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BENZOCYCLOBUTENES—X[1]

SYNTHESIS OF CYCLOBUTA[*l*]PHENANTHRENE DERIVATIVES FROM [2 + 2] PHOTOADDUCTS OF CHLORINATED ETHENES AND PHENANTHRENE

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Abstract—UV irradiation of phenanthrene and 1,1-dichloro-, 1,2-dichloro-, and 1,1,2-trichloroethenes resulted in [2 + 2] cycloaddition to give cyclobutane derivatives. Treatment of the 1,2-dichloro-adducts with *N*-bromosuccinimide resulted in aromatisation to yield *cis*- and *trans*-1,2-dichloro-1,2-dihydrocyclobuta[*l*]phenanthrene, whereas the 1,1-dichloro-adduct resulted in aromatisation and hydrolysis to give cyclobuta[*l*]phenanthren-1(2H)-one. The trichloroethene adducts gave 1,2-dichloro-2a,10b-dihydrocyclobuta[*l*]phenanthrene upon treatment with base, and reaction with *N*-bromosuccinimide resulted in bromine substitution in the cyclobutane ring. The stereochemistry of the adducts and the stereoselectivity of the bromination reactions are discussed.

Cyclobuta[*l*]phenanthrene derivatives have been synthesised by generation of their respective *o*-quinodimethanes,[2–5] by reduction of a ruthenium complex of cyclobuta[*l*]phenanthrene,[6] and by the oxidation of 2a,10b-dihydrocyclobuta[*l*]phenanthrene derivatives.[2,7–9] Although photochemical [2 + 2] cycloaddition reactions between phenanthrene, or substituted phenanthrenes, and alkenes have been extensively studied with regard to exciplex formation,[10–13] few attempts have been made to oxidise these adducts to cyclobuta[*l*]phenanthrene derivatives. To date *trans*-1,2-dichloro-, *trans*-1,2-dimethoxycarbonyl- and tetrachloro-1,2-dihydrocyclobuta[*l*]phenanthrenes have successfully been prepared by oxidation of their respective [2 + 2] cycloadducts with *N*-bromosuccinimide.[2,7,8] This paper records the photochemical reactions between phenanthrene and chlorinated ethenes to yield [2 + 2] cycloadducts and their further transformations with bromination reagents.

Irradiation of phenanthrene with a medium pressure mercury lamp (Pyrex filter) in the presence of 1,2-dichloroethene, 1,1-dichloroethene, and trichloroethene results in the formation of the respective [2 + 2] adducts (**1**, **2**, and **3**) in 29%, 7.5% and 55% yields based on isolated adduct (yields 50–90% based on recovered phenanthrene). The three isomers of adduct **1** could not be separated chromatographically; however, treatment with *N*-bromosuccinimide followed by separation on a dry alumina column gave *trans*-1,2-dichloro-1,2-dihydrocyclobuta[*l*]phenanthrene (**4a**) and the *cis*-isomer (**4b**) in 30 and 35% yields, respectively. The spectral data were consistent with the aromatised phenanthrene structure **4** and the assignment of each isomer is based on the following:

(a) The *cis*-isomer has a lower R_f value (0.4) than the *trans*-isomer (0.7) on silica gel (eluting with light petroleum).[8,14]

(b) The *cis*-isomer has a higher melting point (235–237°) than the *trans*-isomer (131–132°).[8,14]

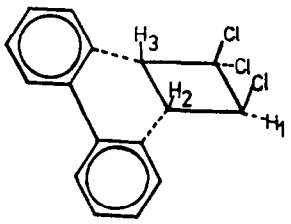
(c) The 1,2-protons appear further downfield in the NMR spectrum of the *cis*-isomer ($\delta = 6.16$ ppm) than the *trans*-isomer ($\delta = 5.62$ ppm), due to the 1,2-protons of the *cis*-isomer being pushed closer together by the 1,2-substituents, resulting in deshielding.[8,14–17]

Treatment of the *trans*- or *cis*-isomer **4a** or **4b** with bromine and irradiation with a 200-W tungsten-filament light bulb, did not result in benzylic bromination to give the compounds **5a** or **5b** (useful intermediates in the synthesis of cyclobuta[*l*]phenanthrene-1,2-dione[2]) but instead yielded phenanthrene-9,10-dicarboxylic anhydride,[18] presumably by aerial oxidation.

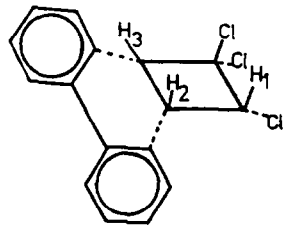
The reaction of the isomeric 1,1-dichloroadduct **2** with *N*-bromosuccinimide under conditions identical to those used previously, did not result in simple aromatisation to yield the phenanthrene **6**, but gave instead a colourless compound, m.p. 168–170°, which exhibited two carbonyl stretching frequencies (1 785 cm^{-1} and 1 750 cm^{-1}) in its IR spectrum, typical for four-membered ring ketones. The mass spectrum showed a molecular ion at 218 m.u. (80%) which fragmented with a loss of 28 m.u. (CO) to 190 m.u. (100%), and elemental analysis confirmed the formula $C_{16}H_{10}O$. The UV spectrum was typical for a phenanthrene nucleus, and the ^1H NMR spectrum contained a multiplet at $\delta = 7.58$–8.69 ppm (8H) and singlet at $\delta = 4.12$ ppm (2H). The ketone structure **8** is consistent with the above spectral data and is confirmed by analogy with benzocyclobutan-1(2H)-one which exhibits two carbonyl stretching frequencies at 1 775 and 1 755 cm^{-1} in the IR spectrum and benzylic protons at $\delta = 3.90$ ppm in its NMR spectrum.[19] The presumed intermediate in this reaction is the dichloro-compound **6**, and its sus-

ceptibility to hydrolysis to the ketone **8** under these conditions is rather surprising when compared with its benzologue 1,1-dichlorobenzocyclobutene. The latter compound requires the presence of Ag^+ ion to effect hydrolysis,[20] and it yields 1,1-dibromo-2,2-dichlorobenzocyclobutene upon treatment with an excess of *N*-bromosuccinimide.[1] The ketone **8** yielded the expected hydrazone derivative **9** when treated with 2,4-dinitrophenylhydrazine reagent. The photochemistry of the ketone has been described elsewhere.[21]

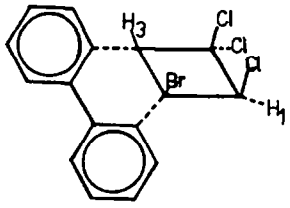
The products from the reaction of either isomer (I or II) of adduct **3** with *N*-bromosuccinimide did not yield the expected 1,1,2-trichloro-1,2-dihydrocyclobuta[*l*]phenanthrene **7**, but each gave an isomeric product which indicated substitution by bromine. The structures of the adducts **3** and their brominated products are based on spectroscopic data and chemical analysis (*vide infra*). The UV spectra of the adducts **3** and their brominated products were typical of those for a strained biphenyl system. The mass spectra of both **3** isomers showed molecular ions at 308 m.u. (*ca* 2%) which fragmented to 178 m.u. (100%) due to loss of trichloroethene (130 m.u.). Similarly, the corresponding brominated products had molecular ions at 386 m.u. (51 and 100%) which fragmented to 256 m.u. (0.2 and 3% respectively), again with loss of trichloroethene indicating a benzylic brominated product. The photochemistry of the adducts **3** and their brominated products was studied to confirm the stereochemistry of the [2 + 2] cycloadducts at the 2a,10b-positions, and to determine the position of Br substitution in their brominated products. Irradiation of either isomer of **3** gave only phenanthrene as the isolated product, after purification by tlc. This indicates that each adduct had *cis*-stereochemistry at the 2a,10b-positions which is consistent with all other adducts isolated from photochemical cycloaddition between phenanthrene and alkenes (the *trans*-isomer would be expected to yield a trichlorinated divinylphenyl product).[22] Irradiation of each isomeric brominated product yielded 9-bromophenanthrene, which similarly confirms the *cis*-stereochemistry at the 2a,10b-positions, and also indicated that bromination had occurred at the benzylic position of the isomeric adducts **3**. Reactions of *N*-bromosuccinimide at a benzylic position are well documented.[9,23] Treatment of either adduct **3** with sodium hydroxide resulted in elimination of HCl to give the same product, namely 1,2-dichloro-2a,10b-



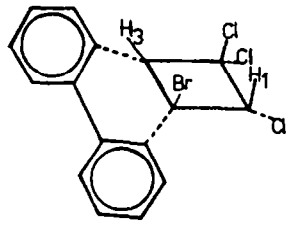
Anti-(3a)



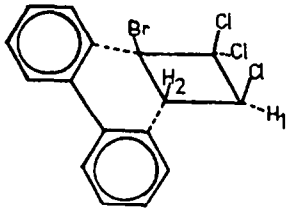
Syn-(3b)



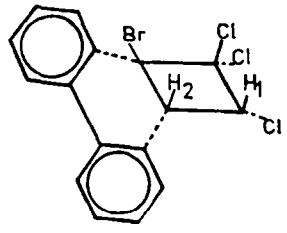
Anti-(11a)



Syn-(11b)



Anti-(12a)



Syn-(12b)

Fig. 1. Stereochemistry of compounds (**3**), (**11**) and (**12**).

dihydro-cyclobuta[*l*]phenanthrene **10**. From the above data there are two possible cycloadducts (*anti*-**3a** and *syn*-**3b** as shown), with *cis*-stereochemistry at the 2a,10b-position (see Fig. 1).

Isomer I melted at 127.5–128.5°, had an R_f value of 0.6 on silica gel plates eluting with light petroleum (phenanthrene $R_f = 0.8$), and was isolated in 48% yield. Isomer II melted at 168–170°C, had an $R_f = 0.2$, and was isolated in 7% yield. The ^{1}H NMR spectrum of isomer I of adduct **3** in deuteriochloroform forms an ABX system. It showed a quartet at $\delta = 3.99$ (one proton, J = 10.0 and 9.0 Hz), a broadened doublet at $\delta = 4.57$ (one proton, J = 10.0 Hz), and a doublet of doublets at $\delta = 4.46$ (one proton, J = 9.0 and 1.0 Hz). However isomer II (AXY system) showed a quartet at $\delta = 4.28$ (one proton, 10.0 and 9.0 Hz), a broadened doublet at $\delta = 4.51$ (one proton, J = 10.0 Hz) and a doublet of doublets at $\delta = 5.44$ (one proton, 9.0 and 1.0 Hz). If the *anti*-(**3a**) and *syn*-(**3b**) isomers are considered, H_1 would appear as a doublet of doublets with strong (H_1 and H_2) and weak (H_1 and H_3) spin–spin coupling. The quartet is due to H_2, which has strong spin–spin coupling with both H_1 and H_3, and the broadened doublet is due to proton H_3 which has strong coupling with H_2 but is broadened due to coupling with H_1 and with the aromatic protons (this phenomenon is also observed in the ^{1}H NMR spectrum of the other nonsymmetrical adduct (**2**)).

However, the greatest change in chemical shift (*ca* 1 ppm) is due to H_1 which appears at $\delta = 4.46$ in isomer I and at $\delta = 5.44$ in isomer II. Clearly isomer I is the *anti*-adduct (**3a**), where H_1 is shielded by the aromatic ring and therefore appears upfield. Isomer II is the *syn*-adduct (**3b**) where H_1 cannot be shielded by the aromatic ring.

Having established that benzylic bromination had occurred [from the mass-spectral data and the photochemical reactions of the brominated products of adducts **3**] there remain four possible structures for these products. Bromination of the two adducts **3** at the 2a-position (i.e. replacing H_2 with Br) would result in the *anti*-(**11a**) and *syn*-(**11b**) products, and substitution at the 10a-position (replacing H_3 with Br) would yield **12a** and **12b** respectively.

Bromination of the *anti*-isomer should yield the *anti*-substituted product **11a** or **12a** and the *syn*-isomer should yield the *syn*-product **11b** or **12b**. The 100 MHz ^{1}H NMR spectrum of the brominated product from adduct **3a** in deuteriochloroform showed a broad singlet at $\delta = 4.14$ (two protons); however the 200 MHz spectrum resolved the "singlet" into two doublets at $\delta = 4.10$ $\delta = 4.14$ (J = 9.8 Hz). These two doublets could be separated

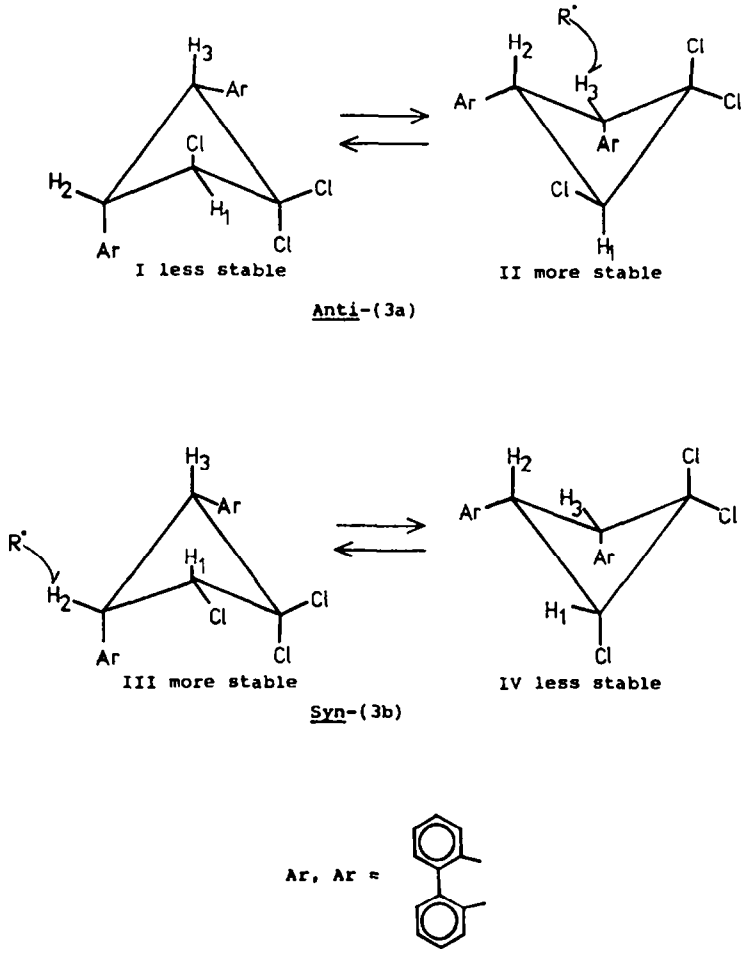


Fig. 2. Conformation of compounds (**3a**) and (**3b**).

further at 200 MHz by using perdeuteriotoluene as the solvent ($\delta = 4.10$ and 4.39, $J = 10.0$ Hz). Clearly these coupling constants are too large for coupling across the cyclobutane ring between H_1 and H_3, as in structure **11a**, and so the brominated product from **3a** must be **12a** with 1,2-*trans*-coupling between H_1 and H_2.

The bromination product from adduct **3b** exhibited a broadened singlet and a doublet in its 100 MHz ^{1}H NMR spectrum in deuteriochloroform at $\delta = 4.93$ (one proton) and 5.85 (one proton) ($J = 1.0$ Hz). These peaks were shifted but not further resolved at 200 MHz using deuteriochloroform or perdeuteriotoluene as solvents. The only structure compatible with these data is *syn*-(**11b**) where bromination has occurred at the 2a-position.

At first sight bromination of both isomers of the adduct **3** would be expected to occur at the 2a-benzylic position, a site further away from the dichloro-substituted carbon than the 10b-benzylic position. However, careful examination of the conformations of the puckered cyclobutane ring system reveals why bromination occurs at the 10b-position in the *anti*-isomer **3a** and at the 2a-position in the *syn*-isomer **3b**.

The *anti*-isomer **3a** has two conformations (see Fig. 2): (I) where H_1, H_2, one Ar, and one Cl are equatorial, and H_3, one Ar, and two Cl substituents are axial; (II) where H_3, one Ar, and two Cl substituents are equatorial and H_1, H_2, one Ar, and one Cl axial.

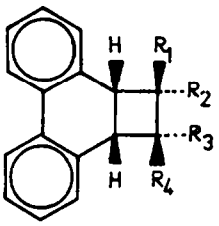
The latter is more stable because it has more of the bulky substituents in the equatorial positions. The less hindered benzylic proton for radical bromination is the equatorial H_3, and so bromination occurs at the 10b-position, i.e. adjacent to the $>CCl_2$ carbon.

Using similar arguments for the conformations of the *syn*-isomer **3b** it is apparent that III has more of the bulky substituents in equatorial positions than IV, and so III is the more stable conformation. In this case the less hindered benzylic proton for radical attack is H_2, and so bromination occurs at the 2b-position, i.e. adjacent to the $>CHCl$ carbon.

Attempts to aromatise either of the brominated adducts **12a** or **11b** using base resulted in an inseparable mixture. This is probably due to elimination of both HCl and HBr to yield a reactive cyclobutadiene species (see the ease of elimination of HCl from either isomer of adducts **3**).

EXPERIMENTAL

General directions for chromatography are given in Ref. 24. IR and UV spectra were measured in Nujol mulls and in 95% ethanol respectively. ^{1}H NMR spectra were recorded in deuteriochloroform solutions on a Varian HA-100 or on a Varian XL 200 MHz spectrometer in deuteriochloroform or perdeuteriotoluene. The chlorinated alkenes were flash



(1a) R_1 and R_3 = Cl; R_2 and R_4 = H

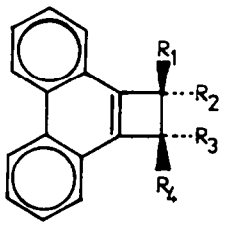
(1b) R_1 and R_4 = Cl; R_2 and R_3 = H

(1c) R_2 and R_3 = Cl; R_1 and R_4 = H

(2) R_1 and R_2 = Cl; R_3 and R_4 = H

(3a) R_1, R_2 and R_4 = Cl; R_3 = H

(3b) R_1, R_2 and R_3 = Cl; R_4 = H



(4a) R_1 and R_3 = Cl; R_2 and R_4 = H

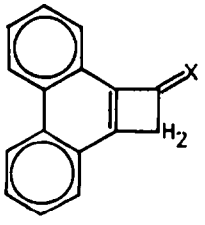
(4b) R_1 and R_4 = Cl; R_2 and R_3 = H

(5a) R_1 and R_3 = Cl; R_2 and R_4 = Br

(5b) R_1 and R_4 = Cl; R_2 and R_3 = Br

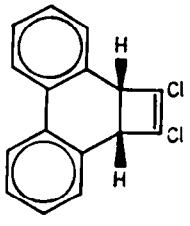
(6) R_1 and R_2 = Cl; R_3 and R_4 = H

(7) R_1, R_2 and R_3 = Cl; R_4 = H



(8) X = O

(9) X = 2,4-$(NO_2)_2C_6H_3$-NH-N=



(10)

distilled prior to use. Light petroleum refers to the fraction of b.p. 60–80°.

1,2-*Dichloro*-1,2,2a,10b-*tetrahydrocyclobuta[l]phenanthrene* (1)

Phenanthrene (13.35 g) in a mixture of *cis*- and *trans*-dichloroethene (36.4 g) and ether (70 ml) was purged with nitrogen and irradiated through Pyrex for 120 h with a 125 W Hanovia medium-pressure mercury lamp. The mixture was evaporated and the residue chromatographed on a column of dry alumina (100 × 2.5 cm) using light petroleum as eluant to yield phenanthrene (*ca* 6 g, 45% recovery), followed by 1,2-dichloro-1,2,2a,10b-tetrahydrocyclobuta[*l*]-phenanthrene **1** (6 g, 29%) m.p. 140–170° as a mixture of isomers (see Ref. 7).

1,1-*Dichloro*-1,2,2a,10b-*tetrahydrocyclobuta[l]phenanthrene* (2)

Phenanthrene (10 g) in 1,1-dichloroethene (100 ml) and ether (200 ml) was irradiated for 38.5 h with a 500 W Hanovia medium-pressure mercury lamp. The solvent was evaporated and the residue chromatographed on a short silica gel column. Elution with light petroleum yielded phenanthrene (8.0 g, 80% recovery), followed by a mixture of phenanthrene and product (*ca* 2 g). The mixture was rechromatographed on a second short silica gel column eluting with light petroleum to yield phenanthrene (0.85 g, 8.5%) and 1,1-*dichloro*-1,2,2a,10b-*tetrahydrocyclobuta[l]-phenanthrene* **2** (1.15 g, 7.5%) as needles (from ethanol) m.p. 110° (Found: C, 70.0; H, 4.6. $C_{16}H_{12}Cl_2$ requires C, 69.85; H, 4.4%); ν_{max} 3 110, 3 075, 3 060, 3 030, 3 020, 860, 795, 780, 760, 730, 700, 675, and 655 cm^{-1}; λ_{max} (log ϵ) 235(3.96), 243(3.73), 262 sh(3.61), 270 sh(3.84), 280(3.94), 289 sh(3.81), 310(3.33), 320(3.15), and 357 nm(2.95); δ(100 MHz) 3.05(1H, ddd, 2-H, J = 1.2, 4.6, 13.0 Hz), 3.67(1H, ddd, 2-H, J = 2.0, 9.0, 13.0 Hz), 4.04(1H, sextet, 2a-H, J = 4.6 Hz), 4.58(1H, br, d, 10b-H, J = 10.0 Hz), 7.29(6H, m, 3, 4, 5, 8, 9, and 10-H), and 7.93(2H, m, 6 and 7-Hz).

Anti- *and* syn-1,1,2-*trichloro*-1,2,2a,10b-*tetrahydrocyclobuta[l]phenanthrene* (3a and 3b)

Phenanthrene (5.0 g) in trichloroethene (100 ml) and hexane (850 ml) was purged with nitrogen and irradiated through Pyrex for 75 h with a 450 W Hanovia medium-pressure mercury lamp. The reaction mixture was chromatographed on a dry alumina column (25 × 3.5 cm) using pentane as eluant: 50 ml fractions were collected and groups of these were united. The eluate, in order of elution, consisted of fractions 1–3, phenanthrene (*ca* 1.3 g, 26% recovery), fractions 4–12 phenanthrene plus isomer I of the cycloadduct (3.2 g) and fractions 13–30 which contained anti-1,1,2,-*trichloro*-1,2,2a,10b-*tetrahydrocyclobuta-[l]phenanthrene* **3a** (1.9 g, 22%) as plates (from ethanol), m.p. 127.5–128.5° (Found: C, 62.1; H, 3.6. $C_{16}H_{11}Cl_3$ requires C, 62.0; H, 3.6%); ν_{max} 3 060, 3 020, 875, 865, 790, 760, 735, 670, and 655 cm^{-1}; λ_{max} (log ϵ), 233(3.85), 252(3.95), 257 sh(3.92), 268(3.89), 277(4.05) and 312 sh(3.36) nm; δ(100 MHz) 3.99(1H, q, 2a-H, J = 10.0, 9.0 Hz), 4.46 (1H, dd, 2-H, J = 9.0, 1.0 Hz), 4.57 (1H, br.d, 10b-H, J = 10.0 Hz), 7.35 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.96 (2H, m, 6 and 7-H); δ(200 MHz) 3.99 (1H, q, 2a-H, J = 9.9, 8.9 Hz), 4.46 (1H, dd, 2-H, J = 8.9, 1.1 Hz), 4.57 (1H, bd, 10b-H, J = 9.9 Hz), 7.34 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.97 (2H, m, 6 and 7-H); $\delta(C_7D_8$, 200 MHz) 3.96 (1H, q, 2a-H, J = 9.8, 8.8 Hz), 4.38 (1H, br.d, 10b-H, J = 10.0 Hz), 4.46 (1H, dd, 2-H, J = 8.8, 1.2 Hz), 7.40 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.97 (2H, m, 6 and 7-H). Fractions 31–48 contained syn-1,1,2-*trichloro*-1,2,2a,10b-*tetrahydrocyclobuta-[l]phenanthrene* (**3b**) (0.3 g, 3.5%) as plates (from ethanol), m.p. 168–170° (dec.) (Found: C, 61.7; H, 3.7. $C_{16}H_{11}Cl_3$ requires C, 62.0; H, 3.6%); ν_{max} 3 100, 3 070, 3 050, 880, 865, 795, 780, 765, 750, 740, 730, 700, and 680 cm^{-1}; λ_{max}(log ϵ), 235(3.98), 243(3.76), 262 sh(3.68), 270 sh(4.05), 280(4.22), 289 sh(4.05), and 306 sh(3.07) nm (log ϵ); δ(100 MHz) 4.28 (1H, q, 2a-H, J = 10.0, 9.0 Hz), 4.51 (1H, br.d, 10b-H, J = 10.0 Hz), 5.44 (1H, dd, 2-H, J = 9.0, 1.0 Hz), 7.32 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.96 (2H, m, 6 and 7-H); δ(200 MHz) 4.28 (1H, q, 2a-H, J = 10.1, 8.8 Hz), 4.50 (1H, br.d, 10b-H, J = 10.1 Hz), 5.44 (1H, dd, J = 8.8, 0.9 Hz), 7.30 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.96 (2H, m, 6 and 7-H); $\delta(C_7D_8$, 200 MHz) 4.04 (1H, q, 2a-H, J = 10.1, 8.9 Hz), 4.22 (1H, br.d, 10b-H, J = 10.1 Hz), 5.18 (1H, dd, J = 8.9, 0.9 Hz), 7.45 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 8.03 (2H, m, 6 and 7-H). Fractions 4–12 and 31–48, were rechromatographed separately, as before, on the same column to yield phenanthrene (0.8 g, 16%), the *anti*-adduct (isomer I, **3a**) (2.25 g, 26%), and the *syn*-adduct (isomer II, **3b**) (0.3 g, 3.5%).

Trans- *and* cis-1,2-*dichloro*-1,2-*dihydrocyclobuta[l]phenanthrene* (4a and 4b)

A mixture of the above adduct (**1**) (2.0 g), *N*-bromosuccinimide (5.5 g), and dibenzoyl peroxide (*ca* 25 mg) in CCl_4 (100 ml) was refluxed for 1.5 h. The hot mixture was filtered, cooled, washed with 0.1 M $Na_2S_2O_3$ (100 ml), then dried and evaporated. The residue was chromatographed on a column of dry alumina eluting with light petroleum to yield trans-1,2-*dichloro*-1,2-*dihydrocyclobuta[l]phenanthrene* (**4a**) (0.6 g, 30%) as needles (from ethanol) m.p. 131-132° (lit.[7] 126.5–127°); ν_{max} 3 070, 3 050, 3 020, 925, 860, 820, 780, 750, 715, 710, and 670 cm^{-1}; δ 5.62 (2H, s, 1 and 2-H), 7.66 (4H, m, 4, 5, 8 and 9-H), 7.92 (2H, m, 3 and 10-H), and 8.65 (2H, m, 6 and 7-H). Further elution with the same solvent yielded cis-1,2-*dichloro*-1,2-*dihydrocyclobuta[l]phenanthrene* (**4b**) (0.7 g, 35%) as needles (from ethanol) m.p. 235–237° (decomp.) (Found: C, 70.7; H, 3.8; Cl, 25.9. $C_{16}H_{10}Cl_2$ requires C, 70.35; H, 3.7; Cl, 25.95%); ν_{max} 3 070, 3 040, 3 020, 950, 930, 890, 870, 830, 775, 750, 720, and 685 cm^{-1}; λ_{max}(log ϵ) (CH_2Cl_2) 230(4.41), 249(4.71), 256(4.83), 264 sh(4.41), 280(3.97), 291(3.93), and 303(4.03) nm; δ6.06 (2H, s, 1 and 2-H), 7.75 (4H, m, 4, 5, 8 and 9-H), 8.01 (2H, m, 3 and 10-H), and 8.75 (2H, m, 6 and 7-H).

9,10-*Phenanthrenedicarboxylic anhydride*

Bromine (0.35 g) in dry carbon tetrachloride (10 ml) was added over 2 h to a refluxing solution of the *trans*-dichloro-compound **5a** (0.1 g) in CCl_4 (50 ml), irradiated with a 200 W tungsten filament light bulb. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2, washed with 0.1 M $Na_2S_2O_3$, and dried. Evaporation yielded the anhydride (50 mg, 55%), m.p. 312° (lit.[2] 317°); ν_{max} 1840, 1805, and 1770 cm^{-1}.

Cis-(**5b**) gave the same product in 60% yield.

1,2-*Dihydrocyclobuta[l]phenanthrenone* (8)

A mixture of the adduct **2** (200 mg), *N*-bromosuccinimide (500 mg), and dibenzoylperoxide (*ca* 25 mg) in dry CCl_4 (5 ml) was refluxed for 1 h. The solvent was evaporated and the residue chromatographed on a dry alumina column (10 × 1 cm) eluting with toluene to yield 1,2-*dihydrocyclobuta[l]phenanthrenone* (**8**) (71 mg, 45%) as needles (from ethanol) m.p. 168–170°C (Found: C, 88.0; H, 4.6. $C_{16}H_{10}O$ requires C, 88.05; H, 4.6%); ν_{max} 3 070, 1 785, 1 750, 1 625, 1 610, 970, 935, 750, and 720 cm^{-1}; λ_{max} (log ϵ) 209(3.96), 243 sh(4.32), 248(4.41), 263(4.24), 283(3.74), 315(3.71), 343(3.31), and 360(3.23) nm; δ 4.12 (2H, s, 2-H), 7.75 (5H, m, 3, 4, 5, 8 and 9-H), 8.08 (1H, m, 10-H) and 8.60 (2H, m, 6 and 7-H).

The ketone gave the 2,4-*dinitrophenylhydrazone* (**9**) m.p. 304° (Found: C, 66.05; H, 3.7; N, 14.0. $C_{22}H_{14}N_4O_4$ requires C, 66.3; H, 3.5; N, 14.1%).

Anti-1,1,2-*trichloro*-10b-*bromo*-1,2,2a,10b-*tetrahydrocyclobuta[l]phenanthrene* (12a)

The anti-adduct **3a** (0.22 g), *N*-bromosuccinimide (0.40 g), and dibenzoylperoxide (*ca* 25 mg) were refluxed for 2 h in CCl_4(25 ml). The hot mixture was filtered, evaporated,

and the residue chromatographed on a column of dry alumina. Elution with light petroleum yielded anti-1,1,2-*trichloro*-10b-*bromo*-1,2,2a,10b-*tetrahydrocyclobuta[l]phenanthrene* (**12a**) (152 mg, 55%) as plates m.p. 170–2.5° (decomp.) (Found: C, 49.1; H, 2.6. $C_{16}H_{10}BrCl_3$ requires C, 49.4; H, 2.6%); ν_{max}, 3 070, 935, 900, 800, 760, 735, 690, and 675 cm^{-1}; $\lambda_{max}(\log \epsilon)$ (CH_2Cl_2) 236(4.11), 244(3.91), 271 sh(4.18), 281(4.32), 289 sh(4.18) and 308 sh(3.18)nm; δ(100 MHz) 4.14 (2H, br.s, 2 and 2a-H), 7.40 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.94 (2H, m, 6 and 7-H); δ (200 MHz) 4.10(1H, d, 2-H, J = 9.9 Hz), 4.14 (1H, d, 2a-H, J = 9.8 Hz), 7.39 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.89 (2H, m, 6 and 7-H); $\delta(C_7D_8$, 200 MHz), 4.10 (1H, d, 2-H, J = 9.9 Hz), 4.39 (1H, d, 2a-H, J = 9.9 Hz), 7.46 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.80 (2H, m, 6 and 7-H).

Syn-1,1,2-*trichloro*-2a-*bromo*-1,2,2a,10b-*tetrahydrocyclobuta[l]phenanthrene* (**11b**)

By the above procedure the *syn-adduct* **3b** (0.22 g) gave the syn-*trichlorotetrahydrocyclobuta[l]phenanthrene* **11b** (169 mg, 61%) as plates m.p. 159–166° (decomp.) (Found: C, 49.5; H, 2.6. $C_{16}H_{10}BrCl_3$ requires C, 49.4; H, 2.6); ν_{max} 3 070, 945, 935, 905, 865, 805, 760, 735 and 690 cm^{-1}, $\lambda_{max}(\log \epsilon)$ (CH_2Cl_2) 335(4.02), 350(4.08), 357 sh(4.01), 368(3.91), 377(4.11), and 412 sh(3.38) nm; δ(100 MHz) 4.93 (1H, br.s, 10b-H), 5.85 (1H, d, 2-H, J = 1.0), 7.51 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.90(2H, m, 6 and 7-H); δ (200 MHz) 4.89 (1H, br.s, 10b-H), 5.82 (1H, d, 2-H, J = 1.0), 7.48 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.97 (2H, m, 6 and 7-H); δ (C_7D_8, 200 MHz) 5.08 (1H, br.s, 10b-H), 6.04 (1H, d, 2-H, J = 1.1), 7.43 (6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.92 (2H, m, 6 and 7-H).

Photolysis of the trichloroethylene-phenanthrene adducts (**3a** and **3b**) *and their brominated products* (**12a** and **11b**)

A solution of the cyclobutane (**3a**, **3b**, **12a**, or **11b**) (5 mg) in dichloromethane (1.0 ml) and ethanol (9.0 ml) was irradiated with one 300 nm Rayonet lamp for 4 h. The solvent was evaporated and the residue purified by thin layer chromatography to give the product (2–3 mg, 60–80% yield) which was identified by R_f value, u.v. absorption spectrum, and m.p. (compared with an authentic sample).

1,2-*Dichloro*-2a,10b-*dihydrocyclobuta[l]phenanthrene* (**10**)

A mixture of the *anti*-adduct **3a** (0.1 g) and sodium hydroxide (0.1 g) in ethanol (10 ml) was refluxed for 1 h. The cooled solution was filtered and the residue washed with water. Recrystallization of the solid from ethanol/water gave 1,2-*dichloro*-2a,10b-*dihydrocyclobuta[l]phenanthrene* (**10**) (60 mg, 67%) as needles, m.p. 168–170° (Found: C, 70.4; H, 3.8. $C_{16}H_{10}Cl_2$ requires C, 70.35; H, 3.7); ν_{max} 3 050, 1 635, 1 615, 940, 760, and 730 cm^{-1}; $\lambda_{max}(\log \epsilon)$ 216(4.68), 234(4.26), 244(3.99), 274 sh(4.13), 281(4.19), 292(4.06), and 311(3.53)nm; δ4.35 (2H, s, 2a,10b-H), 7.33(6H, m, 3, 4, 5, 8, 9 and 10-H), and 7.96 (2H, m, 6 and 7-H).

Similarly the *syn*-adduct (**3b**) (0.1 g) yielded the same product (44 mg, 50%).

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