# Pigments of *Elsinoe* Species. Part VI.[1] A Simple Synthesis of a Related Perylenequinone

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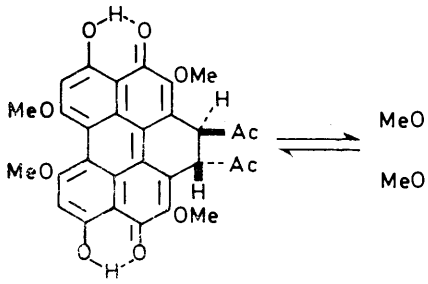
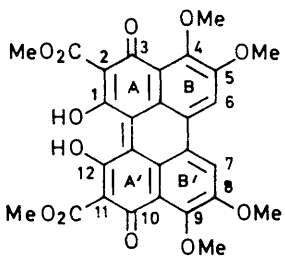
A simple synthesis of dimethyl 3,10-dihydro-1,12-dihydroxy-4,5,8,9-tetramethoxy-3,10-dioxoperylene-2,11-dicarboxylate (2), a key intermediate in the synthesis of the *Elsinoe* pigments, is described, and the unusual mass spectrometric fragmentation of compound (2) and some related compounds, with loss of one oxygen atom, is discussed.

ELSINOCHROME A (1), the main pigment of many species of the phytopathogenic mould genus *Elsinoe* (Elsinoaceae, Ascomycetes), has been formulated as the rapidly interchanging tautomeric system (1a) ⇌ (1b) on the basis of chemical and (particularly) spectroscopic evidence.[2,3] However, further confirmation through synthesis seemed desirable; synthesis of a key intermediate, the perylenequinone (2), is now described. This compound should be capable of being elaborated further, through some appropriate Diels–Alder reaction and additional transformations, to compounds also accessible from (1).



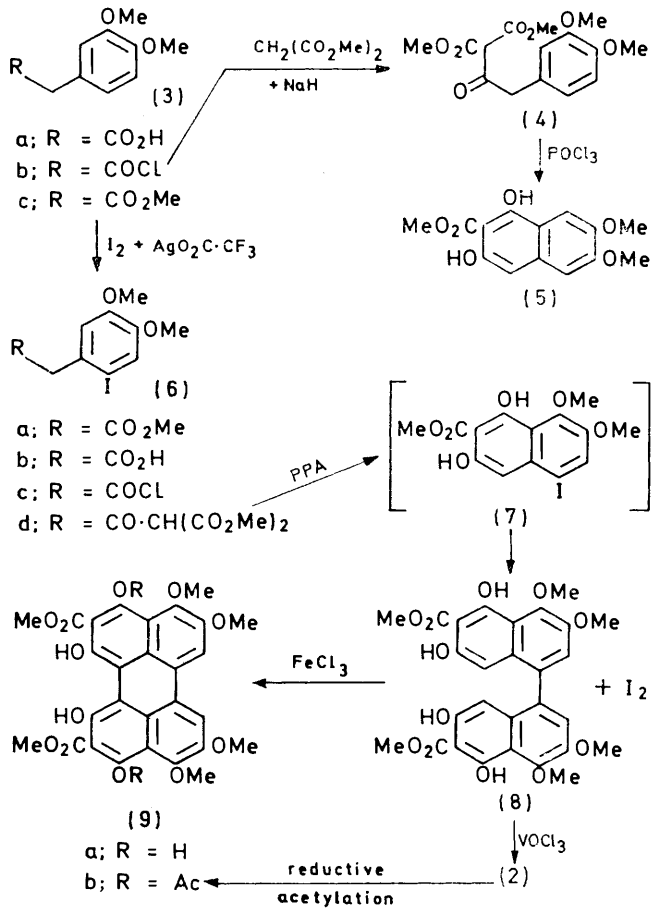
(1a) (1b)



(2)

Our synthetic approach was patterned after the well known synthesis of naphthoresorcinol.[4] The initial attempts to synthesise compound (2) from a suitable biphenyl (10e) corresponding to rings B and B′ of structure (1), by construction of the required additional rings (A and A′) were frustrated by the interaction of the side-chains required for the formation of those rings. This interaction gave rise to a compound (11a) with an unusual ring system, which is discussed later.

Attention was then directed to the synthesis of a naphthol with a suitable oxygenation pattern (see Scheme 1). The cyclisation of compound (4) [from



SCHEME 1

the chloride (3b) of commercial homoveratric acid (3a), dimethyl malonate, and sodium hydride] with phosphoryl chloride took place exclusively in the undesired direction to give methyl 1,3-dihydroxy-6,7-dimethoxy-2-naphthoate (5). However, it seemed probable that this reaction would yield the required orientation of the methoxy-groups if position 6 in structure (4) carried an iodo-substituent, which could be used for a subsequent Ullmann reaction. Iodination of methyl

[1] Part V, R. J. J. Ch. Lousberg, C. A. Salemink, and U. Weiss, *J. Chem. Soc.* (*C*), 1970, 2159.

[2] R. J. J. Ch. Lousberg, C. A. Salemink, U. Weiss, and T. J. Batterham, *J. Chem. Soc.* (*C*), 1969, 1219.

[3] R. J. J. Ch. Lousberg, L. Paolillo, H. Kon, U. Weiss, and C. A. Salemink, *J. Chem. Soc.* (*C*), 1970, 2154.

[4] P. Friedlander and H. Rüdt, *Ber.*, 1896, **29**, 1609; K. Meyer and H. S. Bloch, *Org. Synth.*, 1955, Coll. Vol. III, p. 637.

homoveratrate (3c) with iodine and silver trifluoroacetate [5] readily gave the desired iodo-ester (6a), the structure of which follows from its n.m.r. spectrum (two singlets, 1H each, in the aromatic region, *etc.*). Treatment of the corresponding acid chloride (6c) with dimethyl malonate and sodium hydride gave the iodinated phenylacetyl malonate (6d). Brief heating (25 min) of this compound with polyphosphoric acid in a stream of nitrogen achieved the desired cyclisation. However, the expected iodo-naphthoresorcinol (7) was never observed; instead, two compounds, (8) and (9a), were obtained in yields of about 25% each, together with free iodine. Longer heating times, or omitting the purging with nitrogen, favoured the formation of (9a), which has been isolated in yields up to 60%. Compounds (8) and (9a) were found to be the products of a remarkable dimerisation reaction.

Compound (8) is formulated as a bis-naphthoresorcinol (see Scheme 1) on the basis of the following evidence: a negative Beilstein test, the mass spectrometric molecular weight of 554, and the simple n.m.r. spectrum, which proves a symmetrical structure [two aromatic singlets (2H each), three singlets (6H each) from the methoxy and methoxycarbonyl protons, and two singlets (2H each) from the strongly hydrogen-bonded phenolic hydroxy-groups, which were exchangeable with deuterium oxide]. Compound (8) gave a positive test with diazotised sulphanilic acid and a positive Liebermann reaction, which indicate a phenol with a free *para*-position.

The other product of the reaction of compound (6d) with polyphosphoric acid, a yellow compound of low solubility in the common organic solvents, formed needles from chloroform or hot pyridine. Although no satisfactory elemental analysis could be obtained, there is no doubt that the compound is the perylene-hydroquinone (9a): all spectroscopic findings are consistent with this structure, and it can also be made from compound (8) with iron(III) chloride in acetonitrile. In the mass spectrum, a small peak corresponding to the expected molecular weight (*m/e* 552) was present, accompanied by another minor peak at *m/e* 550 ($M - 2$); similar thermal interconversions of hydroquinone and quinone have been observed before.[6] Neither of these peaks was suitable for precise mass measurement. However, a prominent peak (45%) occurred at *m/e* 536, corresponding to loss of one atom of oxygen from (9a). High precision mass measurement confirmed this assignment. The unusual fragmentation of (9a) (and some of its relatives), with loss of 16 mass units, will be discussed later. The formation of (9a) can be explained as being due to phenol coupling of compound (8), possibly by action of the iodine liberated during the acid-treatment of compound (6d) [*cf.* the increase in yield of (9a) when purging with nitrogen is omitted]. Acetylation gave a pale yellow, intensely blue-fluorescing diacetate (9b), identical with the product of reductive acetylation of the quinone (2) (see later). The quinone (2) itself is formed from (9a) if a solution in conc. sulphuric acid is kept at room temperature for 1—2 days,* or, less satisfactorily, if compound (9a) is treated with iodine in chloroform.

The relatively simple n.m.r. spectra of compounds (9a) and (9b) (see Experimental section) show that they must be symmetrically constituted, and are consistent with the postulated structures.

In the reaction of compound (6d) with polyphosphoric acid to give (8) and hence (9a), the anticipated iodo-naphthoresorcinol (7) must have formed first, since coupling of two molecules of (6d), with loss of iodine, prior to the formation of the naphthalene ring would have given structure (10c), which would have reacted further to yield (11a). Also, compound (6a) did not react at all under these conditions. On the other hand, the observed symmetrical coupling of two molecules of compound (7) in acidic medium, with liberation of iodine, is entirely analogous to a reaction described by Meerwein *et al.*[7] These authors observed that aromatic iodides, especially those substituted with electron-releasing groups (OH, OMe, $NH_2$, etc.) readily transfer their iodine to other molecules under the catalytic influence of acids; *e.g.*, 4-iodoresorcinol dimethyl ether gives the 4,6-di-iodo-derivative and resorcinol dimethyl ether. If, however, the position to be occupied by the migrating iodine is not free, the corresponding symmetrical biphenyl and elemental iodine are formed. Thus, treatment of 5-iodo-1,2,4-trimethoxybenzene with boron trifluoride (or other acidic reagents) gave quantitative yields of 2,2′,4,4′,5,5′-hexamethoxybiphenyl and free iodine.

The quinone (2), available from compound (9a) on treatment with conc. sulphuric acid, can also be obtained directly from (8) by oxidative coupling with vanadium oxychloride in 63% yield. Other reagents often used for phenolic coupling proved unsatisfactory. Compound (2) forms crystals with a green surface colour, giving reddish-brown solutions in chloroform; it does not fluoresce. Its quinonoid nature is apparent from its reduction with neutral dithionite, or with hydrogen over platinum. The reduced solutions are yellow; the original colour is then slowly restored. The i.r. band at 1639 $cm^{-1}$ is indicative of an extended quinone system. The simple n.m.r. spectrum of compound (2) is again compatible only with a symmetrical structure. A singlet (2H) at $\tau$ 2·12 is caused by the strongly hydrogen-bonded hydroxy-groups (not exchangeable with deuterium oxide in presence of sodium carbonate during several h at 75°). The remainder of the spectrum consists of singlets for the aromatic protons and those of methyl ester and two different methyl ether groupings. In the mass spectrum, a small molecular ion was observed at *m/e* 550; loss of 16 mass units gave the base peak at *m/e* 534.

* This reaction was observed by Dr. I. H. Qureshi.

[5] *Cf.* D. E. Janssen and C. V. Wilson, *Org. Synth.*, 1963, Coll. Vol. IV, 547.

[6] R. T. Aplin and W. T. Pike, *Chem. and Ind.*, 1966, 2009.

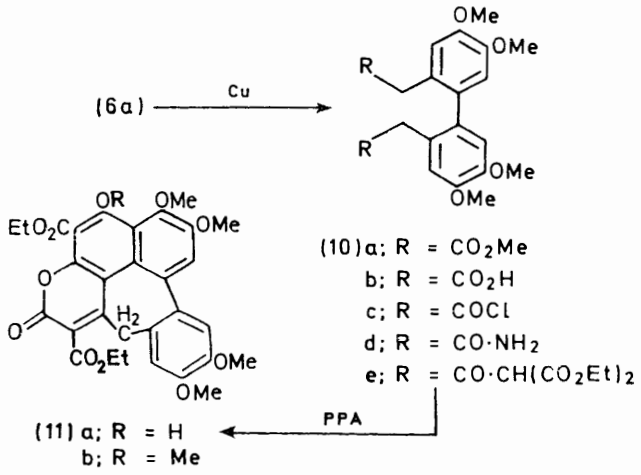
[7] H. Meerwein, P. Hofmann, and F. Schill, *J. prakt. Chem.*, 1940, [2] **154**, 266.

Reductive acetylation of compound (2) with hydrogen over Adams catalyst in pyridine–acetic anhydride gave a diacetate (9b) identical with the acetyl derivative of (9a). Its i.r. spectrum exhibited the acetoxy-absorption at 1779 $cm^{-1}$. The simple n.m.r. spectrum showed a singlet at $\tau$ 7·41 (OAc); integration revealed that only two of the four hydroxy-groups had been acetylated. Since the compound proved resistant to re-oxidation to the quinone, we have assigned the acetoxy-groups to positions 3 and 10 rather than 1 and 12. In this compound too, the hydroxy-protons failed to exchange with deuterium oxide in the presence of sodium carbonate. In the mass spectrum, a small peak due to the molecular ion (*m/e* 636) was observed; again, loss of 16 mass units gave rise to a prominent peak (*m/e* 620).

The spatial proximity of the hydroxy-groups in positions 1 and 12 of structures (9a), (9b), and (2) seems to allow an unusually strong mutual hydrogen bonding. This fact is indicated by their resistance to acetylation and to exchange in the presence of basic deuterium oxide or methan[$^2$H]ol; in contrast, the analogous hydroxy-groups in structure (8), and those in positions 3 and 10 of structure (9a) behave normally. This exceptionally strong bonding also explains some seeming anomalies of the i.r. spectra. The carbonyl-stretching frequencies of the methoxycarbonyl groups of (5), (8), and (9a) (1675, 1671, and 1660 $cm^{-1}$, respectively) fall into the normal range for hydrogen-bonded aromatic carboxylate esters (*ca.* 1670—1690 $cm^{-1}$).[8] If, however, the hydroxy-groups in positions 3 and 10 are absent, as in structures (9b) and (2), this band is shifted to positions (1721 and 1735 $cm^{-1}$, respectively) typical of non-bonded aromatic $CO_2Me$ (*ca.* 1717—1730 $cm^{-1}$), clearly showing that here the 1- and 12-hydroxy-groups are not available for bonding to the ester groups in *ortho*-positions.

To the best of our knowledge, the conversion of (4) into (9a) provides a new, extremely simple, and straightforward synthetic approach to the perylene system, which might also be capable of extension to other ring systems.

In the earlier experiments already mentioned, the iodo-compound (6a) was converted into the biphenyl derivative (10a) by an Ullmann reaction (see Scheme 2). Saponification to the free acid (10b), and treatment with thionyl chloride gave compound (10c), which was characterised by conversion to the amide (10d). The chloride (10c) was utilised for acylating diethyl malonate to give (10e). It was hoped that this, on treatment with polyphosphoric acid, would yield structure (8). However, the yellow, strongly fluorescent compound obtained could not be the then unknown (8) on account of its complex n.m.r. spectrum, which was incompatible with a symmetrical structure. On the basis of this fact, the mass spectrometric molecular weight of 564, and the presence of an i.r. band at 1730 $cm^{-1}$ suggestive of a lactone, the compound is formulated as (11a), a structure which would arise if one of the side-chains of (10e) did actually cyclise in the expected fashion, but the resulting naphthoresorcinol system would react with the other, uncyclised side-chain in a way analogous to a von Pechmann coumarin synthesis to give structure (11a). With diazomethane, (11a) gave the monomethyl ether (11b). The spectroscopic properties of compounds (11a) and (11b) were consistent with the proposed structures.



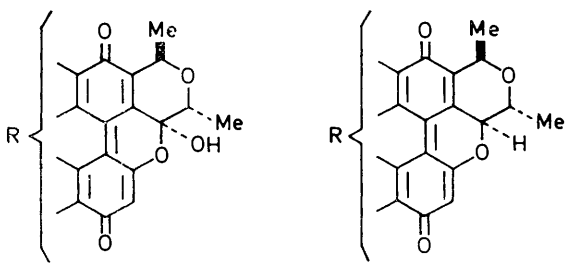

SCHEME 2

*Mass Spectrometric Fragmentation of Compounds* (2), (9a), *and* (9b).—The unusual mass spectrometric fragmentation of the perylene derivatives (9a), (9b), and (2) with loss of 16 mass units, *i.e.* one atom of oxygen, and with very weak molecular ions, seems to be connected with the presence of the pair of strongly bonded hydroxy-groups in positions 1 and 12. No peak ascribable to $M - 16$ occurs in the mass spectra of compounds (8) and (1); here the molecular ion appears as the second most intense peak (*ca.* 40%). This contrasts with the situation in (2), where $M - 16$ is the base-peak, and in (9a) and (9b), where it constitutes a major peak. In the spectra of these compounds, the intensity of the molecular ion is $<3\%$. Exact mass measurement of the $M - 16$ peak from (9a) proves the reality of the loss of one oxygen atom.

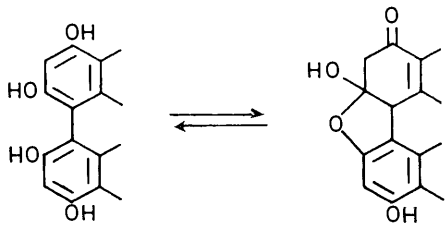
Loss of one oxygen atom has been observed occasionally; examples include some α-hydroxyanthraquinones,[9] dibenzoylmethane [10] and several enamines related to it,[11] 2-hydroxyerythroaphin *fb* (12a),[12] and morin (2′,3,4′,5,7-pentahydroxyflavone).[13] All these compounds, including (2), (9a), and (9b), are actual or potential β-diketones, but the absence of $M - 16$ peaks in the mass spectra of compounds (1), (5), and (8)

[8] *Cf. e.g.*, L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' Wiley, New York, 2nd edn., 1958, p. 179.
[9] J. H. Beynon, ' Mass Spectrometry and its Applications to Organic Chemistry,' Elsevier, Amsterdam, New York, London, and Princeton, 1960, p. 360.
[10] J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, 1966, **31**, 1384, footnote 9.
[11] H. J. Jakobsen, S.-O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc.* (*B*), 1966, 940.
[12] J. H. Bowie and D. W. Cameron, *J. Chem. Soc.* (*B*), 1966, 684.
[13] D. G. I. Kingston, personal communication.

again suggests a specific role for the hydroxy-groups in positions 1 and 12.

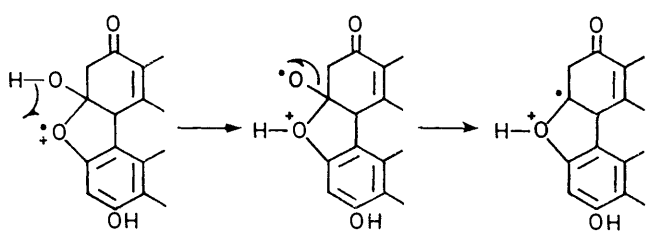


(12a) (12b)



(13)

It seems possible to rationalise these observations by assuming that one of the two resorcinol rings in, *e.g.*, structure (9a) reacts in the tautomeric diketone form, which would interact with the spatially close hydroxy-group on the other ring to give the lactol (13). A plausible mechanism * for loss of oxygen from such a species can be formulated as shown (Scheme 3). This mechanism may find some support through the facts that the observed [13] loss of oxygen from morin can be interpreted in an analogous way, whereas 2′-hydroxyflavonol, which does not have a resorcinol ring, does not lose 16 mass units,[14] and that the postulated lactol system actually pre-exists in structure (12a), which shows loss of oxygen, while erythroaphin *fb* (12b), which lacks the lactol hydroxy-group, does not.



SCHEME 3

The mechanism of this fragmentation is being investigated further, particularly with a view to establishing whether it is a thermal or an electron-impact induced process.

## EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were measured with a Perkin-Elmer 257 spectrometer, u.v. spectra with a Cary 14 spectrometer, n.m.r. spectra with a Varian A-60 or a Varian 100 MHz instrument (tetramethylsilane as internal reference), and mass spectra with an LKB-9000 spectrometer. The mass measurement on compound (9a) was performed with a Hitachi–Perkin-Elmer RMV-7 instrument.

*Methyl* 4-(3,4-*Dimethoxyphenyl*)-2-*methoxycarbonyl*-3-*oxobutyrate* (4).—Homoveratric acid (Aldrich) (3a) (4 g) was warmed on a steam-bath with thionyl chloride (5 ml) for 1 h. The excess of thionyl chloride was removed under vacuum; the crude chloride (3b) was used without purification. To a stirred suspension of sodium hydride (57% oil dispersion; 0·85 g) in tetrahydrofuran, dimethyl malonate (2·70 g) was gradually added, and the mixture was refluxed for 1 h. After cooling, the chloride (3b) in tetrahydrofuran solution was added, and the mixture was stirred for 30 min. Water was added and the solution was acidified with hydrochloric acid and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and concentrated. The residue was crystallised from hexane–chloroform to give the *phenylacetylmalonate* (4) (3 g), m.p. 87·5—88·5° (from methanol); $\nu_{max.}$($CHCl_3$) 1730 and 1760 $cm^{-1}$ (ketone and ester CO); $\lambda_{max.}$ ($CHCl_3$) 381 nm (log ε 3·56); τ ($CDCl_3$) 3·17 (3H, m, aromatic), and 6·13 and 6·21 (6H each, s, OMe and methyl ester) (Found: C, 57·9; H, 5·6%; $M^+$, 310. $C_{15}H_{18}O_7$ requires C, 58·0; H, 5·9%; *M*, 310).

*Methyl* 1,3-*Dihydroxy*-6,7-*dimethoxy*-2-*naphthoate* (5).—The ester (4) (1 g) was warmed in phosphoryl chloride (10 ml) for 30 min. The mixture was poured into ice–water and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and concentrated to a solid, which was treated with methanol to give the *naphthoate* (5) (0·5 g), m.p. 175·5—177° (from chloroform–methanol); $\nu_{max.}$ ($CHCl_3$) 3460 (OH) and 1675 $cm^{-1}$ (ester); $\lambda_{max.}$ ($CHCl_3$) 289, 302, 318, and 381 nm (log ε 3·88, 3·92, and 3·99); τ ($CDCl_3$) −1·18 and 1·21 (1H each, s, OH), 2·53, 3·19, and 3·38 (1H each, s, aromatic), 5·92 (3H, s, Me ester), and 6·04 (6H, s, OMe) (Found: C, 60·6; H, 5·1%; $M^+$, 278. $C_{14}H_{14}O_6$ requires C, 60·4; H, 5·1%; *M*, 278).

*Methyl* (2-*Iodo*-4,5-*dimethoxyphenyl*)*acetate* (6a).—To a stirred suspension of silver trifluoroacetate (25·7 g) in methyl 3,4-dimethoxyphenylacetate (3c) (24 g), iodine (28·9 g) in chloroform was added dropwise. Next day silver iodide was filtered off and the filtrate was concentrated in a rotary evaporator to an oil, which was dissolved in chloroform. The solution was washed with water, 10% sodium hydrogen carbonate, and water, dried ($MgSO_4$), treated with charcoal, filtered and concentrated. The solid residue was crystallised from hexane–chloroform to yield the *iodo-compound* (6a) (31·4 g, 82·5%), m.p. 72—72·5° (from methanol); $\nu_{max.}$ ($CHCl_3$) 1736 $cm^{-1}$ (ester CO); $\lambda_{max.}$ ($CHCl_3$) 287 nm (log ε 3·47); τ ($CDCl_3$) 2·78 (1H, s, aromatic), 3·18 (1H, s, aromatic), 6·17 (6H, s, OMe), and 3·28 (5H, ms, Me ester and benzylic H's) (Found: C, 39·4; H, 3·8; I, 37·8%; $M^+$ 336. $C_{11}H_{13}IO_4$ requires C, 39·3; H, 3·9; I, 37·8%; *M*, 336).

(2-*Iodo*-3,4-*dimethoxyphenyl*)*acetic Acid* (6b).—The ester (6a) (18 g) was refluxed in aqueous 7% potassium hydroxide for 2 h. Acidification with hydrochloric acid gave the acid (6b) (16·6 g), m.p. 165—166·5° (from methanol–water);

* Suggested by Dr. G. W. A. Milne, National Heart and Lung Institute.

[14] A. Pelter and T. Stainton, *J. Chem. Soc.* (*C*), 1967, 1933.

$\nu_{max.}$ ($CDCl_3$) 1755 and 1716 $cm^{-1}$ (acid CO, monomer and dimer) (Found: C, 37·6; H, 3·3; I, 39·5. $C_{10}H_{11}IO_4$ requires C, 37·3; H, 3·4; I, 39·4%).

*Methyl* 4-(6-*Iodo*-3,4-*dimethoxyphenyl*)-2-*methoxycarbonyl*-3-*oxobutyrate* (6d).—Conversion of the acid (6b) (19·80 g) into the crude chloride (6c), and the reaction of this with dimethyl malonate and sodium hydride in tetrahydrofuran were carried out as before. Crystallisation from ether gave the *phenylacetylmalonate* (6d) (20·75 g), m.p. 99—100·5° (from methanol); $\nu_{max.}$ ($CHCl_3$) 1761 and 1731 $cm^{-1}$ (ketone and ester CO); $\lambda_{max.}$ ($CHCl_3$) 288 nm (log ε 3·48); τ ($CDCl_3$) 2·73 and 3·24 (1H each, s, aromatic), 5·47 (1H, s, CH), 5·94 (2H, s, benzylic), 6·15 (3H, s, $CO_2Me$), and 6·19 (6H, s, OMe) (Found: C, 41·1; H, 4·1; I, 29·2%; $M^+$, 436. $C_{15}H_{17}IO_7$ requires C, 41·3; H, 3·9; I, 29·1%; *M*, 436).

*Reaction of the Phenylacetylmalonate* (6d) *with Polyphosphoric Acid.*—The phenylacetylmalonate (6d) (10 g) was heated in PPA (150 g) on a sand-bath at 100—110° under a stream of nitrogen. The reaction was monitored by t.l.c. (silica; 0·5% methanol–chloroform) and judged complete after 25 min. Towards the end of the reaction, free iodine vapour was observed. The mixture was poured into water and extracted with chloroform. The extracts were washed with dilute sodium thiosulphate and water, dried ($MgSO_4$), and concentrated to a solid residue, which was treated with chloroform to give the insoluble, yellow *dimethyl* 1,3,10,12-*tetrahydroxy*-4,5,8,9-*tetramethoxyperylene*-2,11-*dicarboxylate* (9a) (1·35 g), m.p. 264° (decomp.) (from a large volume of chloroform); $\nu_{max.}$ ($CHCl_3$) 1660 $cm^{-1}$ (ester CO); $\lambda_{max.}$ ($CHCl_3$) 328, 343, 396, and 411 nm (log ε 4·09, 4·02, 4·13, and 4·12); τ (100 MHz; $CDCl_3$) −2·45 and 2·05 (2H each, s, OH) (only the low-field peak showed exchange with $D_2O$), 2·09 (2H, s, aromatic), and 5·93, 5·98, and 6·02 (6H each, s, Me ester and OMe) (Found: C, 62·6; H, 4·6%; $M^+$, 550. $C_{28}H_{24}O_{12}$ requires C, 60·9; H, 4·4%; *M*, 552); *m/e* 536·13126 ($M$ − 16) ($C_{28}H_{24}O_{11}$ requires 536·1311).

The chloroform filtrate was concentrated to dryness and the residue crystallised from acetone to give the pale yellow *dimethyl* 5,5′,7,7′-*tetrahydroxy*-3,3′,4,4′-*tetramethoxy*-1,1′-*binaphthyl*-6,6′-*dicarboxylate* (8) (1·65 g), m.p. 270—272° (from acetonitrile–chloroform); $\nu_{max.}$ ($CHCl_3$) 3421 (OH) and 1671 $cm^{-1}$ (ester CO); $\lambda_{max.}$ ($CHCl_3$) 307, 319, and 390 nm (log ε 4·18, 4·19, and 3·77); τ ($CDCl_3$) −1·46 and 0·77 (2H each, s, OH), 2·33 and 3·52 (2H each, s, aromatic), and 5·91, 5·99, and 6·37 (6H each, s, methyl ester and OMe) (Found: C, 60·8; H, 4·8%; $M^+$, 554. $C_{28}H_{26}O_{12}$ requires C, 60·7; H, 4·8%; *M*, 554).

The compound shows greenish yellow fluorescence. Longer reaction times (45 min) favour the formation of (9a), as does omission of the purging with nitrogen.

*Oxidative Coupling of the Binaphthol* (8).—(a) *To dimethyl* 3,10-*dihydro*-1,12-*dihydroxy*-4,5,8,9-*tetramethoxyperylene*-2,11-*dicarboxylate* (2).—To a stirred chloroform solution of compound (8) (1·1 g) was added vanadium oxychloride [15] (0·4 ml). After 15 min the mixture was hydrolysed by stirring for 15 min with 5N-sulphuric acid (50 ml). The aqueous solution was extracted with chloroform, and the extracts were washed with acid and water, dried ($MgSO_4$), and concentrated. The residue was treated with acetone to give the *perylenequinone* (2) (0·7 g,) m.p. 263—265°; crystals with green surface sheen (from chloroform–methanol); $\nu_{max.}$ ($CHCl_3$) 1735 (ester CO) and 1639 $cm^{-1}$ (quinone); $\lambda_{max.}$ ($CHCl_3$) 295, 303, 396, 458, and 557 (log ε 4·15, 4·15, 3·25, 4·35, and 3·87); τ ($CDCl_3$) 2·12 (2H, s, OH), 2·27 (2H, s, aromatic), and 5·97, 6·05, and 6·07 (6H each, s, Me ester and OMe) (Found: C, 61·1; H, 4·1%; $M^+$, 550. $C_{28}H_{22}O_{12}$ requires C, 61·1; H, 4·0%; *M*, 550).

(b) *To the perylenehydroquinone* (9a). To a stirred solution of compound (8) (110 mg) in acetonitrile (10 ml), iron(III) chloride (130 mg) in acetonitrile was added dropwise. The solution was filtered and washed with chloroform to yield dark green crystals (75 mg). Recrystallisation from chloroform gave compound (9a), identical (mixed m.p. and i.r. spectrum) with the sample obtained directly from (6d). T.l.c. of the crude reaction mixture showed the presence of some quinone (2).

*Conversion of the Perylenehydroquinone* (9a) *into the Quinone* (2).—A solution of compound (9a) (30 mg) in conc. sulphuric acid (20 ml) was kept at room temperature for *ca.* 4 days; the original greenish brown colour changed to deep green. The solution was poured into ice–water, and the mixture was extracted with chloroform. The extracts were washed with water, sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), and evaporated. Recrystallisation from chloroform–methanol gave quinone (2) (21 mg), identified by mixed m.p., t.l.c., and i.r. spectrum.

*Reductive Acetylation of Quinone* (2). The perylenequinone (2) (90 mg) was reduced over platinum oxide with hydrogen in a mixture of pyridine (20 ml) and acetic anhydride (1 ml) at *ca.* 60°. The catalyst was filtered off and the filtrate poured into water to precipitate the pale yellow 3,10-*diacetate* (9b) (100 mg), m.p. 278—281° (decomp.) (from chloroform); $\nu_{max.}$ ($CHCl_3$) 1779 (acetate CO) and 1721 $cm^{-1}$ (ester CO); $\lambda_{max.}$ ($CHCl_3$) 299, 317, 329, 372, and 388 nm (log ε 4·10, 3·97, 4·01, 4·24, and 4·23); τ ($CDCl_3$) 1·86 (2H, s, OH), 2·59 (2H, s, aromatic), 5·89 (3H, s, Me ester or OMe), 5·92 (6H, s, methyl ester and/or OMe), and 7·41 (6H, s, acetate) (Found: C, 60·5; H, 4·6%; $M^+$, 636. $C_{32}H_{28}O_{14}$ requires C, 60·4; H, 4·4%; *M*, 636). This substance shows intense blue fluorescence.

*Acetylation of the Hydroquinone* (9a).—The perylenehydroquinone (9a) (1 g) was refluxed with a mixture of pyridine (50 ml) and acetic anhydride (5 ml) for 1·5 h. The mixture was poured into water, and kept overnight at room temperature. The acetylated product (1·12 g) was filtered off and dried; m.p. 278—281° (decomp.) (from chloroform). This product was identical (i.r. and n.m.r. spectra, mixed m.p.) with compound (9b), obtained by reductive acetylation of (2).

*Diethyl* 4,4′,5,5′-*Tetramethoxybiphenyl*-2,2′-*diacetate* (10a).—A mixture of the iodide (6a) (20 g) and copper powder (activated by washing with acetic acid, ethanol, and acetone) (20 g) was placed in three sealed 10 ml ampoules and kept at 210° for 30 min. The ampoules were cooled and broken, and their contents were extracted with chloroform. The combined extracts were treated with charcoal and concentrated, and the product was dissolved in acetone. The *biphenyl* (10a) (7·5 g, 60%) crystallised; m.p. 146—147° (from acetone); $\nu_{max.}$ ($CHCl_3$) 1732 $cm^{-1}$; $\lambda_{max.}$ ($CHCl_3$) 287 nm (log ε 3·84); τ ($CDCl_3$) 3·11 (2H, s, aromatic), 3·24 (2H, s, aromatic), 6·10 (6H, s, OMe), 6·18 (6H, s, OMe), 6·40 (6H, s, Me ester), and 6·63 (4H, s, benzylic) (Found: C, 62·9; H, 6·0%; $M^+$, 418. $C_{22}H_{26}O_8$ requires C, 63·2; H, 6·3%; *M*, 418).

4,4′,5,5′-*Tetramethoxybiphenyl*-2,2′-*diacetic Acid*.—The

[15] W. L. Carrick, G. L. Karapinka, and G. T. Kwiatkowski, *J. Org. Chem.* 1969, **34**, 2388.

ester (10a) (5 g) was added to aqueous 10% potassium hydroxide (100 ml) and refluxed for 2 h. The solution was acidified with concentrated hydrochloric acid. A quantitative yield of the *acid* (10b) precipitated, m.p. 228—232° (from methanol–water); $\nu_{max.}$ ($CHCl_3$) 1723 $cm^{-1}$ (acid CO) (Found: C, 61·4; H, 5·6. $C_{20}H_{22}O_8$ requires C, 61·5; H, 5·7%).

*Tetraethyl* [(4,4′,5,5′-*Tetramethoxy*-2,2′-*biphenylylene*)*bis*-(1-*oxoethylene*)]*dimalonate* (10e).—The acid (10b) (4·18 g) was refluxed with thionyl chloride (10 ml) for 2 h. The dark solution was concentrated to an oil and treated with ether to yield the solid *chloride* (10c) (3·40 g), m.p. 135—138°; $\nu_{max.}$ ($CHCl_3$) 1810 $cm^{-1}$ (acid chloride CO), characterised as the *amide* (10d), prepared by treatment with concentrated ammonia; m.p. 240·5—241·5° (from methanol); $\nu_{max.}$ ($CHCl_3$) 1695 $cm^{-1}$ (amide CO) (Found: C, 62·1; H, 6·0; N, 7·3. $C_{20}H_{24}N_2O_6$ requires C, 61·9; H, 6·2; N, 7·2%).

To magnesium turnings (0·54 g) and ethanol (5 ml), a few drops of carbon tetrachloride were added. The flask was warmed to initiate the reaction, then a solution of diethyl malonate (3·52 g) and ethanol (2 ml) in ether (20 ml) was added dropwise. The mixture was refluxed until nearly all the magnesium had dissolved. The acid chloride (10c) (3·80 g) in dry tetrahydrofuran was added, and the mixture was refluxed for 1 h. It was next diluted with water, acidified with concentrated hydrochloric acid, stirred for 30 min, and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and concentrated. The residue was crystallised from hexane–chloroform to yield the *phenylacetylmalonate* (10e) (4·85 g, 81%), m.p. 106·5—107·5° (from ethanol); $\nu_{max.}$ ($CHCl_3$) 1730 and 1745 $cm^{-1}$ (ester and ketone CO); $\lambda_{max.}$ ($CHCl_3$) 288 nm (log ε 3·85); τ ($CDCl_3$) 3·21 (2H, s, aromatic), 3·28 (2H, s, aromatic), 5·77 (4H, q, *J* 7 Hz, $CH_2$ of ester), 6·09 (6H, s, OMe), 6·17 (6H, s, OMe), 8·77 (6H, t, *J* 7 Hz, Me of ester) (Found: C, 60·6; H, 6·1%; $M^+$, 674. $C_{34}H_{42}O_{14}$ requires C, 60·5; H, 6·3%; *M*, 674).

*Acid-catalysed Condensation of the Dimalonate* (10a) *to Diethyl* 4,6-*Dihydro*-1-*hydroxy*-8,9,12,13-*tetramethoxy*-4-*oxo*-3-*oxabenzo*[5,6]*cyclohepta*[1,2,3,4-def]*phenanthrene*-2,5-*dicarboxylate* (11a).—The phenylacetylmalonate (10e) (1 g) was mixed with polyphosphoric acid (30 g) and warmed (*ca.* 45°) for 5 h. The mixture was poured into water and extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and concentrated. The residue was crystallised from methanol–chloroform to yield the *coumarin* (11a) (0·75 g, 89%), m.p. 190·5—192° (yellow crystals from methanol–chloroform); $\nu_{max.}$ ($CHCl_3$) 1730 $cm^{-1}$ (ester CO); $\lambda_{max.}$ ($CHCl_3$) 265, 288, and 424 (log ε 4·18, 4·19, and 4·03); τ ($CDCl_3$) 2·41, 2·88, and 3·27 (1H each, s, aromatic), 5·49 (4H, q, *J* 7 Hz, $CH_2$ of ester), 5·80, 5·89, 5·92, and 6·11 (3H each, s, OMe), and 8·54 (6H, t, *J* 7 Hz, Me of ester) (Found: C, 63·6; H, 4·8%; $M^+$, 564. $C_{30}H_{28}O_{11}$ requires C, 63·8; H, 5·0%; *M*, 564). Solutions show intense yellow fluorescence.

*Monomethyl ether* (11b).—The coumarin (11a) (0·10 g) in methanol was methylated with diazomethane to give the *monomethyl ether* (11b) (0·095 g), m.p. 192·5—193·5° (from methanol); $\nu_{max.}$ ($CHCl_3$) 1736 $cm^{-1}$ (ester CO); $\lambda_{max.}$ ($CHCl_3$) 366, 381, and 423 nm (log ε 4·21, 4·22, and 4·01); τ ($CDCl_3$) 2·40, 2·89, and 3·27 (1H each, s, aromatic), 5·47 (4H, q, *J* 7 Hz, $CH_2$ of ester), 5·89, 5·95, and 6·12 (3H each, s, OMe), 5·99 (6H, s, OMe), and 8·56 (6H, t, *J* 7 Hz, Me of ester) (Found: C, 64·1; H, 5·1; $M^+$, 578. $C_{31}H_{30}O_{11}$ requires C, 64·4; H, 5·2%; *M*, 578).

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