# Phenanthrene-4,5-quinones: a Synthesis of Morphenol

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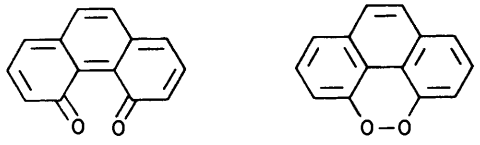
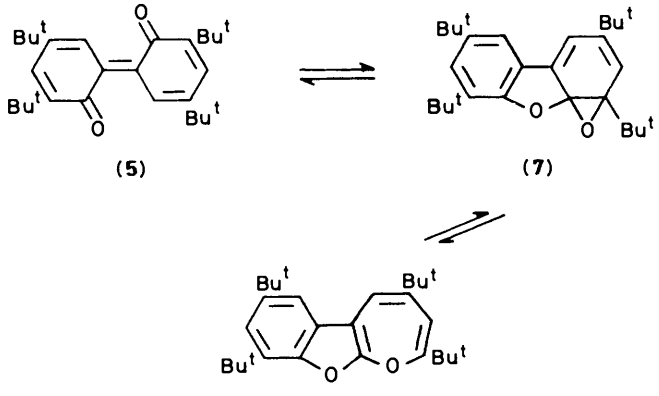
Oxidation of 1,3,6,8-tetra-t-butyl-9,10-dihydrophenanthrene-4,5-diol (**8**), gave the corresponding 4,5-quinone (**9**), isolated as its oxepine valence isomer (**19**). Oxidation of 1,3,6,8-tetra-t-butylphenanthrene-4,5-diol (**3**) gave an even less stable quinone (**4**) which rearranged *via* its arene oxide valence isomer (**26**) to an enone (**22**). Acid-catalysed debutylation of this produced morphenol (**24**). The annelated analogue (**27**) of the phenanthrenequinone (**4**) showed no tendency to rearrange.

Of the 15 possible phenanthrenequinones only four, namely the 1,2-, 1,4-, 3,4-, and 9,10-isomers, have been described and significantly their structures each contain two Kekulé rings. From a theoretical viewpoint the most interesting isomer among the remaining 11 is phenanthrene-4,5-quinone (**1**), in which valence isomerism to a cyclic peroxide (**2**) could restore the phenanthrene aromaticity. Recognizing this possibility Newman *et al.*[2-4] synthesized a number of phenanthrene-4,5-diols, but these on oxidation gave chiefly phenanthrene-1,4-quinones, a polymeric product being obtained from the 1,3.6,8-tetramethyl compound.



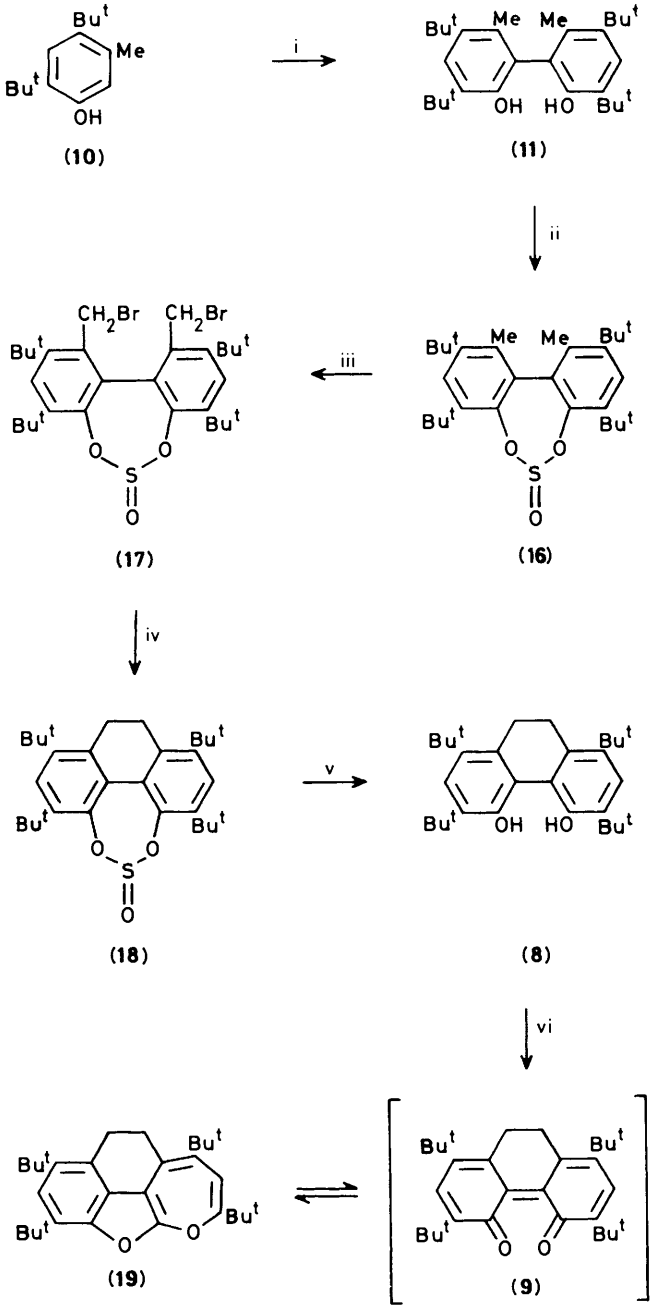
(**1**) (**2**)

To avoid this complication we chose to synthesize the 1,3,6,8-tetra-t-butyl diol (**3**). Moreover, the corresponding quinone (**4**) may be regarded as a bridged dipheno-2,2′-quinone, and such compounds with t-butyl substituents in the 3,3′-positions, *e.g.* (**5**), have been shown to isomerize to oxepino[2,3-*b*]benzofurans (**6**) *via* arene oxides (**7**);[5,6] a possibility of additional interest.



(**5**) (**7**) (**6**)

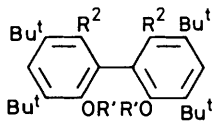
Our first synthetic target was the 9,10-dihydrophenanthrene-4,5-diol (**8**) which on oxidation should give a quinone (**9**) in its own right. The route eventually employed is shown in Scheme 1. Oxidative coupling of the cresol (**10**) with potassium dichromate as reported by Albert[7] was found to give a better yield (75%) of the diol (**11**) than was obtained with alkaline ferricyanide.[8] In a preliminary version of Scheme 1 this diol was quantitatively photobrominated in refluxing carbon tetrachloride to give the bisbromomethyl compound (**12**), but at

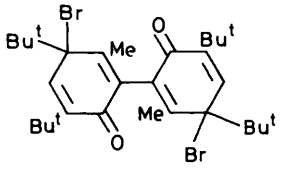


**Scheme 1.** *Reagents:* i, $K_2Cr_2O_7$, $H_2SO_4$, AcOH; ii, $SOCl_2$, pyridine; iii, $Br_2$, *hν*; iv, Mg; v, NaOH, EtOH(aq); vi, $Ag_2O$, $C_6H_6$

40—45 °C the bisdienone (**13**) was obtained, also quantitatively. The structure of (**13**) was deduced from its $^{13}C$ n.m.r. spectrum, from the double carbonyl absorption in the i.r. spectrum, and from the u.v. maximum at 250 nm, consistent with a cross rather than a linearly conjugated dienone.[9] This complete change in the position of bromination with a 30 °C change in reaction temperature is striking. It may reflect a transition from restricted to free rotation about the C(1)–C(1′) bond of the diol which could affect the ease of intramolecular hydrogen transfer between a benzylic radical and a phenolic hydroxy group. The bisdienone (**13**), which is typical of the products produced by bromination of hindered phenols, could not be converted into the bisbromomethyl compound (**12**) by prolonged (40 h) irradiation in boiling carbon tetrachloride, and was recovered unchanged.

As attempted methylation of the bisbromomethyl compound (**12**) gave chiefly the unwanted dioxapyran (**14**), the diol (**11**) was first methylated and then brominated. However, this product (**15**) could not by cyclized to a dihydrophenanthrene on treatment with phenyl lithium, sodium, or copper. Coupling *via* the Grignard reagent, or with lithium amalgam or on pyrolysis with zinc again afforded chiefly the dioxapyran (**14**). These results were not improved by preliminary halide exchange with sodium iodide.

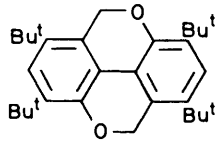



(**12**); $R^1$ = H, $R^2$ = $CH_2Br$

(**15**); $R^1$ = Me, $R^2$ = $CH_2Br$

(**13**)




(**14**)

To preclude this preference for intramolecular ether formation the hydroxy groups were temporarily locked on the same side of the molecule by formation of the cyclic sulphite ester (**16**). This was then photobrominated, and the bisbromomethyl compound (**17**) treated with magnesium to give the dihydrophenanthrene (**18**), which was hydrolysed to the diol (**8**).

Some interesting features are visible in the n.m.r. spectra of these cyclic sulphites. The two aromatic protons of each sulphite are anisochronous in deuteriochloroform solution as are the methyl protons of (**16**). The bromomethyl protons of (**17**) exhibit geminal coupling and are observed as separate AB quartets, whilst the bridge protons of (**18**) are seen as an AA′BB′ multiplet. These features must be attributed to the prochirality of the trigonal-pyramidal co-ordinate sulphur, as discussed by Jennings.[10] The dibromide (**17**) exhibits a double nonequivalence as the bromomethyl carbons are also prochiral and the methylene protons are diastereotopic. This is clearly shown in the $^{13}C$ n.m.r. in which 12 aromatic signals can be observed.

Oxidation of the dihydrophenanthrene (**8**) with either lead(IV) or silver(I) oxide in benzene gave an immediate deep blue colour typical of a dipheno-2,2′-quinone. If the oxidation was done in [$^2H_6$]benzene and the solution quickly filtered into an n.m.r. tube, the symmetrical spectrum of the dihydrophenanthrenequinone (**9**) could be obtained. Within a few minutes this spectrum had decayed as the material isomerized to the oxepin (**19**), although the solution remained blue in accordance with the equilibrium between (**9**) and (**19**). Evaporation of solutions of the quinone left a brown gum from which the oxepine could be crystallized. Yields were higher if the oxidation was done in an inert atmosphere. The n.m.r. spectra were consistent with structure (**19**) and similar to those of other oxepinobenzofurans. No carbonyl carbon resonance was seen in the $^{13}C$ n.m.r. spectrum. Solutions of the oxepine (**19**) became blue as the equilibrium with the quinone (**9**) was re-established. Catalytic hydrogenation regenerated the diol (**8**). Thus, in every respect the quinone (**9**) resembles a dipheno-2,2′-quinone, in which the rings are locked in a (*Z*) configuration.

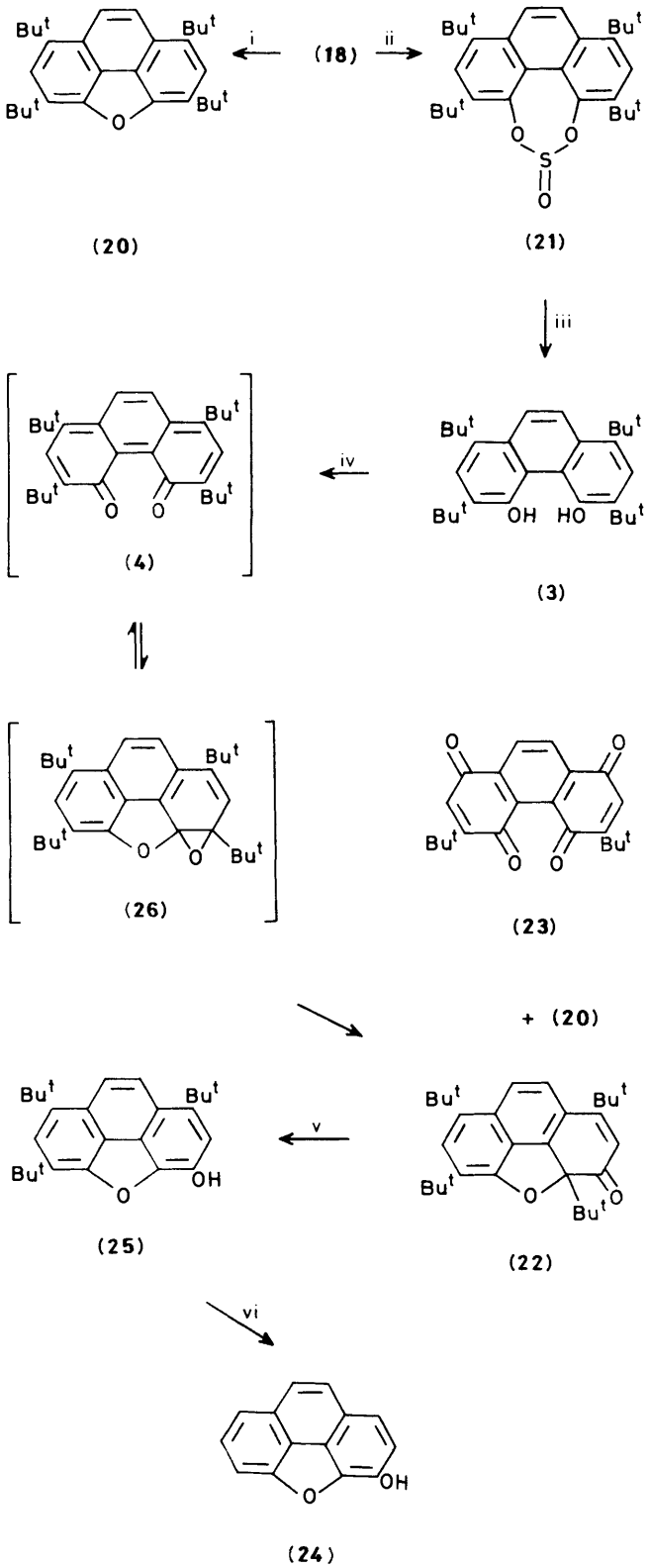
The dehydrogenation needed to obtain the phenanthrenediol (**3**) was attempted on the sulphite ester (**18**), but heating with palladized charcoal, although effecting dehydrogenation, also resulted in extrusion of sulphur dioxide, giving the phenanthrofuran (**20**). A similar result has been reported on pyrolysis of the unsubstituted sulphite ester.[11] Using the milder method of Bowden *et al.*[12] of benzylic bromination followed by dehydrobromination the sulphite ester (**18**) was succcessfully dehydrogenated in high yield, giving (**21**). Alkaline hydrolysis of this sulphite was abandoned as the product was completely autoxidized within minutes on exposure to air. (See a following paper.)* Acid hydrolysis was ineffective, and removal of the sulphite ester group was eventually achieved by reduction with lithium aluminium hydride (Scheme 2) giving the fully aromatic diol (**3**). The extreme sensitivity of the compound to oxidation by air made it necessary to use the Schlenk technique and an argon atmosphere for the reduction.

Since benzene had proved to be the only suitable solvent for oxidation of the dihydro diol (**8**), it was used in the oxidation of the phenanthrenediol (**3**). Treatment of (**3**) with either silver(I) oxide or lead(IV) oxide in an inert atmosphere gave a deep green solution. If exposed to the air the solution became orange almost instantly, and a complex mixture of products was produced. In an inert atmosphere the colour changed to red after *ca.* 10 min. Unfortunately we were unsuccessful in obtaining unambiguous spectroscopic evidence for the presence of the phenanthrene-4,5-quinone (**4**), but we assume that this is the dark green initial product of the oxidation.

From the red solution to which it decayed three products were isolated, the furan (**20**) (18%), the enone (**22**) (56%), and the diquinone (**23**) (7%). Spectroscopic data are in good agreement with the proposed enone structure (**22**). The $^1H$ n.m.r. spectrum in deuteriochloroform shows a singlet at δ 1.02 for the 3a-t-butyl group, and three singlets at δ 1.47, 1.48, and 1.54 for the others; singlets at δ 5.61 and 7.34 for 2-H and 6-H and an AB multiplet at δ 7.70 and 7.96 for 8-H and 9-H. On changing to [$^2H_6$]benzene solution the 3a-t-butyl signal remained fairly constant at δ 1.04, but the vinylic 1-t-butyl signal moved upfield to δ 1.17 while the aromatic t-butyl signals moved downfield to δ 1.54 and 1.56. I.r. absorption at 1 685 $cm^{-1}$, the u.v. spectrum, and the $^{13}C$ n.m.r. resonance at δ 205.5 were consistent with a linearly conjugated enone.

Further evidence for the structure of this enone (**22**) came from its relationship to morphenol (**24**). On heating to *ca.* 170 °C the enone decomposed with loss of colour. The residue crystallized and then melted again at 218—219 °C. The n.m.r. of this material was broadened by the pressure of a free radical (confirmed by e.s.r.). The same material could be obtained by heating the enone (**22**) in acetic acid. The n.m.r. spectrum of the crude product showed it to be the phenol (**25**), but after chromatography it was contaminated by the same radical.

* L. M. Engelhardt, F. R. Hewgill, J. M. Stewart, and A. H. White, *J. Chem. Soc., Perkin Trans. 1*, in the press.

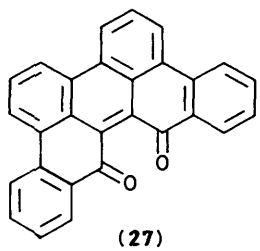



**Scheme 2.** *Reagents:* i. Pd/C, 350 °C; ii, NBS then KOAc, AcOH; iii, $LiAlH_4$; iv, $PbO_2$, benzene; v, AcOH, Zn; vi, HBr, AcOH, Zn

Debutylation of this phenol (**25**) should thus give morphenol. Although this was expected to be straightforward, initial attempts with aluminium chloride in toluene, or in nitromethane, and mixtures of hydrobromic and acetic acids, all resulted in extensive decomposition. With trifluoroacetic acid no reaction was observed. Eventually it was found that alternate additions of zinc dust and hydrobromic acid led to moderate but variable yields of morphenol, the highest being 41%. The morphenol from this reaction was identical with a sample prepared from codeine by the method of Mosettig and Meitzner.[13] Thus the sequence outlined in Schemes 1 and 2 constitutes an unexpected total synthesis of morphenol from *m*-cresol in an overall yield of 5%. The only previous synthesis is that of Horaguchi and Shimizu[14] which proceeded from 8-hydroxytetralone in an overall yield of less than 1%.

The most likely origin of the enone (**22**) is as a result of an N.I.H. rearrangement[15] of the proposed arene oxide valence isomer (**26**) of the quinone (**4**). The formation of the diquinone (**23**) and the furan (**20**) will be discussed in a later paper. There was no indication that a cyclic peroxide structure such as (**2**) is a viable alternative for either of the quinones (**4**) or (**9**), nor are we aware of any reported examples of peroxides where both oxygens are attached to $sp^2$ hybridized carbons. As suggested by Altwicker[16] this may result from the high resonance energy of phenoxy radicals reducing the oxygen–oxygen bond dissociation energy. A biradical derived from such a peroxide could couple intramolecularly to an arene oxide, or redistribute the electrons to form a quinone. An interesting difference between the two quinones (**9**) and (**4**) is the apparent failure of the latter to rearrange to an oxepine. This oxepine, having only one Kekulé ring would be expected on the basis of the Fries rule to be less stable than the arene oxide (**26**) with two. This difference does not occur in the valence isomers of quinone (**9**). The enone (**22**), with its two Kekulé rings, and the inbuilt relief against strain in the form of an $sp^3$ carbon, thus seems to be the most favourable alternative to the quinonoid structure (**4**).

The demonstrated instability of the phenanthrene-4,5-quinone system suggested that structurally similar compounds may also exhibit preferences for isomeric forms. One such compound is dibenzo[*fg,ij*]pentaphene-15,16-quinone (**27**) which can be regarded as an analogue of (**4**) where the t-butyl groups have been replaced by fused aromatic rings. This quinone was prepared by Zinke and Ziegler,[17] by oxidizing the parent hydrocarbon with chromic acid. The formation of a cyclic azine on treatment of the quinone with hydrazine was later provided as proof of structure.[18] However, as the dipheno-2,2′-quinone–arene oxide–oxepinobenzofuran system is an equilibrium mixture, the formation of the cyclic azine would not preclude the presence of the latter valence isomers. As the quinone (**27**) was obtained as a mixture of two crystal types[17] the possibility of an equilibrium mixture is not unreasonable.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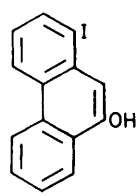
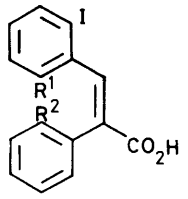

(28)

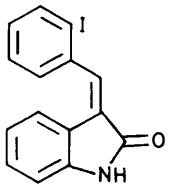
Our intention was to prepare unequivocally the hydroquinone corresponding to (**27**) utilizing the oxidative coupling, in the 10-position, of a 9-phenanthrol.[19] Thus Ullmann coupling of the iodophenanthrol (**28**) followed by oxidative coupling should lead to the desired diol. Unfortunately, lactam formation [*e.g.* (**29**)] on reduction of two possible Pschorr intermediates (**30**) and (**31**) forced this route to be abandoned in favour of the reported synthesis. Cyclization of 9,9′-biphenanthryl to dibenzo-

[*fg,ij*]pentaphene was achieved in low yield as described by Clar and Zander.[20] Thallium tris(trifluoroacetate) has been used to prepare dimers of aromatic compounds[21] and it was hoped that this reagent would afford a higher yield, but although the product resembled the dibenzopentaphene it did not crystalize and the mass spectrum was quite different.



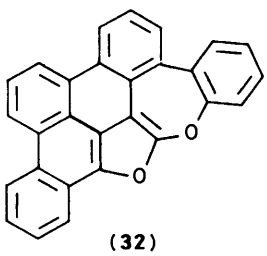
(**30**) $R^1 = H$, $R^2 = NO_2$

(**31**) $R^1 = NO_2$, $R^2 = H$



(**29**)

Spectra of the quinone (**27**) support the quinonoid structure rather than a valence isomer. Thus a typical carbonyl absorption was present in the i.r. spectrum at 1 665 $cm^{-1}$. A 7 H system was seen in the $^1H$ n.m.r. and 14 signals in the $^{13}C$ n.m.r. spectra, the carbonyl carbons being recorded at δ 187.2. This preference for the quinonoid structure, in which five rings may be drawn in the Kekulé form, is again in accordance with the Fries rule. Although the oxepine (**32**) to which it could rearrange can also be drawn with five Kekulé rings, the intermediate arene oxide, *e.g.* (**33**), can have a maximum of only three such rings and the activation energy for this valence isomerism would, therefore, be high. An alternative arene oxide (**34**) can be drawn with five Kekulé rings, but this would lead to a less stable oxepine and is evidently not favoured.



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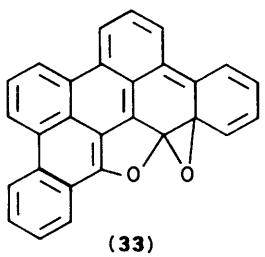

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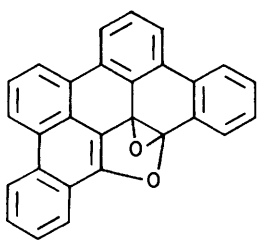

(**34**)

## Experimental

N.m.r. spectra are for deuteriochloroform solutions unless otherwise indicated. Chemical shifts are quoted on the δ scale relative to internal tetramethylsilane. High resolution mass spectra were recorded with a Varian MAT 311 spectrometer at the Department of Obstetrics and Gynaecology, University of Western Australia. Microanalyses are either by the Australian Microanalytical Service, Melbourne, or the Canadian equivalent, Vancouver. Melting points, taken with a Kofler hot stage, are uncorrected. Light petroleum had b.p. 65—70 °C. Extracts were dried with magnesium sulphate.

*6,6′-Bis(bromoethyl)-3,3′,5,5′-tetra-t-butylbiphenyldiol* (**12**) *and 3,3′-dibromo-2,2′-dimethyl-3,3′,5,5′-tetra-t-butylbicyclohexa-1,4-dienyl-6,6′-dione* (**13**).—Oxidation of 2,4-di-t-butyl-*m*-cresol (**10**)[8] as described by Albert[7] gave the diol (**11**), m.p. 244—245 °C (lit.,[7] m.p. 240—241 °C). A stirred solution of this diol (2.0 g) in carbon tetrachloride (50 ml) containing solid sodium carbonate (1.0 g) was heated under reflux and irradiated with a 250 W tungsten lamp, while a solution of bromine (1.5 g) in carbon tetrachloride (4 ml) was added dropwise. After 5 h the mixture was poured into water and the organic layer was separated, washed with aqueous sodium metabisulphite and then water, dried, and evaporated. Crystallization of the residue from dichloromethane–light petroleum gave the *bis(bromomethyl)diol* (**12**) in quantitative yield as small needles, m.p. 206—208 °C (Found: C, 60.6; H, 7.25; Br, 27.0. $C_{30}H_{44}Br_2O_2$ requires C, 60.4; H, 7.4; Br, 26.8%); *m/z* ($M^+$) 594, 596, and 598; $\nu_{max.}(CCl_4)$ 3 515 $cm^{-1}$; $\lambda_{max.}(CHCl_2)$ 300 (log ε 4.03), 244sh (4.24), and 230 nm (4.43); $\delta_H$ 1.43 (s, 18 H, $Bu^t$), 1.51 (s, 18 H, $Bu^t$), 4.43 (m, AA′BB′q, 4 H, $ArCH_2Br$), 4.88 (s, 2 H, OH), and 7.53 (s, 2 H, ArH).

When the otherwise identical reaction was carried out at 45—50 °C a quantitative yield of the *bisdienone* (**13**) was obtained. This crystallized from dichloromethane as pale yellow rods, m.p. 185—187 °C [Found: *m/z* 517.249. $C_{30}H_{44}BrO_2$ ($M$ − Br), requires 517.250]; $\nu_{max.}(CCl_4)$ 1 665 and 1 640 $cm^{-1}$; $\lambda_{max.}$(hexane) 397 (log ε 2.81), 250 (4.47), and 221sh nm (4.08); $\delta_H$ 1.23 (s, 18 H, $Bu^t$), 1.27 (s, 18 H, $Bu^t$), 1.86 (s, 6 H, Me), and 7.09 (s, 2 H, olefinic H); $\delta_C$ 22.4 (vinyl Me), 27.7 and 29.1 ($CMe_3$), 34.6 and 41.8 ($CMe_3$), 76.7 (CBr), 135.9 (C=*C*Me), 142.1 (C-5), 143.8 (C-4), 151.4 (C-1), and 183.2 (C-6).

*2,2′-Dimethoxy-6,6′-dimethyl-3,3′,5,5′-tetra-t-butylbiphenyl.*—Using the method of Stoochnoff and Benoitin[22] sodium hydride (80% dispersion in oil, washed with light petroleum; 4 g) was added to a stirred solution of the diol (**11**) (27.6 g) and methyl iodide (143.2 g) in dry tetrahydrofuran (300 ml). After being stirred overnight, the mixture was concentrated to a slurry under reduced pressure. Ether (600 ml) and water (160 ml) were added and, after shaking, the organic layer was separated, washed with water, dried, and evaporated. The residue was recrystallized from light petroleum to give the *dimethoxybiphenyl* (24 g, 85%) as prisms, m.p. 197—198 °C (Found: C, 82.6; H, 10.4. $C_{32}H_{50}O_2$ requires C, 82.35; H, 10.8%); *m/z* 466 ($M^+$); $\lambda_{max.}$(hexane) 280 (log ε 3.43) and 205 nm (4.94); $\delta_H$ 1.39 (s, 18 H, $Bu^t$), 1.44 (s, 18 H, $Bu^t$), 2.13 (s, 6 H, $ArCH_3$), 3.08 (s, 6 H, OMe), and 7.38 (s, 2 H, ArH).

*6,6′-Bis(bromomethyl)-2,2′-dimethoxy-3,3′,5,5-tetra-t-butylbiphenyl* (**15**).—A solution of bromine (7.6 g) in carbon tetrachloride (20 ml) was added dropwise to a stirred solution of the foregoing dimethoxybiphenyl (10.0 g) in carbon tetrachloride (250 ml) containing suspended sodium carbonate (10 g) at 60—70 °C while illuminated by an incandescent lamp. After 2.5 h the mixture was cooled and water was added. The organic layer was separated, washed with aqueous sodium metabisulphite and water and dried. Evaporation left a yellow gum which crystallized after addition of light petroleum and ethanol. Recrystallization from light petroleum gave the *dibromide* (**15**) (13.4 g), m.p. 150—153 °C (Found: C, 61.8; H, 8.0; Br, 25.5. $C_{32}H_{48}Br_2O_2$ requires C, 61.5; H, 7.75; Br, 25.6%); *m/z* 622 ($M^+$), 624, and 626; $\lambda_{max.}$(EtOH) 293 (log ε 3.75) and 215 nm (4.82); $\delta_H$ 1.41 (s, 18 H, $Bu^t$), 1.54 (s, 18 H, $Bu^t$), 3.28 (s, 6 H, OMe), 4.57 (s, 4 H, $CH_2Br$), and 7.55 (s, 2 H, ArH).

*1,3,6,8-Tetra-t-butyl-5H,10H-4,9-dioxapyrene* (**14**).—(*a*) An intimate mixture of the dibromide (**15**) (300 mg) and zinc dust (100 mg) was melted in a vacuum sublimation apparatus, which

was then evacuated to *ca.* 0.01 mmHg. After 2 min, air was readmitted and, when cool, the sublimate was taken up in ether and washed with water. Concentration of the dried ether solution and crystallization of the residue from light petroleum gave the *dioxapyrene* (**14**) (75%), m.p. 242 °C (decomp. sealed tube) (Found: C, 82.8; H, 9.75. $C_{30}H_{42}O_2$ requires C, 82.9; H, 9.7%); *m/z* 434 ($M^+$); $\lambda_{max.}$(hexane) 325 (log ε 4.13), 316 (4.14), 277 (4.20). 267 (4.08), 256 (3.88), and 224 nm (4.87); $\delta_H$ 1.41 (s, 36 H, Bu$^t$), 5.28 (s, 4 H, $ArCH_2O$), and 7.25 (s, 2 H, ArH).

(*b*) The dibromide (**15**) (224 mg) was heated under reflux with sodium iodide (250 mg) in butan-2-one (2 ml) for 16 h. After evaporation, the residue was taken up in light petroleum and water, and the organic layer was washed with aqueous sodium metabisulphite and then water. Concentration of the dried extract afforded the dioxapyrene (**14**) in 83% yield.

1,11-*Dimethyl*-2,4,8,10-*tetra-t-butyldibenzo*[d,f][1,3,2]*dioxathiepine* 6-*Oxide* (**16**).—Thionyl chloride (40 ml) was added dropwise to a stirred solution of the diol (**11**) (25 g) in dry pyridine (100 ml) at room temperature; cooling in a water-bath was needed. After a further 2 h stirring, the mixture was cautiously poured into *ca.* 1 l of an ice–aqueous hydrochloric acid slurry with stirring. The product was filtered off, washed with water, and recrystallized (charcoal) from ethyl acetate to give the *sulphite ester* (**16**) in 82% yield, as needles, m.p. 293—295 °C (Found: C, 74.4; H, 9.1; S, 6.4. $C_{30}H_{44}O_3S$ requires C, 74.3; H, 9.15; S, 6.6%); *m/z* 484 ($M^+$); $\nu_{max.}$($CCl_4$) 1 190 cm$^{-1}$ (S=O); $\lambda_{max.}$($CH_2Cl_2$) 229 nm (log ε 4.22); $\delta_H$ 1.44 (s, 36 H, Bu$^t$), 2.07 (s, 3 H, ArMe), 2.10 (s, 3 H, ArMe), 7.45 (s, 1 H, ArH), and 7.51 (s, 1 H. ArH).

1,11-*Bis*(*bromomethyl*)-2,4,8,10-*tetra-t-butyldibenzo*[d,f]-[1,3,2]*dioxathiepine* 6-*Oxide* (**17**).—A solution of bromine (15 g) in carbon tetrachloride (45 ml) was added dropwise over 7 h to a stirred, refluxing solution of the sulphite (**16**) (22.3 g) in carbon tetra-chloride (600 ml) containing suspended sodium carbonate (11 g), irradiated with an incandescent lamp. After a further hour the solution was decanted, and washed with aqueous sodium metabisulphite, saturated aqueous sodium hydrogen carbonate, and water. Evaporation of the dried solution left a yellow oil which crystallized after addition of light petroleum and further evaporation. Recrystallisation from light petroleum and recovery from the mother liquors gave the *dibromo compound* (**17**) (28.4 g, 96%), m.p. 220—221.5 °C [Found: *m/z* 425.218. $C_{26}H_{33}O_3S$ requires 425.215 ($M - C_4H_9Br_2$)]: *m/z* (%) 644 (1.5), 642 (3), 640 (1.5) $M^+$, 482 (2), 425 (30). 417 (24). 377 (17), 370 (14), 369 (52), 321 (13), 313 (22), 305 (11), 193 (10), 57 (100); $\nu_{max.}$($CCl_4$) 1 190 cm$^{-1}$ (S=O); $\lambda_{max.}$(hexane) 230 nm (log ε 4.58); $\delta_H$ 1.44 (s, 9 H, Bu$^t$), 1.47 (s, 9 H, Bu$^t$), 1.51 (s, 18 H, Bu$^t$), 4.23, 4.78 (ABq, *J* 10.5 Hz, 2 H, $ArCH_2Br$), 4.24, 4.79 (ABq, *J* 10.5 Hz, 2 H, $ArCH_2Br$), 7.52 (s, 1 H, ArH), and 7.57 (s, 1 H, ArH); $\delta_C$ 30.8 ($CMe_3$ and 2-$CH_2Br$), 31.5 ($CMe_3$), 32.2 (2-$CMe_3$), 35.4 ($CMe_3$), 36.6 (2-$CMe_3$), 125.9 and 126.8 (ArCH), and 132.1, 133.1, 133.3, 133.6, 141.5, 142.2, 143.5, 145.5, 146.7 and 147.3 (ArC).

1,3,7,9-*Tetra-t-butyl*-10,11-*dihydrophenanthro*[4,5-def]-[1,3,2]*dioxathiepine* 5-*Oxide* (**18**).—A stirred suspension of magnesium turnings (2.0 g) in 1,2-dibromoethane (1.0 g) and dry tetrahydrofuran (50 ml) contained in flame-dried apparatus under nitrogen was warmed until reaction set in. A solution of the dibromo compound (**17**) (10.0 g) in dry tetrahydrofuran (220 ml) was then added, and the temperature was raised to reflux. After 3 days a solution of 1,2-dibromoethane (5.0 g) in dry tetrahydrofuran (50 ml) was added over several hours, and the mixture was refluxed overnight. Dilute sulphuric acid was added to the cooled mixture to dissolve the excess of magnesium, followed by water, and the whole was extracted with ethyl acetate. The extract was washed with water, dried, and filtered through Celite. The residue obtained on evaporation was recrystallized from ethyl acetate to give the *dihydrophenanthrene* (**18**) (5.53 g, 74%), m.p. 300 °C (Found: C, 74.5; H, 9.0; S, 6.8. $C_{30}H_{42}O_3S$ requires C, 74.65; H. 8.8; S, 6.6%); *m/z* 482 ($M^+$); $\nu_{max.}$(Nujol) 1 200 cm$^{-1}$ (SO); $\lambda_{max.}$($CH_2Cl_2$) 295sh (log ε 3.38), 268 (3.99), and 229 nm (4.51); $\delta_H$ 1.44 (s, 18 H, Bu$^t$), 1.47 (s, 18 H Bu$^t$), 2.23—3.58 (AA′BB′m, 4 H, $ArCH_2CH_2Ar$), 7.46 (s, 1 H, ArH), and 7.52 (s, 1 H, ArH).

1,3,6,8-*Tetra-t-butyl*-9,10-*dihydrophenanthrene*-4,5-*diol* (**8**).—A solution of the sulphite (**18**) (3.58 g) in ethanol (50 ml) containing sodium hydroxide (5.0 g) was boiled under reflux under nitrogen for 3 h. When cool, it was poured into dilute hydrochloric acid and extracted with ether. Evaporation of the washed and dried extract gave the *diol* (**8**) as a foam which crystallized from ethanol as plates (2.58 g, 80%), m.p. 235—237 °C (Found: C, 82.8; H, 10.2. $C_{30}H_{44}O_2$ requires C, 82.5; H, 10.2%); *m/z* 436 ($M^+$); $\nu_{max.}$($CCl_4$) 3 540 cm$^{-1}$; $\lambda_{max.}$(EtOH) 295 (log ε 3.64), 263 (4.09), and 222 nm (4.52); $\delta_H$ 1.44 (s, 18 H, Bu$^t$), 1.47 (s, 18 H, Bu$^t$), 2.16—3.55 (AA′BB′m, $ArCH_2CH_2Ar$), 5.51 (s, 2 H, OH), and 7.34 (s, 2 H, ArH).

4,5-*Dimethoxy*-1,3,6,8-*tetra-t-butyl*-9,10-*dihydrophenanthrene*.—Sodium hydride (50 mg) was added to a stirred solution of the diol (**8**) (0.3 g) and methyl iodide (1.56 g) in dry tetrahydrofuran (4 ml) under nitrogen. After 2 days water was added and the mixture was extracted with ether. The extract was washed with water, dried, and evaporated. Crystallization of the residue from light petroleum and vacuum sublimation of the mother liquor gave the *dimethyl ether* (combined yield 0.26 g, 81%), m.p. 260—261 °C (Found: C, 82.6; H, 10.25. $C_{32}H_{48}O_2$ requires C, 82.7; H, 10.4%); *m/z* 464 ($M^+$); $\lambda_{max.}$(hexane) 270 (log ε 4.10) and 233 nm (4.62); $\delta_H$ 1.43 (s, 18 H, Bu$^t$), 1.44 (s, 18 H, Bu$^t$), 2.15—3.46 (AA′BB′ m, 4 H, $ArCH_2CH_2Ar$), 3.04 (s, 6 H, OMe), and 7.25 (s, 2 H, ArH).

1,3,6,8-*Tetra-t-butyl*-9,10-*dihydrophenanthrene*-4,5-*quinone* (**9**).—A solution of the diol (**8**) (4.0 mg) in [$^2H_6$]benzene (1 ml) was shaken with lead dioxide (10 mg) for 5 s. The dark blue solution was filtered through a little Celite into an n.m.r. tube; $\delta_H$ 1.10 (s, 18 H, Bu$^t$), 1.48 (s, 18 H, Bu$^t$), 2.28 (s, 4 H, $CH_2CH_2$), and 7.03 (s, 2 H, vinyl H). The u.v. spectrum was similarly obtained: $\lambda_{max.}$($C_6H_6$) 600, 372, 295, and 278 nm.

2,4,7,9-*Tetra-t-butyl*-5,6-*dihydro*-1,10-*dioxanaphtho*[2,1,8-bcd]*azulene* (**19**).—Silver oxide (0.5 g) was added to a stirred solution of the diol (**8**) (250 mg) in benzene (20 ml). After 3 min the oxidant was removed by filtration of the mixture through Celite and the deep blue filtrate was concentrated at room temperature to give a brown gum. Crystallization from light petroleum gave the *oxepine* (**19**) (60 mg, 24%) as pale blue to green clusters of needles, m.p. 150—151 °C, which faded to pale yellow after several days (Found: C, 82.9; H, 9.9. $C_{30}H_{42}O_2$ requires C, 82.9; H, 9.7%); $\nu_{max.}$($CCl_4$) 1 660 and 1 600 cm$^{-1}$; $\lambda_{max.}$(hexane) 329 (log ε 3.27), 280sh (3.62), 240 (4.38), and 226 nm (4.25); *m/z* 436 (14%, $M$ + 2), 435 (30, $M$ + 1), 434 (81, $M^+$), 419 (13), 379 (17), 378 (56), 365 (10), 364 (28), 363 (100), and 57 (68); $\delta_H$ 1.23 (s, 9 H, Bu$^t$), 1.27 (s, 9 H, Bu$^t$), 1.40 (s, 9 H, Bu$^t$), 1.44 (s, 9 H, Bu$^t$), 2.77—3.35 (AA′BB′ m, 4 H, $ArCH_2CH_2$), 5.35 (s, 1 H, vinyl H), and 7.02 (s, 1 H, ArH); $\delta_C$ 28.4 ($CMe_3$), 29.2 and 29.7 ($ArCH_2CH_2$), 30.2, 31.0, and 31.3 ($CMe_3$), 34.3, 34.5, 35.8, and 37.5 ($CMe_3$), 97.5 and 109.7 (vinyl CH), 117.7 (ArCH), and 124.6, 127.5, 128.2, 131.7, 137.6, 141.5, 144.0, 154.5, and 161.2 (OCO). The same compound (**19**) was obtained in higher yield (41%) using lead dioxide in degassed benzene under argon.

*Hydrogenation of the Oxepine* (**19**).—The oxepine (**19**) (30 mg) was hydrogenated over 10% palladized charcoal (3 mg) in ethanol. Removal of the catalyst gave a quantitative yield of the diol (**8**)

*Attempted Dehydrogenation of the Sulphite* (**18**).—The sulphite (**18**) (205 mg) and 10% palladized charcoal (20 mg) were mixed and heated to 350 °C for 30 min. The cooled mixture was triturated with boiling ethyl acetate several times and filtered. Preparative t.l.c. (silica, light petroleum) of the residue after evaporation gave 1,3,5,7-*tetra-t-butylphenanthro*[4,5-bcd]-*furan* (**20**) (125 mg, 71%), m.p. 320 °C (sealed tube) after recrystallization from light petroleum (Found: C, 86.7; H, 9.9. $C_{30}H_{40}O$ requires C, 86.5; H, 9.7%); *m/z* 416 ($M^+$); $\lambda_{max.}$(hexane) 343 (log ε 3.84), 337 (3.91), 323 (3.98), 311sh (3.73), 280sh (3.84), 269 (4.25), 260sh (4.13), 240 (4.51), and 232sh nm (4.34); $\delta_H$ 1.67 (s, 36 H, Bu$^t$), 7.67 (s, 2 H, ArH), and 8.25 (s, 2 H, ArH).

*Dehydrogenation of the Sulphite* (**18**).—A stirred solution of the sulphite (**18**) (5.5 g), *N*-bromosuccinimide (2.25 g), and benzoyl peroxide (0.2 g) in carbon tetrachloride (500 ml) was refluxed for 30 min. Potassium acetate (5.5 g) and acetic acid (5 ml) were then added and refluxing was continued for 30 min. When cool, water was added and the organic layer was separated, washed with aqueous sodium hydrogen carbonate and water, and dried. Evaporation left a pale yellow solid which was chromatographed on alumina. Elution with light petroleum–dichloromethane (10:1) gave 1,3,7,9-*tetra-t-butylphenanthro*[4,5-def][1,3,2]*dioxathiepine* 5-*oxide* (**21**) (4.78 g, 87%), m.p. 242—243 °C, from light petroleum (Found: C, 75.2; H, 8.4; S, 6.5. $C_{30}H_{40}O_3S$ requires C, 75.0; H, 8.4; S, 6.7%); *m/z* 480 ($M^+$); $\nu_{max.}$($CCl_4$) 1 190 cm$^{-1}$ (S=O); $\lambda_{max.}$($CH_2Cl_2$) 328 (log ε 4.07), 314 (4.10), 304sh (3.90), 277sh (4.19), 265sh (4.39), 260 (4.41), and 227 nm (4.29); $\delta_H$ 1.55 (s, 18 H, Bu$^t$), 1.64 (s, 18 H, Bu$^t$), 7.79 (s, 2 H, ArH), and 8.18 (s, 2 H, ArH).

*Dehydrogenation of* 4,5-*Dimethoxy*-1,3,6,8-*tetra-t-butyl*-9,10-*dihydrophenanthrene*.—Dehydrogenation of the dimethyl ether was effected by the method of Bowden *et al.*[12] using *N*-bromosuccinimide followed by potassium acetate in acetic acid, as above. 4,5-*Dimethoxy*-1,3,6,8-*tetra-t-butylphenanthrene* was obtained in 57% yield after crystallization from acetone, and had m.p. 227—228 °C (Found: C, 83.4; H, 10.1. $C_{32}H_{46}O_2$ requires C, 83.1; H, 10.0%); *m/z* 462 ($M^+$); $\lambda_{max.}$(hexane) 340 (log ε 4.21), 328 (4.20), 296 (4.32), 266 (4.58), 239 (4.24), and 222 nm (4.47); $\delta_H$ 1.54 (s, 18 H, Bu$^t$), 1.62 (s, 18 H, Bu$^t$), 3.11 (s, 6 H, OMe), 7.55 (s, 2 H, ArH), and 8.05 (s, 2 H, ArH).

1,3,6,8-*Tetra-t-butylphenanthrene*-4,5-*diol* (**3**).—Lithium aluminium hydride (20 mg) was added to a stirred solution of the sulphite (**21**) (20 mg) in dry degassed tetrahydrofuran (1.5 ml) in a Schlenk apparatus under argon. After 4.5 h the solvent was removed under reduced pressure and degassed, dilute sulphuric acid, and ether were added under argon. The aqueous phase was drawn off and the etheral solution dried. This was filtered under argon and the solvent was removed. The residual solid was dissolved in degassed [$^2H_6$]benzene (1 ml) and sealed in an n.m.r. tube under argon; $\delta_H$ (relative to $C_6H_6$) 1.63 (s, 36 H, Bu$^t$), 6.41 (s, 2 H, OH), 7.84 (s, 2 H, ArH), and 8.12 (s, 2 H, ArH).

*Oxidation of the Diol* (**3**).—A sample of the diol (**3**), prepared as above from the sulphite (**21**) (200 mg) and lithium aluminium hydride (70 mg), was dissolved in degassed benzene (10 ml). Addition of lead dioxide (400 mg) produced a deep green colour which gradually faded to brown. The mixture was stirred under argon overnight and then filtered through Celite. The crude product obtained on evaporation was subjected to rapid silica chromatography. Elution with light petroleum gave the furan (**20**) (31 mg, 18%). Elution with light petroleum–dichloromethane (4:1) gave 1,3a,5,7-*tetra-t-butylphenanthro*[4,5-bcd]-*furan*-3(3aH)-*one* (**22**) (100 mg, 56%) as orange crystals from light petroleum, m.p. 166—168 °C, with loss of colour, crystallizing and then melting at 218—219 °C (Found: C, 83.4; H, 9.6. $C_{30}H_{40}O_2$ requires C, 83.3; H, 9.3%); *m/z* 432 ($M^+$); $\nu_{max.}$($CCl_4$) 1 685, 1 620, and 1 600 cm$^{-1}$; $\lambda_{max.}$(hexane) 466 (log ε 2.79), 340 (3.17), 311 (4.00), 300 (3.96), 280sh (3.70), 232 (4.28), and 220sh nm (4.20); $\delta_H$ ($C_6D_6$, relative to $C_6H_6$) 1.04 (s, 9 H, Bu$^t$), 1.17 (s, 9 H, Bu$^t$), 1.54 (s, 9 H, Bu$^t$), 1.56 (s, 9 H, Bu$^t$), 5.55 (s, 1 H, vinyl H), 7.49 (s, 1 H, ArH), and 7.38 and 7.79 (ABq, *J* 9.2 Hz, 2 H, ArH); $\delta_C$ 25.7 ($CMe_3$), 30.1 (2-$CMe_3$), 31.4 ($CMe_3$), 34.2, 35.9, 36.0, and 42.4 ($CMe_3$), 100.7 (C-4), 119.7 (C-2), 124.7 and 125.0 (C-9 and C-10), 124.8, 125.3, and 125.7 (C-7), and 127.0, 131.4, 137.0, 145.6, 157.5, 162.7, and 205.5 (C-3). Elution with dichloromethane gave a yellow gum, which after preparative t.l.c. afforded the diquinone (**23**) (10 mg), m.p. 230—231.5 °C (lit.,[23] m.p. 229—229.5); $\delta_H$ 1.40 (s, 18 H, Bu$^t$), 6.66 (s, 2 H), and 8.08 (s, 2 H).

1,5,7-*Tri-t-butylphenanthro*[4,5-bcd]*furan*-3-*ol* (**25**).—A mixture of the enone (**22**) (42 mg), zinc dust (30 mg), and acetic acid (1 ml) was heated briefly under reflux until colourless. The mixture was poured into water and extracted with ether. The extract was washed with water, aqueous sodium hydrogen carbonate, and water, dried, and evaporated to give a pale orange gum. Purification by radial chromatography (light petroleum–ethyl acetate 9:1) and crystallization from light petroleum gave the phenol (**25**) (29 mg, 79%), m.p. 218—219 °C (Found: C, 82.8; H, 8.4. $C_{26}H_{32}O_2$ requires C, 82.9; H, 8.6%); *m/z* 376 ($M^+$); $\nu_{max.}$($CCl_4$) 3 595 cm$^{-1}$; $\lambda_{max.}$(MeOH) 360 (log ε 4.01), 343 (4.15), 328 (4.25), 263 (4.50), and 239 nm (4.69); $\delta_H$($CCl_4$) 1.61 (s, 9 H, Bu$^t$), 1.62 (s, 9 H, Bu$^t$), 1.65 (s, 9 H, Bu$^t$), 5.90 (br, 1 H, OH), 7.23 (s, 1 H, ArH), 7.56 (s, 1 H, ArH), and 8.03 and 8.10 (2 H, ABq, *J* 9.0 Hz, ArH).

*Dealkylation of the Phenol* (**25**) *to Morphenol* (**24**).—Zinc dust (60 mg) and hydrobromic acid (48%; 3 ml) were added in portions over 12 h to a stirred refluxing solution of the phenol (**25**) (40 mg) in acetic acid (2 ml). The mixture was heated for a further 5 h and then cooled, poured into water, and extracted with ether. The combined extracts were washed with water, aqueous sodium hydrogen carbonate, and water, dried, and evaporated. Preparative t.l.c. (dichloromethane) of the residue gave a brown gum which was dissolved in ethyl acetate and filtered through activated charcoal. Concentration of the filtrate gave morphenol (**24**) (9 mg, 41%) identical (t.l.c. and $^1$H n.m.r.) with a sample prepared from codeine as described by Mosettig and Meitzner.[13] After recrystallization from benzene it had m.p. 136—140 °C (lit.,[24] m.p. 145 °C) and mixed m.p. 137—141 °C.

(E)-3-(2-*Iodobenzylidene*)*indol*-2(3H)-*one* (**29**).—(*E*)-3-(2-Iodophenyl)-2-(2-nitrophenyl)propenoic acid (**30**), m.p. 187—189 °C (lit.,[25] m.p. 185—185.5 °C) was prepared as described.[25] It was reduced using conditions described by Nesmeyanov *et al.*[26] Thus, a solution of ferrous sulphate (4.3 g) in water (7 ml) was added to a stirred suspension of the acid (**30**) in ammonia (*d* 0.880; 25 ml) and water (5 ml) and stirred under reflux for 1 h. After cooling, the mixture was filtered through Celite, and the residue was washed with ether until the washings were colourless. The ether extract was washed with water, dried, and evaporated to leave a residue which was recrystallized from ethanol to give the *indolone* (**29**) as orange–yellow crystals (0.58 g, 66%), m.p. 173—175 °C (Found: *m/z* 346.977. $C_{15}H_{10}INO$ requires $M^+$, 346.981); *m/z* 347 (2%), 346 (13), 221 (17), 220 (100), 219 (11), 190 (11), 165 (13), and 110 (13); $\nu_{max.}$($CCl_4$) 3 470 (NH), 1 715 (CO), and 1 620 cm$^{-1}$ (CO); $\lambda_{max.}$(MeOH) 315 (log

ε 3.60), 257 (3.81), and 204 nm (4.18); $\delta_H$ 6.79—7.71 (m, 7 H, ArH), 7.68 (s, 1 H, vinyl H), 7.92—8.06 (m, 1 H, ArH), and 7.95 (br, 1 H, =NH).

2-*Amino*-6-*nitrobenzyl Alcohol*.—A mixture of 2,6-dinitrobenzyl alcohol (0.5 g), cyclohexane (1.3 ml), palladium–charcoal (10%; 0.15 g) and ethanol (5 ml) was heated on a steam-bath for 3.5 h and then filtered. (These conditions are similar to those described by Entwistle *et al.*[27]) Evaporation of the solvent and chromatography of the residue on alumina gave the *amine* (280 mg, 66%) as yellow needles, m.p. 96.5—97.5 °C (from dichloromethane–light petroleum) (Found: C, 50.0; H, 5.0; N, 16.6. $C_7H_8N_2O_3$ requires C, 50.0; H, 4.8; N, 16.7%); $\delta_H$ 4.10 (br, 2 H, $NH_2$ and OH), 4.66 (s, 2 H, $CH_2$), and 6.84—7.33 (m, 3 H, ArH).

2-*Iodo*-6-*nitrobenzaldehyde*.—A cold solution of sodium nitrite (0.76 g) in water (5 ml) was added dropwise to a stirred, cooled suspension of the foregoing amine (1.49 g) in water (5 ml) and hydrochloric acid (5 ml). When diazotization was complete a solution of potassium iodide (1.5 g) in water (5 ml) was added. After 2 h at room temperature the mixture was heated on a steam-bath for 1 h. When cool, the product was extracted with ether, and the extract was washed with aqueous sodium metabisulphite and water, and dried. Removal of the solvent left the *iodo compound* as a rather unstable orange oil (1.8 g, 73%), b.p. 150 °C/0.2 mmHg; *m/z* 279; $\delta_H$ 2.68 (br s, 1 H, OH), 4.87 (s, 2 H, $CH_2$), 7.06—7.27 (1 H, X of ABX, $J_{AX}$ 7.8 Hz, $J_{BX}$ 8.1 Hz, 4-H), and 7.82 and 8.12 (2 H, AB of ABX, $J_{AB}$ 1.4 Hz, 3-H, 5-H).

The foregoing iodo alcohol (1.8 g) was oxidized in benzene (100 ml) with alkaline manganese dioxide (3.75 g) in a Dean-Stark apparatus for 2 h. The oxidant was removed by filtration of the mixture through Celite, which was washed with chloroform, and the filtrate was evaporated. Rapid silica chromatography of the residue and elution with chloroform gave the *aldehyde* (1.65 g, 92%), m.p. 120—122 °C (from ethanol) (Found: C, 30.1; H, 1.5; I, 45.5; N, 5.0. $C_7H_4INO_3$ requires C, 30.35; H, 1.5; I, 45.8; N, 5.1%); *m/z* 277 ($M^+$); $\nu_{max.}$($CCl_4$) 1 730 $cm^{-1}$ (CO); $\delta_H$ 7.26—7.45 (1 H, X of ABX, $J_{AX}$ 7.4 Hz, $J_{BX}$ 8.0 Hz, 4-H), 8.06 and 8.19 (2 H, AB of ABX, $J_{AB}$ 1.1 Hz, 3-H, 5-H), and 10.07 (1 H, s, CHO).

(*E*)-3(2-*Iodo*-6-*nitrophenyl*)-2-*phenylpropenoic acid* (**31**).—A mixture of 2-iodo-6-nitrobenzaldehyde (0.67 g), phenylacetic acid (0.33 g), acetic anhyride (0.7 ml), and triethylamine (0.35 ml) was heated on a steam-bath for 5 h. Water (2 ml) was then added and the mixture was boiled for a few minutes. After cooling, the mixture was extracted with ether and the extract was washed with water, dried, and evaporated. (These conditions have been described by Covello *et al.*[25]) The residue was recrystallized from dichloromethane–light petroleum to give the *cinnamic acid* (**31**) (0.47 g, 49%), m.p. 211—214 °C (Found: C, 45.9; H, 2.6; I, 32.0; N, 3.6. $C_{15}H_{10}INO_4$ requires C, 45.6; H, 2.55; I, 32.1; N, 3.5%); $\delta_H$ 4.60 (br s, 1 H, OH), 6.96—7.26 (m, 6 H, ArH), 7.70—7.82 (m, 1 H, ArH), 7.95—8.11 (m, 1 H, ArH), and 8.00 (s, 1 H, vinyl H).

Reduction of the acid (**31**) as described for (**30**), and crystallization of the product from methanol gave a 7% yield of material tentatively identified as 5-*iodo*-3-*phenylquinolin*-2(1H)-*one*, needles, m.p. 272—273 °C; $\nu_{max.}$($CHCl_3$) 3 400, 1 660, and 1 570 $cm^{-1}$; $\delta_H$([$^2H_6$]acetone) 7.16—7.90 (m, 9 H, ArH and NH), and 8.09 (s, 1 H, vinyl H). The mother liquor appeared to contain a little of the desired amine, which decomposed on attempted crystallization.

*Dibenzo*[fg,ij]*pentaphene*-15,16-*quinone* (**27**).—9,9′-Biphenanthryl, prepared in 42% yield as described by Bachmann,[28] except that ether was replaced by tetrahydrofuran, was converted into dibenz[*fg,ij*]pentaphene as described by Clar and Zander[20] (12%), m.p. 332—334 °C (lit.,[20] m.p. 343—345 °C). This was oxidized to the quinone (**27**) as described by Zinke and Ziegler[17] (18%), m.p. (sealed tube) 336 °C (lit.,[17] m.p. 330 °C); $\nu_{max.}$($CCl_4$) 1 665 $cm^{-1}$ (CO); $\delta_H$ (at 360 MHz) 7.52—7.58 (m, 2 H), 7.68—7.80 (m, 4 H), 8.16—8.19 (m, 2 H), 8.31—8.35 (m, 4 H), and 8.62—8.66 (m, 2 H); $\delta_C$ 123.1, 123.7, 124.0, 126.6, 127.9, 128.7, 129.0, 129.3, 131.4, 133.3, 133.6, 135.3, 135.6, and 187.2.

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