On the Synthesis of a Phenanthrene-2,7-quinone

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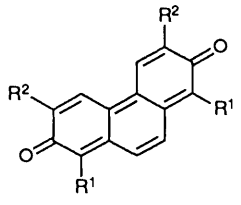
Oxidative coupling of 2,2',4,4'-tetramethoxystilbene-3,3'-diol **51** gave a 51% yield of 1,3,6,8-tetramethoxyphenanthrene-2,7-quinone **52**, the first isolated example of a quinone of this type. Similar oxidation of the corresponding diphenylethane **55** gave the 9,10-dihydrophenanthrene-2,7-quinone **56**. Attempts to synthesize the tetramethoxyphenanthrene-2,7-diol **25** from a 2,2'-bis(hydroxymethyl)hexamethoxybiphenyl precursor **28** were thwarted by the ease of intramolecular cyclization to 2,3,4,8,9,10-hexamethoxydibenz[*c*,*e*]oxepine **32**. Selective demethylation of the 3- and 9-methoxy groups of this compound, and oxidation of the resulting diol **58** gave the dibenzoxepine quinone **59**.

The synthesis of 3,6-di-*tert*-butylphenanthrene-2,7-diol **3** is also described, but this could not be oxidized to the quinone. However, the preparation of 3,6-di-*tert*-butyl-9,10-dihydrophenanthrene-2,7-quinone **12** was successful.

The four stable phenanthrenequinones, 1,2-, 1,4-, 3,4- and 9,10-, each contain two Kekulé rings. Of the other eleven isomers, three, the 1,9-, the 2,3- and the 3,9-, contain only one Kekulé ring, and the remaining eight none. Unsuccessful attempts to oxidize the diols corresponding to three of these, the 1,6-, 2,7- and 3,6-, with silver oxide have been made,[1,2] and it seems likely that in order to isolate examples of these quinones suitable blocking or electron-donating groups will have to be incorporated. In this paper we describe attempts to prepare a stabilized phenanthrene-2,7-quinone **1**.

It was claimed that 1,3,5-trimethoxyphenanthrene-2,7-quinone occurs in the plant *Tamus communis*,[3] but the structure was subsequently revised to 4,6,7-trimethoxyphenanthrene-1,2-quinone.[4] The only other reference to a phenanthrene-2,7-quinone appears to be that of Newman and Childers,[2] who obtained UV–VIS spectroscopic evidence for the formation of 1,8-dibromophenanthrene-2,7-quinone **2** when the corresponding diol was oxidized with lead tetraacetate, but the quinone could not be isolated.

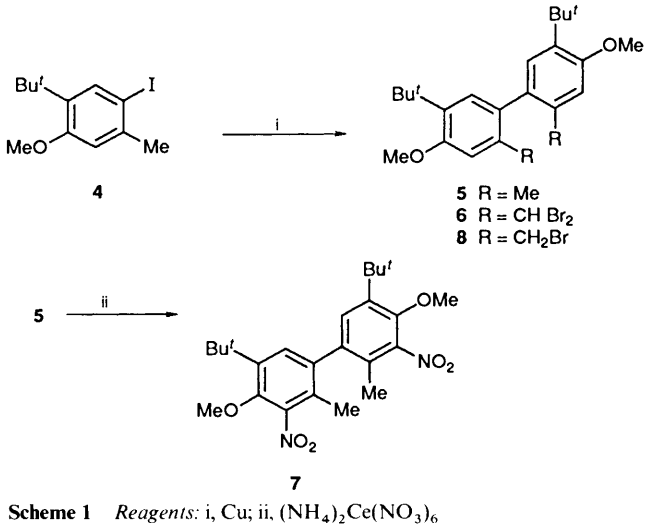


1 $R^1 = R^2 = H$
2 $R^1 = Br$, $R^2 = H$

Results and Discussion

Following our successful entry into the phenanthrene-4,5-quinone system by the use of *tert*-butyl blocking groups at the 1,3,6,8-positions,[5] we attempted to *tert*-butylate phenanthrene-2,7-diol, but without success. As synthesis of 1,3,6,8-tetra-*tert*-butylphenanthrene-2,7-diol by other routes would be difficult, 3,6-di-*tert*-butylphenanthrene-2,7-diol **3** was perceived as an acceptable compromise.

For this, a route involving cyclization of a biphenyl-2,2'-dicarbaldehyde with hydrazine, by the method of Bacon and Lindsay[6] was envisaged. Iodination of 5-methyl-2-*tert*-butylanisole gave the iodo compound **4**, which underwent Ullmann coupling to the biphenyl **5**. Photobromination of this gave the bis(dibromomethyl) compound **6**, but attempts to hydrolyse this to the dialdehyde failed (Scheme 1). Alternative oxidation of **5** with ceric ammonium nitrate[7] led only to the dinitro compound **7**, and oxidation with lead tetraacetate was also unsuccessful.

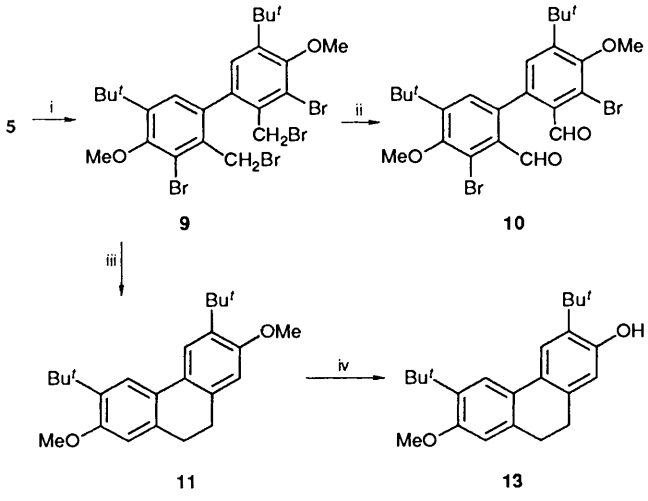


Scheme 1 *Reagents*: i, Cu; ii, $(NH_4)_2Ce(NO_3)_6$

Oxidation of benzyl halides with dimethyl sulphoxide also yields aldehydes,[8] but attempts to convert **5** into the bisbenzyl bromide **8** by photobromination gave a mixture of **5**, **6** and **8**. However, ring-bromination of **5** followed by photobromination gave a quantitative yield of the tetrabromo compound **9** (Scheme 2). Oxidation of this with dimethyl sulphoxide gave low and variable yields of the dialdehyde **10**, but further reaction with hydrazine gave mainly polymer. The alternative ring closure of **9** with magnesium gave the dihydrophenanthrene **11**, the traces of ring-brominated material being removed by hydrogenation during work-up.

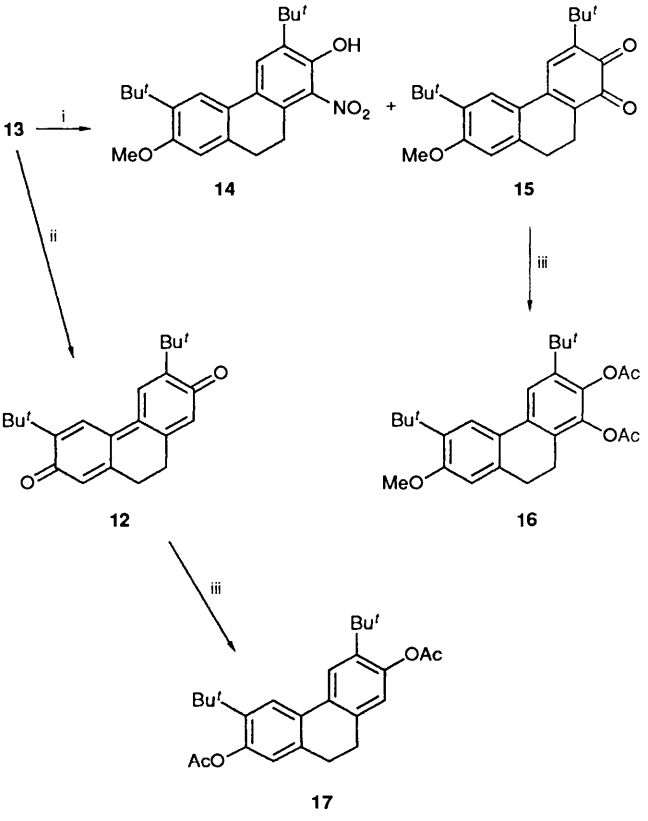
With the dihydrophenanthrene **11** in hand, it was decided to convert this into the 9,10-dihydro-2,7-quinone **12** as a preliminary. Surprisingly, **11** could not be demethylated cleanly with pyridinium chloride. Below 200 °C no reaction was

observed, and at higher temperatures demethylation was accompanied by extensive debutylation. Reaction of **11** with sodium thioethoxide, which does not effect debutylation, led to monodemethylation, giving **13**. Presumably formation of the phenoxide anion of **13** inhibits further nucleophilic attack by thioethoxide.[9] The remaining methoxy group could not be removed with boron tribromide.



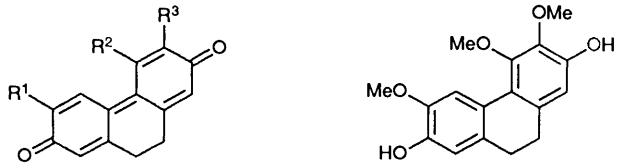
Scheme 2 *Reagents:* i, Br_2; ii, Me_2SO; iii, Mg; iv, EtSNa

Ceric ammonium nitrate has been used successfully to oxidize the dimethyl ether of a hydroquinone to a quinone.[10] When applied to the methoxyphenol **13**, two products were isolated: the nitrophenol **14** and the unstable, purple *ortho* quinone **15** (Scheme 3). Oxidation with ceric sulphate[11] was more successful, giving the reddish brown dihydrophenanthrene-2,7-quinone **12**. This quinone was also unstable. The ^1H NMR spectrum consists of four singlets, reflecting the high degree of symmetry. Reductive acetylation gave the diacetate **17**.



Scheme 3 *Reagents:* i, $(NH_4)_2Ce(NO_3)_6$; ii, $Ce(SO_4)_2$; iii, Zn, Ac_2O

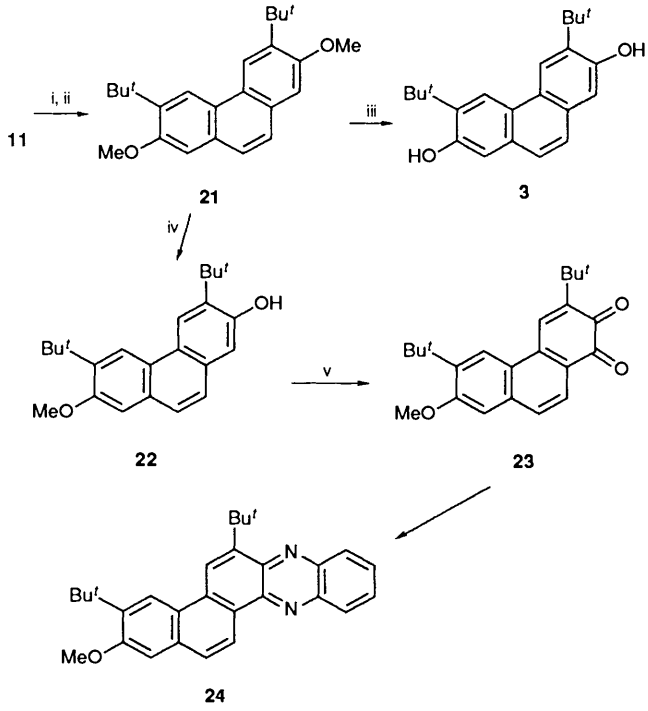
The only previous examples of 9,10-dihydrophenanthrene-2,7-quinones appear to be the 3,6-dihydroxyquinone **18** described by Horner and Weber,[12] which rearranges on heating to a phenanthrenetetrol, and the recent account by G. R. Pettit *et al.*[13] of the oxidation of a diol **19** obtained from *Combretum caffrum* to the quinone **20**.



18 $R^1 = R^3 = OH$, $R^2 = H$
20 $R^1 = R^2 = R^3 = OMe$

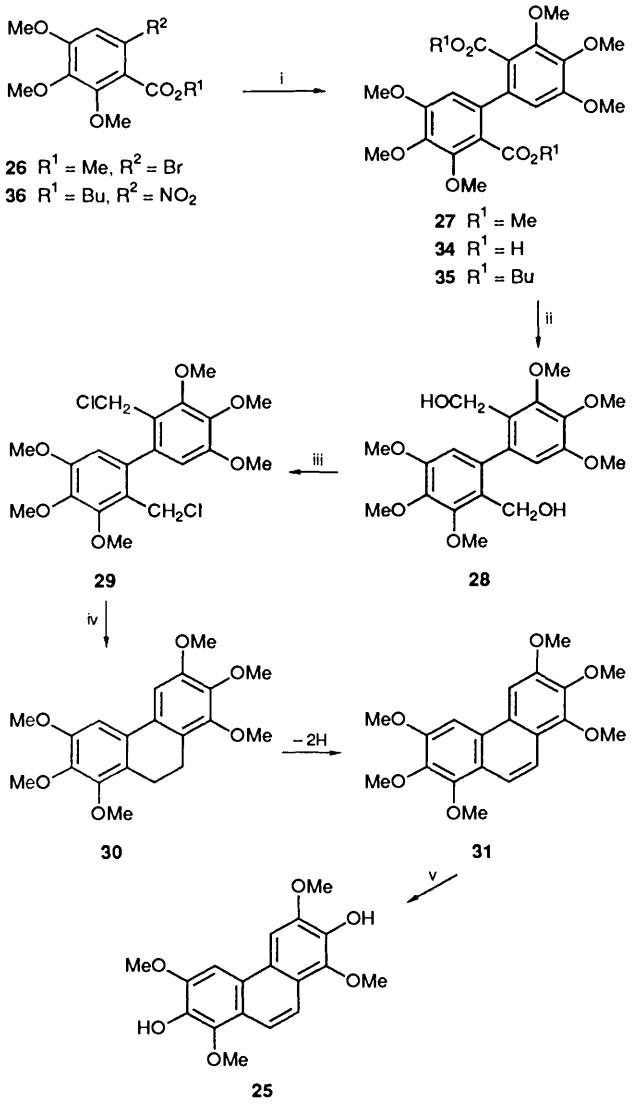
19

Access to the phenanthrene series was obtained by dehydrogenation of the dimethyl ether **11**, using the bromination–dehydrobromination procedure of Bowden *et al.*[14] Attempts to demethylate the product **21** with boron tribromide also led to debutylation, but with pyridinium chloride this was reduced to an acceptable level. However, the resulting diol **3** (Scheme 4) was unstable, and attempts to oxidize it gave only tar. Success with the oxidative demethylation of the dihydro compound **13** suggested a similar approach. Accordingly the dimethyl ether **21** was partially demethylated to **22** with sodium thioethoxide, but oxidation of this with ceric sulphate gave only the red phenanthrene-1,2-quinone **23**. Sodium periodate oxidation[15] led to the same result. By contrast with the dihydrophenanthrene-1,2-quinone **15**, the phenanthrene-1,2-quinone **23** was quite stable. Its structure was confirmed spectroscopically, and by formation of the phenazine **24**. The reaction of *o*-phenylenediamine with **23** was extremely slow, requiring 14 weeks before all the latter was consumed: no doubt a result of steric hindrance. All attempts to oxidize **22** with other reagents were unsuccessful. Sodium bismuthate[11] or ceric sulphate, made soluble in benzene with dibenzo-18-crown-6 ether,[16] gave only polymeric material.



Scheme 4 *Reagents:* i, NBS; ii, AcOK; iii, pyridine, HCl; iv, EtSNa; v, $Ce(SO_4)_2$

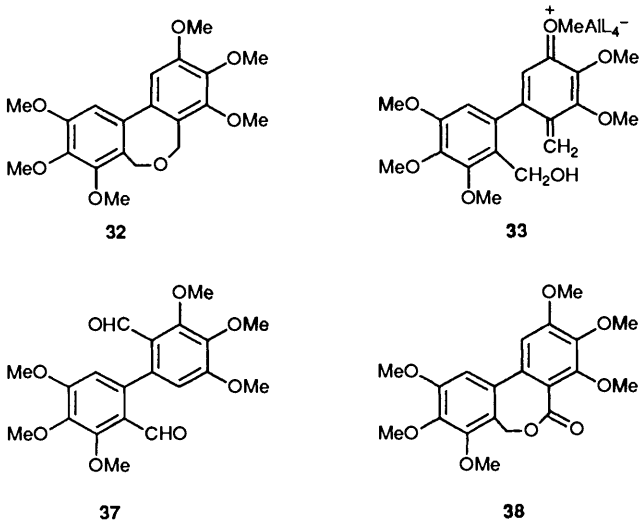
The formation of an *ortho* quinone on oxidation of **22** and a polymer on oxidation of **3** reinforced the need for blocking groups at positions 1, 3, 6 and 8, as well as for free hydroxy groups at positions 2 and 7, as a prerequisite for formation of a phenanthrene-2,7-quinone. As the tetra-*tert*-butyl diol appeared to be out of reach, 1,3,6,8-tetramethoxyphenanthrene-2,7-diol **25** seemed the next best alternative. A logical route to **25** might proceed from the known methyl 6-bromo-2,3,4-trimethoxybenzoate **26**[17] as shown in Scheme 5.



Scheme 5 *Reagents:* i, Cu; ii, $LiAlH_4$; iii, $SOCl_2$; iv, Mg; v, MeMgI

Although Ullmann coupling of **26** gave a satisfactory yield of the dimethyl ester **27**, the latter was very difficult to dissolve in ether, so that for lithium aluminium hydride reduction the ester was placed in the thimble of a Soxhlet extractor. Even using this method, some of the ester remained undissolved after several days. The product, however, was the required diol **28**. Using tetrahydrofuran, in which the ester **27** was much more soluble, a mixture of the reduction products was obtained, consisting of the diol **28** and the dibenzoxepine **32**. The structure of the latter was evident from its NMR and IR spectra. At the higher temperature of boiling tetrahydrofuran, an intermediate such as **33**, stabilized by both *ortho* and *para* methoxy groups, may have been formed, and reacted intramolecularly to give the oxepine.

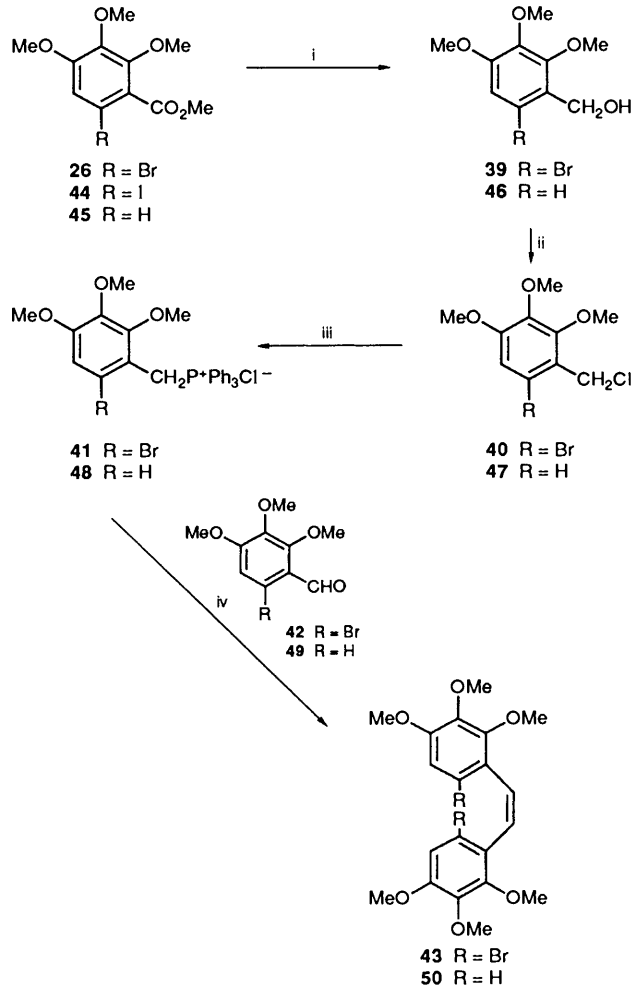
To circumvent this difficulty the dimethyl ester **27** was hydrolysed to the diphenic acid **34**, and converted into the much more soluble dibutyl ester **35**. Alternative routes to the dibutyl ester involved elaboration of the butyl nitrobenzoate **36**, and are described in the Experimental section. Reduction of the dibutyl ester **35** with lithium aluminium hydride, if stopped after 10 min, gave the diol **28** in 90% yield, but longer reaction times led principally to the oxepine **32**. Unfortunately, subsequent reaction of the diol **28** with thionyl chloride gave a very low yield of the dichloride **29**, the major product again being the oxepine **32**.



Attempts to form the dialdehyde **37** for subsequent conversion into the phenanthrene with hydrazine also failed. Thus, oxidation of the diol **28** with activated manganese dioxide, barium manganate,[18] or dinitrogen tetroxide[19] all gave the lactone **38** as the major product.

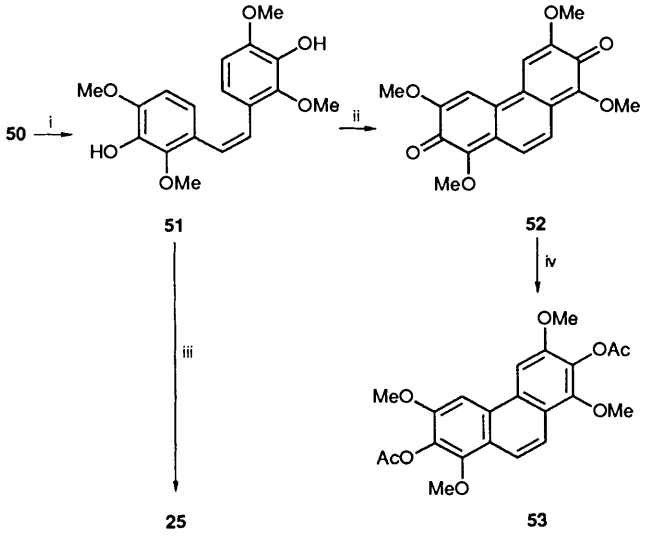
Because of the marked tendency of the 2,2′-disubstituted hexamethoxybiphenyls to react intramolecularly the biphenyl route to the phenanthrene was abandoned in favour of coupling the aryl rings of a suitably substituted stilbene. Moreover, it has been shown[20] that the Wittig reaction between a benzaldehyde and a benzylphosphonium halide gives mainly the required (*Z*)-stilbene if the reaction is promoted by lithium methoxide in *N*,*N*-dimethylformamide. Accordingly, the phosphonium chloride **41** was prepared from the bromo ester **26** *via* the alcohol **39** and the chloride **40**, and was treated in this way with the bromo aldehyde **42**, obtained by oxidation of **39** with barium manganate, to give the dibromostilbene **43** (Scheme 6). But this could not be coupled to the phenanthrene **31** either with copper or with tetrakis(triphenylphosphine)nickel(0).[21] The presumably more reactive diiodo analogue of **43** could not be prepared in this way, because lithium aluminium hydride reduction of the iodo ester **44** also reduced the iodo group.

The alternative method of proceeding to the phenanthrene system was to demethylate preferentially the 3 and 3′ positions of the stilbene **50** and to couple oxidatively the resulting diol. Using the method of Hurd and Winberg,[22] the major product from the reaction of methylmagnesium iodide with **50** was the diol **51**. Oxidation of this with freshly prepared silver oxide gave the desired quinone **52** in 51% yield (Scheme 7). This quinone was reddish purple and of moderate stability. Its structure was confirmed by its ^1H NMR spectrum which showed two singlets, each for six methoxy protons, and two singlets for the four ring protons. Reductive acetylation gave the diacetate **53**, the UV spectrum of which was clearly that of a phenanthrene. Other modes of phenolic oxidative coupling, although possible, would not lead to products which satisfy these spectroscopic data. Oxidation of the diol **51** with alkaline potassium ferricyanide gave a 30% yield of the quinone **52**, but in this case an ink-blue, water soluble by-product was formed, which showed indicator



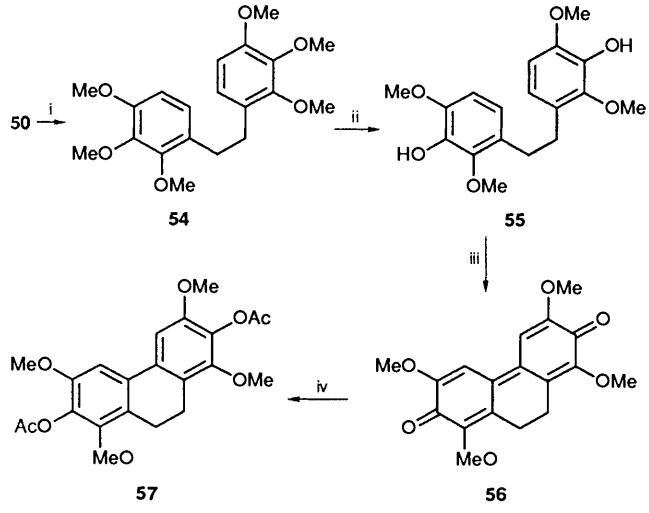
Scheme 6 *Reagents:* i, $LiAlH_4$; ii, $SOCl_2$; iii, PPh_3; iv, LiOMe

properties, reversibly changing to pale yellow on addition of acid. This was not identified. Oxidation of the diol **51** with (diacetoxyiodo)benzene[23] gave a low yield of the phenanthrenediol **25**.



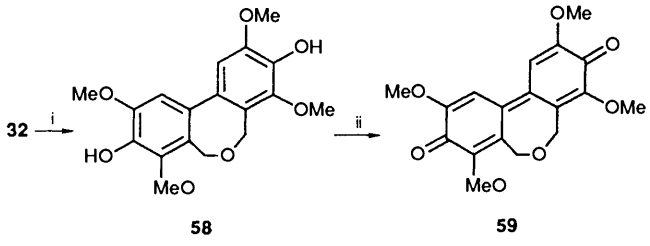
Scheme 7 *Reagents:* i, MeMgI; ii, Ag_2O; iii, $PhI(OAc)_2$; iv, Zn, Ac_2O

Reaction of the hexamethoxydiphenylethane **54**, obtained on hydrogenation of the stilbene **50**, with methylmagnesium iodide gave the diol **55**. Oxidation of this with alkaline ferricyanide gave polymeric material, and oxidation with ruthenium dioxide[24] was also unsuccessful, as was anodic oxidation.[25] However, oxidation of **55** with silver oxide gave the 9,10-dihydrophenanthrene-2,7-quinone **56** in 78% yield (Scheme 8). The spectroscopic data for this red quinone were in agreement with structure **56**. This quinone was again of moderate stability. On reductive acetylation it gave the diacetate **57**.



Scheme 8 *Reagents:* i, H_2, Pd/C; ii, MeMgI; iii, Ag_2O; iv, Zn, Ac_2O

For comparison, the oxepine **32** was also selectively demethylated with methylmagnesium iodide, giving the diol **58**. On oxidation with alkaline ferricyanide or silver oxide, this also gave a red quinone **59** (Scheme 9), but this quinone was less



Scheme 9 *Reagents:* i, MeMgI; ii, Ag_2O

stable than either **52** or **56**, presumably because the 7-membered ring prevents coplanarity of the two quinonoid rings. This is reflected in the unusually high carbonyl absorption at 1720 cm^{-1}.

In conclusion, it appears that methoxy groups may be used as effectively as *tert*-butyl groups to increase the stability of non-aromatic polycyclic quinones. In fact methoxy groups may be a source of even greater stability when, as in the present case, they are in conjugation with the carbonyl groups, and the quinone may thus be considered to be a vinylogous ester.

Experimental

NMR spectra are for deuteriochloroform solutions unless otherwise stated. Chemical shifts are quoted on the δ scale relative to internal tetramethylsilane and J-values are given in Hz. Microanalyses are by M.H.W., Arizona. M.p.s, taken with a Kofler hot stage, are uncorrected. Light petroleum had b.p. 65–70 °C. Extracts were dried with magnesium sulphate.

2-Iodo-5-methoxy-4-tert-butyltoluene **4**.—Iodine (32 g) was added in portions to a stirred solution of 3-methoxy-4-*tert*-butyltoluene (20.5 g) in dichloromethane (200 cm^3) in the presence of silver trifluoroacetate (28 g) during 20 min. After

being stirred for a further 10 min, the mixture was filtered, and the residue was washed with dichloromethane. The combined filtrates were washed with aqueous sodium hydrogen sulphite and water, and dried. The residue obtained on evaporation was recrystallized from methanol (charcoal) giving the *iodo compound* **4** (22.3 g, 64%), m.p. 101–102 °C (Found: C, 47.7; H, 5.6; I, 41.25. $C_{12}H_{17}IO$ requires C, 47.4; H, 5.6; I, 41.7%); δ_H 1.32 (9 H, s, Bu^t), 2.36 (3 H, s, $ArCH_3$), 3.77 (3 H, s, OMe), 6.72 (1 H, s, ArH) and 7.60 (1 H, s, ArH); *m/z* 304 (M^+).

4,4′-*Dimethoxy*-2,2′-*dimethyl*-5,5′-*di*-tert-*butylbiphenyl* **5**.—An intimate mixture of the iodide **4** (14.6 g) and copper bronze (20 g) was heated in a sealed ampoule at 240–250 °C for 4 h. The cooled solid was triturated with hot chloroform, and filtered through Celite. Evaporation gave a residue which was chromatographed on silica. Elution with light petroleum–dichloromethane (9:1) and crystallization from light petroleum gave the *biphenyl* **5** (6.65 g, 78%), m.p. 185–187 °C (Found: C, 81.4; H, 9.6. $C_{24}H_{34}O_2$ requires C, 81.3; H, 9.7%); δ_H 1.37 (18 H, s, Bu^t), 2.05 (6 H, s, $ArCH_3$), 3.84 (6 H, s, OMe), 6.75 (2 H, s, ArH) and 7.03 (2 H, s, ArH); λ_{max}(hexane)/nm (log ε) 284 (3.75), 275 (3.77), 227sh (4.22) and 204 (4.86); *m/z* 354 (M^+).

2,2′-*Bis*(*dibromomethyl*)-4,4′-*dimethoxy*-5,5′-*di*-tert-*butylbiphenyl* **6**.—A solution of bromine (0.2 g) in carbon tetrachloride (1 cm^3) was added dropwise during 15 min to a stirred solution of the biphenyl **5** (100 mg) in carbon tetrachloride (10 cm^3) under reflux, and illuminated with a tungsten lamp. After 1 h, the solution was cooled, washed with aqueous sodium bisulphite and water, and dried. Evaporation, and recrystallization from dichloromethane–light petroleum gave the *bisbenzalbromide* **6** (127 mg, 67%), m.p. 276–278 °C (Found: C, 42.9; H, 4.25; Br, 47.9. $C_{24}H_{30}Br_4O_2$ requires C, 43.0; H, 4.5; Br, 47.7%); δ_H 1.39 (18 H, s, Bu^t), 3.98 (6 H, s, OMe), 6.30 (2 H, s, $-CHBr_2$), 6.99 (2 H, s, 6-H) and 7.49 (2 H, s, 3-H) assigned by NOE; $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 305 (3.75) and 230 (4.57); *m/z* 674, 672, 670, 668 and 666 (M^+).

Attempted Oxidation of 4,4′-*Dimethoxy*-2,2′-*dimethyl*-5,5′-*di*-tert-*butylbiphenyl* **5**.—A solution of ammonium hexanitratocerate(IV) (1.25 g) in water (1 cm^3) and acetic acid (5.5 cm^3) was added during 5 h to a stirred suspension of the biphenyl **5** (100 mg) in 90% acetic acid (2 cm^3) at 80 °C. The mixture was heated under reflux overnight and then diluted with water, and extracted with ether. The ether extract was washed with aqueous sodium hydrogen carbonate and water, and evaporated to leave a residue which was purified by preparative TLC in dichloromethane. This gave 4,4′-*dimethoxy*-2,2′-*dimethyl*-3,3′-*dinitro*-5,5′-*di*-tert-*butylbiphenyl* **7** as tan crystals from methanol (24 mg, 19%), m.p. 189–190 °C (Found: C, 65.0; H, 7.4; N, 6.0. $C_{24}H_{32}N_2O_6$ requires C, 64.85; H, 7.3; N, 6.3%); δ_H 1.39 (18 H, s, Bu^t), 1.95 (6 H, s, $ArCH_3$), 3.88 (6 H, s, OMe) and 7.14 (2 H, s, ArH); *m/z* 444 (M^+).

2,2′-*Bis*(*bromomethyl*)-3,3′-*dibromo*-4,4′-*dimethoxy*-5,5′-*di*-tert-*butylbiphenyl* **9**.—A solution of bromine (16.3 g) in carbon tetrachloride (90 cm^3) was added during 4 h to a cooled, stirred solution of the biphenyl **5** (17.2 g) in carbon tetrachloride (450 cm^3). After 28 h, the solution was heated to reflux under illumination from a tungsten lamp while a solution of bromine (15 g) in carbon tetrachloride (90 cm^3) was added during 4 h. Heating and illumination were continued overnight. The cooled solution was washed with aqueous sodium bisulphite and water and dried. Concentration to about a third of its volume and dilution with light petroleum, followed by recrystallization from dichloromethane–light petroleum gave the *tetrabromide* **9** (32.2 g, 99%), m.p. 207–209 °C (Found: C, 43.25; H, 4.5; Br, 48.1. $C_{24}H_{30}Br_4O_2$ requires C, 43.0; H, 4.5; Br, 47.7%); δ_H 1.42 (18 H, s, Bu^t), 4.0 (6 H, s, OMe), 4.10–4.56 (4 H, AA′BB′m, $ArCH_2Br$) and 7.25 (2 H, s, ArH); $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 294 (3.49) and 233 (4.56); *m/z* 674, 672, 670, 668 and 666 (M^+).

2,7-*Dimethoxy*-3,6-*di*-tert-*butyl*-9,10-*dihydrophenanthrene* **11**.—A little of a solution of the tetrabromide **9** (6.7 g) in dry tetrahydrofuran (200 cm^3) containing 1,2-dibromoethane (6.6 g) was run into a flask containing magnesium turnings (1.85 g) under nitrogen. The mixture was heated with stirring until reaction set in. The remainder was added dropwise over 1.5 h with gentle heating to maintain reflux. After being heated and stirred for a further 2 h, the mixture was cooled and acidified with dilute sulphuric acid. After addition of water (300 cm^3), the mixture was extracted with ether, and the combined extracts were washed with water, dried, and concentrated to a yellow foam (5.5 g). This was dissolved as far as possible in ethanol (100 cm^3) and hydrogenated overnight over palladium–charcoal. The catalyst was filtered off through Celite and the filtrate was evaporated leaving a yellow residue (3.5 g). Rapid chromatography on silica and elution with light petroleum gave the *dihydrophenanthrene* **11** (1.86 g, 53%) as a colourless oil which crystallized on standing, m.p. 135–138 °C from ethanol (Found: C, 81.7; H, 9.1. $C_{24}H_{32}O_2$ requires C, 81.8; H, 9.15%); δ_H 1.43 (18 H, s, Bu^t), 2.78 (4 H, s, $ArCH_2CH_2Ar$), 3.81 (6 H, s, OMe), 6.69 (2 H, s, ArH) and 7.63 (2 H, s, ArH); λ_{max}(EtOH)/nm (log ε) 314sh (3.96), 287 (4.44), 277sh (4.23), 219 (4.34), 212sh (4.41) and 210 (4.44); *m/z* 352 (M^+).

2-*Hydroxy*-7-*methoxy*-3,6-*di*-tert-*butyl*-9,10-*dihydrophenanthrene* **13**.—A solution of ethanethiol (50 mg) in dry dimethylformamide (2 cm^3) was added to sodium hydride (60 mg; 80% dispersion) in the same solvent (1 cm^3) under nitrogen with stirring. After 5 min, a similar solution of the diether **11** (100 mg) was added. The mixture was stirred under reflux for 3 h, cooled, diluted with dilute hydrochloric acid, then poured into water and extracted with ether. Evaporation of the washed and dried extract, and preparative TLC gave the *monomethyl ether* **13** (48 mg, 50%), m.p. 139–142 °C, from aqueous methanol (Found: C, 81.3; H, 8.8. $C_{23}H_{30}O_2$ requires C, 81.6; H, 8.9%); δ_H 1.43 (9 H, s, Bu^t), 1.47 (9 H, s, Bu^t), 2.77 (4 H, s, $ArCH_2CH_2Ar$), 3.86 (3 H, s, OMe), 4.68 (1 H, s, OH), 6.52 (1 H, s, ArH), 6.72 (1 H, s, ArH) and 7.60 (2 H, s, ArH); $\nu_{max}(CCl_4)$/cm^{-1} 3600; λ_{max}(MeOH)/nm (log ε) 320sh (3.30), 287 (3.86), 262sh (3.59) and 208 (4.25); *m/z* 338 (M^+). On a larger scale a 72% yield was obtained.

Oxidation of the Monomethyl Ether **13**.—(*a*) *With ammonium hexanitratocerate*(IV). Oxidation of **13** using the conditions described by Laatsch[10] gave, after preparative TLC (dichloromethane–light petroleum), two major components. The first was 2-*hydroxy*-7-*methoxy*-1-*nitro*-3,6-*di*-tert-*butyl*-9,10-*dihydrophenanthrene* **14** (17%), m.p. 187–189 °C, from hexane (Found: C, 72.0; H, 7.7; N, 3.8. $C_{23}H_{29}NO_4$ requires C, 72.0; H, 7.6; N, 3.65%); δ_H 1.42 (9 H, s, Bu^t), 1.49 (9 H, s, Bu^t), 2.60–3.20 (4 H, AA′BB′m, $ArCH_2CH_2Ar$), 3.88 (3 H, s, OMe), 6.75 (1 H, s, 8-H), 7.54 (1 H, s, ArH), 7.86 (1 H, s, ArH) and 10.0 (1 H, s, OH); ν_{max}/cm^{-1} 3250br (OH); λ_{max}(MeOH)/nm (log ε) 285 (4.30) and 208 (4.62); *m/z* 383 (M^+). The more polar fraction consisted of the purple, unstable 7-*methoxy*-3,6-*di*-tert-*butyl*-9,10-*dihydrophenanthrene*-1,2-*quinone* **15** (16%), isolated as a gum; δ_H 1.33 (9 H, s, Bu^t), 1.42 (9 H, s, Bu^t), 2.50–3.00 (4 H, AA′BB′m, $ArCH_2CH_2$), 3.93 (3 H, s, OMe), 6.79 (1 H, s, 8-H), 7.44 (1 H, s, 4-H) and 7.56 (1 H, s, 6-H); $\nu_{max}(CCl_4)$/cm^{-1} 1630 (C=O) and 1610 (C=C); λ_{max}(MeOH)/nm (log ε) 528 (3.56), 375 (3.85), 284 (4.18) and 208 (4.53); *m/z* 356 (10%, M + 4), 355 (26, M + 3), 354 (100, M + 2), 353 (8, M + 1), 352 (6, M^+), 340

(17), 339 (40), 325 (12), 324 (40), 323 (21), 322 (59), 312 (11), 310 (44), 309 (21), 308 (12), 307 (45), 272 (36), 271 (46) and 57 (66).

(*b*) *With ceric sulphate.* Oxidation of **13** using the conditions described by Hewgill *et al.*[26] gave the unstable red–brown 3,6-*di*-tert-*butyl*-9,10-*dihydrophenanthrene*-2,7-*quinone* **12** (27%) after preparative TLC (dichloromethane), m.p. 112–114 °C from benzene–light petroleum; δ_H 1.37 (18 H, s, Bu^t), 2.77 (4 H, s, $-CH_2CH_2-$), 6.29 (2 H, s), and 7.72 (2 H, s); $\nu_{max}(CCl_4)/cm^{-1}$ 1620 (C=O) and 1600 (C=C); λ_{max}(MeOH)/nm (log ε) 408 (4.62), 323 (3.45), 283 (3.76) and 205 (4.38); *m/z* 326 (3%, M + 4), 325 (24, M + 3), 324 (100, M + 2), 323 (24, M + 1), 322 (87, M$^+$), 310 (12), 309 (53), 308 (18), 307 (70), 305 (32), 293 (17), 281 (20), 280 (45), 279 (32), 266 (29), 265 (88), 253 (20), 252 (68), 251 (24), 238 (45), 167 (24), 149 (53) and 57 (29).

1,2-*Diacetoxy*-7-*methoxy*-3,6-*di*-tert-*butyl*-9,10-*dihydrophenanthrene* **16**.—The 1,2-quinone **15** (29 mg), zinc dust (50 mg), sodium acetate (50 mg) and acetic anhydride (5 cm^3) were heated under reflux for 10 min. The supernatant liquid was decanted, and the residue washed with hot acetic acid. The combined extracts were diluted with water and extracted with ether. Evaporation of the ether from the washed (aq. $NaHCO_3$) and dried extract gave a gum which was purified by preparative TLC (dichloromethane). Crystallization from methanol gave the *diacetate* **16**, m.p. 193–195 °C (Found: C, 74.2; H, 7.7. $C_{27}H_{34}O_5$ requires C, 73.9; H, 7.8%); δ_H 1.39 (9 H, s, Bu^t), 1.42 (9 H, s, Bu^t), 2.30 (3 H, s, OAc), 2.33 (3, s, OAc), 2.55–2.90 (4 H, AA′BB′m, $ArCH_2CH_2Ar$), 3.86 (3 H, s, OMe), 6.72 (1 H, s, 8-H) and 7.62 (2 H, s, 4-H and 5-H); $\nu_{max}(CCl_4)/cm^{-1}$ 1770 (C=O); λ_{max}(MeOH)/nm (log ε) 285 (4.46) and 215 (4.76).

2,7-*Diacetoxy*-3,6-*di*-tert-*butyl*-9,10-*dihydrophenanthrene* **17**.—Reductive acetylation of the 2,7-quinone **12** as above gave the *diacetate* **17** (62%) (Found: *m/z*, 408.228. $C_{26}H_{32}O_4$ requires 408.230); δ_H 1.40 (18 H, s, Bu^t), 2.34 (6 H, s, OAc), 2.80 (4 H, s, $ArCH_2CH_2Ar$), 6.87 (2 H, s, ArH) and 7.71 (2 H, s, ArH); $\nu_{max}(CCl_4)/cm^{-1}$ 1755 (C=O); λ_{max}(MeOH)/nm (log ε) 304 (3.84), 271 (4.18) and 211 (4.54); *m/z* 408 (13%), 366 (33), 325 (26), 324 (100), 309 (27) and 57 (17).

2,7-*Dimethoxy*-3,6-*di*-tert-*butylphenanthrene* **21**.—A solution of the dihydrophenanthrene **11** (536 mg), *N*-bromosuccinimide (292 mg), and benzoyl peroxide (37 mg) in carbon tetrachloride (50 cm^3) was stirred under reflux for 30 min, then potassium acetate (5 g) and acetic acid (5 cm^3) were added. The mixture was stirred under reflux for a further 30 min, then cooled and poured into water. The organic layer was separated, washed with sodium hydrogen carbonate, then water, and dried and evaporated. Rapid chromatography of the residue on silica (dichloromethane–light petroleum), and recrystallization from light petroleum gave the *phenanthrene* **21** (474 mg, 89%), m.p. 207–210 °C (Found: C, 82.3; H, 8.8. $C_{24}H_{30}O_2$ requires C, 82.2; H, 8.6%); δ_H 1.55 (18 H, s, Bu^t), 3.91 (6 H, s, OMe), 7.15 (2 H, s, ArH), 7.54 (2 H, s, ArH) and 8.52 (2 H, s, ArH); λ_{max}(hexane)/nm (log ε) 359 (3.55), 341 (3.47), 325 (3.27), 295 (4.33), 283 (4.38), 257 (4.96), 250sh (4.73), 229 (4.35) and 213 (4.44); *m/z* 350 (M$^+$).

3,6-*Di*-tert-*butylphenanthrene*-2,7-*diol* **3**.—A mixture of the dimethyl ether **21** (158 mg) and pyridinium chloride (1 g) was heated under reflux for 45 min. After being cooled the mixture was taken up in ether and water. The organic layer was washed with dilute sulphuric acid and water, and dried. The residue after evaporation was purified by rapid chromatography on silica (dichloromethane–light petroleum) and crystallization from benzene–light petroleum giving the *diol* **3** (113 mg, 78%), m.p. 190–200 °C, as rather unstable material; δ_H 1.58 (18 H, s, Bu^t), 5.08 (2 H, s, OH), 7.04 (2 H, s, ArH), 7.46 (2 H, s, ArH) and 8.50 (2 H, s, ArH); *m/z* 323 (24%, M + 1), 322 (100, M$^+$), 308 (22), 307 (97), 266 (12), 251 (20), 118 (12) and 57 (16).

2-*Hydroxy*-7-*methoxy*-3,6-*di*-tert-*butylphenanthrene* **22**.—Reaction of the dimethyl ether **21** with sodium thioethoxide as for **11** gave the *monomethyl ether* **22** (59%), m.p. 200 °C from light petroleum (Found: C, 82.2; H, 8.5. $C_{23}H_{28}O_2$ requires C, 82.1; H, 8.4%); δ_H 1.54 (9 H, s, Bu^t), 1.58 (9 H, s, Bu^t), 3.98 (3 H, s, OMe), 5.02 (1 H, s, OH), 7.05 (1 H, s, ArH), 7.19 (1 H, s, ArH), 7.48, 7.56 (2 H, AB, *J* 9.0, ArH) and 8.50 (2 H, br s, ArH); $\nu_{max}(CCl_4)/cm^{-1}$ 3600; λ_{max}(MeOH)/nm (log ε) 362 (3.29), 345 (3.12), 328 (2.82), 297 (4.30), 284 (4.33), 258 (4.92), 228 (4.32) and 213 (4.53).

7-*Methoxy*-3,6-*di*-tert-*butylphenanthrene*-1,2-*quinone* **23**.—Oxidation of the phenanthrol **22** with ceric sulphate as for **13** gave the 1,2-*quinone* **23** (26%) as red needles, m.p. 234–235 °C from benzene–light petroleum (Found: C, 78.8; H, 7.6. $C_{23}H_{26}O_3$ requires C, 78.8; H, 7.5%); δ_H 1.41 (9 H, s, Bu^t), 1.52 (9 H, s, Bu^t), 4.02 (3 H, s, OMe), 7.13 (1 H, s, 8-H), 7.68, 8.01 (2 H, AB, *J* 8.8, 9-H and 10-H), 8.10 (1 H, s) and 8.13 (1 H, s); $\nu_{max}(CCl_4)/cm^{-1}$ 1660 (C=O) and 1615 (C=C); λ_{max}(MeOH)/nm (log ε) 408 (3.72), 308 (4.13), 249 (4.37) and 217 (4.25); *m/z* 352 (8%, M + 2), 350 (3, M$^+$), 323 (22), 322 (100), 308 (15), 307 (63), 294 (11), 279 (13) and 57 (15).

4-*Methoxy*-5,8-*di*-tert-*butylnaphtho*[2,1-a]*phenazine* **24**.—A solution of the quinone **23** (19 mg) and freshly sublimed *o*-phenylenediamine (8 mg) in chloroform (2 cm^3) was set aside over anhydrous sodium sulphate (50 mg) for 14 weeks. The solution was filtered and concentrated. Preparative TLC (dichloromethane) gave the yellow *phenazine* **24** (11 mg, 48%), m.p. 233–234 °C from benzene (Found: *m/z* 422.236. $C_{29}H_{30}N_2O$ requires 422.236); δ_H 1.60 (9 H, s, Bu^t), 1.90 (9 H, s, Bu^t), 4.06 (3 H, s, OMe), 7.36 (1 H, s, 3-H), 7.77–7.95 (2 H, m, ArH), 7.98 (1 H, B of ABq, *J* 9.2, 2-H), 8.25–8.42 (2 H, m, ArH), 8.68 (1 H, s, ArH), 8.89 (1 H, s, ArH) and 9.38 (1 H, A of ABq, *J* 9.2, 1-H); λ_{max}(hexane)/nm (log ε) 408 (4.36), 391 (4.36), 309 (4.84), 296 (4.68), 272 (5.04), 251 (4.64) and 220 (4.51).

Methyl 6-*Iodo*-2,3,4-*trimethoxybenzoate* **44**.—Sodium nitrite (5.73 g) in water (13 cm^3) was added dropwise with stirring to an ice-cold solution of methyl 6-amino-2,3,4-trimethoxybenzoate[27] (20 g) in hydrochloric acid (40 cm^3 of 17%). This solution was added to an aqueous solution of potassium iodide (14 g), and heated on the steam bath until evolution of nitrogen had ceased. The cooled mixture was extracted with ether, and the extract was washed with aqueous sodium hydrogen sulphite and water, and dried. The residue obtained on evaporation was purified by rapid chromatography on silica (ethyl acetate–light petroleum) and recrystallized from dichloromethane–light petroleum to give the *iodo compound* **44** (22.8 g, 78%), m.p. 90–91.5 °C (Found: C, 37.5; H, 3.7; I, 36.1. $C_{11}H_{13}O_5I$ requires C, 37.5; H, 3.7; I, 36.0%); δ_H 3.81–3.88 (12 H, OMe) and 7.01 (1 H, s, ArH); *m/z* 352 (M$^+$).

Dimethyl 3,3′,4,4′,5,5′-*Hexamethoxybiphenyl*-2,2′-*dicarboxylate* **27**.—Methyl 6-iodo-2,3,4-trimethoxybenzoate **44** (5.0 g) was mixed with copper bronze (8 g) and heated at 240 °C for 45 min. The cooled mixture was extracted with dichloromethane. Evaporation of the extract and recrystallization of the residue from ethanol gave the *biphenyl* **27** (2.9 g, 45%), m.p. 153–153.5 °C (Found: C, 58.9; H, 6.1. $C_{22}H_{26}O_{10}$ requires C, 58.65; H, 5.8%); δ_H 3.59 (6 H, s, OMe), 3.79 (6 H, s, OMe), 3.85 (6 H, s, OMe), 3.90 (6 H, s, OMe) and 6.52 (2 H, s, ArH); *m/z* 450 (M$^+$). A higher yield (63%) was obtained on subjecting the bromo ester **26**[17] to exactly the same conditions.

Reduction of Dimethyl 3,3′,4,4′,5,5′-Hexamethoxybiphenyl-2,2′-dicarboxylate **27** *with Lithium Aluminium Hydride.*—(*a*) The dimethyl ester **27** (2.0 g) was dissolved in ether with great difficulty. This solution was added dropwise with stirring to a suspension of lithium aluminium hydride (0.3 g) in ether (75 cm^3) and the mixture was then heated under reflux for 2 h. After being cooled, water, and dilute sulphuric acid were added, the ether layer was separated, and the aqueous layer was further extracted with ether. The extracts were combined, dried and evaporated. The residue was recrystallized from chloroform–light petroleum giving the *diol* **28** as needles (1.63 g, 93%), m.p. 114–114.5 C (Found: C, 60.6; H, 6.6. $C_{20}H_{26}O_6$ requires C, 60.9; H, 6.7%); δ_H 3.84 (6 H, s, OMe), 3.92 (6 H, s, OMe), 4.02 (6 H, s, OMe), 4.57 (4 H, AB, *J* 11.6, $ArCH_2$), 3.59–2.79 (2 H, br s, OH) and 6.48 (2 H, s, ArH); $\nu_{max}(CCl_4)/cm^{-1}$ 3599 (OH) and 3460–3300 (bonded OH); *m/z* 394 (M^+).

(*b*) The ester **27** (2.0 g) was placed in the thimble of a Sohxlet extractor mounted above a flask containing lithium aluminium hydride (0.5 g) and dry ether (100 cm^3). After being heated under reflux for 2 d, the diol **28** (0.83 g) was obtained, but 0.72 g of the ester still remained undissolved in the thimble.

(*c*) The ester **27** (3.0 g) was treated with lithium aluminium hydride (0.75 g) as in (*a*), but in dry tetrahydrofuran (150 cm^3) and heated under reflux for 4 h. The crude product was chromatographed on silica (ethyl acetate–light petroleum) giving the diol **28** (0.72 g), and 2,3,4,8,9,10-*hexamethoxydibenz*[c,e]*oxepine* **32** (1.7 g), m.p. 138–139.5 °C (Found: C, 64.0; H, 6.3. $C_{20}H_{24}O_7$ requires C, 63.8; H, 6.4%); δ_H 3.83 (18 H, s, OMe), 4.23 (4 H, s, OCH_2) and 6.68 (2 H, s, ArH); *m/z* 376 (M^+).

6-*Bromo*-2,3,4-*trimethoxybenzoic Acid.*—The methyl ester **26** (6.0 g) was heated under reflux in aqueous sodium hydroxide (100 cm^3; 10%) for 13 h. After being cooled, the mixture was acidified and extracted with ethyl acetate. The dried extract was evaporated, and the residue was recrystallized from dichloromethane–light petroleum giving the *acid* (5.51 g), m.p. 113–114.5 °C (Found: C, 41.4; H, 4.0; Br, 27.6. $C_{10}H_{11}O_5Br$ requires C, 41.25; H, 3.8; Br, 27.4%); δ_H 3.79–3.90 (9 H, OMe), 6.75 (1 H, s, ArH) and 7.95 (1 H, br s, CO_2H); *m/z* 292 (100%) and 290 (94.7, M^+).

Butyl 2,3,4-*Trimethoxybenzoate.*—2,3,4-Trimethoxybenzoic acid (15 g), butyl bromide (37.5 cm^3) and anhydrous potassium carbonate (40 g) were stirred and heated in *N,N*-dimethylformamide (150 cm^3) for 12 h at 80 °C. After being cooled, the mixture was diluted with water and extracted with ether. Removal of the solvent and distillation gave the butyl ester (16.4 g, 87%), b.p. 162 °C at 1.6 mmHg; δ_H 0.90–2.00 (7 H, m, Pr), 3.80 (3 H, s, OMe), 3.85 (3 H, s, OMe), 3.90 (3 H, s, OMe), 4.25 (2 H, t, *J* 7, OCH_2), 6.62 (1 H, AB, *J* 8.4, ArH) and 7.44 (2 H, AB, *J* 8.4, ArH).

Butyl 6-*Nitro*-2,3,4-*trimethoxybenzoate* **36.**—Concentrated nitric acid (25 cm^3) was added dropwise with stirring to butyl 2,3,4-trimethoxybenzoate (5.0 g) at 0 °C. The colour changed to blood red. The mixture was poured onto ice and extracted with ethyl acetate. The extract was washed with water, aqueous sodium hydrogen carbonate and water, and dried. Evaporation of the solvent and rapid chromatography of the residue on silica (ethyl acetate–light petroleum) gave the *nitro ester* **36** (7.4 g, 79%), m.p. 29–31 °C (Found: C, 53.7; H, 5.85; N, 4.6. $C_{14}H_{19}O_7N$ requires C, 53.7; H, 6.1; N, 4.5%); δ_H 0.80–2.0 (7 H, m, Pr), 3.85–3.90 (9 H, OMe), 4.29 (2 H, t, *J* 7, OCH_2) and 7.4 (1 H, s, ArH); *m/z* 313 (M^+).

Butyl 6-*Amino*-2,3,4-*trimethoxybenzoate.*—The nitro ester **36** (5.0 g) was hydrogenated in ethyl acetate over palladium–charcoal (10%). The filtered solution was evaporated and the residue distilled to give the *amino ester* (4.3 g, 95%), b.p. (bath temp.) 230 °C at 2 mmHg (Found: C, 59.1; H, 7.3; N, 5.05. $C_{14}H_{21}O_5N$ requires C, 59.35; H, 7.5; N, 4.9%); δ_H 0.75–2.00 (7 H, m, Pr), 3.70 (3 H, s, OMe), 3.75 (3 H, s, OMe), 3.85 (3 H, s, OMe), 4.29 (2 H, t, *J* 7, OCH_2), 4.60–5.20 (2 H, br s, NH_2) and 5.91 (1 H, s, ArH); *m/z* 283 (M^+).

Butyl 6-*Iodo*-2,3,4-*trimethoxybenzoate.*—Diazotization of butyl 6-amino-2,3,4-trimethoxybenzoate (10.0 g) and reaction with potassium iodide as described for the methyl ester gave the *iodo ester* as a yellow oil (12.9 g, 92%), b.p. 194–196 °C at 3 mmHg (Found: C, 42.8; H, 5.0; I, 32.4. $C_{14}H_{19}O_5I$ requires C, 42.7; H, 4.9; I, 32.2%); δ_H 0.90–2.01 (7 H, m, Pr), 3.81 (6 H, s, OMe), 3.87 (3 H, s, OMe), 4.28 (2 H, t, *J* 7, OCH_2) and 6.99 (1 H, s, ArH); *m/z* 394 (M^+).

3,3′,4,4′,5,5′-*Hexamethoxybiphenyl*-2,2′-*dicarboxylic Acid* **34.**—The dimethyl ester **27** (0.7 g) was heated under reflux in aqueous sodium hydroxide (50 cm^3; 10%) overnight. After being cooled, the mixture was acidified and extracted with ethyl acetate. Evaporation of the dried extract and recrystallization of the residue from chloroform–light petroleum gave the *diphenic acid* **34** (0.64 g, 97%), m.p. 208–210.5 °C (Found: C, 56.8; H, 5.4. $C_{20}H_{22}O_{10}$ requires C, 56.9; H, 5.4%); δ_H 3.75 (6 H, s, OMe), 3.80 (6 H, s, OMe), 3.91 (6 H, s, OMe) and 6.38 (2 H, s, ArH); *m/z* 422 (M^+).

Dibutyl 3,3′,4,4′,5,5′-*Hexamethoxybiphenyl*-2,2′-*dicarboxylate* **35.**—The diphenic acid **34** (340 mg), butyl bromide (570 mg) and anhydrous potassium carbonate (1 g) were heated at 100 °C in *N,N*-dimethylformamide (10 cm^3) with stirring for 7 h. When cool, the mixture was diluted with water and extracted with ether. Distillation of the dried extract gave the *dibutyl ester* **35** (414 mg, 96%), b.p. (bath temp.) 220 °C at 2 mmHg (Found: C, 62.9; H, 7.2. $C_{28}H_{38}O_{10}$ requires C, 62.9; H, 7.2%); δ_H 0.72–1.63 (14 H, m, Pr), 3.79–3.89 (18 H, OMe), 3.98 (4 H, t, *J* 7, OCH_2) and 6.50 (2 H, s, ArH); *m/z* 534 (M^+).

Ullmann Coupling of Butyl 6-*Iodo*-2,3,4-*trimethoxybenzoate.*—The iodo ester (2.0 g) was mixed with copper bronze (4.0 g) and heated at 250 °C for 2 h. When cool, the mixture was extracted with dichloromethane. Evaporation left 1.78 g of crude product. This was shown by GLC to contain di-butyl 3,3′4,4′5,5′-hexamethoxybiphenyl-2,2′-dicarboxylate **35** and butyl 2,3,4-trimethoxybenzoate in a 3:1 ratio.

A similar result was obtained with *butyl* 6-*bromo*-2,3,4-*trimethoxybenzoate* (Found: C, 48.5; H, 5.6; Br, 23.3. $C_{14}H_{19}O_5Br$ requires C, 48.4; H, 5.5; Br, 23.1%), obtained by esterification of the bromo acid.

Reduction of Dibutyl 3,3′,4,4′,5,5′-*Hexamethoxybiphenyl*-2,2′-*dicarboxylate* **35** *with Lithium Aluminium Hydride.*—A solution of the ester **35** (10.0 g) in dry ether was added dropwise with stirring to a suspension of lithium aluminium hydride (1.5 g) in dry ether at such a rate that the ether boiled. After being heated for a further 10 min, the reaction mixture was cooled, and quenched with water, followed by dilute sulphuric acid. The ether layer was separated and the aqueous layer further extracted with ether. The combined extracts were dried and evaporated to give the diol **28** (6.82 g, 83%). Reaction for 30 min gave the oxepine **32** as the major product.

2,2′-*Bis*(*chloromethyl*)-3,3′,4,4′,5,5′-*hexamethoxybiphenyl* **29.**—A solution of thionyl chloride (0.8 g) in dry dichloromethane was added dropwise with stirring to a solution of the diol **28** (1.0 g) in dry dichloromethane (50 cm^3) containing pyridine (0.2 cm^3). Stirring was continued for 1 h, after which the mixture was washed with water, and the organic layer was

dried and evaporated. Rapid chromatography of the residue on silica (ethyl acetate–light petroleum) gave the crude chloro compound **29** (0.47 g) and the oxepine **32** (0.48 g). After five recrystallizations from chloroform–light petroleum the pure *dichloro compound* **29** was obtained (130 mg), m.p. 116–118 °C (Found: C, 56.0; H, 5.7; Cl, 16.35. $C_{20}H_{24}O_6Cl_2$ requires C, 55.8; H, 5.6; Cl, 16.3%); δ_H 3.80 (6 H, s, OMe), 3.88 (6 H, s, OMe), 3.90 (6 H, s, OMe), 4.16 (2 H, A of ABq, *J* 10, CH_2), 4.50 (2 H, B of ABq, *J* 10, CH_2), 6.59 (2 H, s, ArH); *m/z* 434 (4%), 432 (24) and 430 (37, M^+).

Reaction of 2,2′-*Bishydroxymethyl*-3,3′,4,4′,5,5′-*hexamethoxybiphenyl* **28** *with Carbon Tetrachloride and Triphenylphosphine.*—A solution of the diol **28** (200 mg) and triphenylphosphine (400 mg) in dry carbon tetrachloride (5 cm^3) was heated under reflux overnight. Rapid chromatography on silica (ethyl acetate–light petroleum) gave the oxepine **32** (168 mg). Shorter reaction times did not give the dichloro compound **29**.

Oxidation of 2,2′-*Bis*(*hydroxymethyl*)-3,3′,4,4′,5,5′-*hexamethoxybiphenyl* **28**.—A solution of the diol **28** (0.56 g) in dichloromethane (100 cm^3) was stirred with barium manganate (7.5 g) for 16 h. It was then filtered, the residue was washed with more solvent, and the filtrate was evaporated leaving a residue which was recrystallized from chloroform–light petroleum to give prisms, m.p. 157–159 °C, of 2,3,4,8,9,10-*hexamethoxydibenz*[c,e]*oxepin*-5-*one* **38** (0.52 g) (Found: C, 61.4; H, 5.8. $C_{20}H_{22}O_8$ requires C, 61.5; H, 5.7%); δ_H 3.92 (3 H, s, OMe), 3.94 (3 H, s, OMe), 3.95 (3 H, s, OMe), 3.96 (3 H, s, OMe), 3.97 (3 H, s, OMe), 4.02 (3 H, s, OMe), 4.66 (1 H, AB, *J* 12.23, CH_2O), 5.41 (1 H, AB, *J* 12.23, CH_2O), 6.70 (1 H, s, ArH) and 6.80 (1 H, s, ArH); δ_C 56.21 (OCH_3), 56.34 (OCH_3), 60.99 (OCH_3), 61.05 (OCH_3), 61.56 (CH_2), 62.10 (OCH_3), 62.30 (OCH_3), 106.59 (C-11), 107.23 (C-1), 119.15, 122.32, 133.29, 134.99, 142.25, 142.58, 151.14, 153.22, 154.43, 155.63 (ArC) and 166.73 (C=O); $\nu_{max}(CCl_4)/cm^{-1}$ 1720 (C=O); *m/z* 390 (100%, M^+), 362 (11), 301 (15), 270 (5) and 239 (5).

Oxidation of the diol **28** with active manganese dioxide, or with dinitrogen tetroxide gave the same lactone **38** as the only identifiable product.

6-*Bromo*-2,3,4-*trimethoxybenzyl Alcohol* **39**.—A solution of the methyl ester **26** (300 mg) in dry ether (25 cm^3) was added dropwise with stirring to a suspension of lithium aluminium hydride (41 mg) in dry ether (25 cm^3). After being heated under reflux for 30 min, the mixture was cooled and treated with water and dilute sulphuric acid. Evaporation of the washed and dried extract, and distillation of the residue gave the *alcohol* **39** as a pale yellow liquid (210 mg, 77%), b.p. 190 °C (bath temp.) at 0.8 mmHg (Found: C, 43.2; H, 4.6; Br, 28.8. $C_{10}H_{13}O_4Br$ requires C, 43.3; H, 4.7; Br, 28.8%); δ_H 2.25–2.35 (1 H, br s, OH), 3.80 (6 H, s, OMe), 3.89 (3 H, s, OMe), 4.68 (2 H, s, CH_2) and 6.81 (1 H, s, ArH); *m/z* 278 (100%) and 276 (97, M^+).

6-*Bromo*-2,3,4-*trimethoxybenzaldehyde* **42**.—Barium manganate (25 g) was added in portions to a solution of the bromo alcohol **39** (5.0 g) in dry dichloromethane (300 cm^3). This mixture was stirred at room temperature for 5 d, then filtered. The solvent was removed from the filtrate and the residue was subjected to rapid chromatography on silica (ethyl acetate–light petroleum) to give the *bromo aldehyde* **42** (3.2 g, 65%), b.p. (bath temp.) 195 °C at 0.8 mmHg; δ_H 3.92 (6 H, s, OMe), 3.99 (3 H, s, OMe), 6.90 (1 H, s, ArH) and 10.13 (1 H, s, CHO).

6-*Bromo*-2,3,4-*trimethoxybenzyl Chloride* **40**.—A solution of thionyl chloride (2 cm^3) in dry dichloromethane (25 cm^3) was added dropwise with stirring to a solution of the bromo alcohol **39** (7.0 g) in dry dichloromethane containing pyridine (3 cm^3). After being further stirred the solution was washed with dilute sulphuric acid and water, and dried. Evaporation of the solvent and crystallization of the residue from ethyl acetate–light petroleum gave the *benzyl chloride* **40** (7.2 g, 95%) as pale yellow prisms, m.p. 50–53 °C; δ_H 3.81 (6 H, s, OMe), 3.94 (3 H, s, OMe), 4.71 (2 H, s, CH_2) and 6.88 (1 H, s, ArH); *m/z* 298 (8%), 297 (5), 296 (34), 295 (3), 294 (26, M^+).

6-*Bromo*-2,3,4-*trimethoxybenzyl*(*triphenyl*)*phosphonium Chloride* **41**.—A solution of the benzyl chloride **40** (7.0 g) in dry toluene was added dropwise with stirring to a solution of triphenylphosphine (6.3 g) in dry toluene. The temperature was maintained at 60 °C for 45 h. When cool, the precipitate was filtered off, washed with dry light petroleum and then dry ether, and dried *in vacuo* to give the *phosphonium salt* **41** (8.6 g, 72%), m.p. 177–179 °C (Found: C, 66.0; H, 5.4. $C_{28}H_{27}BrClO_3P$ requires C, 66.0; H, 5.3%).

6,6′-*Dibromo*-2,2′,3,3′,4,4′-*hexamethoxystilbene* **43**.—6-Bromo-2,3,4-trimethoxybenzaldehyde **42** (0.9 g) in dry *N*,*N*-dimethylformamide (10 cm^3) was added dropwise with stirring to a solution of the phosphonium salt **41** (2.1 g) in dry *N*,*N*-dimethylformamide (50 cm^3) at 90 °C. This was followed by the slow, dropwise addition of a solution of lithium methoxide in methanol [from lithium (26.4 mg) and dry methanol (5 cm^3)] under argon. Heating and stirring were continued for 4.5 h at 90 °C. The cooled reaction mixture was poured into water and extracted with ethyl acetate. Triphenylphosphine oxide was removed by rapid chromatography on silica (ethyl acetate–light petroleum, 1:9), and the crude *stilbene* **43** was recrystallized from ethyl acetate–light petroleum giving 800 mg (47%), m.p. 159–161 °C (Found: C, 46.5; H, 4.4; Br, 30.8%. $C_{20}H_{22}Br_2O_6$ requires C, 46.4; H, 4.3; Br, 30.8%); δ_H 3.81 (18 H, s, OMe), 6.87 (2 H, s, olefinic H) and 7.33 (2 H, s, ArH); *m/z* 520 (11%), 518 (20), 516 (11, M^+), 358 (58), 181 (35), 179 (97) and 166 (34).

Attempted coupling of this material with copper bronze or tetrakis(triphenylphosphine)nickel(0) was not successful.

2,3,4-*Trimethoxybenzyl Chloride* **47**.—A solution of thionyl chloride (11 cm^3) in dry dichloromethane (25 cm^3) was added dropwise with stirring to a solution of 2,3,4-trimethoxybenzyl alcohol **46** (18 g), in dry dichloromethane (50 cm^3) containing pyridine (1 cm^3). After being stirred for 30 min, the solution was poured into water, and the organic layer was washed with dilute sulphuric acid and water. The dried solution was distilled to give the benzyl chloride **47** (18.6 g, 95%), b.p. 106–107 °C at 0.3 mmHg; δ_H 3.82 (3 H, s, OMe), 3.91 (3 H, s, OMe), 3.98 (3 H, s, OMe), 4.58 (2 H, s, CH_2), 6.78 (1 H, AB, *J* 8.8, ArH) and 6.92 (1 H, AB, *J* 8.8, ArH). This compound has been mentioned in the literature.[28]

2,3,4-*Trimethoxybenzyl*(*triphenyl*)*phosphonium Chloride* **48**.—Reaction of 2,3,4-trimethoxybenzyl chloride **47** (12.88 g) with triphenylphosphine (16 g) as described for **41** gave the *phosphonium salt* **48** (18.98 g, 67%), m.p. 177–178 °C (Found: C, 70.5; H, 6.0; Cl, 7.3. $C_{28}H_{28}ClO_3P$ requires C, 70.2; H, 5.9; Cl, 7.4%).

2,2′3,3′4,4′-*Hexamethoxystilbene* **50**.—Reaction of 2,3,4-trimethoxybenzaldehyde **49** (6.0 g) with the phosphonium salt **48** (13.5 g) as described for **43** gave the *stilbene* **50** as needles, m.p. 69–70 °C (9.16 g, 82%), from ethyl acetate (Found: C, 66.5; H, 6.85. $C_{20}H_{24}O_6$ requires C, 66.65; H, 6.7%); δ_H 3.79 (18 H, s, OMe), 6.43 (2 H, AB, *J* 8.8, 6,6′ArH), 6.60 (2 H, s, olefinic H) and 6.82 (2 H, AB, *J* 8.8, 5,5′ ArH); *m/z* 361 (22%, M + 1), 360 (100, M^+).

2,2′,3,3′,4,4′-*Hexamethoxybibenzyl* **54**.—The silbene **50** (3.0 g)

was hydrogenated over palladium–charcoal (10%) in ethyl acetate to give the bibenzyl **54**[29] (2.93 g, 97%) as prisms, m.p. 126–127 °C, from ethyl acetate–light petroleum (Found: C, 66.4; H, 7.3. Calc. for $C_{20}H_{26}O_6$: C, 66.3; H, 7.3%); δ_H 2.79 (4 H, s, olefinic H), 3.79 (6 H, s, OMe), 3.87 (12 H, s, OMe), 6.57 (2 H, AB, *J* 8.8, 6,6′ ArH) and 6.82 (2 H, AB, *J* 8.8, 5,5′ ArH).

3,3′-*Dihydroxy*-2,2′,4,4′-*tetramethoxystilbene* **51**.—A solution of the hexamethoxystilbene **50** (1.0 g) in dry toluene (40 cm^3) was added dropwise with stirring to a solution of methyl magnesium iodide [from magnesium (540 mg) and methyl iodide (2.06 g)] in dry ether (15 cm^3) under nitrogen. The ether was removed by distillation, more toluene being added to make up the volume. This mixture was heated under reflux for 10 h. When cool, it was poured into ice-cold dilute hydrochloric acid. The toluene layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were extracted with aqueous sodium hydroxide (5%), and this extract was acidified with dilute sulphuric acid (5%), and then extracted with ether. Evaporation of the washed and dried extract gave a dark residue which was purified on silica by radial chromatography. Elution with ethyl acetate–light petroleum (19:1) gave the *diol* **51** (273 mg) as crystals, m.p. 121–123 °C from ethyl acetate–light petroleum (Found: C, 64.85; H, 6.1. $C_{18}H_{20}O_6$ requires C, 65.0; H, 6.1%); δ_H 3.78 (6 H, s, OMe), 3.82 (6 H, s, OMe), 5.30–5.70 (2 H, br s, OH), 6.45 (2 H, AB, *J* 8.4, ArH) and 6.54 (2 H, AB, *J* 8.4, ArH and 6.54 (2 H, s, olefinic H); λ_{max}(MeOH)/nm (log ε) 291 (5.05), 235 (5.41) and 202 (5.48); *m*/*z* 332 (M^+).

1,3,6,8-*Tetramethoxyphenanthrene*-2,7-*quinone* **52**.—(*a*) A solution of the diol **51** (150 mg) in chloroform (30 cm^3) was shaken for 30 min with freshly precipitated silver oxide (1.5 g). Evaporation of the filtered solution and recrystallization of the residue from benzene gave the *quinone* **52** (76.4 mg, 51%) as reddish purple needles, m.p. 222–224 °C (Found: C, 65.8; H, 5.1. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.9%); δ_H 3.90 (6 H, s, OMe), 4.17 (6 H, s, OMe), 6.6 (2 H, s, quinonoid H) and 7.13 (2 H, s, quinonoid H); ν_{max}(KBr)/cm^{-1} 1662 (C=O) and 1600 (C=C); λ_{max}(CH_2Cl_2)/nm (log ε) 484 (4.12), 344sh (3.64), 310sh (3.83), 280sh (4.09) and 258 (4.19); *m*/*z* 330 (100%, M + 2), 328 (28, M^+), 315 (47), 314 (35), 287 (12), 286 (40), 272 (16), 271 (25), 225 (11), 215 (15), 213 (10), 171 (15) and 165 (15).

(*b*) A solution of the diol **51** (100 mg) in dichloromethane (25 cm^3) was shaken for 5 min with a solution of potassium ferricyanide (400 mg) and potassium hydroxide (150 mg) in water (25 cm^3). The organic layer was separated, and the dark blue aqueous layer further extracted with dichloromethane. Evaporation of the combined, washed, and dried extracts gave the quinone **52** (33 mg).

2,7-*Diacetoxy*-1,3,6,8-*tetramethoxyphenanthrene* **53**.—Reductive acetylation of the quinone **52** (29 mg) as described for **12** gave the *diacetate* **53** (27 mg) as prisms, m.p. 170–171.5 °C, from aqueous methanol (Found: C, 63.7; H, 5.45. $C_{22}H_{22}O_8$ requires C, 63.8; H, 5.35%); δ_H 2.44 (6 H, s, OAc), 4.00 (6 H, s, OMe), 4.05 (6 H, s, OMe), 7.67 (2 H, s, olefinic H) and 7.93 (2 H, s, ArH); λ_{max}(MeOH)/nm (log ε) 323sh (4.06), 314 (4.19), 310 (4.22), 298 (4.23), 284 (4.19), 279 (4.21), 262 (4.49), 259sh (4.44), 237 (4.35), 213sh (4.41) and 204 (4.44); *m*/*z* 414 (22%, M^+), 372 (19), 331 (21), 330 (100) and 315 (38).

1,3,6,8-*Tetramethoxyphenanthrene*-2,7-*diol* **25**.—Benzene iododiacetate (95 mg) was added to a stirred solution of the stilbenediol **51** (100 mg) in dichloromethane (100 cm^3) and trifluoroacetic acid (46 cm^3) under nitrogen. After 2.5 h, water was added, and the residue obtained by evaporation of the washed and dried dichloromethane solution was purified by preparative TLC on silica (ethyl acetate–light petroleum) giving the *diol* **25** (7 mg) as prisms, m.p. 169–170 °C; δ_H 4.08 (6 H, s, OMe), 4.15 (6 H, s, OMe), 5.30 (2 H, s, OH), 7.62 (2 H, s, ArH) and 7.95 (2 H, s, ArH); λ_{max}(MeOH)/nm (log ε) 340 (2.15), 312 (2.85), 300 (3.11), 290 (3.21), 277 (3.48), 264 (3.71), 234 (3.28) and 220 (3.43); *m*/*z* 330 (100%, M^+), 316 (7), 315 (41), 272 (9.5), 269 (5), 257 (6) and 165 (13).

3,3′-*Dihydroxy*-2,2′,4,4′-*tetramethoxybibenzyl* **55**.—The hexamethoxybibenzyl **54** (900 mg) was treated with methyl magnesium iodide [from magnesium (238 mg)] as described for **50**. Recrystallization of the crude product from dichloromethane–light petroleum gave the *diol* **55** (376 mg, 45%) as prisms, m.p. 164–166 °C (Found: C, 64.9; H, 6.6. $C_{18}H_{22}O_6$ requires C, 64.7; H, 6.5%); δ_H 2.83 (4 H, s, CH_2), 6.59 (2 H, AB, *J* 8.4, ArH), 6.65 (2 H, AB, *J* 8.4, ArH); *m*/*z* 334 (11%, M^+), 181 (7), 168 (10), 167 (100) and 107 (19).

1,3,6,8-*Tetramethoxy*-9,10-*dihydrophenanthrene*-2,7-*quinone* **56**.—A solution of the diol **55** (50 mg) in chloroform (10 cm^3) was shaken with freshly precipitated silver oxide (500 mg) for 30 min. Evaporation of the filtered solution left a residue which was recrystallized from benzene giving the *quinone* **56** (39 mg, 78%) as red needles, m.p. 170–172 °C (Found: C, 65.3; H, 5.2. $C_{18}H_{18}O_6$ requires C, 65.45; H, 5.5%); δ_H 2.84 (4 H, s, CH_2), 3.93 (6 H, s, OMe), 3.99 (6 H, s, OMe) and 6.72 (2 H, s, quinonoid H); ν_{max}(KBr)/cm^{-1} 1610 (C=O) and 1593 (C=O); λ_{max}(CH_2Cl_2)/nm (log ε) 456 (4.71); *m*/*z* 332 (100%, M + 2), 330 (92, M^+), 315 (17), 287 (15), 269 (13), 257 (11), 211 (11), 199 (10), 165 (10) and 115 (11).

2,7-*Diacetoxy*-1,3,6,8-*tetramethoxy*-9,10-*dihydrophenanthrene* **57**.—Reductive acetylation of the quinone **56** (50 mg) as described for **12** gave the *diacetate* **57** as plates, m.p. 224–226 °C (Found: C, 63.3; H, 6.0. $C_{22}H_{24}O_8$ requires C, 63.45; H, 5.8%); δ_H 2.37 (6 H, s, OAc), 2.79 (4 H, s, CH_2), 3.78 (6 H, s, OMe), 3.91 (6 H, s, OMe) and 7.05 (2 H, s, ArH); *m*/*z* 416 (7%, M^+), 374 (14), 333 (17), 332 (100) and 43 (12).

2,4,8,10-*Tetramethoxydibenz*[c,e]*oxepine*-3,9-*diol* **58**.—Reaction of the hexamethoxyoxepine **32** (1.16 g) with methyl magnesium iodide (from 600 mg of magnesium) as described for **50** gave a crude product (502 mg) which was separated by radial chromatography and gradient elution with ethyl acetate–light petroleum into three fractions. Fraction 1 was crystallized from dichloromethane–light petroleum giving 2,3,4,8,10-*pentamethoxydibenz*[c,e]*oxepin*-9-*ol* (107 mg) as prisms, m.p. 149–151 °C (Found: C, 62.75; H, 6.3. $C_{19}H_{22}O_7$ requires C, 63.0; H, 6.1%); δ_H 4.0 (15 H, s, OMe), 4.40 (4 H, s, CH_2), 6.03 (1 H, br s, OH) and 6.86 (2 H, s, ArH); *m*/*z* 362 (100%, M^+).

Fraction 2 was crystallized from dichloromethane–light petroleum giving a pentamethoxydibenz[*c*,*e*]oxepinol of unidentified substitution pattern (73 mg) as cubes, m.p. 81–83 °C. Fraction 3 was crystallized from dichloromethane–light petroleum giving the *diol* **58** (223 mg) as needles, m.p. 191–193 °C (Found: C, 62.0; H, 5.8. $C_{18}H_{20}O_7$ requires C, 62.1; H, 5.8%); δ_H 3.97 (12 H, s, OMe), 4.36 (4 H, s, CH_2), 5.83 (2 H, s, OH) and 6.80 (2 H, s, ArH); *m*/*z* 348 (100%, M^+), 320 (5), 317 (7), 315 (9), 301 (6), 299 (11), 288 (7), 287 (26), 273 (11) and 257 (10).

2,4,8,10-*Tetramethoxydibenz*[c,e]*oxepine*-3,9-*quinone* **59**.—(*a*) A solution of the diol **58** (40 mg) in dichloromethane (25 cm^3) was shaken for 3 min with a solution of potassium ferricyanide (160 mg) and potassium hydroxide (150 mg) in water (20 cm^3). The organic layer was washed with water, dried and evaporated. The residue was recrystallized from benzene giving the *quinone* **59** (34 mg) as dark red crystals, m.p. 186–188 °C; δ_H 3.93 (6 H, s, OMe), 4.10 (6 H, s, OMe), 4.61 (4 H, s,

CH_2) and 6.73 (2 H, s, quinonoid H); *m/z* 348 (100%, M + 2), 346 (5, M^+), 315 (11), 287 (21), 273 (13), 257 (13) and 213 (10); ν_{max}(KBr)/cm^{-1} 1720 (C=O) and 1600 (C=C). Solutions of the quinone in dichloromethane lost their colour before a meaningful absorption spectrum could be obtained.

(*b*) A solution of the diol **58** (11.8 mg) in chloroform (5 cm^3) was shaken with freshly precipitated silver oxide (118 mg) for 30 min. Evaporation of the filtered solution and recrystallization of the residue from benzene gave the quinone **59** (10.8 mg, 92%).

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