-region benzo-[*g*]chrysene diarene oxide **14**[14] by use of an excess of *N*-bromoacetamide (NBA) reagent upon 3,4-dihydrobenzo[*g*]-chrysene **13** suggested that a modification of this procedure (starting with a *trans*-bromo acetate precursor) should provide a general synthetic route to other diarene oxides, *e.g.* **18**, **22**, **26** and **30**.

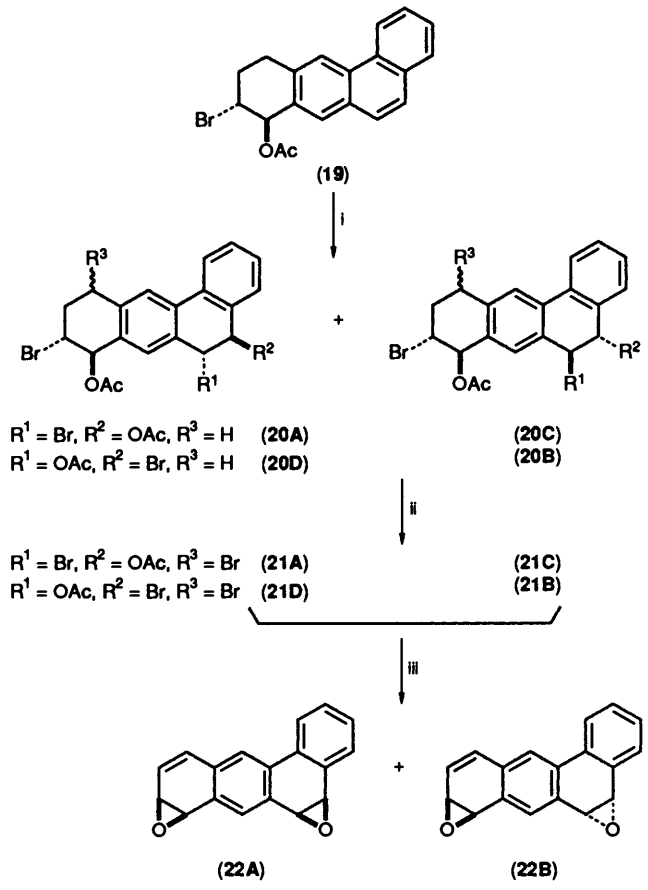
Thus, formation of diarene oxides **18**, **22**, **26** and **30** involved a three-step synthetic sequence starting from the appropriate *trans*-bromo acetates **15**, **19**, **23** and **27** (Schemes 1–4) using a



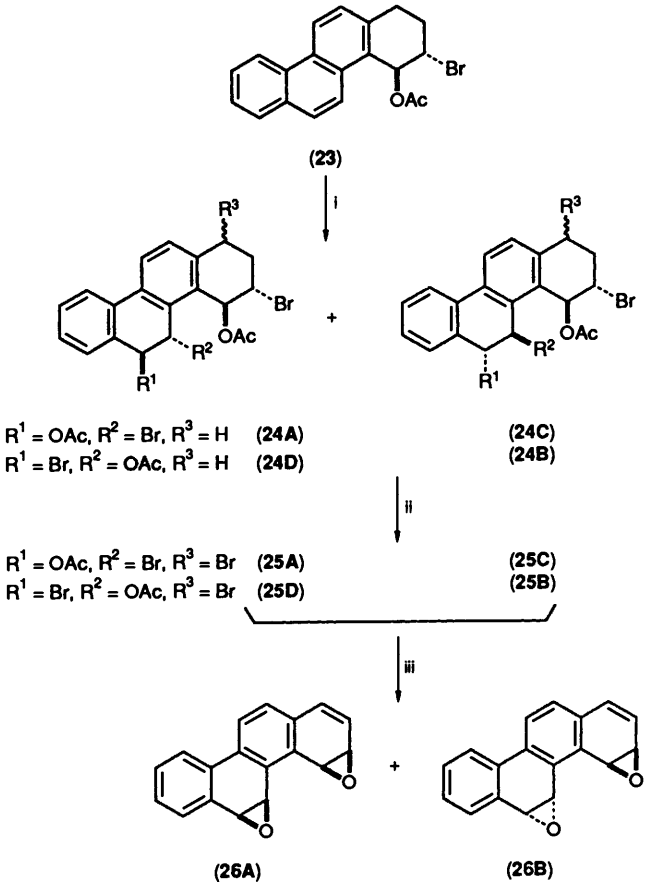
Scheme 1. *Reagents:* i, NBA–$MeCO_2H$–THF–LiOAc; ii, NBS–CCl_4; iii, NaOMe–THF.

modified form of the bromo ester route to monoarene oxides[20] on the corresponding dihydroarenes. By analogy with the reaction of NBA at the K-region of other PAHs[21] it was expected that the dibromo diacetates **16**, **20**, **24** and **28** would be formed from opening of the cyclic bromonium ion intermediate. ^{1}H NMR analyses of the products indicated that the dibromo diacetates **16**, **20**, **24** and **28** were in each case found to be the major components. A minor proportion (< 20%) of unchanged bromo acetate **15**, **19**, **23** and **27** was consistently observed and was in each case removed by multi-elution preparative TLC prior to recycling. Using the latter procedure the dibromo diacetates **16**, **20**, **24** and **28** were obtained in isolated yields of 80–90%.

Using high resolution ^{1}H NMR spectral analysis (400 MHz) it was possible to identify the individual dibromo diacetate diastereoisomers **24A**, **24B**, **24C** and **24D** in the product mixture (Scheme 3) and to determine their relative proportion, *i.e.* 45:26:26:3 respectively. The assignment of stereochemistry was based on 2D-COSY and NOE difference spectroscopy. A larger NOE value (13–14%) was thus obtained upon irradiation of the ^{1}H NMR signal at 4-H and observation of signal 5-H in



Scheme 2. Reagents as in Scheme 1.



Scheme 3. Reagents as in Scheme 1.

isomers **24C** and **24B**. A value of 9% enhancement was observed for isomer **24A**. Because of the very small proportion (3%) of isomer **24D** present in the mixture a reliable NOE value could not be obtained. The percentages of isomers present may thus be rationalized in terms of steric approach control. Two isomeric cyclic bromonium ion intermediates are possible in the formation of these dibromo diacetates (Fig. 1). Bromonium ion **I** is probably favoured over **II** on steric considerations. The nucleophilic acetate ion would be expected to attack preferentially the cyclic bromonium ion at the less hindered C-6 position rather than the more hindered C-5 position. Attack at both positions would yield the dibromodiacetates **24A** and **24B** respectively. A similar argument can be applied to the bromonium ion **II** which would give the dibromo acetates **24C** and **24D** as the major and minor isomers respectively. ^{1}H NMR coupling constants from compounds **24A–D** are indicative of a pseudo diaxial conformation of the vicinal bromine atom and acetoxy group as a result of steric congestion in the bay region.

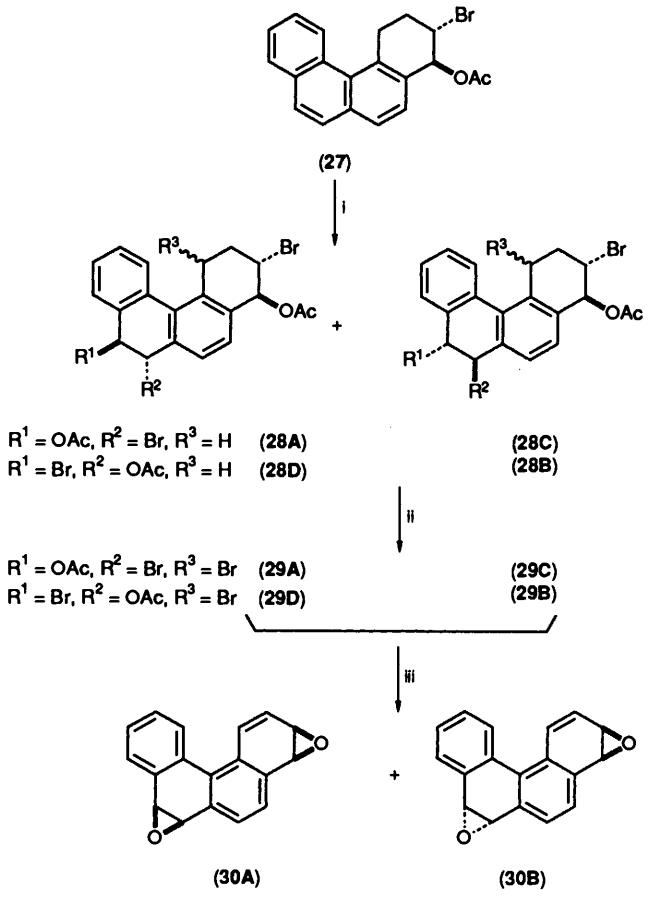
It was not possible to detect and to identify individual diastereoisomers of the dibromo diacetates **16**, **20** and **28** on the basis of ^{1}H NMR analysis owing to the similarity of chemical shift values. It is assumed, however, that as observed for the dibromodiacetates **24A–D**, the analogous diastereoisomers were present in compounds **16**, **20** and **28** (Schemes 1, 2 and 4).

Because of evidence of instability no attempts at chromatographic separation of the diastereoisomers of the dibromo diacetates **16**, **20**, **24** and **28**, were made. The latter dibromo acetate isomers were thus converted directly into the corresponding tribromo diacetates **17**, **21**, **25** and **29** by benzylic bromination using *N*-bromosuccinimide. Periodic ^{1}H NMR analysis was used to ensure complete bromination and to avoid decomposition of the relatively unstable tribromo diacetate products **17**, **21**, **25** and **29**. Further treatment of the latter crude reaction products with sodium methoxide in THF gave the corresponding diarene oxide products **18**, **22**, **26** and **30** in good yield (87–95%).

The formation of both *cis* and *trans* diarene oxide isomers **26A** and **26B** was deduced from ^{1}H NMR and NOE difference spectroscopy at 400 MHz. Thus, a larger NOE value (11%) was found upon irradiation of 4-H and observation of 5-H in the *cis* isomer **26A**. A similar procedure on the *trans* isomer **26B** yielded an NOE value of 7%. The *cis*:*trans* ratio (72%, **26A**:28%, **26B**) was in good agreement with the ratio expected based upon the relative proportions of the dibromo diacetate isomers **24A–D**. Attempted separations of the diarene oxide isomers **26A** and **26B** by TLC on silica-gel containing a trace of triethylamine, showed partial decomposition into phenolic isomers without evidence of isomer separation.

Both *cis* **22A** and *trans* **22B** diarene oxides in the benz[*a*]anthracene series were found to be present in almost equal proportions, based upon ^{1}H NMR spectral data. Although individual *cis* and *trans* isomers of the diarene oxides **18** and **30** were not distinguishable from ^{1}H NMR spectral data, it is expected that the ratio of **18A**:**18B** and **30A**:**30B** will be similar to that observed for diarene oxides **22A** and **22B**, *i.e.* 1:1. Unfortunately, a sufficient quantity of any of the diarene oxide isomers **18**, **22**, **26** and **30** was unavailable for detection of individual stereoisomers by ^{13}C NMR analysis.

The configurational stability of arene oxides of PAHs has previously been successfully predicted on the basis of PMO calculations.[22] It is probable that these calculations and predictions will be equally applicable to direne oxides. Since each of the diarene oxides **18**, **22**, **26** and **30** are derivatives of tetracyclic PAH systems, they can be considered as a



Scheme 4. Reagents as in Scheme 1.

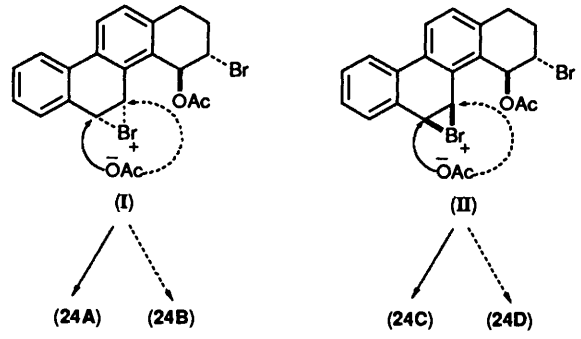


Fig. 1.

combination of naphthalene 1,2-oxide **1** and phenanthrene 9,10-oxide **9** units. Thus diarene oxide **22** can be dissected into mono arene oxide derivatives **1** and **9** (Fig. 2) which are known to be configurationally stable. A similar configurational stability is predicted for diarene oxides **22**, **26** and **30** which, in principle, should allow their existence as separate isomers at ambient temperature. Using a similar rationale it is predicted that the diarene oxide **14** which has previously been synthesised[14] will be configurationally unstable, *i.e. cis* and *trans* isomers will spontaneously equilibrate. The diarene oxide **14** can be considered as a combination of chrysene 5,6-oxide and phenanthrene 1,2-oxide units. The latter molecule was predicted[22] to racemize spontaneously (*via* an oxepine intermediate, Figure 2).

Treatment of the diarene oxides **18**, **22**, **26** and **30** with trifluoroacetic acid (TFA) yielded totally aromatic products which are assumed to be diphenols from ^{1}H NMR and MS data.

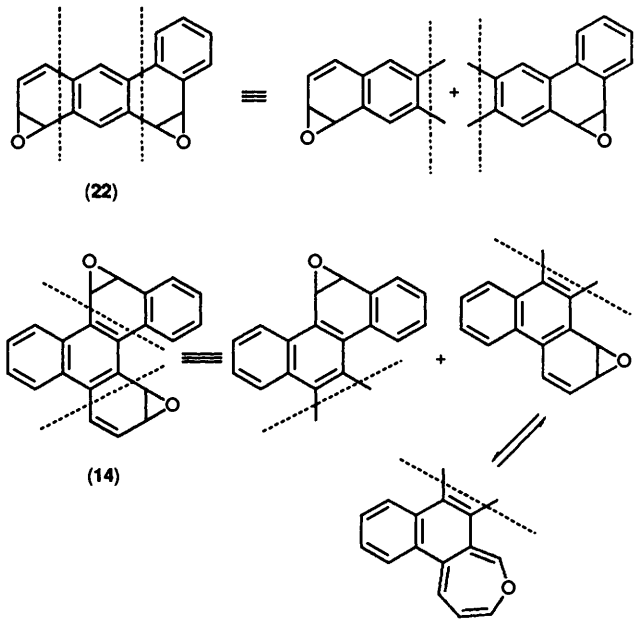


Fig. 2.

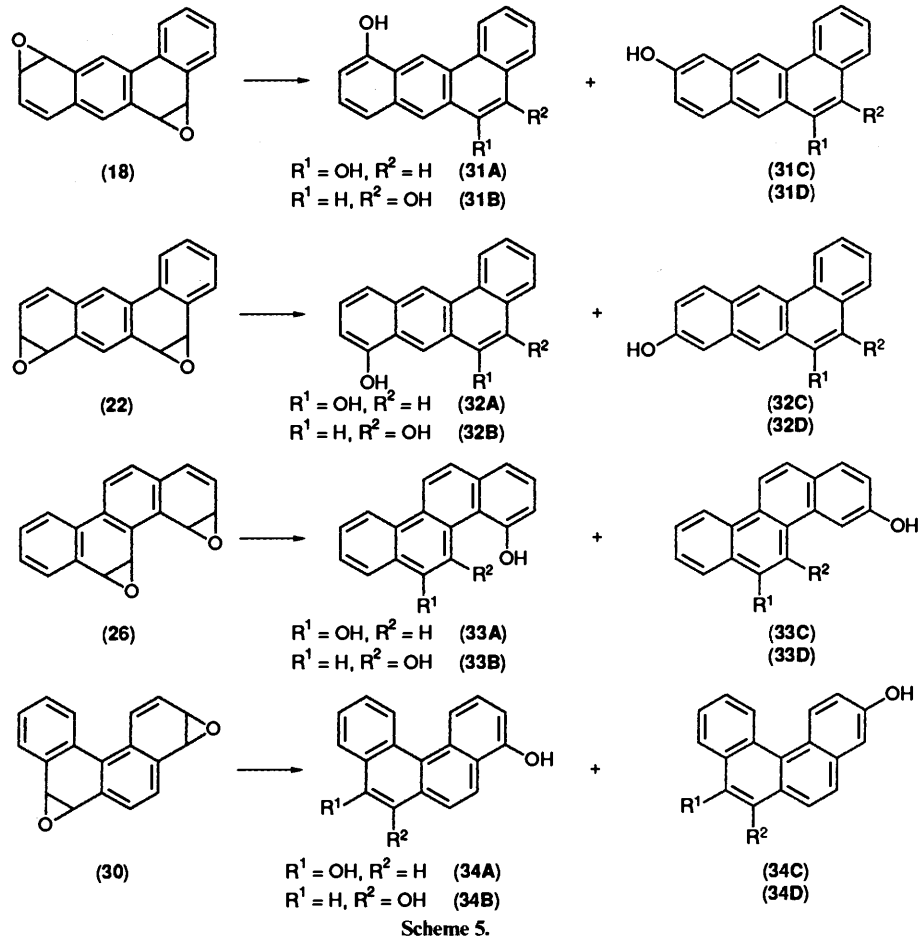
The facile aromatization of arene oxides under acidic conditions is well documented with the stability of the intermediate carbocation controlling the structures of the resultant phenols.[12,23] The possible phenols which could be formed from the diarene oxides **18**, **22**, **26** and **30** are shown (Scheme 5).

The product mixtures obtained by acidification of the diarene oxides **18**, **22** **26** and **30** contained a proportion of material which was insoluble in $CDCl_3$. Since diphenols of PAHs are susceptible to aerial oxidation they have usually been isolated as diacetates.[24,25] Attempts to identify the diphenol products of **18**, **22**, **26** and **30** were confined to 400 MHz ^{1}H NMR analysis (normal decoupling, 2D-COSY and NOE difference spectroscopy) of the $CDCl_3$-soluble portion.

The diphenols derived from the diarene oxide **18** appeared to be present as a mixture of two products in the ratio 5:2 which were tentatively assigned as **31A** and **31B**. Similarly, the diarene oxide **22** upon acidification with trifluoroacetic acid appeared to yield diphenols **32B**, **32C** and **32D** in a ratio of 2:1:1. The diarene oxide **30** appeared to give the diphenols **34A** and **34B** in the ratio 5:1. Because of the presence of other impurity peaks it was not possible to identify the diphenols derived from the diarene oxide **26**. As a result of the unstable nature of many of the diphenolic products, no further attempts were made to separate and purify individual diphenol isomers. Furthermore, the differing degree of instability associated with each diphenol diminishes the significance of the ratio of isomers observed. Despite these limitations, the major diphenols identified in each case **31A**, **32B** and **34A** are those expected when the non-K region arene oxide forms the more stable allylic carbocation. Since further metabolism of the monophenolic metabolites of PAHs has been established[9] it is probable that diphenols of similar type to those formed in the present study will be formed *in vivo*. The synthesis of diarene oxides **18**, **22**, **26** and **30**, allied to their phenolic isomerization products may thus prove to be of value in the quest for new polyoxygenated metabolites of PAHs.

Experimental

^{1}H NMR spectra were recorded at 250 MHz (Bruker WH250), at 300 MHz (General Electric QE300) and at 400 MHz (Bruker WH400, SERC service at the University of Warwick).



Scheme 5.

Tetramethylsilane was used as internal reference and deuteriochloroform as solvent unless otherwise stated.

Mass spectra were recorded at 70 eV on an AEI-MS902 model instrument updated by V.G. instruments. Accurate molecular weights were determined by the peak-matching method using perfluorokerosene as standard reference and were accurate to within ±0.000 006 amu. Analytical TLC was carried out on Merck Kieselgel $60F_{254}$ plates and the spots were visualised using a Hanovia chromatolite UV lamp. Preparative TLC was carried out with glass plates coated with Merck Kieselgel $PF_{254+366}$. Diethyl ether and tetrahydrofuran were dried with sodium wire and superdry tetrahydrofuran was obtained by distillation over sodium and benzophenone. Light petroleum refers to that fraction boiling in the range 40–60 °C. Sodium methoxide was prepared by dissolving sodium in dry methanol, evaporating the solution to dryness, and by vacuum drying overnight of the residue. *N*-Bromoacetamide (NBA) was purified by recrystallization from dichloromethane–light petroleum prior to the reaction. *N*-Bromosuccinimide was purified by recrystallization from hot (*ca.* 75 °C) water prior to the reaction. The *trans*-bromo acetates **15**,[26] **19**,[27] **23**[28] and **27**[29] were available from previous studies in these laboratories.

(±)-trans-*Dibromo Diacetates* **16**, **20**, **24** *and* **28**.—NBA (49 mg, 3.6×10^{-4} mol) was added to a stirred solution of the appropriate *trans*-bromo acetate (120 mg, 3.2×10^{-4} mol) and lithium acetate (120 mg, 1.8×10^{-3} mol) in a mixture of tetrahydrofuran (1 ml)–glacial acetic acid (7 ml) and stirring was continued for a further 1.5 h at 5–10 °C. The mixture was poured into cold water, extracted with chloroform, washed with aqueous sodium hydrogen carbonate solution (5%), dried ($MgSO_4$) and evaporated to dryness to give the dibromo diacetate. Preparative plate chromatography eluting three times with chloroform–light petroleum (50:50) afforded pure samples of the required dibromo diacetate and a minor proportion (<20%) of the starting material. The latter bromo acetate was isolated and treated as before. The dibromo diacetates **16**, **20**, **24** and **28** being isomeric mixtures which could be not be separated were crystalline solids of indefinite melting point.

r-5,5,c-11-*Diacetoxy*,t-6,t-10-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **16A**, r-5,t-6,t-11-*diacetoxy*,5,c-10-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **16B**, r-5,5,t-11-*diacetoxy*,t-6,c-10-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **16C**, r-5,t-6,c-11-*diacetoxy*,5,t-10-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **16D**: **16A–D** (145 mg, 88%) (Found: M^+, 507.972. $C_{22}H_{20}O_4Br_2$ requires *M*, 507.971); ν_{max}(KBr) 1735 cm^{-1} (C=O); δ_H(400 MHz) 1.90–2.17 (8 × 3 H, 8s, 8 × CH_3), 2.28–2.51 (4 × 2 H, m, 9-H_A, 9-H_B, 9-H_C, 9-H_D), 2.92–3.11 (4 × 2 H, m, 8-H_A, 8-H_B, 8-H_C, 8-H_D), 4.51 (4 × 1 H, m, 10-H_A, 10-H_B, 10-H_C, 10-H_D), 5.35 (4 × 1 H, m, 6-H_A, 5-H_B, 6-H_C, 5-H_D), 6.12–6.15 (4 × 1 H, m, 5-H_A, 6-H_B, 5-H_C, 6-H_D), 6.22 (4 × 1 H, m, 11-H_A, 11-H_B, 11-H_C, 11-H_D), 7.22 (4 × 1 H, s, 7-H), 7.33–7.51 (4 × 3 H, m, 4 × ArH) and 7.71–7.88 (4 × 2 H, m, 4 × ArH).

r-5,5,c-7-*Diacetoxy*,t-6,t-8-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **20A**, r-5,t-6,t-8-*diacetoxy*,5,c-9-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **20B**, r-5,5,t-8-*diacetoxy*,t-6,c-9-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **20C** and r-5,t-6,c-8-*diacetoxy*,5,t-9-*dibromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **20D**: **20A–D** (141 mg, 85%) (Found: $M - 120^+$, 387.9288. $C_{18}H_{12}Br_2$ requires *M*, 387.9287); ν_{max}(KBr) 1740 cm^{-1} (C=O); δ_H(400 MHz) 1.87–2.16

(8 × 3 H, 8s, 8 × CH_3), 2.22–2.35 and 2.46–2.56 (4 × 2 H, m, 10-H_A, 10-H_B, 10-H_C, 10-H_D), 2.96–3.23 (4 × 2 H, m, 11-H_A, 11-H_B, 11-H_C, 11-H_D), 4.45–4.59 (4 × 1 H, m, 9-H_A, 9-H_B, 9-H_C, 9-H_D), 5.36 (4 × 1 H, m, 6-H_A, 5-H_B, 6-H_C, 5-H_D), 6.05–6.09 (4 × 1 H, m, 5-H_A, 6-H_B, 5-H_C, 6-H_D), 6.13–6.38 (4 × 1 H, m, 8-H_A, 8-H_B, 8-H_C, 8-H_D), 7.33–8.62 (4 × 6 H, m, 4 × ArH).

r-3,t-4,t-6-*Diacetoxy*,3,c-5-*dibromo*-1,2,3,4,5,6-*hexahydrochrysene* **24A**, r-3,t-4,t-5-*diacetoxy*,3,c-6-*dibromo*-1,2,3,4,5,6-*hexahydrochrysene* **24B**, r-3,t-4,c-6-*diacetoxy*,3,t-5-*dibromo*-1,2,3,4,5,6-*hexahydrochrysene* **24C** and r-3,t-4,c-5-*diacetoxy*,3,t-6-*dibromo*-1,2,3,4,5,6-*hexahydrochrysene* **24D**, (148 mg, 90%) (Found: M^+, 507.9707. $C_{22}H_{20}Br_2O_4$ requires *M*, 507.9709); ν_{max}(KBr) 1725 cm^{-1} (C=O).

24A δ_H(400 MHz) 1.86 (3 H, s, CH_3), 2.13 (3 H, s, CH_3), 2.16–2.53 (2 H, m, 2-H), 2.87–2.97 and 3.19–3.22 (2 H, m, 1-H), 4.61 (1 H, m, 3-H), 5.48 (1 H, d, $J_{5,6}$ 3.2 Hz, 5-H), 6.09 (1 H, d, $J_{6,5}$ 3.2 Hz, 6-H), 6.35 (1 H, d, $J_{4,3}$ 2.9 Hz, 4-H) and 7.27–7.92 (6 H, m, ArH).

24B δ_H(400 MHz) 1.86–2.15 (2 × 3 H, 2s, 2 × CH_3), 2.16–2.53 (2 H, m, 2-H), 2.87–2.97 and 3.19–3.22 (2 H, m, 1-H), 4.65 (1 H, m, 3-H), 5.42 (1 H, d, $J_{6,5}$ 2.9 Hz, 6-H), 6.13 (1 H, d, $J_{5,6}$ 2.9 Hz, 5-H), 6.20 (1 H, d, $J_{4,3}$ 2.0 Hz, 4-H) and 7.27–7.92 (6 H, m, ArH).

24C δ_H(400 MHz) 1.86–2.15 (2 × 3 H, 2s, 2 × CH_3), 2.16–2.53 (2 H, m, 2-H), 2.87–2.97 and 3.19–3.22 (2 H, m, 1-H), 4.65 (1 H, m, 3-H), 5.33 (1 H, d, $J_{3,4}$ 2.9 Hz, 5-H), 6.02 (1 H, d, $J_{6,5}$ 2.9 Hz, 6-H), 6.31 (1 H, d, $J_{4,3}$ 2.0 Hz, 4-H) and 7.27–7.92 (6 H, m, ArH).

24D δ_H(400 MHz) 1.86–2.15 (2 × 3 H, 2s, 2 × CH_3), 2.16–2.53 (2 H, m, 2-H), 2.87–2.97 and 3.19–3.22 (2 H, m, 1-H), 4.72 (1 H, m, 3-H), 5.18 (1 H, d, $J_{5,6}$ 2.9 Hz, 5-H), 6.05 (1 H, d, 6-H), 6.38 (1 H, m, 4-H) and 7.27–7.92 (6 H, m, ArH).

r-3,t-4,t-8-*Diacetoxy*,3,c-7-*dibromo*-1,2,3,4,7,8-*hexahydrobenzo*[c]*phenanthrene* **28A**, r-3,t-4,t-7-*diacetoxy*,3,c-8-*dibromo*-1,2,3,4,7,8-*hexahydrobenzo*[c]*phenanthrene* **28B**, r-3,t-4,c-8-*diacetoxy*,3,t-7-*dibromo*-1,2,3,4,7,8-*hexahydrobenzo*[c]*phenanthrene* **28C** and r-3,t-4,c-7-*diacetoxy*,3,t-8-*dibromo*-1,2,3,4,7,8-*hexahydrobenzo*[c]*phenanthrene* **28D**: **28A–D** (143 mg, 87%) (Found: M^+, 507.9707. $C_{22}H_{20}O_4Br_2$ requires *M*, 507.9709); ν_{max}(KBr) 1740 cm^{-1} (C=O); δ_H(400 MHz) 1.84, 1.85, 1.90, 1.91, 2.11, 2.12, 2.20, 2.21 (8 × 3 H, 8s, 8 × CH_3), 2.08–2.65 (4 × 2 H, m, 2-H_A, 2-H_B, 2-H_C, 2-H_D) 3.07–3.62 (4 × 2 H, m, 1-H_A, 1-H_B, 1-H_C, 1-H_D), 4.52 (4 × 1 H, m, 3-H_A, 3-H_B, 3-H_C, 3-H_D), 5.26–5.31 (4 × 1 H, m, 7-H_A, 8-H_B, 7-H_C, 8-H_D), 5.98–6.03 (4 × 1 H, 4d, $J_{7D,8D}$ 2.9 Hz, 8-H_A, 7-H_B, 8-H_C, 7-H_D), 6.18 and 6.43 (4 × 1 H, m, 4-H_A, 4-H_B, 4-H_C, 4-H_D) and 7.28–7.91 (4 × 6 H, m, 4 × 4 ArH).

(±)-*Tribromo Diacetates* **17**, **21**, **25** *and* **29**.—A mixture of the appropriate dibromo diacetate (135 mg, 2.6 × 10^{-4} mol), NBS (52 mg, 2.9 × 10^{-4} mol), α,α′-azoisobutyronitrile (6 mg) in carbon tetrachloride (25 ml) was maintained under an atmosphere of nitrogen and at 60 °C using a heat lamp until a fluffy precipitate of succinimide formed (*ca.* 30 min). Activated charcoal (150 mg) was added after which the solution was stirred, filtered and evaporated to dryness on a cool water-bath to give the corresponding tribromo diacetate. The latter were isomeric mixtures which were not separated and thus of indefinite melting point. The crude products were used without further purification.

6,11-*Diacetoxy*-5,8,10-*tribromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **17B**, **17D** and 5,11-*diacetoxy*-6,8,10-*tribromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **17A**, **17C** (145 mg, 93%); δ_H(250 MHz) 1.91–2.16 (8 × 3 H, 8s, 8 × CH_3), 2.28–2.98 (4 × 2 H, m, 9-H_A, 9-H_B, 9-H_C, 9-H_D), 4.73 (4 × 1 H, m, 10-H_A, 10-H_B, 10-H_C, 10-H_D), 5.34 (4 × 1 H, m, 6-H_A, 5-H_B, 6-H_C, 5-H_D), 5.53 (4 × 1 H, m, 8-H_A, 8-H_B, 8-H_C, 8-H_D), 6.14–6.38 (8 × 1 H, m, 5-H_A, 6-H_B, 5-H_C, 6-H_D, 11-H_A, 11-H_B, 11-H_C, 11-H_D) and 7.28–8.51 (4 × 6 H, m, 4 × ArH).

6,8-*Diacetoxy*5,9,11-*tribromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **21B**, **21D** and 5,8-*diacetoxy*-6,9,11-*tribromo*-5,6,8,9,10,11-*hexahydrobenz*[a]*anthracene* **21A**, **21C** (132 mg, 85%), δ_H(250 MHz) 1.72–2.21 (8 × 3 H, 8s, 8 × CH_3), 2.23–2.96 (4 × 2 H, m, 10-H_A, 10-H_B, 10-H_C, 10-H_D), 4.41–4.83 (4 × 1 H, m, 9-H_A, 9-H_B, 9-H_C, 9-H_D), 5.37 (4 × 1 H, m, 6-H_A, 5-H_B, 6-H_C, 5-H_D), 5.57 (4 × 1 H, m, 11-H_A, 11-H_B, 11-H_C, 11-H_D), 6.04–6.41 (8 × 1 H, m, 5-H_A, 6-H_B, 5-H_C, 6-H_D, 8-H_A, 8-H_B, 8-H_C, 8-H_D) and 7.28–8.60 (4 × 6 H, m, ArH).

4,5-*Diacetoxy*-1,3,6-*tribromo*-1,2,3,4,5,6-*hexahydrochrysene* **25B**, **25D** and 4,6-*Diacetoxy*-1,3,5-*tribromo*-1,2,3,4,5,6-*hexahydrochrysene* **25A**, **25C** (148 mg, 95%), δ_H(250 MHz) 1.86–2.13 (8 × 3 H, 8s, 8 × CH_3), 2.87–3.15 (4 × 2 H, m, 2-H_A, 2-H_B, 2-H_C, 2-H_D), 4.49–4.70 (4 × 1 H, m, 3-H_A, 3-H_B, 3-H_C, 3-H_D), 5.22–5.55 (4 × 1 H, m, 5-H_A, 6-H_B, 5-H_C, 6-H_D), 5.61–5.79 (4 × 1 H, m, 1-H_A, 1-H_B, 1-H_C, 1-H_D), 6.09–6.75 (8 × 1 H, m, 6-H_A, 5-H_B, 6-H_C, 5-H_D, 4-H_A, 4-H_B, 4-H_C, 4-H_D) and 7.36–7.99 (4 × 6 H, m, 4 × ArH).

4,7-*Diacetoxy*-1,3,8-*tribromo*-1,2,3,4,7,8-*hexahydrobenzo*[c]*phenanthrene* **29B**, **29D** and 4,8-*diacetoxy*-1,3,7-*tribromo*-1,2,3,4,7,8-*hexahydrobenzo*[c]*phenanthrene* **29A**, **29C** (140 mg, 90%), δ_H(250 MHz) 1.72–2.25 (8 × 3 H, 8s, 8 × CH_3), 2.76–3.19 (4 × 2 H, m, 2-H_A, 2-H_B, 2-H_C, 2-H_D), 4.53 (4 × 1 H, m, 3-H_A, 3-H_B, 3-H_C, 3-H_D), 5.21–5.39 and 5.71 (8 × 1 H, 7-H_A, 8-H_B, 7-H_C, 8-H_D, 1-H_A, 1-H_B, 1-H_C, 1-H_D), 5.96–6.04 (4 × 1 H, 8-H_A, 7-H_B, 8-H_C, 7-H_D), 6.19–6.71 (4 × 1 H, 4-H_A, 4-H_B, 4-H_C, 4-H_D), 7.29–7.91 and 8.65 (4 × 6 H, m, 4 × ArH).

(±)-*Diarene Oxides* **18**, **22**, **26** *and* **30**.—A solution of the appropriate tribromo diacetate (*ca.* 140 mg, 2.4 × 10^{-4} mol) was stirred at 0 °C in dry tetrahydrofuran (5 ml) under an atmosphere of nitrogen and dry sodium methoxide (500 mg) was added. The mixture was stirred for 1 h and then stored at −70 °C for 12 h. Prior to work-up, glassware was washed with triethylamine. The reaction mixture was diluted with cold chloroform and then washed with cold water, and aqueous potassium hydroxide (10%), dried (potassium carbonate) and evaporated to dryness to give the corresponding diarene oxide isomers. The product was recrystallized at −78 °C.

cis,trans-5,6;10,11-*Diepoxy*-5,6,10,11-*tetrahydrobenz*[a]*anthracene* **18A**/**18B** (60 mg, 93%), m.p. 120–125 °C [(mixture of diastereoisomers), (from chloroform–pentane)] (Found: M^+, 260.0840. $C_{18}H_{12}O_2$ requires *M*, 260.0837); δ_H(400 MHz), 4.15 (2 × 1 H, ddd, $J_{10,8}$ 1.6 Hz, $J_{10,9}$ 3.8 Hz, $J_{10,11}$ 3.8 Hz, 10-H_A, 10-H_B), 4.56 (6 × 1 H, m, 5-H_A, 6-H_A, 11-H_A, 5-H_B, 6-H_B, 11-H_B), 6.49 (2 × 1 H, dd, $J_{9,8}$ 9.6 Hz, $J_{9,10}$ 3.8 Hz, 9-H_A, 9-H_B), 6.81 (2 × 1 H, dd, $J_{8,9}$ 9.6 Hz, $J_{8,10}$ 1.6 Hz, 8-H_A, 8-H_B), 7.40 (2 × 1 H, ddd, $J_{3,1}$ 1.1 Hz, $J_{3,2}$ 7.4 Hz, $J_{3,4}$ 7.4 Hz, 3-H_A, 3-H_B), 7.51 (2 × 1 H, ddd, $J_{2,1}$ 7.5 Hz, $J_{2,3}$ 7.4 Hz, $J_{2,4}$ 1.5 Hz, 2-H_A, 2-H_B), 7.59 (2 × 1 H, s, 7-H_A, 7-H_B), 7.66 (2 × 1 H, dd, 4-H_A, 4-H_B), 8.17 (2 × 1 H, d, 1-H_A, 1-H_B) and 8.34 (2 × 1 H, s, 12-H_A, 12-H_B).

cis,trans-5,6;8,9-*Diepoxy*-5,6,8,9-*tetrahydrobenz*[a]*anthracene* **22A**/**22B** (51 mg, 87%), m.p. 132–135 °C [(decomp.) (mixture of diastereoisomers) (from chloroform–pentane)] (Found: M^+, 260.0841. $C_{18}H_{12}O_2$ requires *M*, 260.0837); δ_H(400 MHz), 4.14 (2 × 1 H, m, 9-H_A, 9-H_B), 4.52 (2 × 1 H, $J_{8,9}$ 3.8 Hz, 8-H_A, 8-H_B), 4.56 (2 × 1 H, m, 5-H_A, 5-H_B), 4.60 (2 × 1 H, d, $J_{6,5}$ 4.0 Hz, 6-H_A, 6-H_B), 6.50 (2 × 1 H, dd, $J_{10,9}$ 3.8 Hz, $J_{10,11}$ 9.6 Hz, 10-H_A, 10-H_B), 6.84 and 6.85 (2 × 1 H, dd, $J_{11,9}$ 1.6 Hz, 11-H_A, 11-H_B), 7.39 (2 × 1 H, ddd, $J_{3,1}$ 1.2 Hz, $J_{3,2}$ 7.4 Hz, $J_{3,4}$ 7.4 Hz, 3-H_A, 3-H_B), 7.49 (2 × 1 H, ddd, $J_{2,1}$ 7.6 Hz, $J_{2,4}$ 1.4 Hz, 2-H_A, 2-H_B), 7.66 (2 × 1 H, dd, 4-H_A, 4-H_B), 7.87 and 7.90 (2 × 1 H, 2s, 12-H_A, 12-H_B), 8.00 and 8.01 (2 × 1 H, 2s, 7-H_A, 7-H_B) 8.09 and 8.12 (2 × 1 H, 2d, 1-H_A, 1-H_B).

cis,trans-3,4;5,6-*Diepoxy*-3,4,5,6-*tetrahydrochrysene* **26A**/**26B** (61 mg, 93%), m.p. 190–195 °C [(decomp.) (mixture of

diastereoisomers) (from chloroform–pentane)] (Found: M^+, 260.0838. $C_{18}H_{12}O_2$ requires M, 260.0837). **26A** δ_H(400 MHz) 4.22 (1 H, ddd, $J_{3,1}$ 1.6 Hz, $J_{3,2}$ 3.8 Hz, $J_{3,4}$ 4.0 Hz, 3-H_A), 4.64 (1 H, d, $J_{6,5}$ 4.2 Hz, 6-H_A), 5.13 (1 H, d, 4-H_A), 5.21 (1 H, d, 5-H_A), 6.48 (1 H, dd, $J_{2,1}$ 9.6 Hz, 2-H_A), 6.79 (1 H, dd, 1-H_A) and 7.38–8.18 (6 H, m, ArH); **26B** δ_H(400 MHz) 4.12 (1 H, ddd, $J_{3,1}$ 1.6 Hz, $J_{3,2}$ 3.8 Hz, $J_{3,4}$ 4.0 Hz, 3-H_B), 4.54 (1 H, d, $J_{6,5}$ 4.1 Hz, 6-H_B), 5.00 (1 H, d, 4-H_B), 5.06 (1 H, d, 5-H_B), 6.46 (1 H, dd, $J_{2,1}$ 9.6 Hz, 2-H_B), 6.71 (1 H, dd, 1-H_B) and 7.38–8.18 (6 H, m, ArH).

cis,trans-3,4;7,8-*Diepoxy*-3,4,7,8-*tetrahydrobenzo*[c]*phenanthrene* **30A**/**30B** (59 mg, 95%), m.p. 148–150 °C [(decomp.) (mixture of diastereoisomers) (from chloroform–pentane) (Found: M^+, 260.0837. $C_{18}H_{12}O_2$ requires M, 260.0838); δ_H(400 MHz) 4.30 (2 × 1 H, ddd, $J_{3,1}$ 1.8 Hz, $J_{3,2}$ 3.9 Hz, $J_{3,4}$ 3.9 Hz, 3-H_A, 3-H_B), 4.55 (2 × 1 H, d, $J_{7,8}$ 4.0 Hz, 7-H_A, 7-H_B), 4.60 (2 × 1 H, d, 4-H_A, 4-H_B), 4.68 (1 H, d, 8-H_A, 8-H_B), 6.44 (2 × 1 H, dd, $J_{2,1}$ 9.8 Hz, 2-H_A, 2-H_B), 7.40 (2 × 1 H, ddd, $J_{11,9}$ 1.3 Hz, $J_{11,10}$ 7.3 Hz, $J_{11,12}$ 7.5 Hz, 11-H_A, 11-H_B), 7.45 (2 × 1 H, ddd, $J_{10,9}$ 7.8 Hz, $J_{10,12}$ 1.6 Hz, 10-H_A, 10-H_B), 7.48 (2 × 1 H, d, 1-H_A, 1-H_B), 7.65 (2 × 3 H, m, 6-H_A, 6-H_B, 5-H_A, 5-H_B, 9-H_A, 9-H_B) and 7.93 (2 × 1 H, d, 12-H_A, 12-H_B).

Diphenols **31**, **32**, **33** *and* **34**.—Reaction of each diarene oxide with trifluoroacetic acid (30 mg) gave the corresponding diphenol. The diphenols were identified by TLC analysis and visualization as a violet–blue spot with Gibbs reagent.

6,11-*Dihydroxybenz*[a]*anthracene* **31A** and 5,11-*dihydroxybenz*[a]*anthracene* **31B** (Found: M^+, 260.0837. $C_{12}H_{12}O_2$ requires M, 260.0838); ν_{max}(KBr) 3440 cm^{-1} (OH, br). Although the ^1H NMR spectrum of each compound is recorded separately the diphenols were not physically separated due to their similar properties and unstable nature.

31A δ_H(400 MHz), 6.88 (1 H, d, $J_{10,9}$ 7.2 Hz, 10-H_A), 6.93 (1 H, s, 5-H_A), 7.38 (1 H, m, 9-H_A), 7.53 (2 H, m, 2-H_A, 4-H_A), 7.65 (1 H, m, 3-H_A), 7.69 (1 H, m, 8-H_A), 8.75 (1 H, s, 7-H), 8.80 (1 H, m, 1-H_A) and 9.54 (1 H, s, 12-H_A).

31B δ_H(400 MHz), 6.79 (1 H, d, $J_{10,9}$ 7.0 Hz, 10-H_A), 7.04 (1 H, s, 6-H_B), 7.32 (1 H, m, 9-H_B), 7.57 (1 H, m, 8-H_B), 7.65 (1 H, m, 3-H_B), 7.73 (1 H, m, 2-H_B), 8.10 (1 H, s, 7-H_B), 8.28 (1 H, m, 4-H_B), 8.88 (1 H, d, $J_{1,2}$ 8.1 Hz, 1-H_B) and 9.47 (1 H, s, 12-H_B).

5,8-*Dihydroxybenz*[a]*anthracene* **32B**, 6,9-*dihydroxybenz*[a]*anthracene* **32C** and 5,9-*dihydroxybenz*[a]*anthracene* **32D** (Found: M^+, 260.0838. $C_{18}H_{12}O_2$ requires M, 260.0837); ν_{max}(KBr) 3440 cm^{-1} (OH, br).

32B δ_H(400 MHz), 6.83 (1 H, d, $J_{9,10}$ 7.2 Hz, 9-H_B), 7.08 (1 H, s, 6-H_B), 7.30 (1 H, dd, $J_{10,11}$ 7.8 Hz, 10-H_B), 6.79 (3 H, m, 1-H_B, 2-H_B, 11-H_B), 8.28 (1 H, d, $J_{4,3}$ 7.2 Hz, 4-H_B), 8.45 (1 H, s, 7-H_B), 8.79 (1 H, d, $J_{1,2}$ 8.0 Hz, 1-H_B) and 9.03 (1 H, s, 12-H_B).

32C δ_H(400 MHz), 6.97 (1 H, s, 6-H_C), 7.11 (1 H, d, $J_{10,11}$ 8.9 Hz, 10-H_C), 7.21 (1 H, m, 8-H_C), 7.69 (2 H, m, 2-H_C, 3-H_C), 7.91 (1 H, s, 7-H_C), 7.97 (1 H, d, 11-H_C), 8.74 (1 H, d, $J_{1,2}$ 8.0 Hz, 1-H_C) and 9.06 (1 H, s, 12-H_C).

32D δ_H(400 MHz), 6.90 (1 H, s, 5-H_D), 7.21 (1 H, m, 10-H_D), 7.35 (1 H, m, 8-H_D), 7.50 (2 H, m, 2-H_D, 4-H_D), 7.69 (1 H, m, 3-H_D), 8.03 (1 H, d, $J_{11,10}$ 8.9 Hz, 11-H_D), 8.58 (1 H, s, 7-H_D), 8.67 (1 H, m, 1-H_D) and 9.06 (1 H, s, 12-H_D).

4,7-*Dihydroxybenzo*[c]*phenanthrene* **34B** and 4,8-*dihydroxybenzo*[c]*phenanthrene* **34A** (Found: M^+, 260.0838. $C_{18}H_{12}O_2$ requires M, 260.0837); ν_{max}(KBr) 3400 cm^{-1} (OH, br).

34B δ_H(400 MHz) 6.99 (1 H, d, $J_{3,2}$ 7.6 Hz, 3-H_A), 7.18 (1 H, s, 8-H_A), 7.46 (1 H, m, 2-H_A), 7.80 (1 H, m, 9-H_A), 8.31 (1 H, m, 5-H_A), 8.35 (1 H, m, 6-H_A), 8.68 (1 H, d, $J_{1,2}$ 8.6 Hz, 1-H_A) and 8.99 (1 H, d, $J_{12,11}$ 7.4 Hz, 12-H_A).

34B δ_H(400 MHz), 6.92 (1 H, d, $J_{3,2}$ 6.5 Hz, 3-H_B), 7.10 (1 H, s, 7-H_B), 7.46 (1 H, m, 2-H_B), 7.69 (3 H, m, 6-H_B, 10-H_B, 11-H_B), 8.27 (1 H, d, $J_{5,6}$ 8.4 Hz, 5-H_B), 8.41 (1 H, d, $J_{9,10}$ 7.9 Hz, 9-H_B), 8.60 (1 H, d, $J_{1,2}$ 8.6 Hz, 1-H_B) and 9.09 (1 H, d, $J_{12,11}$ 8.3 Hz, 12-H_B).

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