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PREPARATION OF FUNCTIONALISED ANTHRA[*b*]CYCLOBUTENES FROM 3,6-DIMETHOXYBENZOCYCLOBUTENONE

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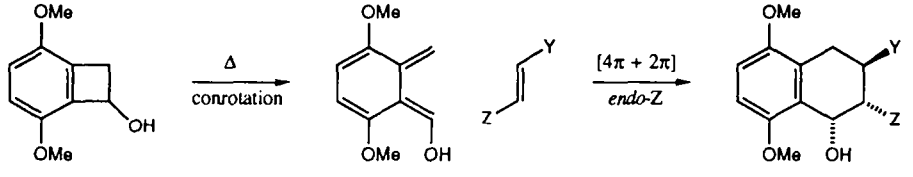
Abstract: 3,10-Dimethoxyclobut[*b*]anthracene-1,4,9-trione **9**, a potential anthracycline precursor, has been prepared from 3,6-dimethoxybenzocyclobutenone **4** *via* quinone acetal and phthalide anion chemistry. Diels-Alder and electrophilic phthaloylation approaches to **9** were unsuccessful.

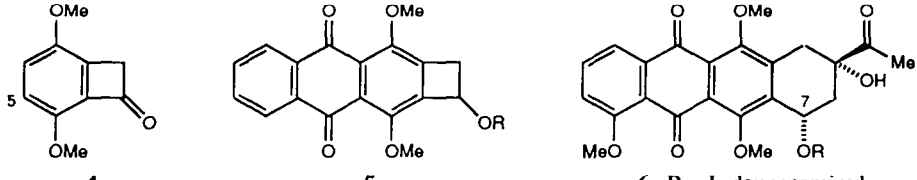
Our interest in developing routes to naturally occurring quinone and hydroquinone derivatives prompted us to investigate the chemistry of 3,6-dimethoxybenzocyclobutenol **1**, whose *peri*-oxygenation pattern matches that frequently encountered into polyketide-derived systems, and we found that the electrocyclic ring-opening of **1** proceeds readily at 110–115 °C to give the (*Z*)-hydroxy-*o*-quinone dimethide **2**, which can be intercepted with dienophiles to generate 1,2,3,4-tetrahydro-1-naphthols **3** in a stereoselective manner (Scheme 1).[1]



1 **2** **3**

Scheme 1

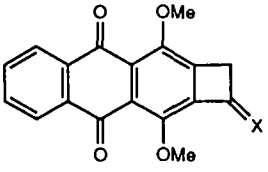
We were also attracted by the notion that annulation of the benzocyclobutenone **4** might provide, *inter alia*, anthra[*b*]cyclobutenes **5** suitable for direct conversion into analogues of the anthracycline anticancer agent daunomycin **6** and its aglycone, daunomycinone **7**,[2] using a sequence analogous to that shown in Scheme 1.



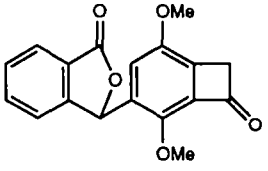
4 **5**

6 R = L-daunosaminyl
7 R = H

Oda and coworkers[3] demonstrated the feasibility of such an approach using the quinone **8**, which on heating to 220 °C in the presence of methyl vinyl ketone gave a good yield of the desired [4π + 2π] cycloadduct, a known anthracycline precursor. Our own efforts in this area have been directed towards the preparation of the trione **9**, which incorporates in latent form the potentially problematic 7-substituent of the anthracycline nucleus,[4] and other fused cyclobutenes suitable for exploitation in synthesis, and we herein describe our progress.



8 X = H_2
9 X = O



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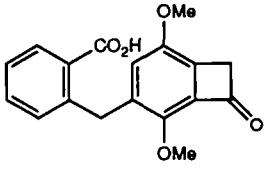

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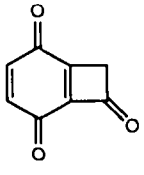
Although the benzocyclobutenone **4** could be efficiently nitrated and halogenated at C-5, electrophilic benzoylation proceeded only in poor yield, and attempts to convert the readily available phthalide **10** into the reduction product **11**, set up for cyclisation by acid treatment, proved fruitless.[1] We were further disappointed to find that attempts to convert **4** directly into the anthraquinone **9**, *via* electrophilic phthaloylation (phthalic anhydride, $AlCl_3$-NaCl melt, 190 °C)[5] and remethylation of the phenolic oxygens, gave a complex mixture containing no significant amount of the desired product. We therefore turned our attention to the chemistry of the hitherto unknown trione **12**, which offered an opportunity for annulation using [4π + 2π] cycloadditions. Molecules of this type are of considerable theoretical interest, as their physicochemical properties (*e.g.* reduction potentials) provide data of use in evaluating bond-order preference and angle strain effects.[6] In the event our attempts to prepare the trione **12** were unsuccessful. Oxidative demethylation of the ketone **4** with silver(II) oxide[7] or silver(II) dipicolinate[8] gave complex red mixtures in each case, while ammonium cerium(IV) nitrate[9] failed to induce any reaction. The conversion of **4** into the hydroquinone **13** using boron tribromide was straightforward, but oxidation of the derived bis(trimethylsilyl) ether **14** with pyridinium chlorochromate[10] gave only tars. It is presumably the parallel effects of enhanced strain and electrophilicity within the quinone **12** which render it inaccessible using these conventional reagents and procedures.



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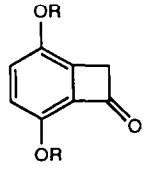
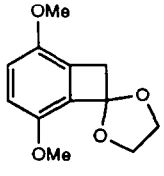


13 R = H
14 R = $SiMe_3$



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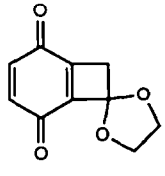

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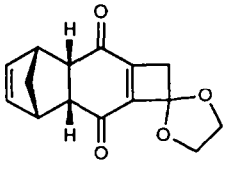

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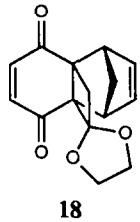

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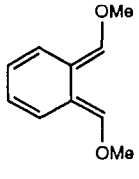

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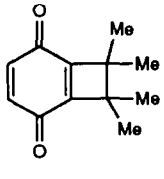

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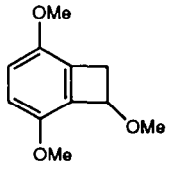
Oxidation of the acetal **15** proved less demanding, and treatment with silver(II) dipicolinate[8] gave the unstable quinone **16** in 69% yield as a yellow solid. However, the quinone **16** reacted with cyclopentadiene at 0 °C at either double bond with equal facility, giving a 1:1 mixture of unstable adducts tentatively assigned as **17** and **18** by ^{1}H n.m.r. spectroscopy. Attempted cycloaddition of the quinone **16** to the diene **19**, formed *in situ* by heating *trans*-1,2-dimethoxybenzocyclobutene at 80 °C,[11] gave a complex mixture consistent with the thermal decomposition of the quinone **16**. These results are disappointing from a synthetic point of view, especially in the context of the behaviour of the related quinone **20**, which reacts with cyclopentadiene exclusively at the less hindered 'external' double bond despite the greater electrophilicity of the 'internal' double bond.[12]



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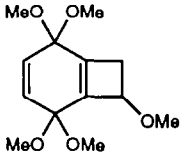

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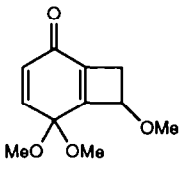

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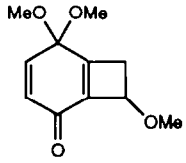

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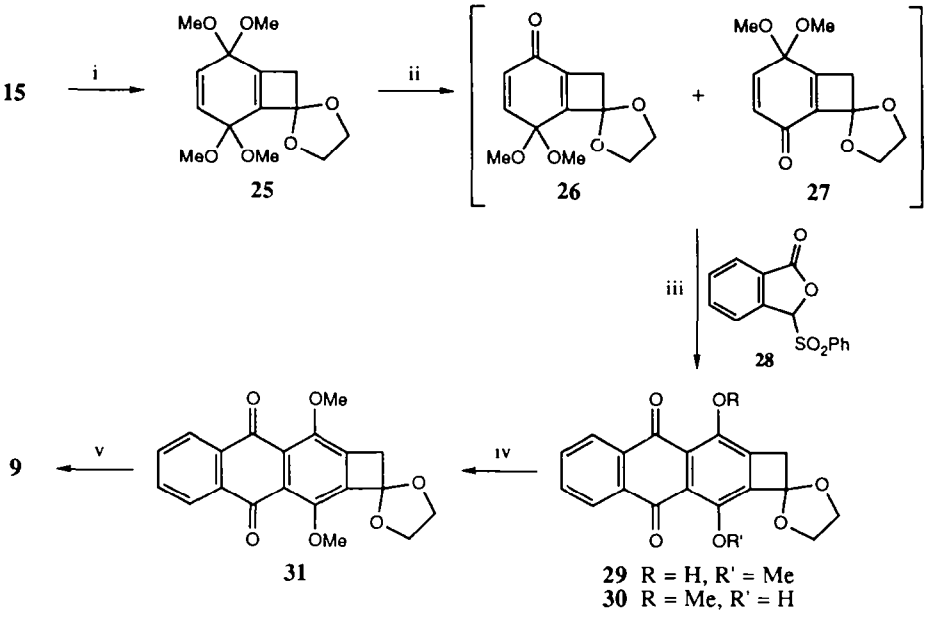
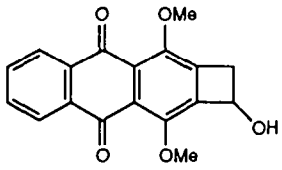
Application of the anodic oxidation/partial hydrolysis technique developed by Swenton and coworkers for the preparation of quinone monoacetals[13] eventually provided intermediates suitable for conversion into the anthraquinone **9** *via* the phthalide anion addition method.[14] Oxidation of the trimethoxybenzocyclobutene **21** in methanolic KOH using a flat cell with a platinised titanium anode[15] gave the quinone bis(dimethyl)acetal **22** in 78% yield, but the product of partial hydrolysis, expected to be a mixture of the enones **23** and **24** with the former predominant for steric reasons,[13] was unstable. In contrast, the acetal **15** gave intermediate dienones which were relatively stable, and these were converted into the desired anthraquinone **9** as shown in Scheme 2.



Scheme 2 *Reagents:* i, Pt anode, 6 V, MeOH, KOH (75%); ii, HOAc, H_2O, acetone, 0 °C to room temp., 3.5 h (90%); iii, LDA, hexane-THF, HMPT, **28**, –78 °C to reflux (47%); iv, Me_2SO_4, K_2CO_3, acetone (91%); v, H_2O, THF, H_2SO_4, reflux, 16 h (92%).

Anodic oxidation of **15** gave the tetramethoxy compound **25**, hydrolysis of which gave two products presumed to be **26** and **27** (ratio *ca.* 4:1). Treatment of this mixture with the lithium derivative of the sulphone **28** gave a corresponding mixture of the hydroxyquinones **29** and **30**, which was methylated to obtain the acetal **31**. Hydrolysis of **31** then afforded the trione **9** as a red crystalline solid, m.p. 207–209 °C. Chemoselective reduction of the cyclobutenone carbonyl of **9** was readily effected by treatment with sodium borohydride in methanol/dichloromethane at –78 °C, and provided the corresponding alcohol **32** in good yield. This could be converted into the ether **33** (97%) by treatment with silver(I) oxide and iodomethane.



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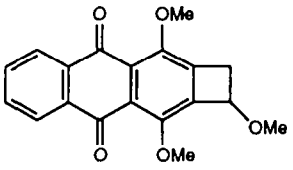

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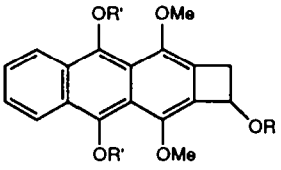

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The chemistry of the anthra[*b*]cyclobutene quinones **32** and **33**, and their reduced forms **34**, is currently under investigation. Other synthetic applications of the enones **26** and **27**, which may function as dienophiles as well as Michael acceptors, will be described in due course.

EXPERIMENTAL

All compounds are racemic. M.p.s were determined on an Electrothermal apparatus and are uncorrected. I.r. spectra were recorded on Perkin-Elmer 1710FT or 297 spectrometers. ^{1}H N.m.r. spectra were measured for solutions in deuteriochloroform unless otherwise indicated, with tetramethylsilane as the internal standard, on Varian EM 360 (60 MHz), Varian CFT-20 (80 MHz), Perkin-Elmer R32 (90 MHz), or Bruker AC300 (300 MHz) instruments. Mass spectra were measured on Kratos MS30 or Finnigan 4500 instruments.

Starting materials and solvents were routinely purified by conventional techniques.[16] Distillation of liquid products was performed using a bulb-to-bulb (Kugelrohr) apparatus, and the temperatures quoted are those of the oven. Organic solutions were dried using anhydrous magnesium sulphate and concentrated by rotary evaporation. Analytical thin layer chromatography (t.l.c.) was carried out on Camlab Polygram SIL G/UV$_{254}$ silica gel plates. Column chromatography was carried out using 60H silica gel (Merck 7736 and hand-bellows pressure, or Merck 9385 and the flash technique[17]). Compositions of solvent mixtures are quoted as ratios of volume. 'Petroleum' refers to light petroleum, b.p. 40–60 °C. 'Ether' refers to diethyl ether.

*3,6-Dihydroxybenzocyclobuten-1(2*H*)-one* **13**. – A solution of boron tribromide (0.75 g, 3 mmol) in dichloromethane (2 ml) was added dropwise to a stirred solution of 3,6-dimethoxybenzocyclobutenone **4**[1] (178 mg, 1 mmol) in dichloromethane (5 ml) at –78 °C. The mixture was then allowed to reach room temperature and stirred for 18 h. Water (10 ml) was then added, the mixture extracted with dichloromethane (3 x 15 ml), and the extract washed with water (2 x 10 ml), dried, and evaporated. The residue was sublimed (140 °C, 0.01 mmHg) to obtain the pure *title compound* **13** (130 mg, 87%) as a white solid, m.p. 189–190 °C (Found: C, 63.9; H, 4.1. $C_8H_6O_3$ requires C, 64.0; H, 4.0%); ν_{max} (Nujol) 3275 br, 1715, and 1620 cm^{-1}; δ (60 MHz, d_6-acetone) 3.72 (2 H, s, 2-H$_2$), 6.65 (1 H, d, *J* 8 Hz, 5-H), 6.85 (1 H, d, *J* 8 Hz, 4-H), and 8.6 (2 H, br s, exchanges with D_2O, OH).

3,6-Bis(trimethylsilyloxy)benzocyclobuten-1(2H)-one **14**. – A solution of the hydroquinone **13** (70 mg, 0.47 mmol) and *O,N*-bis(trimethylsilyl)acetamide (100 mg, 0.5 mmol) in acetonitrile (2.5 ml) was stirred at room temperature for 1.5 h, after which the starting material was no longer detectable by t.l.c. The solvent was then evaporated and the title compound **14** (122 mg, 89%) isolated by bulb-to-bulb distillation (90–92 °C, 0.01 mmHg) as an unstable colourless oil; δ (60 MHz) 0.30 (9 H, s, $SiMe_3$), 0.32 (9 H, s, $SiMe_3$), 3.72 (2 H, s, 2-H_2), 6.65 (1 H, d, *J* 8.5 Hz, 5-H), and 6.85 (1 H, d, *J* 8.5 Hz, 4-H); M^+, 294.
Attempted oxidation[10] of **14** using pyridinium chlorochromate in dichloromethane gave only tarry material.

Spiro[bicyclo[4.2.0]octa-1(6),3-diene-7,2'-[1,3]dioxolane]-2,5-dione **16**. – To a stirred solution of the acetal **15**[1] (222 mg, 1.0 mmol) in acetonitrile - water (5.6:1 v/v; 6 ml) at room temperature was slowly added a slurry of silver(II) dipicolinate[8] (2.2 g, 6.3 mmol) in acetonitrile - water (5.6:1 v/v; 18 ml). When the reaction was over (white solid formed), sodium acetate (0.82 g, 10 mmol) was added and the mixture was stirred for a further 1.5 h. Water (20 ml) was then added, the mixture was filtered, and the solid was washed on the filter with chloroform (20 ml). The combined filtrate and washings were extracted with chloroform (3 x 15 ml) and the extract washed with water (2 x 25 ml), dried, and evaporated. Chromatography over silica gel (ether - petroleum 3:2) gave the *title compound* **16** (132 mg, 69%) as an unstable yellow solid, m.p. 83–84 °C (M^+ 192.0420. $C_{10}H_8O_4$ requires 192.0423); ν_{max} (Nujol) 1660 cm^{-1}; δ (300 MHz) 3.42 (2 H, s, 2-H_2), 4.05–4.15 (4 H, m, 4'-H_2, 5'-H_2), and 6.60 (2 H, ABq, *J* 10.5 Hz, 4-H and 5-H).

Reaction of the Quinone **16** *with Cyclopentadiene*. – A solution of the quinone **16** (131 mg, 0.68 mmol) and freshly distilled cyclopentadiene (47 mg, 0.71 mmol) in dichloromethane (5 ml) was stirred at 0 °C and monitored by t.l.c. When the starting material had been consumed (0.5 h), the solvent was evaporated. The ^1H n.m.r. spectrum of the residue [δ (60 MHz) 6.1 (4 H, m) and 6.6 (2 H, s)] suggested that both adducts had been formed in essentially equal proportions. Chromatography [ether - petroleum (1:1)] gave the 'internal' adduct **18** [δ (60 MHz) 1.3–1.6 (1 H, m), 2.0–2.3 (1 H, m), 2.55 (2 H, d), 3.2–3.4 (2 H, m), 3.8–4.2 (4 H, m), 6.1 (2 H, m), and 6.6 (2 H, s)] and the 'external' adduct **17** [δ (60 MHz) 1.3–1.6 (1 H, m), 2.0–2.1 (1 H, m), 2.6–2.8 (2 H, m), 3.2–3.5 (4 H, m), 3.8–4.2 (4 H, m), and 6.1 (2 H, m)]. The structural assignments for **17** and **18** are tentative, and are based on comparison of the above data with those of the analogous products obtained by Oda *et al.*[12] On crystallisation from ether, each of these compounds decomposed to give a product with no olefinic hydrogens apparent in the ^1H n.m.r. spectrum.

Attempted Reaction of the Quinone **16** *with the Diene* **19**. – A solution of the quinone **16** (110 mg, 0.57 mmol) and freshly prepared *trans*-1,2-dimethoxybenzocyclobutene[11] (containing *ca.* 20% of the *cis*-isomer; 470 mg, 2.3 mmol) in benzene (10 ml) under nitrogen was heated under reflux and monitored by t.l.c. The starting material **16** was rapidly consumed (<0.5 h) and a complex mixture formed.

1,3,6-Trimethoxybenzocyclobutene **21**. – 3,6-Dimethoxybenzocyclobuten-1-ol **1**[1] (0.90 g, 5.0 mmol) was stirred with iodomethane (10 ml) and silver(I) oxide (1.2 g, 5.2 mmol) in dichloromethane (50 ml) at room temperature for 24 h. The mixture was then filtered and the residue washed with dichloromethane. The combined filtrate and washings were evaporated to obtain the *title compound* **21** (0.97 g, 100%) as a pale yellow oil. Distillation (85–87 °C, 0.1 mmHg) gave the analytical sample, m.p. 32–33 °C (Found: C, 68.3; H, 7.3. $C_{11}H_{14}O_3$ requires C, 68.0; H, 7.3%); δ (60 MHz) 3.15 (1 H, dd, *J* 2, 14 Hz, 2-H *cis* to OMe), 3.47 (1 H, dd, *J* 4, 14 Hz, 2-H *trans* to OMe), 3.47 (3 H, s, OMe), 3.80 (3 H, s, OMe), 3.85 (3 H, s, OMe), 5.00 (1 H, dd, *J* 2, 4 Hz, 1-H), and 6.66 (2 H, s, 4-H and 5-H).

2,2,5,5,7-Pentamethoxybicyclo[4.2.0]octa-1(6),3-diene **22**. – A stirred solution of the benzocyclobutene **21** (97 mg, 0.5 mmol) in 1% methanolic potassium hydroxide (40 ml) was oxidised at a platinised titanium anode (6 V flat cell,[15] 16–18 °C, 0.82–0.89 A) until the starting material was no longer detectable by t.l.c. (50 min). The solution was then evaporated to one-half of the original volume (bath ≤ 25 °C), extracted with ether (6 x 10 ml), and the extract washed with water (2 x 20 ml) and brine (20 ml). The solution was dried and evaporated to obtain the title compound **22** (100 mg, 78%) as a pale yellow oil which was homogeneous by ^{1}H n.m.r. spectroscopy; δ (90 MHz) 2.70 (1 H, dd, *J* 1.5, 13.5 Hz, 2-H *cis* to OMe), 3.07 (1 H, dd, *J* 3.5, 13.5 Hz, 2-H *trans* to OMe), 3.25–3.4 (15 H, m, 5 x OMe), 4.60 (1 H, dd, *J* 2, 3.5 Hz, 1-H), and 6.07 (2 H, s, 4-H and 5-H); M^+, 256.

Partial hydrolysis of **22**. – To a stirred solution of the pentamethoxy compound **22** (250 mg) in acetone (12.5 ml) at 0 °C was added dropwise 2% aqueous acetic acid (5 ml).[13] After 0.5 h the mixture was allowed to warm to room temperature and monitored by t.l.c. (ether - petroleum 1:1). After 4 h the starting material had been consumed, and the reaction was quenched by the dropwise addition of saturated aqueous sodium hydrogen carbonate (5 ml). The products were extracted into dichloromethane (3 x 20 ml) and the extract washed with water (25 ml), dried, and evaporated. The resulting pale yellow oil, presumed to contain the dienones **23** and **24**, rapidly decomposed.

2,2,5,5-Tetramethoxyspiro[bicyclo[4.2.0]octa-1(6),3-diene-7,2'-[1,3]dioxolane] **25**. – A stirred solution of the acetal **15** (222 mg, 1.0 mmol) in 1% methanolic potassium hydroxide (40 ml) was oxidised at a platinised titanium anode (6 V flat cell,[15] 19–20 °C, 0.85–0.90 A) until the starting material was no longer detectable by t.l.c. (60 min). The solution was then evaporated to one-half of the original volume (bath ≤ 25 °C), extracted with ether (6 x 10 ml), and the extract washed with water (2 x 20 ml) and brine (20 ml). The solution was dried and evaporated, giving the title compound **25** (214 mg, 75%) as a pale yellow oil, homogeneous by ^{1}H n.m.r. spectroscopy; δ (60 MHz) 3.20 (2 H, s, 2-H$_2$), 3.39 (12 H, s, 4 x OMe), 4.12 (4 H, s, 4'-H$_2$, 5'-H$_2$), and 6.10 (2 H, s, 4-H and 5-H).

Partial hydrolysis of **25**. – To a stirred solution of the tetramethoxy compound **25** (130 mg, 0.46 mmol) in acetone (3 ml) at 0 °C was added dropwise 2% aqueous acetic acid (1 ml).[13] After 0.5 h the mixture was allowed to warm to room temperature and monitored by t.l.c. After 3.5 h the starting material had been consumed, and the reaction was quenched by the dropwise addition of saturated aqueous sodium hydrogen carbonate (1 ml). The products were extracted into dichloromethane (3 x 10 ml) and the extract washed with water (15 ml), dried, and evaporated. The ^{1}H n.m.r. spectrum of the resulting oil (96 mg, 90%) indicated that both possible dienones **26** and **27** had been formed (ratio *ca.* 4:1); δ (90 MHz) 6.15 (d, *J* 10.5 Hz, C*H*C=O of major product), 6.22 (d, *J* 10.5 Hz, C*H*C=O of minor product), 6.70 (d, *J* 10.5 Hz, C*H*CHC=O of major product), and 6.71 (d, *J* 10.5 Hz, C*H*CHC=O of minor product). The crude mixture was used in the next step. The structures assigned to **26** and **27** are tentative and may be reversed.

1,2-Dihydro-3,10-dimethoxyspiro[cyclobut[b]anthracene-1,2'-[1,3]dioxolane]-4,9-dione **31**. – To a stirred solution of lithium diisopropylamide, prepared in the usual way from diisopropylamine (166 mg, 1.64 mmol) and *n*-butyllithium in hexane (1.6M; 0.94 ml, 1.5 mmol), in tetrahydrofuran (15 ml) at –78 °C under nitrogen was added hexamethylphosphoric triamide (0.26 ml, 1.5 mmol). After 0.5 h the sulphone **28** [prepared by oxidation[14] of 3-(phenylthio)-1(3*H*)-isobenzofuranone;[18] 411 mg, 1.5 mmol] was added as a solid, and the mixture stirred for a further 1 h at –78 °C. A solution of **26** and **27** (total 357 mg, 1.5 mmol) in tetrahydrofuran (5 ml) was then added dropwise, and the mixture stirred for a further 0.5 h at –78 °C, then at room temperature for 0.5 h, and finally heated under reflux for 1.5 h. The mixture was cooled, treated with 2M hydrochloric acid

(25 ml), and stirred at room temperature for 16 h. The organic solvents were then removed by evaporation and the resulting solid was collected and dissolved in dichloromethane (40 ml). The red solution was washed with water (20 ml) and brine (20 ml), dried, and evaporated. Chromatography of the residual red solid, eluting with ether - petroleum (7:3), gave unreacted sulphone **28** (63 mg, 15%), followed by the isomeric hydroxyquinones **29** and **30** (total 238 mg, 47%). This mixture was dissolved in acetone (30 ml) and methylated by heating under reflux with anhydrous potassium carbonate (6.35 g, 46 mmol) and dimethyl sulphate (4.4 ml, 5.9 g, 47 mmol) for 5 h. After cooling, the excess of methylating agent was quenched by stirring the reaction mixture with 2M ammonium hydroxide (25 ml) overnight at room temperature. Acetone was then removed by evaporation, and the product extracted into dichloromethane (40 ml). The extract was washed with water (20 ml) and brine (20 ml), dried, and evaporated. The residue was crystallised from ethanol to afford the pure *title compound* **31** (226 mg, 43% over two steps) as maroon needles, m.p. 202–205 °C (Found: C, 68.0; H, 4.65. $C_{20}H_{16}O_6$ requires C, 68.2; H, 4.6%); ν_{max} (FT, neat) 1666 and 1571 cm^{-1}; δ (300 MHz) 3.69 (2 H, s, 2-H_2), 4.01 (3 H, s, OMe), 4.10 (3 H, s, OMe), 4.1–4.2 (4 H, br s, 4'-H_2, 5'-H_2), 7.65–7.7 (2 H, m, 6-H and 7-H), and 8.05–8.15 (2 H, m, 5-H and 8-H).

*1,2-Dihydro-3,10-dimethoxycyclobut[*b*]anthracene-1,4,9-trione* **9**. – The acetal **31** (153 mg, 0.435 mmol) in a mixture of tetrahydrofuran (8 ml) and water (2 ml) containing three drops of concentrated sulphuric acid was heated under reflux for 16 h, cooled, extracted with dichloromethane (3 x 15 ml), and the extract washed with water (2 x 15 ml) and brine (15 ml). Drying and evaporation gave a red solid residue which, on crystallisation from methanol - dichloromethane, gave the *title compound* **9** (123 mg, 92%), m.p. 207–209 °C (Found: C, 70.25; H, 3.7. $C_{18}H_{12}O_5$ requires C, 70.1; H, 3.9%); ν_{max} (Nujol) 1765, 1670, 1650, and 1580 cm^{-1}; δ (300 MHz) 4.07 (3 H, s, OMe), 4.26 (2 H, s, 2-H_2), 4.27 (3 H, s, OMe), 7.65–7.75 (2 H, m, 6-H and 7-H), and 8.05–8.15 (2 H, m, 5-H and 8-H); M^+, 308.

*1,2-Dihydro-3,10-dimethoxy-4,9-dioxocyclobut[*b*]anthracen-1-ol* **32**. – The ketone **9** (618 mg, 2.0 mmol) in dichloromethane (40 ml) was added dropwise to a stirred solution of sodium borohydride (19 mg, 0.5 mmol) in methanol (10 ml) at –78 °C. After 0.5 h, more sodium borohydride (19 mg, 0.5 mmol) was added portionwise to the reaction mixture, which was then allowed to warm up to room temperature. A mixture of 2M hydrochloric acid (25 ml) and ice (25 g) was added to the mixture, which was then extracted with dichloromethane (3 x 20 ml). The extract was washed with water (2 x 20 ml) and brine (20 ml), dried, and evaporated. Flash chromatography of the residue, eluting with dichloromethane - methanol (49:1), gave a small amount of unreacted ketone **9** (31 mg, 5%), followed by the *title compound* **32** (549 mg, 88%), which formed orange crystals, m.p. 174–176 °C (ethanol) (Found: C, 69.9; H, 4.5. $C_{18}H_{14}O_5$ requires C, 69.7; H, 4.55%); ν_{max} (FT, neat) 3440 br, 1661, and 1592 cm^{-1}; δ (300 MHz) 3.26 (1 H, d, *J* 14.5 Hz, 2-H *cis* to OH), 3.46 (3 H, s, OMe), 3.74 (1 H, dd, *J* 4.5, 14.5 Hz, 2-H *trans* to OH), 4.12 (3 H, s, OMe), 4.6 (1 H, br d, *J* 12 Hz, OH; chemical shift and multiplicity markedly solvent and concentration dependent), 5.24 (1 H, dd, *J* 4.5, 12 Hz, 1-H), 7.6–7.7 (2 H, m, 6-H and 7-H), and 8.05–8.1 (2 H, m, 5-H and 8-H); M^+, 310.

*1,2-Dihydro-1,3,10-trimethoxycyclobut[*b*]anthracene-4,9-dione* **33**. – A mixture of the alcohol **32** (46.5 mg, 0.15 mmol), freshly prepared silver(I) oxide (140 mg, 0.6 mmol), and iodomethane (1.0 ml, 2.28 g, 16 mmol) in dichloromethane (4 ml) was stirred at room temperature for 16 h and then filtered. Evaporation of the filtrate gave the *title compound* **33** (47 mg, 97%), which formed orange rosettes, m.p. 154–156 °C (ethyl acetate) (Found: C, 69.95; H, 5.0. $C_{19}H_{16}O_5$ requires C, 70.35; H, 5.0%); ν_{max} (FT, neat) 1667 and 1593 cm^{-1}; δ (300 MHz) 3.42 (3 H, s, 1-OMe), 3.44 (1 H, dd, *J* 2, 14 Hz, 2-H *cis* to OMe), 3.69 (1 H, dd, *J* 4, 14 Hz, 2-H *trans* to OMe), 4.03 (3 H, s, ArOMe), 4.12 (3 H, s, ArOMe), 5.12 (1 H, dd, *J* 2, 4 Hz, 1-H), 7.6–7.7 (2 H, m, 6-H and 7-H), and 8.05–8.1 (2 H, m, 5-H and 8-H).

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