Studies in the cycloproparene series: chemistry of 1*H*-cyclopropa[*b*]naphthalene-3,6-dione and its transformation into 1*H*-cyclopropa[*b*]anthracene-3,8-dione[1]

Brian Halton,*[a] Carissa S. Jones,[a] Andrew J. Kay,[a]† Davor Margetic[b] and Sanja Sretenovic[a]

[a] *School of Chemical & Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand*
[b] *Centre for Molecular Architecture, Central Queensland University, Rockhampton, Queensland 4702, Australia*

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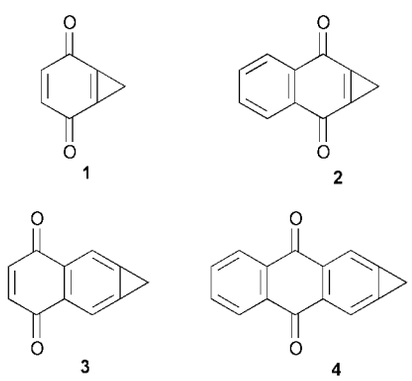
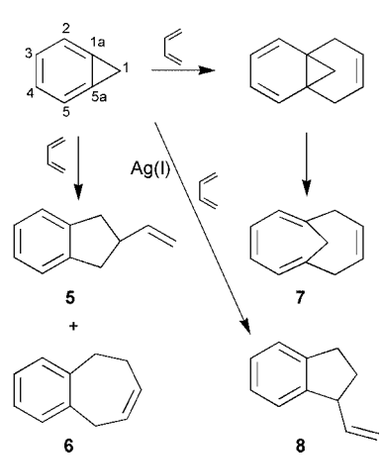
1*H*-Cyclopropa[*b*]naphthalene-3,6-dione **3** adds bromine stoichiometrically across the enedione C=C bond to give dibromodihydrocyclopropanaphthalenedione **10** while with an excess of the reagent (bromomethyl)tribromonaphthoquinone **12** is formed. Typical quinone character is exhibited by **3** in Diels–Alder cycloadditions and it gives the *endo*-methanocyclopropanthraquinone **14** with cyclopentadiene. With buta-1,3-diene the analogous tetrahydrocyclopropanthraquinone **15** is formed from a temperature dependent reaction. Above 45 °C opening of the three-membered ring of **4** also occurs and the cyclopentanthracenedione **16** is obtained from [π2 + π4] and [σ2 + π2] additions; it is the sole product at 100 °C. Enolisation of the tetrahydroanthraquinone **15** provides diphenolate **18** and this can be diverted to diether **19** or readily oxidized to the dihydroanthraquinone **20**. In turn, **20** is dehydrogenated to the fully aromatic cyclopropa[*b*]anthracene-3,8-dione **4**, the first anthraquinone of the cycloproparene series.

Although the chemistry of the cycloproparenes has received significant attention over the past years,[2] only three cyclopropaquinones (**1**–**3**) have been reported.[3–5] The first and



simplest of these, 1*H*-cyclopropabenzene-2,5-dione **1**, was prepared by Oda and his colleagues, but it was too reactive for isolation under normal conditions and its formation was deduced from appropriate trapping experiments.[3] The same was found to hold[4] for the cyclopropa[*b*]naphthalene analogue **2**. However, incorporation of an enedione moiety into the ring remote from cyclopropa fusion led to cyclopropa[*b*]-naphthalene-3,6-dione **3** as a stable, yellow crystalline compound whose structure has been confirmed by X-ray analysis.[5] This compound is intermediate to naphthoquinone and anthraquinone in its ease of reduction as established from cyclic voltammetry.[5] We now report on the essential chemical reactivity of quinone **3** that provides for its use as a synthon to more complex polycyclic assemblies by way of [4 + 2] Diels–Alder methodology. As the cycloproparene framework is usually retained in the absence of electrophilic reagents,[2] this allows for the elaboration of the series from cyclopropanaphthalene-3,6-dione **3** to cyclopropanthracene-3,8-dione **4**. Quinone **4** has possible use as a new molecular spacer and is a desired precursor to derivatives with extended conjugation through a C-1 exocyclic olefin.

It is known that cyclopropabenzene behaves as an electron rich dienophile in Diels–Alder cycloadditions and adds electron deficient dienes across the C-1a–C-5a bridge bond.[2] However, opening of the three-membered ring can also occur.[6] Thus, with butadiene at 80 °C cyclopropabenzene gives 2-vinylindane **5** from [3 + 2] addition across the σ bond, small amounts of the analogous [3 + 4] adduct **6**, and some of the dihydro[10]-annulene **7** that arises from sequential [2 + 4] addition across the C1a–C5a bond followed by norcaradiene valence isomerization (Scheme 1).[7] Under Ag(I) catalysis the regioselectivity of addition to the σ bond is changed and it is the regioisomeric 1-vinylindane **8** that is obtained.[8] In similar vein, easy



Scheme 1

† Present address: Industrial Research Ltd., Gracefield Research Centre, PO Box 31-310, Lower Hutt, New Zealand.

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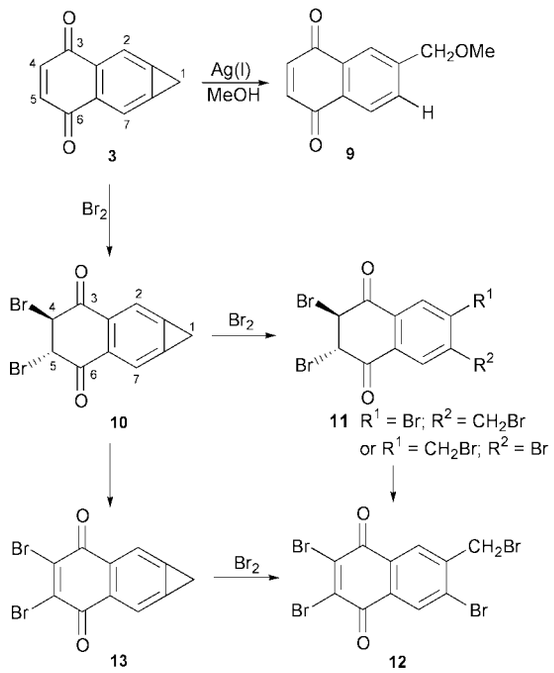
ring-opening with electrophilic reagents is illustrated by the formation of benzyl ethers from reaction with alcohols in a reaction that is catalysed by Ag(I) (Scheme 2).[8–10] In order to

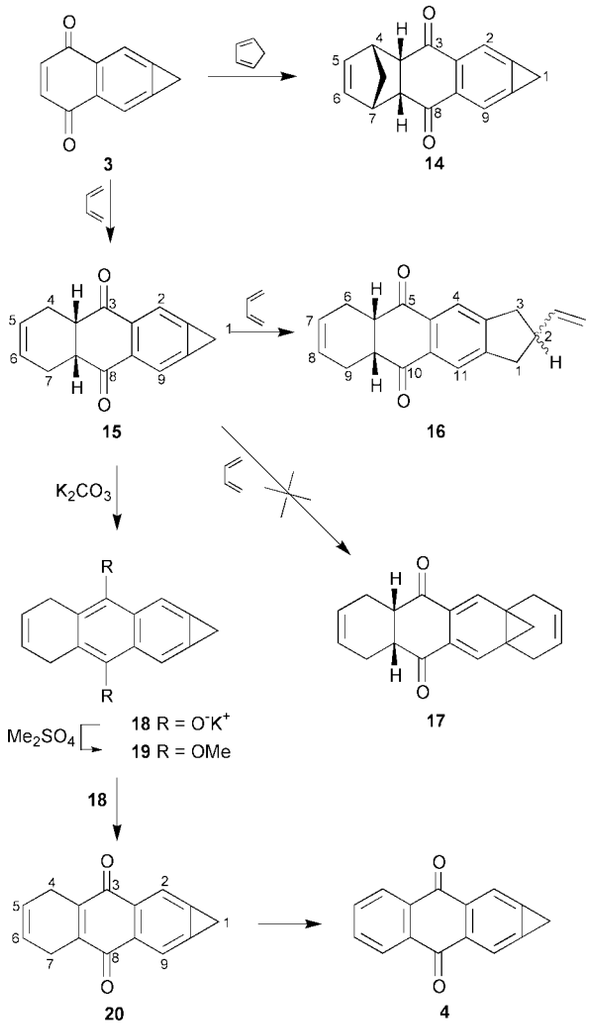


Scheme 2

compare the reactivity of the three-membered ring σ bond with that of the enedione olefinic bond of quinone **3**, the behaviour with methanol, bromine, cyclopentadiene and butadiene has been examined.

As part of the formal characterization of quinone **3**, we reported[5] that Ag(I)-catalysed methanolysis results in the known[11] 6-(methoxymethyl)naphthalene-1,4-dione **9** from electrophilic opening of the three-membered ring (Scheme 2). What is more relevant here, however, is the fact that in competition for molecular bromine (1 mol equiv.) it is the enedione π bond that adds the reagent and the *trans*-dibromide **10** is formed almost quantitatively from reaction in tetrachloromethane. The structure of the product is fully compatible with the spectroscopic data. The two proton singlet at δ 4.99 is expected for a *trans*-1,2-dibromocyclohexane ring[12] and it replaces that at δ 6.95 for 4-H/5-H of **3**. The retention of the methylene moiety [**10**: δ 3.44/19.7; **3**: δ 3.36/19.1], the presence of only two methine signals, one of which corresponds to the shielded C-2(5) carbon atoms (δ 114.4), and the appearance of three quaternary carbons are fully consistent with the assigned structure. In a modification of the experimental procedure tetrachloromethane–methanol was employed as the solvent system whereupon a different outcome was recorded. In this case the product is precipitated as the reaction proceeds and addition of a further aliquot of bromine provides more of the same compound. The product is insoluble in common solvents and is neither dibromide **10** nor the diastereomeric tetrabromides **11** from dibromination. Rather, facile oxidation of **11** provides the aromatic tetrabromide **12** as the isolated compound (Scheme 2). While the path from **3** to **12** *via* **10** and **11** is entirely plausible, we cannot exclude the alternative route *via* **9** in which the oxidative dehydrogenation precedes opening of the three-membered ring (Scheme 2). Compound **12** displays the molecular ion cluster of a tetrabromide (*m*/*z* 484/486/488/490/492 : 4/15/20/13/3) and the three ^{1}H NMR signals (δ 4.65, CH_2; 8.22, CH; 8.36, CH) closely resemble the corresponding peaks of 2-bromo-3-(bromomethyl)naphthalene.[13]

Reaction of quinone **3** with excess cyclopentadiene at ambient temperature results in a 1 : 1 adduct that is assigned as the

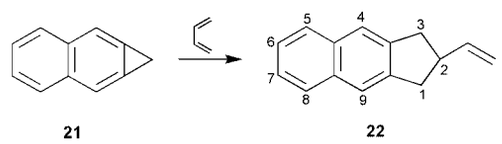


Scheme 3

endo-product **14** from Diels–Alder addition across the enedione olefinic double bond (Scheme 3). The presence of only nine signals in the ^{13}C NMR spectrum is nicely compatible with **14** and excludes the product from addition across the three-membered ring σ bond. The highly stereoselective formation of the *endo*-adduct is deduced from the characteristic coupling between the bridge (3a-H/7a-H: δ 3.44) and bridgehead protons (4-H/7-H: δ 3.65) that requires the bridge protons to be oriented *exo*.

The ease with which quinone **3** adds not only cyclopentadiene but also isobenzofuran[1] across the olefinic π bond suggests its use as a synthon for the annelated cyclopropanthracene-3,8-dione **4** (Scheme 3). Indeed, the addition of buta-1,3-diene occurs easily under sealed tube conditions but the excess of this reagent that is invariably present impacts upon the outcome. When the Carius tube reaction is effected at 100 °C cycloaddition takes place at *both* the enedione π bond and the cyclopropene σ bond to give a symmetrical diadduct that is identified as [5aα,9aα]-2-ethenyl-5a,6,9,9a-tetrahydro-1*H*-cyclopenta[*b*]anthracene-5,10-dione **16** rather than the desired mono-addition product **15** (Scheme 3). The symmetry of **16** is evident from the ^{13}C NMR spectrum which displays only 11 lines for the centrosymmetric molecule (Experimental section). These observations *exclude* the unsymmetrical regioisomeric homologue of **8** with the vinyl substituent at C-1, as well as the benzocycloheptene equivalent to **6** from [4 + 3] addition across the three-membered ring σ bond (Scheme 1). The assignment of the product as indane **16** rather than the norcaradiene **17** (or its ring opened valence bond isomer) from addition across the C-1a–9a bridge also follows from the spectroscopic data. The ^{1}H NMR resonances at δ 5.01, 5.10, and 5.93 are compatible

with the monosubstituted vinyl group, that at δ 5.73 with the symmetrical disubstituted olefin (7-H/8-H), and the two-proton aromatic singlet (δ 7.84) is required for **16** but not **17** (Scheme 3). Although the opening of the three-membered ring recorded for **3** matches the behaviour of cyclopropabenzene discussed above (Scheme 1), a more appropriate model for cyclopentanthracene **16** was sought. Hence cyclopropa[*b*]naphthalene **21** was reacted with buta-1,3-diene at 100 °C. The single product isolated in 57% yield is confidently assigned as 2-ethenyl-2,3-dihydrocyclopenta[*b*]naphthalene **22** (Scheme 4)



21 **22**

Scheme 4

and the NMR data for its 2-vinylindane moiety mirror those found for **16** (Experimental section).

On the scale at which this work was performed it was not possible to exclude excess butadiene from the cycloadditions, but by careful adjustment of the reaction conditions the outcome can be controlled. As the temperature of the reaction is decreased from 100 °C the proportion of cyclopentanthracene **16** decreases and at 45 °C the addition of butadiene is predominantly to the enedione C=C bond of quinone **3**. After 4 days the crude reaction mixture contains mono-adduct **15** and substrate **3** with only traces of di-adduct **16**. Crystallization of the crude product mixture (benzene, 5 °C) provides two distinct crystal types, green and pale yellow, that are easily separated by hand. The green material is a mixture of **3** and **15** (*ca.* 2:1; NMR) whereas the pale yellow crystals are almost pure **15** that can be used directly for subsequent transformations. An analytical sample of dione **15** was obtained, however, only after several recrystallizations because of easy oxidation (*vide infra*).[14] Retention of the cycloproparene skeleton in **15** is evident from the NMR spectra as the C-1 methylene protons appear as a broadened singlet (δ 3.36) and the *ortho* carbon atoms C-2/9 are characteristically[2] shielded and appear at δ 113.2. The resonances recorded for the AMX spin system of 4-H/7-H at δ 2.19–2.29 and 2.47–2.57, and 3a-H/7a-H at δ 3.36–3.41, respectively, are complex. Dreiding molecular models of **15** show a distinct preference for the new ring that spans C-4 to C-7 to adopt a half-chair conformation and molecular orbital calculations at the 6-31G* level (without geometrical constraints) confirm this as the energy minimum (Fig. 1a) with dihedral angles for 3a-H–C-3a–C-7a–7a-H and C-4–C-3a–C-7a–C-7 of 58.2° and 58.0°, respectively; calculated bond lengths and angles are shown in Fig. 2. By constraining the 3a-H–C-3a–C-7a–7a-H dihedral angle to 0° the calculations also detect four shallow energy wells *ca.* 32–37 kJ mol^{-1} above the minimum and these correspond to the distinct conformers of **15** shown in Fig. 1b–e. Despite cooling to −50 °C the ^{1}H NMR spectrum of **15** remains unchanged.

The ring-fused tetrahydroanthraquinone **15** contains a dihydroxynaphthalene valence isomer and aromatization of this moiety to **18** is achieved quantitatively with K_2CO_3. This salt has been characterized in solution from its NMR data and by conversion into the dimethoxy derivative **19**. Attempts to protonate **18** have been frustrated because upon workup its oxidation product, dihydrocyclopropanthraquinone **20** is isolated (Experimental section). Apart from displaying comparable 1-H and 2-H/9-H proton singlets, and shielded C-2/9 carbon resonances, **18** and **19** display oxygen-substituted *ipso* aromatic carbons at δ 144.2 and 150.9 whereas diones **15** and **20** have the carbonyl resonances at δ 198.1 and 184.8, respectively; 1,4-dihydroxybenzene is likewise transformed to its dianion with K_2CO_3 under the same reaction conditions and it provides comparable NMR data. The 4,7-dihydroanthraquinone **20**,

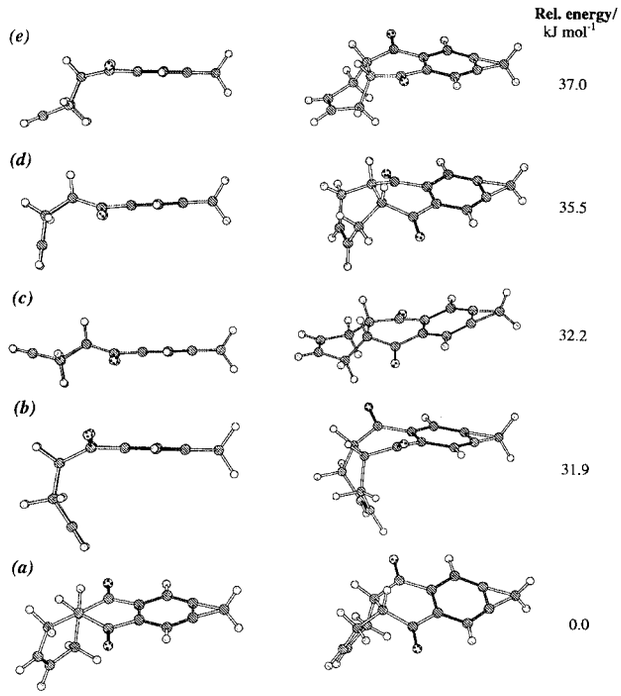


Fig. 1 Calculated (6-31G*) conformations of Diels–Alder adduct **15** in order of increasing energy (*a*) without constraint and (*b*)–(*e*) with the 3a-H–C-3a–C-7a–7a-H dihedral angle constrained to 0°.

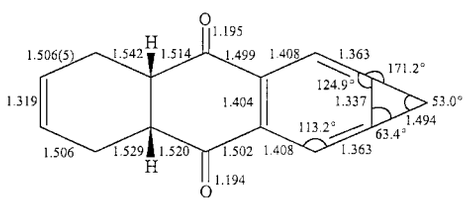


Fig. 2 Calculated geometry of tetrahydroanthracenedione **15**; bond lengths in Å and angles in degrees.

obtained by oxidation of **18**, is a yellow solid isolated in 41% yield and it displays the spectral characteristics expected of a ring-annelated variant of cyclopropanaphthalenedione **3**. More notable, however, is the relative instability of the compound as standing for a period of days results in darkening and even at −16 °C some 9% of **20** is oxidized to cyclopropanthraquinone **4** over 17 days. This desired transformation can be brought about more efficiently by passing oxygen through a solution of **20** (80% yield), by treating the dihydro derivative with DDQ (58%), or by standing **20** over K_2CO_3 (69%). The cyclopropanthraquinone **4** so obtained is a yellow crystalline compound that is markedly more stable than the only other oxygenated cyclopropanthracene recorded, namely the 3,8-dioxa derivative which dimerizes below 0 °C.[15] It is the first quinone in the cyclopropanthracene series and, to the best of our knowledge, only the seventh cyclopropa[*b*]anthracene prepared.[10,15,16] The compound provides a cyclic voltammogram[5] almost identical to that of 9,10-anthraquinone recorded under the same conditions. This shows that in the anthracene series cyclopropa[*b*] fusion does not alter the quinone redox characteristics. Quinone **4** shows the conjugated carbonyl stretching frequency at 1668 cm^{-1} and in the NMR spectra the methylene group appears at δ 3.55/19.2, CH(2/9) at 8.14/113.5, and 4-H/7-H as an AA′BB′ coupled system at δ 7.76–7.82 and 8.28–8.32 with their respective carbons at δ 134.0 and 127.2. This AA′BB′ system and the carbonyl carbon resonance match well those of 9,10-anthraquinone in the same solvent. In like manner the resonances of the cyclopropabenzenediyl moiety complement those of cyclopropabenzene and demonstrate that the impact

of cyclopropa fusion on the NMR parameters cannot be detected beyond the ring in which it is located.

The potential of naphthoquinone **3** as a synthon for other linear cycloproparene homologues forms a part of our continuing studies.

Experimental

General

Microanalyses were performed by the Analytical Facility of Otago University, Dunedin. Low-resolution mass spectra were recorded on a Hewlett Packard HP-5995C instrument and accurate mass measurements made either by Mr B. Clark of the Chemistry Department, University of Canterbury, Christchurch, on a Kratos MS80 RFA instrument or Mr O. Zubkov on Victoria University PE Biosystems Mariner operating in electrospray mode. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity INOVA 300 MHz instrument for (D)chloroform solutions, except where stated, using the residual solvent peak as internal standard. ^{1}H NMR multiplicities are defined by the usual notation and coupling constants are in hertz. The assignment of ^{13}C and ^{1}H NMR resonances were made with the aid of DEPT and ^{1}H–^{1}H COSY and ^{13}C–^{1}H HSQC experiments, and heteronuclear multiple bond connectivity (HMBC) experiments. IR spectra of solid samples were recorded for KBr disks and all other samples between NaCl plates using a Biorad FTS 7 spectrophotometer. UV measurements were acquired from a Hewlett-Packard 8452A diode array spectrophotometer. Melting points were determined on a Reichert hot-stage melting point apparatus and are uncorrected. Geometry optimizations were performed using the SPARTAN programme[17] employing the *ab initio* 6-31G* basis set[18] on a Silicon Graphics O2 R5000 workstation.

Thin layer chromatographic (TLC) analyses were performed using Merck Kieselgel (Alufoilen) 60 F_{254} to a thickness of 0.2 mm. Components were detected under an ultraviolet lamp at 254 or 350 nm, or in an iodine chamber. Preparative TLC plates were coated with Merck Kieselgel GF_{254} to a thickness of 0.75 mm and radial chromatography plates were coated with Merck Kieselgel 60 GF_{254} to a thickness of 2.0 or 4.0 mm. Column chromatography employed Riedel-de Haën silica gel S (230–400 ASTM) unless otherwise stated.

Reactions of 1*H*-cyclopropa[*b*]naphthalene-3,6-dione 3 with bromine

A. In tetrachloromethane: *trans*-4,5-dibromo-4,5-dihydro-1*H*-cyclopropa[*b*]naphthalene-3,6-dione 10. To a stirred solution of dione **3** (85 mg, 0.5 mmol) in dry tetrachloromethane (10 ml) under oxygen-free nitrogen was added dropwise bromine (88 mg, 28 L, 0.55 mmol) in the same solvent (2 ml). The pale-orange solution was stirred for 1 h, concentrated under vacuum and light petroleum (*ca.* 15 ml) added. The mixture was then shaken vigorously, the upper petroleum layer decanted from the dark insoluble residue, and the extraction repeated. The combined organic extracts were then concentrated under vacuum to afford **10** as a thick orange oil (150 mg, 91%) (Found: M^+ 329.8712 and 327.8736. $C_{11}H_6{}^{81}Br^{79}Br$ and $C_{11}H_6{}^{79}Br_2$ require M^+ 329.8714 and 327.8735, respectively); ν_{max}/cm^{-1} 3001, 2951, 1703, 1698, 1694, 1557, 1410, 1283, 1223, 1127, 1063, 978, 880, 735; NMR δ_H 3.44 (2 H, s, CH_2), 4.99 (2 H, s 4-H/5-H), 7.95 (2 H, s, 2-H/7-H); δ_C 19.7 (C-1), 45.9 (C-4/5), 114.4 (C-2/7), 133.8 (C-2a/6a), 134.5 (C-1a/7a), 186.6 (C-3/6); *m*/*z* 332/330/328 (M^+, 19/42/20%), 251/249 (91/100, M − Br), 170 (45), 114 (47), 88 (29).

B. In tetrachloromethane–methanol: 2,3,6-tribromo-7-(bromomethyl)naphthalene-1,4-dione 12. To a stirred solution of **3** (50 mg, 0.29 mmol) in tetrachloromethane (10 ml) at 0 °C under oxygen-free nitrogen, was added dropwise a solution of bromine (47 mg, 15 L, 0.29 mmol) in the same solvent (1.5 ml). The solution was stirred for 10 min and methanol (10 ml) was added rapidly. The solution stirred for 24 h and the pale-yellow precipitate collected by filtration. A further portion of bromine (0.29 mmol) in tetrachloromethane (1.5 ml) was added to the filtrate and stirring was continued for 36 h. More of the pale-yellow precipitate formed and was collected by filtration. Mass spectrometry and ^{1}H NMR spectroscopy indicated the isolated precipitates to be identical. The compound, insoluble in common solvents, is assigned as **12** (106.4 mg, 75%), mp 242–244 °C (Found: C, 27.1; H, 0.67; Br, 65.0. $C_{11}H_4Br_4O_2$ requires C, 27.1; H, 0.83; Br, 65.5%); ν_{max}/cm^{-1} 3088, 3028, 1676, 1588, 1539, 1283, 1213, 1190, 1092, 970, 943, 831, 797, 725, 718; NMR δ_H 4.65 (2 H, s, CH_2Br), 8.22 (1 H, s, 4-H), 8.36 (1 H, s, 1-H); *m*/*z* 492/490/488/486/484 (3.4/13.4/20.3/14.6/3.8%, M), 411/409/407/405 (32/100/100/34, M − Br), 383/381/379/377 (9/27/27/10, M − Br − CO).

Reaction of 1*H*-cyclopropa[*b*]naphthalene-3,6-dione 3 with cyclopenta-1,3-diene: [3aα,4α,7α,7aα]-4,7-methano-3a,4,7,7a-tetrahydro-1*H*-cyclopropa[*b*]anthracene-3,8-dione 14

To a stirred solution of **3** (170 mg, 1.0 mmol) in benzene (20 ml) at RT and under oxygen-free nitrogen was added dropwise freshly distilled cyclopenta-1,3-diene (225 mg, 0.28 ml, 3.4 mmol). The bright yellow solution was stirred until colourless (4 h) and then concentrated under vacuum to a white solid. TLC (dichloromethane) indicated two components (R_F 0.0, 0.8) and the most mobile fraction was isolated by radial chromatography (dichloromethane elution). The resultant white solid (216 mg) was recrystallized (light petroleum) to afford **14** as fine white platelets (190 mg, 80%), mp 90–91.5 °C (Found: C, 81.5; H 4.95. $C_{16}H_{12}O_2$ requires C, 81.3; H, 5.1%); ν_{max}/cm^{-1} 3061, 3005, 2936, 2874, 1667, 1564, 1402, 1335, 1294, 1265, 1229, 1084, 1061, 982, 893, 785, 712; NMR δ_H 1.52–1.59 (2 H, m, 10-H), 3.33 (2 H, s, 1-H), 3.44 (2 H, dd, 1.5, 2.3, 3a-H/7a-H), 3.63–3.66 (2 H, m, 4-H/7-H), 5.96 (2 H, t, 1.8, 5-H/6-H), 7.84 (2 H, s, 2-H/9-H); δ_C 19.2 (C-1), 49.2 (C-10), 49.3/49.4 (C-3a/7a and C-4/7), 113.0 (C-2/9), 132.7 (C-1a/9a), 135.5 (C-5/6), 139.9 (C-2a/8a), 197.9 (C-3/8); *m*/*z* 237/236 (M^+, 2.1/12.4%), 171 (15, M − C_5H_5), 114 (17), 66 (100, C_5H_6).

cis-3a,4,7,7a-Tetrahydro-1*H*-cyclopropa[*b*]anthracene-3,8-dione 15

To a calibrated Carius tube (300 ml) was added naphthoquinone **3** (1.5 g, 8.8 mmol), a magnetic follower and benzene (30 ml). The mixture was cooled to −50 °C and buta-1,3-diene (5 ml, 56.8 mmol) was added by vapour transfer. The sealed tube was warmed to 45 °C and the contents maintained at this temperature with stirring for 4 days. The cooled tube (liquid nitrogen) was opened, slowly warmed to RT and the mixture filtered though a plug of cotton wool. The filtrate was concentrated under reduced pressure to a yellow–brown oily solid (1.90 g) that contained (^{1}H NMR) unchanged **3** and tetrahydrocycloproparene **15** (*ca.* 3:17) and only traces of diadduct. The crude solid product was purified by:

Method A. Recrystallization from benzene at 5 °C predominantly gave pale yellow crystals (565 mg, 27%) together with some green crystals (50 mg) that were separated by hand. The pale yellow crystals contained (^{1}H NMR) **15** with traces (<2%) of **3** while the green crystals contained these same compounds in a 2:1 ratio. The pale yellow crystals, suitable for subsequent use (see below), were recrystallized first from benzene and then from ether–tetrahydrofuran (1:1) to give an analytical sample (19.4 mg) of adduct **15** as pale yellow diamond-shaped crystals, mp 96–97 °C (Found: C, 80.2; H, 5.5. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.4%); λ_{max}(acetonitrile)/nm 235 (log ε 4.42), 273 (3.81); ν_{max}/cm^{-1} 3029, 2974, 2938, 2900, 2851, 1678, 1556, 1431, 1246, 1178, 1053, 878, 706; NMR δ_H 2.19–2.29 (2 H_A, AMX, 4-H/7-

H), 2.47–2.57 (2 H_M, AMX, 4-H/7-H), 3.36 (2 H, s, 1-H); 3.36–3.41 (2 H_X, AMX, 3a-H/7a-H), 5.73 (2 H, t, 1.5, H5/6), 7.87 (2 H, s, H2/9); δ_C 19.5 (C-1), 24.4 (C-4/7), 46.5 (C-3a/7a), 113.2 (C2/9), 124.6 (C5/6), 133.0 (C-1a/9a), 137.7 (C-2a/8a), 198.2 (C-3/8); *m*/*z* 225/224 (M^+, 10/60%,), 196 (69, M − 28), 178 (52), 152 (31), 116 (30), 105 (38), 89 (51), 88 (82), 87 (33), 77 (52), 63 (43), 62 (100).

Method B. Radial chromatography (dichloromethane–light petroleum elution; 1 : 1) to give a yellow solid (1.3–1.6 g, *ca.* 65–80%) that contained enedione **15**, dihydroquinone **20** (see below), and naphthoquinone **3** in varying ratios from 15 : 0 : 5 to 150 : 1 : 0.5. The appearance of dihydroquinone **20** depends on the time that the product mixture resides on the column and this purification procedure is the method of choice for subsequent transformation into anthraquinone **4**.

[5a*α*,9a*α*]-2-Ethenyl-5a,6,9,9a-tetrahydro-1*H*-cyclopenta[*b*]anthracene-5,10-dione 16

A freshly prepared solution of dione **3** (400 mg, 2.35 mmol) in benzene (7 ml) was placed in a calibrated Carius tube (30 ml). The solution was frozen (liquid nitrogen) and buta-1,3-diene (*ca.* 3 ml, *ca.* 35 mmol) added by vapour transfer. After warming to RT the sealed tube was heated at 100 °C for 24 h (Carius furnace). The tube was cooled, refrozen to liquid air temperature, opened and the contents slowly warmed to RT. The liquid was concentrated under reduced pressure to a yellow oily solid (1.49 g) that was pumped under vacuum for 4 h to give a white solid (1.07 g). TLC (dichloromethane–light petroleum; 5 : 1 elution) indicated three components (R_F 0.0, 0.5, 0.7) and column chromatography (silica gel; dichloromethane–light petroleum, 5 : 1 elution) provides a first fraction (140 mg) thought to be (NMR) the dimer of butadiene. The second and major component provided a solid which gave **16** (200 mg, 31%) as colourless crystals (dichloromethane–light petroleum, 1 : 2; *ca.* −16 °C), mp 128–129 °C (Found: C, 81.7; H, 6.6. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); λ_{max}(hexane)/nm 214 sh (log ε 3.58), 235 sh (4.63), 240 (4.70), 268 (4.00); ν_{max}/cm^{-1} 3077, 3025, 2880, 2828, 1682, 1603, 1418, 1364, 1341, 1288, 1172, 1130, 920, 868, 835, 752; NMR δ_H 2.20 (2 H_A, br d, 15.2, 6-H/9-H), 2.50 (2 H_B, br d, 15.2, 6-H/9-H), 2.80–2.89 (2 $H_{A'}$, m, 1-H/3-H), 3.09–3.21 (3 H, m, 2$H_{B'}$, 1-H/3-H *and* 2-H), 3.35 (2 H, br t, 10.2, 5a-H/9a-H), 5.01 (1 H, br d, 10.2, 13_A-H), 5.10 (1 H, br d, 17.0, 13_B-H), 5.73 (2 H, s, 7-H/8-H), 5.87–5.98 (1 H, m, 12-H), 7.84 (2 H, s, 4-H/11-H); δ_C 24.4 (C-6/9), 39.0 (C-1/3), 43.9 (C-2), 46.5 (C-5a/9a), 114.4 (C-13), 122.5 (C-4/11), 124.6 (C-7/8), 133.1 (C-4a/10a), 140.7 (C-12), 150.5 (C-3a/11a), 198.3 (C-5/10); *m*/*z* 279/278 (M^+, 17/82%), 250 (38, M − 28), 170 (17), 115 (100).

3,8-Dihydroxy-4,7-dihydro-1*H*-cyclopropa[*b*]anthracene dipotassium salt 18

To an NMR tube flushed with argon and containing anhydrous potassium carbonate (24 mg, 0.17 mmol) was added butadiene adduct **15** (24 mg, 0.17 mmol) in d_6-acetone (0.45 ml). After 1 h cycloproparene **15** was unchanged (^{1}H NMR). The tube was then sonicated for 30 min after which time substrate **15** and salt **18** were present in a *ca.* 10 : 1 ratio. Further sonication for 30 min showed complete conversion into the dipotassium salt **18**; NMR (d_6-acetone) δ_H 3.42 (2 H, s, CH_2), 3.50 (4 H, d, 1.0, 2 × CH_2, 4-H/7-H), 5.96 (2 H, t, 1.3, 5-H/6-H), 7.95 (2 H, s, 2-H/9-H); δ_C 18.2 (C-1), 25.3 (C-4/7), 107.0 (C-2/9), 117.7 (C-3a/7a), 122.1 (C-1a/9a), 124.4 (C-5/6), 127.8 (C-2a/8a), 144.2 (C-3/8).

1,4-Dihydroxybenzene displays a single OH resonance in d_6-acetone and this was likewise transformed into its dianion under the same conditions.

3,8-Dimethoxy-4,7-dihydro-1*H*-cyclopropa[*b*]anthracene 19

To a stirred solution of **15** (100 mg, 0.45 mmol) and anhydrous potassium carbonate (222 mg, 1.62 mmol) in anhydrous acetone (7 ml) under argon at 0 °C, was added dimethyl sulfate (0.106 ml, 1.13 mmol) over 30 s by syringe. After stirring overnight (RT) the lemon coloured mixture was filtered under vacuum though Celite and the residue was washed with acetone (4 × 25 ml). The combined filtrates were concentrated (reduced pressure) to a dark yellow solid which gave a strongly fluorescent pure white solid (72 mg, 63%) as the major and most mobile component on radial chromatography (dichloromethane–light petroleum elution; 1 : 1). Recrystallization (dichloromethane–light petroleum, 1 : 1, −16 °C) provided **19** (22 mg, 20%) as colourless plates, mp 126–130 °C (Found: C, 80.7; H 6.3. $C_{15}H_{12}O_2$ requires C, 80.9; H, 6.4%); λ_{max}(acetonitrile)/nm 216 (log ε 4.45), 246 (4.62), 300 (3.69); ν_{max}/cm^{-1} 3072, 3029, 2993, 2932, 2876, 2827, 1744, 1671, 1600, 1451, 1423, 1330, 1297, 1063, 1052, 995, 950, 853; NMR δ_H 3.49 (2 H, s, CH_2), 3.56 (4 H, d, 1.2, 2 × CH_2), 3.91 (6 H, s, 2 × OMe), 6.02 (2 H, t, 1.4, 5-H/6-H), 7.82 (2 H, s, 2-H/9-H); δ_C 18.4 (C-1), 24.3 (C-4/7), 61.0 (2 × OMe), 106.8 (C-2/9), 122.9 (C-1a/9a), 124.1 (C-5/6), 124.5 (C-3a/7a), 130.0 (C-2a/8a), 150.0 (C-3/8); *m*/*z* 253/252 (M^+, 19/100%), 237 (62, M − Me), 206 (70), 205 (38), 178 (69), 177 (34), 176 (44), 165 (77), 163 (30), 89 (36), 88 (47), 87 (41), 77 (65), 76 (35), 75 (33), 63 (58), 62 (48), 51 (67), 50 (37).

Further elution of the chromatotron plate (same solvent mixture) gave an oily yellow solid (24 mg) that contained (^{1}H NMR) **19**, cyclopropanthraquinone **4** (see below) and unreacted dimethyl sulfate in a 20 : 6 : 1 ratio; purification was not attempted.

4,7-Dihydro-1*H*-cyclopropa[*b*]anthracene-3,8-dione 20

To a stirred solution of adduct **15** (100 mg, 0.45 mmol) in anhydrous acetone (10 ml) under argon, was added anhydrous potassium carbonate (620 mg, 4.49 mmol) under a stream of argon. The mixture instantly darkened and was stirred for a further 2.5 h then filtered though a pad of Celite under vacuum. The residue was washed with acetone (4 × 25 ml) and the combined filtrates concentrated under reduced pressure to a purple–blue sparingly soluble solid (97 mg) shown (^{1}H NMR) to be a mixture of dihydroquinone **20** with varying amounts of cyclopropanthraquinone **4** (see below). The solid was either left in air until it became yellow or stirred as a suspension in dichloromethane until it dissolved; use of an oxygen atmosphere accelerates the oxidation. Radial chromatography (dichloromethane–light petroleum elution; 1 : 4) gave, as the major and most mobile component, dihydrodione **20** as a yellow solid (41 mg, 41%) that rapidly darkened on standing. Recrystallization (diethyl ether, −16 °C) provided an analytical sample of **20** (23 mg, 23%) as yellow crystals, mp 122–124 °C (decomp.) after sublimation at 111 °C (Found: C, 81.2; H 4.5(5). $C_{15}H_{10}O_2$ requires C, 81.1; H, 4.5%); λ_{max}(acetonitrile)/nm 260 (log ε 4.41), 326 (3.30); ν_{max}/cm^{-1} 3037, 3010, 2948, 2923, 2852, 1655, 1626, 1557, 1416, 1294, 1123, 1058, 980, 933, 875, 856, 723, 715; NMR δ_H 3.25 (4 H, d, 1.2, 2 × CH_2), 3.34 (2 H, s, CH_2), 5.87 (2 H, t, 1.2, 5-H/6-H), 7.94 (2 H, s, 2-H/9-H); δ_C 19.1 (C-1), 24.4 (C-4/7), 112.7 (C-2/9), 122.7 (C-5/6), 131.9 (C-1a/9a), 135.4 (C-2a/8a), 141.1 (C-3a/7a), 184.8 (C-3/8); *m*/*z* (electrospray) 223 $(M + H)^+$.

Quinone **20** is readily oxidised to cycloproanthracene **4** and on storing in the freezer for 17 days 9% conversion to compound **4** was observed. It is best that **4** be stored under an inert atmosphere.

1*H*-Cyclopropa[*b*]anthracene-3,8-dione 4

Method A. A slow stream of oxygen was bubbled through a mixture of quinones **20** and **4** (from above) (103 mg, *ca.* 0.46 mmol) suspended in dichloromethane (15 ml). After 2 h the solid had dissolved but the oxygen flow was continued for 12 days with constant volume being maintained by solvent

addition as required. Solvent removal under reduced pressure gave a yellow solid that was purified by column chromatography (dichloromethane elution) (yellow powder; 82 mg, 80%). Recrystallization (dichloromethane, −16 °C) gave the anthracenedione **4** (28 mg, 27%) as yellow crystals, mp 132 °C (subl., sublimate mp >350 °C (Found: C, 81.7; H 3.7; *m*/*z* $(M + H)^+$ 221.0601. $C_{15}H_8O_2$ requires C, 81.8; H, 3.7%; $(M+H)^+$ 221.0602); λ_{max}(acetonitrile)/nm 206 (log ε 4.27), 259 (4.65), 280 sh (4.04), 324 (3.61); ν_{max}/cm^{-1} 2924, 2853, 1668, 1592, 1581, 1557, 1317, 1292, 1123; NMR δ_H 3.41 (2 H, s, CH_2), 7.79–7.81 (2 H, AA′, 5-H/6-H), 8.16 (2 H, s, 2-H/9-H), 8.31–8.34 (2 H, BB′, 4-H/7-H); δ_C 19.2 (C-1), 113.5 (C-2/9), 127.2 (C-4/7), 132.8 (C-1a/9a), 133.1 (C3a/7a), 134.0 (C-5/6), 137.0 (C2a/8a), 183.3 (C-3/8).

Method B. The quinones **20** and **4** (50 mg, 0.22 mmol) and DDQ (128 mg, 0.56 mmol) were suspended in anhydrous benzene (5 ml) at RT for 6.5 days under argon. Workup as in **A** above gave a mixture of **4** and DDQ, and further chromatography provided **4** (29 mg, 58%) identical to that described in **A** above.

Method C. To the mixture of **20** and **4** (50 mg, 0.22 mmol) in dry acetone (5 ml) under argon was added anhydrous potassium carbonate (311 mg, 2.26 mmol) and the suspension was stirred for 24 h. Workup as in **A** above gave **20** and **4** in a 1:5 ratio (^{1}H NMR). However, upon repeating the procedure **4** (34 mg, 69%) was obtained as a yellow solid. If the reaction is left uninterrupted for 48 h a yellow oil (20 mg) that contains only traces of **4** is obtained; a similar outcome follows from reaction with potassium hydroxide.

2-Ethenyl-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene 22

A solution of cyclopropanaphthalene **21** (200 mg, 1.4 mmol) in benzene (5 ml) was placed in a calibrated Carius tube (20 ml), cooled to liquid air temperature and buta-1,3-diene (*ca.* 1 ml, *ca.* 12 mmol) added by vapour transfer. The sealed tube was slowly warmed and then heated at 100 °C for 18–19 h (Carius furnace). The cooled tube (liquid nitrogen) was opened, slowly warmed to room temperature and then excess diene and solvent were removed under vacuum. The product was pumped under vacuum (5–6 h) to give a white solid (300 mg) and column chromatography (silica gel; dichloromethane–light petroleum, 1:4 elution) afforded from the most mobile fraction a white solid (180 mg, 64%). Recrystallization (dichloromethane, *ca.* −16 °C) gave **22** as colourless crystals (160 mg, 57%), mp 55–57 °C (Found: C, 92.5; H, 7.5. $C_{15}H_{14}$ requires C, 92.7; H, 7.3%); λ_{max}(hexane)/nm 248 (log ε 3.46), 268 (3.72), 279 (3.76), 290 (3.60), 308 (3.09), 320 (3.15); ν_{max}/cm^{-1} 3079, 3054, 2980, 2834, 1640, 1605, 1429, 1337, 1267, 1148, 992, 911, 868, 741; NMR δ_H 2.87–2.95 (2 H_A, m, 1-H/3-H), 3.10–3.25 (2 H, 2H_B, m, 1-H/3-H and 2-H), 5.09 (1 H, br d, 10.3, 11$_A$-H), 5.14 (1 H, br d, 17.3, 11$_B$-H), 5.95–6.06 (1 H, m, 10-H), 7.36–7.39 (2 H, AA′, 5-H/8-H), 7.62 (2 H, s, 4-H/9-H), 7.73–7.76 (2 H, BB′, 6-H/7-H); δ_C 38.8 (C-1/3), 44.8 (C-2), 113.8 (C-11), 122.1 (C-5/8), 124.9 (C-4/9), 127.4 (C-6/7), 132.9 (C-4a/8a), 141.8 (C-10), 142.2 (C-3a/9a); *m*/*z* 195/194 (M^+, 12/77%), 193 (18, M − H), 179 (100, M − CH_3), 116 (38, M − C_2H_4), 165 (83, M – C_2H_5), 152 (20, M − C_3H_6), 139 (15, M − C_4H_7).

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