Preparation of 3,4-Dihydroanthracen-1(2*H*)-ones. A Synthetic Approach to Islandicin and Digitopurpone *via* Difluoro[anthracen-1(2*H*)-onato-O^1,O^9]boron Chelates

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Three 9,10-dihydroxyanthracen-1(2*H*)-one derivatives (2a—c) have been obtained by the catalytic hydrogenation of quinizarin, 1-hydroxy-5-methoxyanthraquinone, and 1-hydroxy-8-methoxyanthraquinone, respectively; in the last two reactions, monohydroxyanthracen-1(2*H*)-ones (4a) and (4b) are formed as by-products. The anthracenone derivatives (2a—c) were *O*-methylated by methyl toluene-*p*-sulphonate and the selective demethylation of the dimethoxy derivative (2d) to the monomethoxy derivative (2e) was effected by $AlCl_3$. The silyl enolate (5) was unreactive toward *C*-methylation but the lithium enolate of the anthracenone (2d) reacted with methyl iodide to give a mixture of *C*-mono (2f) and *C*-di (6a) alkylated derivatives; in contrast, the boron enolate of (2d) reacted with methyl iodide to give exclusively the *C*-monomethylated derivative (2f) and this procedure was extended to the synthesis of 5-methoxy (2g) and 8-methoxy (2h) analogues of (2f). Whereas the dimethoxyanthracenone derivative (2d) is brominated (Br_2–$CHCl_3$, 0 °C) in separate reactions to give monobromo (2i) and dibromo (6b) derivatives, the difluoroboron chelate (9a) [from (2d) and BF_3–Et_2O] was converted by photochemical bromination into a product (9g) of benzylic substitution; the analogue (9h) was similarly obtained from the difluoroboron chelate (9b). The boron derivatives (9g) and (9h) were transformed by methanol into hydroxydimethoxyanthracenone derivatives (2l) and (2m), and (9g) was also converted by wet alumina into the dihydroxymethoxyanthracenone (2n). The hydroxydimethoxyanthracenones (2l) and (2m) were transformed by 2,3-dichloro-5,6-dicyanobenzoquinone [for (2l)] and selenium dioxide [for (2n)] into 1-hydroxy-4-methoxyanthraquinone and 1-hydroxy-4-methoxy-2-methylanthraquinone, respectively.

The commercial success of adriamycin [1]† as an antineoplastic agent has generated a renewed interest [2] in the synthesis of hydroxyanthraquinones with particular regard to regiochemical problems inherent in compounds such as islandicin (1a) and digitopurpone (1b).[3] We describe an approach to the synthesis of these derivatives (1a) and (1b) from 1,5- and 1,8-dihydroxyanthraquinones.

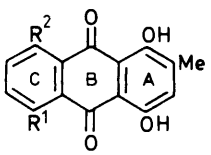
It was considered that regiospecific functionalisation of the A ring [*cf.* (1)] might be achieved by conversion of the anthraquinone system into a 3,4-dihydroanthracen-1(2*H*)-one derivative [*cf.* (2)]. Methylation (introducing R^1), bromination and ensuing hydrolysis (introducing R^2) and finally oxidation of appropriately substituted anthracenones (2; R^5 or R^6 = OMe) would provide relatively simple syntheses of islandicin and digitopurpone (1a) and (1b). The ensuing discussion describes separately the catalytic hydrogenation of hydroxyanthraquinones, alkylation and related nucleophilic reactions of the ensuing 3,4-dihydroanthracen-1(2*H*)-ones, the manner in which such anthracenones can be regioselectively brominated *via* aryloxydifluoroboron chelates, and finally the transformation of bromoanthracenone difluoroboron chelates into anthraquinones.

Catalytic Hydrogenation of Hydroxyanthraquinones.—The conversion by catalytic reduction (H_2–Ni) of 1-hydroxyanthraquinone and 1,4-dihydroxyanthraquinone into 3,4-dihydro-9,10-dihydroxyanthracen-1(2*H*)-one (2a) was described in 1938 by Zahn and Koch.[4] In a modified procedure we have obtained (2a) in 85% yield by catalytic hydrogenation (H_2, 5% Pd–C) of quinizarin in dimethylformamide. No success was achieved in an attempt to prepare 2-substituted 3,4-dihydroanthracenones [*cf.* (2; R^1 = Cl or SO_3H)] by catalytic hydrogenation of appropriately substituted quinizarin derivatives. In each case the only identifiable product was leucoquinizarin (3). Since leucoquinizarin is probably an intermediate in the transformation of 1,4-dihydroxyanthraquinone into (2a) it must be assumed that elimination of HCl or H_2SO_4 during the hydrogenation causes a reduction in the efficiency of the palladium catalyst. 5-Methoxy (2b) and 8-methoxy (2c) derivatives of (2a) were prepared in similar fashion by catalytic hydrogenation of 1-hydroxy-5-methoxy- and 1-hydroxy-8-methoxy-anthraquinones respectively, but in each reaction additional anthracenone derivatives (4a) and (4b) were isolated. The regiochemical outcome of these hydrogenations followed from a comparison of ^1H n.m.r. chemical-shift values for the hydroxy protons of (4a) and (4b) (δ 14.04 and 14.80 respectively) with those of (2a) [δ (9-OH and 10-OH) 13.77 and 8.56, respectively].

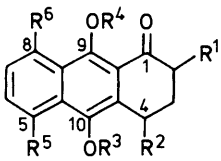
Alkylation and Related Reactions.—The anthracenone (2a) was methylated routinely (p-$MeC_6H_4SO_3Me$–Na_2CO_3) to give the dimethoxy derivative (2d) and this could be selectively dealkylated [5] (CH_3COCl–$AlCl_3$) [6] to give the monomethoxy derivative (2e); the latter was identical with the compound obtained by the selective methylation (Me_2SO_4–NaOH) of (2a) using the method of Zahn and Koch.[4] Confirmation of the regiochemistry of demethylation follows from the ^1H n.m.r. spectrum which includes an exchangeable OH resonance at δ 14.05 [*cf.* values of δ 14.04 and 14.80 for the chelated 9-OH protons of (4a) and (4b) respectively].

Initial attempts to prepare the anthracenone (2f) from (2d) *via* the silyl enolate (5) failed, perhaps because of steric inhibition of nucleophilic attack by fluoride ion at silicon. Treatment of the lithium enolate of (2d) with methyl iodide at −78 °C, and warming to room temperature gave the desired trimethyl derivative (2f) (48%), but the *C*-dialkylated product (6a) (10%) was also formed, and was isolated only after a difficult chromatographic separation from (2f). The problem of dialkylation was overcome by methylating the boron

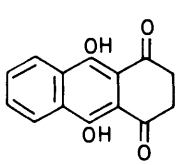
† Marketed by Montedison as Doxorubicin Hydrochloride.



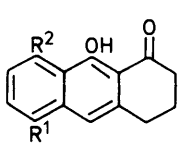
(1) a; R^1 = MeO, R^2 = H
b; R^1 = H, R^2 = MeO



(2) a; R^1 - R^6 = H
b; R^1 - R^4 = R^6 = H, R^5 = MeO
c; R^1 - R^5 = H, R^6 = MeO
d; R^1 = R^2 = R^5 = R^6 = H, R^3 = R^4 = Me
e; R^1 = R^2 = R^4 - R^6 = H, R^3 = Me
f; R^1 = R^3 = R^4 = Me, R^2 = R^5 = R^6 = H
g; R^1 = R^3 = R^4 = Me, R^2 = R^6 = H, R^5 = MeO
h; R^1 = R^3 = R^4 = Me, R^2 = R^5 = H, R^6 = MeO
i; R^1 = Br, R^2 = R^5 = R^6 = H, R^3 = R^4 = Me
j; R^1 = R^2 = H, R^3 = R^4 = Me, R^5 = MeO, R^6 = H
k; R^1 = R^2 = H, R^3 = R^4 = Me, R^5 = H, R^6 = MeO
l; R^1 = R^4 = R^5 = R^6 = H, R^2 = MeO, R^3 = Me
m; R^1 = R^3 = Me, R^2 = MeO, R^4 = R^5 = R^6 = H
n; R^1 = R^4 = R^5 = R^6 = H, R^2 = OH, R^3 = Me



(3)

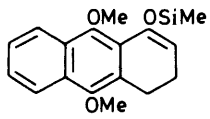


(4) a; R^1 = MeO, R^2 = H
b; R^1 = H, R^2 = MeO

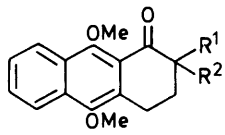
enolate [Li enolate-$B(OCH_2CH_2)_3N$][7] to give the monomethyl derivative (2f) in 79% yield, and this procedure was applied successfully to the synthesis of 5- and 8-methoxy analogues, (2g) and (2h), of (2f) from (2j) and (2k) respectively.

Introduction of R^2 Substituent into Compound (2).—It was intended that the C(4)-oxygen function [*cf.* (2; R^2 = OH or OMe)] could be introduced *via* bromo derivatives [*cf.* (2; R^2 = Br)]. It was recognised that successful benzylic free radical bromination could only be effected by masking the carbonyl group [(2d) was converted rapidly (Br_2–$CHCl_3$, 0 °C) in separate reactions into mono- (2i) and dibromo-anthracenones (6b), and (2f) formed a monobromo derivative (6c) under similar conditions], but an acetal could not be prepared [*e.g.* from (2d), $HOCH_2CH_2OH$-*p*-$MeC_6H_4SO_3H$ and related reactions], and bromo derivatives (7b) and (8b) could not be isolated from separate reactions of the oxime acetate (7a) with *N*-bromosuccinimide[8] or the trimethoxy derivative (8a) with bromine in u.v. light.

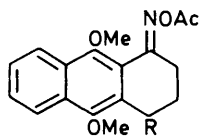
A procedure for the regioselective bromination *via* masked carbonyl compounds was eventually developed using aryloxy-



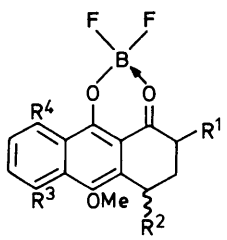
(5)



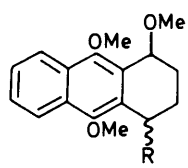
(6) a; R^1 = R^2 = Me
b; R^1 = R^2 = Br
c; R^1 = Br, R^2 = Me



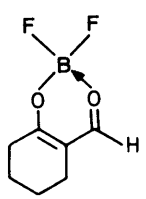
(7) a; R = H
b; R = Br
c; R = OMe



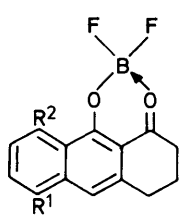
(9) a; R^1 - R^4 = H
b; R^1 = Me, R^2 - R^4 = H
c; R^1 = R^2 = R^4 = H, R^3 = MeO
d; R^1 = R^2 = R^3 = H, R^4 = MeO
e; R^1 = Me, R^2 = R^4 = H, R^3 = MeO
f; R^1 = Me, R^2 = R^3 = H, R^4 = MeO
g; R^1 = R^3 = R^4 = H, R^2 = Br
h; R^1 = Me, R^2 = Br, R^3 = R^4 = H



(8) a; R = H
b; R = Br



(10)



(11) a; R^1 = MeO, R^2 = H
b; R^1 = H, R^2 = MeO

difluoroboron chelates [*cf.* (9)] derived from 9,10-dimethoxyanthracenones [*cf.* (2)] during studies of their demethylation. For example, treatment of the dimethoxyanthracenone (2d) with boron trifluoride–diethyl ether in dichloromethane gave an air-stable orange crystalline complex (9a) in 79% yield. This formulation (9a) is supported by analytical data, by the mass spectrum ($M^{\cdot+}$ at *m/e* 290), by the ^1H n.m.r. spectrum [one MeO resonance and no exchangeable signal at δ *ca.* 14 which would be expected from an H-bonded 9-OH proton, *cf.* (2e)], and a slight shift (205 ⟶ 199 p.p.m.) in the ^{13}C n.m.r. carbonyl carbon resonance in passing from (2d) to (9a). The i.r. spectrum of (9a) shows strong absorption bands at 1 580 and 1 483 cm^{-1} which are characteristic of difluoroboron chelates derived from related enolisable 1,3-dicar-

bonyl compounds [*cf.* values[9] of 1 612 and 1 495 cm^{-1} in (10)]. Air-stable difluoroboron chelates (9b—d), (11a) and (11b) were prepared in similar fashion from appropriate 9-methoxy- (2f—h) or 9-hydroxy- (4a), and (4b) anthracenones, respectively, but unfortunately it proved impossible to prepare pure samples of 2-methyl-5-methoxy and 2-methyl-8-methoxy derivatives (9e) and (9f).

Photochemical bromination (sunlamp, ABIN) of the difluoroboron chelate (9a) by bromine in carbon tetrachloride gave an orange derivative (9g) of benzylic substitution, and the 2-methyl analogue (9h) was obtained by a similar procedure. The 2-methyl ^1H n.m.r. resonance of (9h) appears as a doublet at δ 1.42 and the C-2 hydrogen appears as a seven-line signal at δ 3.55. These data demonstrate that bromination occurs regioselectively at C-4 [the remaining hydrogens at C-4 of (9g) and (9h) appear at δ 5.98 and 5.90, respectively]. Regrettably, impure 2-methyl-5- and -8-methoxy difluoroboron chelates (9e) and (9f) failed to react with bromine under conditions of photolysis (n.m.r. analysis).

Conversion of Bromo Derivatives (9g) *and* (9h) *into Anthraquinones*.—The difluoroboron chelates (9g) and (9h) are thermally unstable at room temperature and decompose within one day to give intractable black oils. However, treatment of the crude difluoroboron chelates (9g) and (9h) with methanol at −20 °C for 3 days gave the hydroxydimethoxyanthracenones (2l) (85%) and (2m) (55%). Solvolysis of the difluoroboron moiety was recognised in each compound (2l) and (2m) by the appearance of exchangeable ^1H n.m.r. resonances for the 9-OH proton at δ 14.02 and 14.26, respectively. The difluoroboron chelate (9g) could also be solvolysed by chromatographing it through wet alumina using toluene as eluant to give the dihydroxymethoxyanthracenone (2n) (89%); the ^1H n.m.r. spectrum of this material also exhibited the low-field exchangeable 9-OH proton (δ 14.02) in addition to the 4-OH resonance (δ 2.65).

The hydroxydimethoxyanthracenone (2l) was transformed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) into 1-hydroxy-4-methoxyanthraquinone (46%). Using the same reaction conditions, the 2-methyl analogue (2m) of (2l) was transformed by DDQ into 1-hydroxy-2-methylanthraquinone in a process of oxidation with concomitant elimination of methanol. This substrate (2m) was successfully converted into 1-hydroxy-4-methoxy-2-methylanthraquinone (madeirin), albeit in poor yield (18%), by treating it with selenium dioxide in dioxan, but the major product (70%) was again 1-hydroxy-2-methylanthraquinone.

Experimental

Catalytic Hydrogenation.—Catalytic hydrogenation experiments were conducted with equal facility using either a Frings apparatus or rocking Baskerville autoclaves (300 ml or 1 l capacity). The catalyst was 5% palladium-on-charcoal (Koch-Light).

Preparation of 3,4-*Dihydro*-9,10-*dihydroxyanthracen*-1(2H)-*one* (2a).—1,4-Dihydroxyanthraquinone (20 g, 87 mmol) in dimethylformamide (250 ml) was heated at 70 °C for 20 h in a rocking autoclave, with palladium (0.5 g, 5% Pd on charcoal) under H_2 (40 atm). On cooling, the reaction mixture was filtered through Celite, concentrated to half volume and poured onto ice (200 g). The precipitate was air dried and recrystallised from ethyl acetate–toluene to yield 3,4-dihydro-9,10-dihydroxyanthracen-1(2*H*)one (2a) (16.0 g, 84%), m.p. 154—156 °C (lit.,[4] 170—171 °C); δ(^1H) ($CDCl_3$; 100 MHz) 13.77 (1 H, s, exch, chelated OH), 8.56 (1 H, s, exch, OH), 8.3 (2 H, m), 7.62 (2 H, m), 3.03 (2 H, t, *J* 6 Hz), 2.68 (2 H, t, *J* 6 Hz), and 2.06 (2 H, t, *J* 6 Hz); *m/e* 228 ($M^{\cdot+}$).

Hydrogenation of 1-*Hydroxy*-5-*methoxyanthraquinone*.—1-Hydroxy-5-methoxyanthraquinone (10.0 g, 40 mmol) in dimethylformamide (200 ml) was hydrogenated (40 atm H_2) over palladium (0.5 g, 5% Pd on charcoal) for 12 h at 80 °C. The product was filtered through Celite, evaporated to *ca.* 100 ml and poured on to ice. The pale brown precipitate was separated, washed with cold water, dried at 60 °C *in vacuo*, and purified chromatographically [silica gel, dichloromethane–light petroleum (1 : 5) as eluant] to give initially 3,4-*dihydro*-9-*hydroxy*-5-*methoxyanthracen*-1(2H)-*one* (4a) (0.83 g, 8.3%), m.p. 118—119 °C (from diethyl ether–light petroleum); δ(^1H)($CDCl_3$) 14.04 (1 H, s, exch, chelated OH), 7.88 (1 H, d, *J* 8 Hz, 8-H), 7.36 (1 H, s, 10-H), 7.30 (1 H, t, *J* 8 Hz, 7-H), 6.86 (1 H, d, *J* 8 Hz, 6-H), 3.92 (3 H, s, OMe), 2.95 (2 H, t, *J* 6 Hz, 2-H), 2.70 (2 H, t, *J* 6 Hz, 4-H), and 2.1 (2 H, m, 3-H); *m/e* 242 ($M^{\cdot+}$); $\nu_{max.}$ 2 930, 1 620, 1 590, 1 490, 1 450, 1 390, 1 260, 1 240, 1 125, 1 080, 1 055, 880, and 810 cm^{-1}; $\lambda_{max.}$ (MeOH) 225, 262, 285, 295, 307, and 390 nm (Found: C, 74.25; H, 5.85. $C_{14}H_{14}O_3$ requires C, 74.38; H, 5.78%). The second fraction was 3,4-*dihydro*-9-10-*dihydroxy*-5-*methoxyanthracen*-1(2H)-*one* (2b) (4.98 g, 50%), m.p. 142—143 °C (from dichloromethane–light petroleum); $\nu_{max.}$ 2 930, 1 620, 1 590, 1 490, 1 450, 1 390, 1 260, 1 240, 1 125, 1 080, 1 055, 880, and 810 cm^{-1}; δ(^1H) ($CDCl_3$) 13.28 (1 H, s, exch, 9-OH), 8.92 (1 H, s, exch, 10-OH), 7.96 (1 H, d, *J* 8 Hz, 8-H), 7.26 (1 H, t, *J* 8 Hz, 7-H), 6.90 (1 H, d, *J* 8 Hz, 6-H), 4.00 (3 H, s, OMe), 2.96 (2 H, t, *J* 6 Hz, 2-H), 2.70 (2 H, t, *J* 6 Hz, 4-H), and 2.10 (2 H, m, 3-H); *m/e* 258 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 224, 263, 327, 422 nm (Found: C, 69.75; H, 5.4. $C_{14}H_{14}O_4$ requires C, 69.73; H, 5.48%).

Hydrogenation of 1-*Hydroxy*-8-*methoxyanthraquinone*.—1-Hydroxy-8-methoxyanthraquinone (10.0 g, 40 mmol) was hydrogenated as in the preceding experiment to give a brown oily residue (10.0 g) after filtration and evaporation. The oil was purified chromatographically [silica gel, diethyl ether–light petroleum (1 : 10) eluant] to give initially 3,4-*dihydro*-9-*hydroxy*-8-*methoxyanthracen*-1(2H)-*one* (4b) (0.47 g, 4.5%), m.p. 152—153 °C (from dichloromethane–diethyl ether); $\nu_{max.}$ 2 930, 1 625, 1 570, 1 405, 1 350, 1 260, 1 060, 970, 810, and 730 cm^{-1}; δ(^1H) ($CDCl_3$) 14.80 (1 H, s, exch, 9-OH), 7.12—7.60 (2 H, m, 6-, 7-H), 6.86 (1 H, s, 10-H), 6.78 (1 H, d, *J* 8 Hz, 5-H), 4.00 (3 H, s, OMe), 2.96 (2 H, t, *J* 6 Hz, 2-H), 2.72 (2 H, t, *J* 6 Hz, 4-H), and 2.12 (2 H, m, 3-H); *m/e* 242 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 227, 262, 290, 302, 315, and 395 nm (Found: C, 74.65; H, 5.8. $C_{15}H_{14}O_3$ requires C, 74.38; H, 5.78%).

The second component (28%) was starting material and the third fraction [eluant diethyl ether–light petroleum (1 : 1)] was 3,4-*dihydro*-9,10-*dihydroxy*-8-*methoxyanthracen*-1(2H)-*one* (2c) (4.25 g, 43%), m.p. 165—166 °C (from chloroform); $\nu_{max.}$ 3 460, 2 960, 2 910, 1 625, 1 595, 1 585, 1 455, 1 390, 1 250, 1 180, 1 120, 1 075, 1 050, 975, 940, 900, 815, 775, and 765 cm^{-1}; δ(^1H) [$(CD_3)_2SO$] 14.30 (1 H, s, exch, 9-OH), 8.80—8.00 (1 H, br s, exch, 10-OH), 7.80—7.40 (2 H, m, 6-, 7-H), 6.94 (1 H, d, *J* 8 Hz, 5-H), 3.90 (3 H, s, OMe), 2.94 (2 H, t, *J* 6 Hz, 2-H), 2.70 (2 H, t, *J* 6 Hz, 4-H), and 1.98 (2 H, m, 3-H); *m/e* 258 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 227, 263, 295, 307, 320, and 418 nm (Found: C, 69.75; H, 5.4. $C_{15}H_{14}O_4$ requires C, 69.73; H, 5.48%).

Preparation of 3,4-*Dihydro*-9,10-*dimethoxyanthracen*-1(2H)-*one* (2d).—3,4-Dihydro-9,10-dihydroxyanthracen-1(2*H*)-one (2a) (20 g, 88 mmol), anhydrous sodium carbonate (20 g) and methyl toluene-*p*-sulphonate (40 g, 0.21 mol) were

heated under reflux in *o*-dichlorobenzene (300 ml) for 12 h. The mixture was poured into water (300 ml) and the organic phase was washed with water (100 ml), dried ($MgSO_4$), filtered and evaporated under reduced pressure to yield a brown solid. This was heated under reflux with toluene and decolourising charcoal (2 g), filtered through Celite, and allowed to crystallise to yield 3,4-dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (2d) (18.4 g, 82%), m.p. 117—119 °C (lit.,[4] 115 °C), $\nu_{max.}$ ($CHCl_3$) 3 010, 2 935, 1 681, 1 621, 1 565, 1 357, 1 287, and 1 008 cm^{-1}; $\delta(^1H)$ ($CDCl_3$; 60 MHz) 8.32 (1 H, m, 5-H), 8.08 (1 H, m, 8-H), 7.52 (2 H, m, 6-, 7-H), 3.98, 3.88 (2 × 3 H, s, OCH_3), 3.10 (2 H, t, *J* 6 Hz, 4-H), 2.70 (2 H, t, *J* 6 Hz, 2-H), and 2.14 (2 H, m, 3-H); $\delta(^{13}C)$ ($CDCl_3$; 50.32 MHz) 22.4, 24.0, 41.0, 61.0, 62.9, 121.5, 124.4, 125.4, 128.2, and 196.7 p.p.m., *m/e* 256 ($M^{\cdot+}$).

3,4-*Dihydro*-5,9,10-*trimethoxyanthracen*-1(2H)-*one* (2j).—This was prepared (66% yield) from 3,4-dihydro-9,10-dihydroxy-5-methoxyanthracen-1(2*H*)-one (2b) by the method described above. The initial dark oily yellow product was purified chromatographically (silica gel, toluene as eluant) to give 3,4-*dihydro*-5,9,10-*trimethoxyanthracen*-1(2H)-*one* (2j) as a yellow oil, $\nu_{max.}$ ($CHCl_3$) 2 920, 1 680, 1 610, 1 560, 1 450, 1 255, 1 075, and 770 cm^{-1}; $\delta(^1H)$ ($CDCl_3$) 7.94 (1 H, d, *J* 8 Hz, 8-H), 7.36 (1 H, d, *J* 8 Hz, 7-H), 6.96 (1 H, d, *J* 8 Hz, 6-H), 4.00 (6 H, s, 5- and 9-MeO), 3.80 (3 H, s, 10-MeO), 3.12 (2 H, t, *J* 6 Hz, 2-H), 2.64 (2 H, t, *J* 6 Hz, 4-H), and 2.06 (2 H, m, 3-H); *m/e* 286 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 255, 292, 304, 315, and 372 nm (Found: C, 69.05; H, 6.6. $C_{17}H_{18}O_4$ requires C, 71.33; H, 6.3%).

3,4-*Dihydro*-8,9,10-*trimethoxyanthracen*-1(2H)-*one* (2k).—This was prepared (58% yield) from 3,4-dihydro-9,10-dihydroxy-8-methoxyanthracen-1(2*H*)-one (2c) by the method described for (2d) and (2j) above. The initial dark yellow oily product was purified chromatographically [silica gel, diethyl ether–light petroleum (4 : 1) as eluant] to give 3,4-*dihydro*-8,9,10-*trimethoxyanthracen*-1(2H)-*one* (2k), m.p. 92—94 °C (from diethyl ether–light petroleum); $\nu_{max.}$ 2 930, 1 680, 1 610, 1 580, 1 550, 1 430, 1 380, 1 360, 1 330, 1 275, 1 240, 1 175, 1 105, 1 075, 1 055, 960, 820, 785, and 770 cm^{-1}; $\delta(^1H)$ ($CDCl_3$) 7.72—7.20 (2 H, m, 6-, 7-H), 6.84 (1 H, d, *J* 8 Hz, 5-H), 4.00 (3 H, s, 8-OMe), 3.92 (3 H, s, 9-OMe), 3.84 (3 H, s, 10-OMe), 2.82 (2 H, t, *J* 6 Hz, 2-H), 2.66 (2 H, t, *J* 6 Hz, 4-H), and 2.04 (2 H, m, 3-H); *m/e* 286 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 252, 263, 293, 304, 316, and 372 nm (Found: C, 71.7; H, 6.35. $C_{17}H_{18}O_4$ requires C, 71.33; H, 6.29%).

3,4-*Dihydro*-9-*hydroxy*-10-*methoxyanthracen*-1(2H)-*one* (2e).—This compound was prepared according to a literature procedure[4] and is included here to provide full spectral characterisation. To 3,4-dihydro-9,10-dihydroxyanthracen-1(2*H*)-one (2a) (912 mg, 4 mmol) in sodium hydroxide solution (2M; 20 ml) was added dimethyl sulphate (0.5 g; 1 equiv.). After stirring for 4 h at room temperature, the mixture was neutralised with hydrochloric acid (conc.) and extracted with ether (2 × 15 ml). The ether extract was washed with water (20 ml), dried ($MgSO_4$), and evaporated to yield a brown solid. This was recrystallised from methanol–toluene (10 : 1) to yield 3,4-dihydro-9-hydroxy-10-methoxyanthracen-1(2*H*)-one (2e) (794 mg, 84%) as yellow cubes, m.p. 128—129 °C (lit.,[4] 128—129 °C); $\nu_{max.}$ ($CHCl_3$) 3 300—2 500, 3 000, 2 945, 1 614, 1 440, 1 376, 1 352, 1 083, and 1 003 cm^{-1}; $\delta(^1H)$ ($CDCl_3$; 60 MHz) 14.05 (1 H, s, exch, 9-OH), 8.42 (1 H, m, 5-H), 8.00 (1 H, m, 8-H), 7.60 (2 H, m, 6-, 7-H), 3.83 (3 H, s, OCH_3), 3.08 (2 H, t, *J* 6 Hz, 4-H), 2.73 (2 H, t, *J* 6 Hz, 2-H), 2.13 (2 H, m, 2-H); *m/e* 242 ($M^{\cdot+}$); $\delta(^{13}C)$ ($CDCl_3$; 50.32 MHz) 22.4, 23.5, 38.8, 61.0, 110.8, 121.6, 124.8, 125.2, 127.7, 130.3, 132.5, 143.7, 159.9, and 204.8 p.p.m.

Compound (2e) was also obtained by treating 3,4-dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (2d) (0.51 g, 2 mmol) in carbon disulphide (20 ml) with acetyl chloride (1.1 g, 15 mmol) and $AlCl_3$ (0.6 g) and heating the mixture under reflux for 45 min. It was then acidified with 2M-hydrochloric acid (50 ml) and extracted with diethyl ether. The ether was evaporated and the residual brown oil was chromatographed (silica gel, 10% diethyl ether in light petroleum as eluant) to give (2e) (0.25 g, 52%), m.p. 128—129 °C, which was spectroscopically (i.r., n.m.r.) identical with the sample described above.

3,4-*Dihydro*-9,10-*dimethoxy*-1-*trimethylsilyloxyanthracene* (5).—To a solution of 3,4-dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (0.512 g, 2 mmol) in tetrahydrofuran (THF) (5 ml) was added lithium di-isopropylamide[10] (1.1 equiv., 0.4M in THF–hexane) at −78 °C under N_2. The solution was stirred for 15 min, chlorotrimethylsilane (0.34 g, 3 mmol, 1.5 equiv.) was added and the solution was stirred for 1 h until room temperature was attained. The solution was added to cold saturated sodium hydrogen carbonate solution (15 ml) and extracted with ether (10 ml). The organic phase was washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated to yield (5) as a pure yellow oil (660 mg, 100%) (n.m.r. and t.l.c. analysis), $\nu_{max.}$ (film) 2 958, 2 842, 1 633, 1 456, 1 358, 1 071, 1 018, and 842 cm^{-1}; $\delta(^1H)$ ($CDCl_3$; 60 MHz) 8.64 (2 H, m), 7.98 (2 H, m), 5.94 (1 H, t, *J* 5.4 Hz, =CHR), 4.36, 4.27 (2 × 3 H, s, OCH_3), 3.43 (2 H, m), 2.77 (2 H, m), and 0.10 (9 H, m, $SiMe_3$); *m/e* 329 ($M^{\cdot+}$). Attempted distillation of this product (Kugelrohr, 165 °C, 1 mmHg) yielded an impure yellow oil (0.52 g, 78%) (n.m.r. and mass spectral data).

Alkylation (MeI–CH_2Cl_2–$SnCl_4$, −20 °C) of the material (5) prior to distillation was unsuccessful.

Methylation of 3,4-*Dihydro*-9,10-*dimethoxyanthracen*-1(2H)-*one* (2d).—(*a*) Via *lithium enolate*. 3,4-Dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (512 mg, 2 mmol) in dry THF (15 ml) under nitrogen, at −78 °C, was treated with lithium di-isopropylamide (1.1 equiv., 2.2 mmol, 5.5 ml; 0.4M in THF–hexane) dropwise during 2 min and stirred for a further 10 min. Iodomethane (1.4 g, 10 mmol, 5 equiv.) was added and the solution was stirred for 2 h until room temperature was attained. The product was extracted with diethyl ether and the extract was dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The residue was chromatographed (silica gel, 3% diethyl ether in light petroleum as eluant) to yield 3,4-*dihydro*-9,10-*dimethoxy*-2,2-*dimethylanthracen*-1(2H)-*one* (6a) (56 mg, 10%) as a brown oil; $\nu_{max.}$ ($CHCl_3$) 3 018, 1 682, 1 354, and 1 210 cm^{-1}; $\delta(^1H)$ ($CDCl_3$; 60 MHz) 7.8 (4 H, m, arom.) 3.95, 3.85 (2 × 3 H, s, OCH_3), 3.10 (2 H, t, *J* 7 Hz, 4-H), 2.00 (2 H, t, *J* 7 Hz, 3-H), and 1.70 (6 H, s, 2 × CH_3); *m/e* 284, ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 235, 290, and 351 nm (Found: C, 74.2; H, 6.9. $C_{18}H_{20}O_3$ requires C, 76.06; H, 7.04%).

Further elution with 4% ether in light petroleum gave 3,4-*dihydro*-9,10-*dimethoxy*-2-*methylanthracen*-1(2H)-*one* (2f) as colourless cubes from methanol (257 mg, 48%), m.p. 86—88 °C; $\nu_{max.}$ (KBr) 2 918, 1 688, 1 618, 1 580, 1 560, and 1 353 cm^{-1}; $\delta(^1H)$ ($CDCl_3$; 100 MHz) 7.8 (4 H, m, aromatic), 3.95, 3.82 (2 × 3 H, s, OCH_3), 3.5—1.6 (5 H, m), and 1.23 (3 H, d, *J* 6 Hz, CH_3); *m/e* 270, ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 219, 252, 287, and 353 nm (Found: C, 75.45; H, 6.5. $C_{17}H_{18}O_3$ requires C, 75.56; H, 6.67%). Further elution with 5% ether in light petroleum gave starting material (93 mg, 19%).

(*b*) Via *boron enolate*.[7] The lithium enolate of (2d) [from

(2d) (1.02 g, 4 mmol) and lithium di-isopropylamide (1.1 equiv., 6 ml, 0.75M in THF–hexane)] in THF (20 ml) was treated with triethanolamine borate (1.0 equiv., 0.66 g) in dimethyl sulphoxide (10 ml) at −78 °C. Iodomethane (1.41 g, 10 mmol) was added at −20 °C and the mixture was stirred for 2 h with the coolant removed. The product was extracted with ether (10 ml) and the organic phase was washed (H_2O), dried ($MgSO_4$) and evaporated to leave a yellow oil. This was crystallised from methanol to give 3,4-dihydro-9,10-dimethoxy-2-methylanthracen-1(2*H*)-one (2f) (0.71 g, 66%), m.p. 85—87 °C. The filtrate was evaporated and the residue was chromatographed (silica gel, toluene as eluant) to give a further crop (0.15 g, 13%; total yield 79%), m.p. 86—88 °C.

3,4-*Dihydro*-5,9,10-*trimethoxy*-2-*methylanthracen*-1(2H)-*one* (2g).—This was prepared (79% yield) by methylation of 3,4-dihydro-5,9,10-trimethoxyanthracen-1(2*H*)-one (2j) using method (*b*) described above: m.p. 121—122 °C (from diethyl ether–light petroleum); $\nu_{max.}$ 2 920, 1 685, 1 610, 1 565, 1 450, 1 365, 1 350, 1 260, 1 135, and 1 080 cm^{-1}; $\delta(^1H)$ ($CDCl_3$) 7.96 (1 H, d, *J* 8 Hz, 8-H), 7.44 (1 H, t, *J* 8 Hz, 7-H), 7.00 (1 H, d, *J* 8 Hz, 6-H), 4.00 (6 H, s, 5- and 9-MeO), 3.80 (3 H, s, 10-MeO), 3.60—1.70 (5 H, m, methylene-H), and 1.28 (3 H, d, *J* 6 Hz, 2-CH_3); *m/e* 300 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 253, 266, 292, 302, 315, and 375 nm (Found: C, 72.2; H, 6.75. $C_{18}H_{20}O_4$ requires C, 72.0; H, 6.66%).

3,4-*Dihydro*-8,9,10-*trimethoxy*-2-*methylanthracen*-1(2H)-*one* (2h).—This was prepared (73% yield) by methylation of 3,4-dihydro-8,9,10-trimethoxyanthracen-1(2*H*)-one (2k) using method (*b*) described above. The initial oily yellow product was purified chromatographically [silica gel, diethyl ether–light petroleum (8 : 1) as eluant] to give the title *compound* (2h), m.p. 98—100 °C (from diethyl ether–light petroleum); $\nu_{max.}$ 2 940, 1 685, 1 610, 1 555, 1 450, 1 430, 1 380, 1 360, 1 330, 1 270, 1 070, 1 045, 1 020, 995, 820, 780, and 760 cm^{-1}; $\delta(^1H)$ ($CDCl_3$) 7.76—7.20 (2 H, m, 6-, 7-H), 6.84 (1 H, d, *J* 8 Hz, 5-H), 4.00 (3 H, s, 8-MeO), 3.92 (3 H, s, 9-MeO), 3.86 (3 H, s, 10-MeO), 3.40—1.60 (5 H, m, methylene-H), and 1.18 (3 H, d, *J* 6 Hz, 2-Me); *m/e* 300 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 252, 267, 290, 302, 315, and 375 nm (Found: C, 72.15; H, 6.35. $C_{18}H_{20}O_4$ requires C, 72.00; H, 6.66%).

2-*Bromo*-3,4-*dihydro*-9,10-*dimethoxyanthracen*-1(2H)-*one* (2i).—To a stirred solution of 3,4-dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (1.02 g, 4 mmol) in chloroform (20 ml) at 0 °C was added bromine (1.0 equiv., 4 mmol, 1M in $CHCl_3$) dropwise during 5 min with dry nitrogen purging. After a further 5 min the solution was poured into water (30 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated to yield a brown oil which crystallised from methanol–toluene (10 : 1) to yield 2-*bromo*-3,4-*dihydro*-9,10-*dimethoxyanthracen*-1(2H)-*one* (1.3 g, 92%), m.p. 91—93 °C; $\nu_{max.}$ (KBr) 2 925, 1 673, 1 604, 1 354, 1 063, and 777 cm^{-1}; $\delta(^1H)$ ($CDCl_3$; 60 MHz) 8.28 (1 H, m, 8-H), 8.00 (1 H, m, 5-H), 7.45 (2 H, m, 6-, 7-H), 4.71 (1 H, t, *J* 4.5 Hz, CHBr), 3.96, 3.85, (2 × OCH_3), 3.13 (2 H, m, 4-H), and 2.46 (2 H, m, 3-H); *m/e* 336, ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 222, 233, 259, 298, and 361 nm (Found: C, 57.45; H, 4.5; Br, 24.9. $C_{16}H_{15}BrO_3$ requires C, 57.31; H, 4.48; Br, 23.88%).

2,2-*Dibromo*-3,4-*dihydro*-9,10-*dimethoxyanthracene*-1(2H)-*one* (6b).—To a solution of 3,4-dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (256 mg, 1 mmol) in dichloromethane (10 ml) was added bromine (2.2 equiv., 350 mg, 1M in dichloromethane) and the mixture was stirred at room temperature for 0.5 h. The solution was washed with water (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure to yield a yellow oil. This was crystallised from methanol–toluene (10 : 1) to yield 2,2-*dibromo*-3,4-*dihydro*-9,10-*dimethoxyanthracene*-1(2H)-*one* as yellow crystals (380 mg, 92%), m.p. 80.5—81 °C; $\nu_{max.}$ (KBr) 2 930, 2 845, 1 693, 1 614, 1 355, 1 282, 1 069, and 772 cm^{-1}; $\delta(^1H)$ (60 MHz; $CDCl_3$) 8.28 (1 H, m, 8-H), 8.00 (1 H, m, 5-H), 7.55 (2 H, m, 6-, 7-H), 4.02 (3 H, s, OCH_3), 3.88 (3 H, s, OCH_3), and 3.15 (4 H, m); *m/e* 416 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 222, 262, 302, 313, and 378 nm (Found: C, 46.35; H, 3.6; Br, 37.8. $C_{16}H_{15}Br_2O_3$ requires C, 46.27; H, 3.61; Br, 38.55%).

2-*Bromo*-3,4-*dihydro*-9,10-*dimethoxy*-2-*methylanthracen*-1(2H)-*one* (6c).—To a solution of 3,4-dihydro-9,10-dimethoxy-2-methylanthracen-1(2*H*)-one (143 mg, 0.55 mmol) in carbon tetrachloride (10 ml) was added bromine during 10 min at 0 °C under nitrogen. After a further 5 min the mixture was washed with water (20 ml), dried ($MgSO_4$), and evaporated to yield a yellow oil. Chromatography of this oil (silica-gel column, 10% ether in light petroleum as eluant) yielded yellow 2-*bromo*-3,4-*dihydro*-9,10-*dimethoxy*-2-*methylanthracen*-1(2H)-*one* (171 mg, 89%), m.p. 74—76 °C (dec.) (from MeOH); $\nu_{max.}$ (KBr) 2 935, 2 843, 1 688, 1 616, 1 563, 1 357, 1 296, 1 046, 1 000, and 772 cm^{-1}; $\delta(^1H)$ (60 MHz; $CDCl_3$) 8.32 (1 H, m, ArH), 8.08 (1 H, m, ArH), 7.6 (2 H, m, ArH), 3.98, 3.88 (2 × OCH_3), 3.30 (2 H, m, methylene), 2.40 (2 H, m, methylene), and 2.01 (3 H, s, CH_3); *m/e* 350 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 222, 261, 311, and 361 nm. Satisfactory analytical data could not be obtained for this substance owing to its low thermal stability.

Preparation and Attempted Bromination of 3,4-*Dihydro*-9,10-*dimethoxyanthracen*-1(2H)-*one* O-*Acetyloxime* (7a).—3,4-Dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (0.5 g, 2 mmol), pyridine (5 ml), ethanol (95%, 5 ml), and hydroxylamine hydrochloride (0.5 g) were heated under reflux for 1 h. The product was evaporated under reduced pressure and the resulting solid was triturated with water (15 ml), filtered, washed with water until pyridine-free, and air dried. Recrystallisation from toluene–methanol (10 : 1) yielded 3,4-*dihydro*-9,10-*dimethoxyanthracen*-1(2H)-*one oxime* (494 mg, 93%), m.p. 225.5—227.5 °C (dec.); $\nu_{max.}$ (KBr) 3 210, 2 945, 2 842, 1 581, 1 347, 1 084, 979, and 777 cm^{-1}; $\delta(^1H)$ ($CDCl_3$) 8.28 (1 H, m, 8-H), 8.09 (1 H, m, 5-H), 7.45 (2 H, m, 6-, 7-H), 3.88 (6 H, s, OCH_3), 2.90 (4 H, m, 2-, 4-H), and 1.92 (2 H, m, 3-H); *m/e* 271 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 219, 256, and 302 nm (Found: C, 70.9; H, 6.2; N, 5.15. $C_{16}H_{17}NO_3$ requires C, 70.84; H, 6.27; N, 5.17%).

The oxime described above (350 mg, 1.3 mmol) in pyridine (5 ml) and acetic anhydride (5 ml) was maintained at room temperature for 12 h. The solution was evaporated under reduced pressure to yield cream crystals which were dissolved in ether (10 ml), washed with water (2 × 10 ml), dried ($MgSO_4$), filtered and the solution evaporated. The solid obtained was recrystallised from methanol to yield 3,4-*dihydro*-9,10-*dimethoxyanthracen*-1(2H)-*one* O-*acetyloxime* (7a) (372 mg, 92%), m.p. 125—126 °C; $\nu_{max.}$ (KBr) 2 945, 2 842, 1 760, 1 602, 1 350, 1 192, 1 009, and 779 cm^{-1}; $\delta(^1H)$ ($CDCl_3$) 8.0 (2 H, m, 5-, 8-H), 7.4 (2 H, m, 6-, 7-H), 4.08 (3 H, s, OCH_3), 3.84 (3 H, s, OCH_3), 2.23 (3 H, s, $COCH_3$), 2.55 (4 H, m, 2-, 4-H), and 1.80 (2 H, m, 3-H); *m/e* 313 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 218, 256, 301, and 351 nm (Found: C, 69.0; H, 5.95; N, 4.35. $C_{18}H_{19}NO_4$ requires C, 69.01; H, 6.07; N, 4.47%).

The *O*-acetyloxime from above (0.16 g, 0.5 mmol), *N*-bromosuccinimide (0.6 g, 3 mmol), and benzoyl peroxide (10 mg) were heated under reflux in carbon tetrachloride (N_2 atmosphere) for 6 h. The product was cooled in ice, and evaporated to leave a yellow oil. The ^1H n.m.r. spectrum indicated that (7b) had probably been formed [$\delta(^1H)$ ($CDCl_3$)

8.0 (2 H, m, 5-, 8-H), 7.42 (2 H, m, 6-, 7-H), 5.95 (1 H, t, *J* 3.5 Hz, CHBr), 3.88 (6 H, s, 2 × OMe), 3.5—2.3 (4 H, m, 2-, 3-H), and 2.08 (3 H, s, $COCH_3$)] but this material blackened on exposure to air, and formed a complex inseparable product when an attempt was made to convert it into (7c) [MeOH–CH_2Cl_2, room temp., 12 h].

Preparation and Attempted Bromination of 1,2,3,4-*Tetrahydro*-1,9,10-*trimethoxyanthracene* (8a).—To a solution of 3,4-dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (512 mg, 2 mmol) in methanol (15 ml) at 0 °C was added a solution of sodium borohydride (120 mg, 2 mmol) in methanol (5 ml) and the mixture stirred for 0.5 h until room temperature had been attained. Water (10 ml) was added and the mixture was stirred for 0.5 h. The solution was extracted with dichloromethane (2 × 15 ml) and the extract was dried ($MgSO_4$) and evaporated to yield a yellow oil. This was purified chromatographically (silica gel, toluene as eluant) to give a colourless oil which crystallised on addition of methanol to yield colourless 1,2,3,4-*tetrahydro*-1,9,10-*trimethoxyanthracene* (8a) (389 mg, 72%), m.p. 66—68 °C; $\nu_{max.}$ (KBr) 2 920, 1 582, 1 447, 1 351, 1 260, 1 184, 1 060, and 766 cm^{-1}; δ(^{1}H) ($CDCl_3$; 60 MHz) 7.61 (2 H, m), 7.04 (2 H, m), 4.55 (1 H, t, *J* 3 Hz, C*H*OMe), 3.74, 3.60, 3.24, (3 × OCH_3), and 3.1—1.25 (6 H, m); *m/e* 272 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 215, 235, 258, 267, 285, 300, and 330 nm (Found: C, 75.05; H, 7.4. $C_{17}H_{20}O_3$ requires C, 75.00; H, 7.35%).

Photochemical reaction (150W sunlamp) of the above material (8a) (272 mg, 1 mmol) and bromine (160 mg, 1 mmol) in carbon tetrachloride (5 ml) for 30 min gave, after evaporation of solvent, a complex inseparable brown oily product (t.l.c. analysis).

Preparation of Difluoroboron Chelates. Difluoro[3,4-*dihydro*-9-*hydroxy*-10-*methoxyanthracen*-1(2H)-*onato*-O^1,O^9]-*boron* (9a).—3,4-Dihydro-9,10-dimethoxyanthracen-1(2*H*)-one (1.50 g, 5.86 mmol) and boron trifluoride–diethyl ether (2 equiv., 11.5 mmol, 3.35 ml) in dichloromethane (20 ml) was maintained at room temperature for 72 h under N_2. The solution was poured into dilute hydrochloric acid (15 ml) and extracted. The organic phase was dried ($MgSO_4$) and evaporated under reduced pressure to yield brown crystals, which were heated under reflux in toluene with activated charcoal (0.25 g) for 2 min. The mixture was filtered through Celite and allowed to crystallise to yield orange difluoro-[3,4-dihydro-9-hydroxy-10-methoxyanthracen-1(2*H*)-onato-O^1,O^9]boron (1.35 g, 79%), m.p. 211—212.2 °C; $\nu_{max.}$ (KBr) 2 945, 2 840, 1 620, 1 580, 1 541, 1 483, and 782 cm^{-1}; δ(^{1}H) ($CDCl_3$; 60 MHz) 8.58 (1 H, m, 5-H), 7.7 (3 H, m, 6-, 7-, 8-H), 3.82 (3 H, s, OCH_3), 3.00 (4 H, m, methylene), and 2.20 (2 H, m, 3-H); *m/e* 290 ($M^{\cdot+}$); $\lambda_{max.}$ (hexane) 273, 307, 317, and 435 nm. δ(^{13}C) (50.32 MHz; $CDCl_3$) 21.9, 22.5, 34.2, 61.3, 121.8, 122.0, 122.5, 124.7, 125.1, 126.3, 126.9, 127.2, 134.4 136.9, and 199.2 p.p.m. (Found: C, 61.85; H, 4.55; B, 3.75. $C_{15}H_{13}BF_2O_3$ requires C, 62.07; H, 4.48; B, 3.79%). The following compounds were prepared by a similar procedure: *difluoro*[3,4-*dihydro*-9-*hydroxy*-10-*methoxy*-2-*methylanthracen*-1(2H)-*onato*-O^1,O^9]*boron* (9b) (83%), m.p. 160—161 °C; $\nu_{max.}$ (KBr) 2 940, 1 620, 1 580, 1 547, 1 483, and 780 cm^{-1}; δ(^{1}H) ($CDCl_3$; 60 MHz) 8.55 (1 H, d, *J* 0.8 Hz, 5-H), 8.25 (3 H, m), 3.88 (3 H, s, OCH_3), 3.15 (3 H, m), 2.15 (2 H, m), and 1.75 (3 H, d, *J* 6 Hz, CH_3); *m/e* 304 ($M^{\cdot+}$); $\lambda_{max.}$ (hexane) 272, 307, 318, and 436 nm (Found: C, 63.2; H, 5.1. $C_{16}H_{15}BF_2O_3$ requires C, 63.16; H, 4.93%). *Difluoro*-[3,4-*dihydro*-9-*hydroxy*-5,10-*dimethoxyanthracen*-1(2H)-*onato*-O^1,O^9]*boron* (9c) (87%), m.p. 168—170 °C (from benzene–light petroleum); $\nu_{max.}$ 2 940, 1 590, 1 560, 1 485, 1 465, 1 385, 1 275, 1 100, 1 080, 1 050, and 765 cm^{-1}; δ(^{1}H) ($CDCl_3$) 8.26 (1 H, d, *J* 8 Hz, 8-H), 7.52 (1 H, t, *J* 8 Hz, 7-H), 7.28 (1 H, d, *J* 8 Hz, 6-H), 4.00 (3 H, s, 5-MeO), 3.76 (3 H, s, 10-MeO), 3.04 (4 H, m, 2-, 4-H), and 2.16 (2 H, m, 3-H); *m/e* 320 ($M^{\cdot+}$); $\lambda_{max.}$ ($CHCl_3$) 282, 308, and 473 nm (Found: C, 60.1; H, 5.0. $C_{16}H_{15}BF_2O_4$ requires C, 60.00; H, 4.69%). *Difluoro*[3,4-*dihydro*-9-*hydroxy*-8,10-*dimethoxyanthracene*-1(2H)-*onato*-O^1,O^9]*boron* (9d) (85%), m.p. 232—234 °C (from toluene); $\nu_{max.}$ 2 930, 1 625, 1 675, 1 530, 1 475, 1 380, 1 322, 1 260, and 1 035 cm^{-1}; *m/e* 320 ($M^{\cdot+}$); δ(^{1}H) ($CDCl_3$) 7.90—7.30 (2 H, m, 6-, 7-H) 7.00 (1 H, d, *J* 8 Hz, 5-H), 4.04 (3 H, s, 8-MeO), 3.84 (3 H, s, 10-MeO), 2.96 (4 H, m, 2-, 4-H), and 2.10 (2 H, m, 3-H); $\lambda_{max.}$ ($CHCl_3$) 269, 276, 304, and 455 nm (Found: C, 60.7; H, 4.9. $C_{16}H_{15}BF_2O_4$ requires C, 60.00; H, 4.69%). *Difluoro*[3,4-*dihydro*-9-*hydroxy*-5-*methoxyanthracen*-1(2H)-*onato*-O^1,O^9]*boron* (11a) (85%), m.p. 217—220 °C (from chloroform); $\nu_{max.}$ 2 940, 1 625, 1 580, 1 540, 1 465, 1 380, 1 320, 1 260, 1 164, 1 150, 1 100, and 1 040; *m/e* 290 ($M^{\cdot+}$); δ(^{1}H) ($CDCl_3$) 7.92 (1 H, d, *J* 8 Hz, 8-H), 7.40—7.08 (2 H, m, 7-, 10-H), 6.96 (1 H, d, *J* 8 Hz, 6-H), 3.90 (3 H, s, MeO), 2.92 (4 H, m, 2-, 4-H), and 2.10 (2 H, m, 3-H); $\lambda_{max.}$ ($CHCl_3$) 277, 304, and 452 nm (Found: C, 61.95; H, 4.35. $C_{15}H_{13}BF_2O_3$ requires C, 62.07; H, 4.48%). *Difluoro*[3,4-*dihydro*-9-*hydroxy*-8-*methoxyanthracen*-1(2H)-*onato*-O^1,O^9]*boron* (11b) (82%), m.p. 237—240 °C (from benzene); $\nu_{max.}$ 2 940, 1 630, 1 577, 1 534, 1 476, 1 382, 1 323, 1 264, 1 180, 1 142, 1 110, 1 080, and 1 040 cm^{-1}; *m/e* 290 ($M^{\cdot+}$); $\lambda_{max.}$ ($CHCl_3$) 268, 274, 305, and 485 nm; δ(^{1}H) ($CDCl_3$) 7.7—7.0 (2 H, m, 6-, 7-H), 6.88 (1 H, s, 10-H), 6.84 (1 H, d, *J* 8 Hz, 5-H), 4.00 (1 H, s, MeO), 2.92 (4 H, m, 2-, 4-H), and 2.1 (2 H, m, 3-H) (Found: C, 62.7; H, 4.4. $C_{15}H_{13}BF_2O_3$ requires C, 62.07; H, 4.48%).

3,4-*Dihydro*-9-*hydroxy*-4,10-*dimethoxyanthracen*-1(2H)-*one* (2l).—This compound (2l) was prepared *via* an unstable 4-bromo derivative (9g). To a solution of difluoro[3,4-dihydro-9-hydroxy-10-methoxyanthracen-1(2*H*)-onato-O^1,O^9]boron (9a) (333 mg, 1.15 mmol) in benzene (10 ml) was added carbon tetrachloride (10 ml) and bromine (2 equiv., 1M in carbon tetrachloride) dropwise during 5 min. The solution was irradiated (150W sunlamp; 1 h) at room temperature under N_2. The solution was washed with water (10 ml), dried ($MgSO_4$), filtered and evaporated to yield the unstable 4-bromo compound (9g) as orange plates. δ(^{1}H) (60 MHz; $CDCl_3$) 8.57 (1 H, m, 5-H), 7.3—8.1 (3 H, m), 5.98 (1 H, t, *J* 2.5 Hz, CHBr), 4.16 (3 H, s, OCH_3), and 2.2—3.6 (4 H, m).

The crude product was dissolved in anhydrous methanol (10 ml) under nitrogen and maintained at −18 °C for 3 days. The mixture was evaporated under reduced pressure and partitioned between water (10 ml) and dichloromethane (10 ml). The organic phase was dried ($MgSO_4$), filtered and evaporated to yield yellow 3,4-*dihydro*-9-*hydroxy*-4,10-*dimethoxyanthracen*-1(2H)-*one* (2l) (265 mg, 85%), m.p. 92—93 °C; $\nu_{max.}$ (KBr) 3 500—2 000, 2 920, 2 815, 1 613, 1 380, 1 080, and 769 cm^{-1}; δ(^{1}H) ($CDCl_3$; 60 MHz) 14.02 (1 H, s, exch, OH), 8.48 (1 H, m, 8-H), 8.07 (1 H, m, 5-H), 7.65 (2 H, m), 5.00 (1 H, t, *J* 2.5 Hz, C*H*OMe), 3.96, 3.45 (2 × OCH_3), and 3.4—1.7 (4 H, m); *m/e* 272 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 220, 260, 270, and 381 nm (Found: C, 70.5; H, 5.95. $C_{16}H_{16}O_4$ requires C, 70.58; H, 5.88%).

3,4-*Dihydro*-9-*hydroxy*-4,10-*dimethoxy*-2-*methylanthracen*-1(2H)-*one* (2m).—An analogous bromination procedure was carried out on difluoro[3,4-dihydro-9-hydroxy-10-methoxy-2-methylanthracen-1(2*H*)-onato-O^1,O^9]boron (9b) (256 mg, 0.84 mmol) to yield an unstable orange bromide (9h), δ(^{1}H) ($CDCl_3$; 60 MHz) 8.40 (1 H, m, 5-H), 7.3—8.0 (3 H, m), 5.90 (1 H, t, *J* 3 Hz, CHBr), 4.05 (3 H, s, OCH_3), 3.55 (1 H,

sept., *J* 6.6 Hz, C*H*Me), 1.75—2.75 (2 H, m), and 1.42 (3 H, d, *J* 6.6 Hz, CH_3). This bromide (9h) was converted by methanol as above into 3,4-*dihydro*-9-*hydroxy*-4,10-*dimethoxy*-2-*methylanthracen*-1(2H)-*one* (2m) as a yellow oil (136 mg, 55%); $\nu_{max.}$ ($CHCl_3$) 2 920, 1 614, 1 497, 1 375, and 772 cm^{-1}; δ(^1H) ($CDCl_3$; 60 MHz) 14.26 (1 H, s, exch, OH), 8.42 (1 H, m, 5-H), 8.05 (1 H, m, 8-H), 7.2—7.8 (2 H, m), 4.90 (1 H, t, *J* 3 Hz, C*H*OMe), 3.88, 3.42 (2 × OCH_3), 3.5—1.5 (3 H, m), and 1.28 (3 H, d, *J* 6.7 Hz, CH_3); *m/e* 286 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 223, 267, 285, 332, 404, and 426 nm (Found: C, 71.25; H, 6.1. $C_{17}H_{18}O_4$ requires C, 71.33; H, 6.29%).

3,4-*Dihydro*-4,9-*dihydroxy*-10-*methoxyanthracen*-1(2H)-*one* (2n).—The difluoroboron compound (9g) (100 mg, 0.34 mmol) was brominated as above. The crude product was dissolved in toluene (10 ml) and placed on an alumina column (neutral, 10 g, 10% w/w water) and eluted with toluene. The solvent was evaporated under reduced pressure to yield 3,4-*dihydro*-4,9-*dihydroxy*-10-*methoxyanthracen*-1(2H)-*one* (2n) (79 mg, 89%), as a yellow oil; $\nu_{max.}$ (film) 3 450, 2 930, 1 622, 1 501, 1 378, 1 067, and 774 cm^{-1}; δ(^1H) ($CDCl_3$; 60 MHz) 8.3 (1 H, m, 8-H), 7.7 (3 H, m), 5.42 (1 H, t, *J* 4 Hz, C*H*OH), 3.94 (3 H, s, OCH_3) 2.65 (1 H, br s, exch, CHO*H*), 2.0—3.3 (4 H, m), and 14.02 (1 H, s, exch, ArOH); *m/e* 258 ($M^{\cdot+}$); $\lambda_{max.}$ (MeOH) 223, 265, 283, 330, 404, and 424 nm (Found: C, 69.85; H, 5.35. $C_{15}H_{14}O_4$ requires C, 69.77; H, 5.43%).

Reaction of 3,4-*Dihydro*-9-*hydroxy*-4,10-*dimethoxyanthracen*-1(2H)-*one* (2l) *with* 2,3-*Dichloro*-5,6-*dicyanobenzoquinone*.—The anthracenone (2l) (185 mg, 0.68 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (503 mg, 2.2 mmol) were heated under reflux in toluene (10 ml) for 6 h under N_2. The product was filtered, and the filtrate was chromatographed (silica gel, toluene as eluant) to yield 1-hydroxyanthraquinone (16 mg, 10%). Further elution with 1% diethyl ether in toluene gave 1-hydroxy-4-methoxyanthraquinone (80 mg, 46%), m.p. 167—169 °C (lit.,[11] 167—168 °C).

Oxidation of 3,4-*Dihydro*-9-*hydroxy*-4,10-*dimethoxy*-2-*methylanthracen*-1(2H)-*one* (2m).—(*a*) *With* 2,3-*dichloro*-5,6-*dicyanobenzoquinone*. The anthracenone (2l) (48 mg, 0.15 mmol), 2,3-dichloro-5,6-dicyanobenzoquinone (165 mg, 0.16 mmol, 4 equiv.), and toluene were heated under reflux for 6 h under N_2. The product was filtered and the filtrate was chromatographed (silica gel, toluene as eluant) to yield 1-hydroxy-2-methylanthraquinone (25 mg, 55%), m.p. 184—185 °C (lit.,[12] 184—185 °C).

(*b*) *With selenium dioxide*. The anthracenone (2l) (93 mg, 0.31 mmol) and selenium dioxide (380 mg) were heated in dioxan (5 ml) under reflux for 4 days (N_2 atmosphere). The product was filtered, the filtrate was evaporated to dryness, and the residue was dissolved in toluene (2 ml). Chromatographic purification (silica gel, toluene as eluant) yielded 1-hydroxy-2-methylanthraquinone (54 mg, 70%). Further elution with 10% v/v ether in toluene gave 1-hydroxy-4-methoxy-2-methylanthraquinone (16 mg, 18%), m.p. 187—189 °C (m.p. lit.,[13] 188—190 °C).

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