Naturally Occurring Compounds related to Phenalenone. Part V.[1] Synthetic Approaches to Structures Based on 8,9-Dihydro-8,8,9-trimethylphenaleno[1,2-*b*]furan-7-one

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A number of possible synthetic routes to 8,9-dihydro-8,8,9-trimethylphenaleno[1,2-*b*]furan-7-one (21b) and its 1,6-dimethoxy- (21a) and 1-hydroxy-6-methoxy- (21c) analogues have been explored. One successful method involved acid-catalysed cyclisation of the keto-lactone (22) [2-(2,7-dimethoxy-1-naphthoyl)-3,3-dimethylpentan-4-olide]; another utilised the Claisen rearrangement of the dimethylallyl ether (24b) [9-hydroxy-4-methoxy-3-(3-methylbut-2-enyloxy)phenalenone].

THE mould metabolites atrovenetin (1a),[2] deoxyherqueinone (1b),[2c,3-5] herqueinone (2a),[2c,4,5] isoherqueinone [C-9 epimer of (2a)],[4,5] norherqueinone (2b),[2c,4,5] and isonorherqueinone [C-9 epimer of (2b)] [4,5] have structures which are derived from 8,9-dihydro-8,8,9-trimethylphenaleno[1,2-*b*]furan-7-one (21b). As a first step towards the synthesis of these naturally-occurring compounds a number of approaches to the preparation of the model compounds (21a—c) have been investigated.

The carboxylic acid (8a) was selected as the first synthetic objective, since it was thought that it might be possible to elaborate the side-chain to produce the alcohol (14a); it was hoped that the hydroxy-group of the latter might be induced to add to the enone system of the phenalenone to give, after dehydrogenation, compound (21a). Reformatsky reaction between 2,7-dimethoxy-1-naphthaldehyde (3) [6] and diethyl α-bromo-ββ-dimethylsuccinate [7] afforded the lactone (4) which was cyclised smoothly with polyphosphoric acid to give the required carboxylic acid (8a). However, despite the use of carefully purified reagents, the Reformatsky reaction gave variable yields, and the following method was found to be superior. Stobbé condensation of the aldehyde (3) with diethyl ββ-dimethylsuccinate using potassium t-butoxide as catalyst gave the unsaturated ester (7a), which was converted into the carboxylic acid (8a), in an overall yield from the aldehyde (3) of 74%, by treatment with polyphosphoric acid. The configuration of the olefinic double bond in compound (7a) was revealed by the very high field n.m.r. signal (τ 9·57) of the methyl group of the ester, indicating that it lies within the shielding zone of the aromatic nucleus.

A number of direct methods for the preparation of the methyl ketone (13a) which could be selectively reduced to the alcohol (14a) were denied to us because we were unable to obtain the acid chloride derived from the acid (8a) in a pure state using thionyl chloride or oxalyl chloride. The preparation of methyl ketones from esters *via* β-keto-sulphoxides has been described.[8] However, treatment of the ester (8b), obtained by the action of diazomethane on the acid (8a), with methylsulphinyl anion gave none of the required β-keto-sulphoxide (8c); instead, the anion added vinylogously to the phenalenone carbonyl group with subsequent elimination of the 9-methoxy-group to yield the sulphoxide (8d). Spectral data did not distinguish between structure (8d) and that arising by replacement of the 4-methoxy-group, but the latter possibility was excluded by the fact that compound (8e), obtained by reduction of the sulphoxide with Raney nickel, was unaffected by treatment with 6N-hydrochloric acid at 100°; phenalenones containing a 9-methoxy-substituent are readily demethylated under acid conditions.[5,9]

When the ester (8e) was reduced with lithium aluminium hydride at −78° two compounds were isolated. The formation of the major product (12a) (50% yield) was unexceptional; its structure followed from its spectra, and from those of the derived acetate (12b). The other product (12% yield) is assigned structure (11) on the basis of its spectra, and in particular on the *meta*-coupling observed in its n.m.r. spectrum between the 7- and 9-hydrogen atoms. Formation of compound (11) is thought to proceed by further reduction of the phenalenone (12a); hydrolysis of the resulting hydroxyphenalenone is effected during work-up under acid conditions (Scheme 1). In agreement with this, it was shown by t.l.c. that treatment of compound (12a) with lithium aluminium hydride in ether at 0° resulted in its conversion into the phenalenone (11).

Treatment of the alcohol (12a) with 2N-hydrochloric acid at room temperature produced 8,9-dihydro-8,8-dimethylphenaleno[1,2-*b*]furan-6-one (15), the structure of which follows from its spectra (see Experimental section). The n.m.r. spectrum clearly shows that the aromatic methyl group and the 2-hydrogen atom are coupled. This compound is considered to arise by the mechanism shown in Scheme 2.

An alternative approach to the carbinol (14a) involved

[1] Part IV, J. S. Brooks and G. A. Morrison, *J.C.S. Perkin I*, 1972, 2990

[2] (*a*) K. G. Neill and H. Raistrick, *Biochem. J.*, 1957, **65**, 166; (*b*) D. H. R. Barton, P. de Mayo, G. A. Morrison, and H. Raistrick, *Tetrahedron*, 1959, **6**, 48; (*c*) I. C. Paul, G. A. Sim, and G. A. Morrison, *Proc. Chem. Soc.*, 1962, 352; (*d*) I. C. Paul and G. A. Sim, *J. Chem. Soc.*, 1965, 1097; (*e*) J. S. Brooks and G. A. Morrison, *Chem. Comm.*, 1971, 1359.

[3] A. B. Kriegler and R. Thomas, *Chem. Comm.*, 1971, 738; D. A. Frost and G. A. Morrison, *Tetrahedron Letters*, 1972, 4729.

[4] J. A. Galarraga, K. G. Neill, and H. Raistrick, *Biochem. J.*, 1955, **61**, 456.

[5] J. S. Brooks and G. A. Morrison, *Tetrahedron Letters*, 1970, 963; *J.C.S. Perkin I*, 1972, 421.

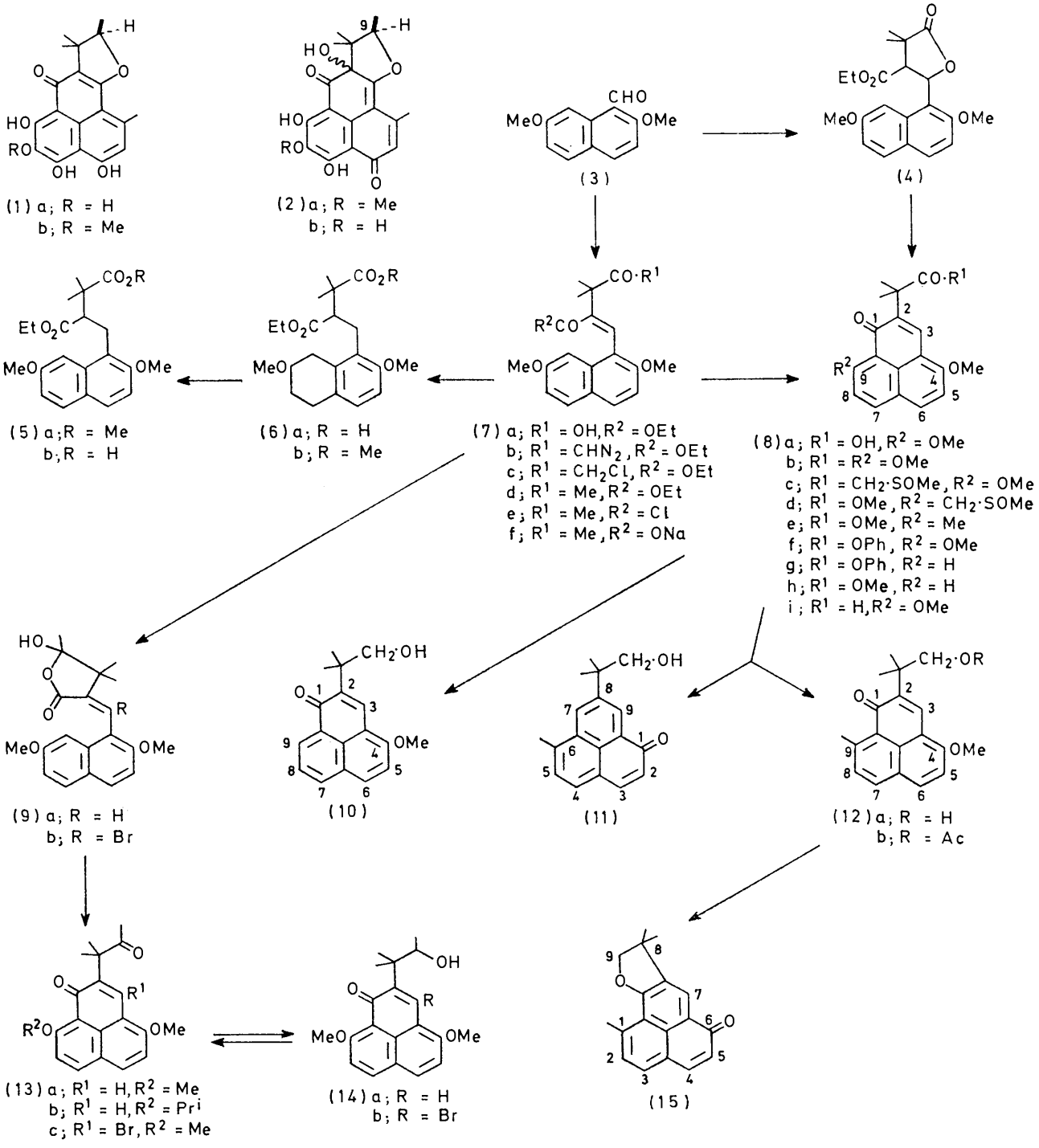
[6] Ng. Ph. Buu-Hoï and D. Lavit, *J. Chem. Soc.*, 1955, 2776.

[7] A. Kandiah, *J. Chem. Soc.*, 1932, 1215.

[8] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1964, **86**, 1639; 1965, **87**, 1345.

[9] B. Laundon and G. A. Morrison, *J. Chem. Soc.* (*C*), 1971, 1694.

preparation of the aldehyde (8i) as its immediate precursor. Aldehydes can be prepared by the reduction of phenyl esters with lithium tri-t-butoxyaluminium hydride.[10] Accordingly, the acid (8a) was converted into its phenyl ester (8f) by treatment with boron trifluoride–ether and phenol,[11] and reduced with lithium tri-t-butoxyaluminium hydride. Once again an addition–elimination process occurred at C-9, hydrogen replacing methoxy to give the phenalenone (8 g).

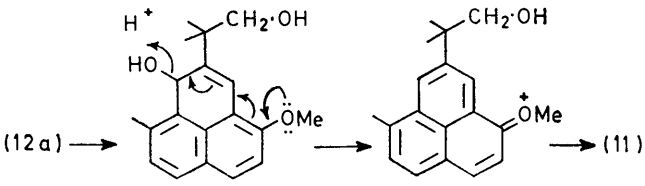


Similarly, an attempt to achieve selective reduction of the ester function of compound (8b) by treatment with lithium aluminium hydride to give a primary alcohol

[10] R. L. Augustine, 'Reduction,' Marcel Dekker, New York, 1968, p. 65.

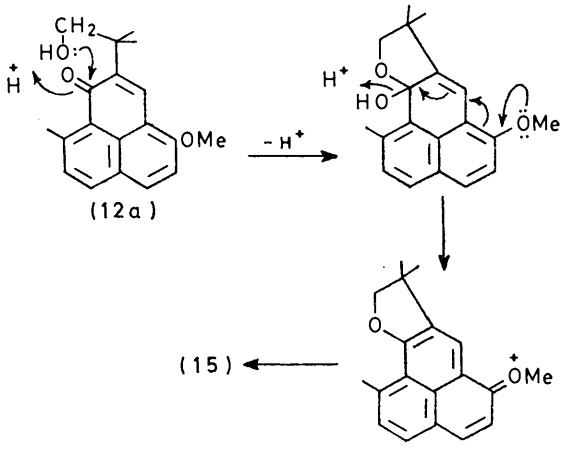
[11] *Cf.* J. L. Marshall, K. C. Erickson, and T. K. Folsom, *Tetrahedron Letters*, 1970, 4011.

which might be oxidised to the aldehyde (8i) resulted in formation of the phenalenone (8h) as the major product (61% yield). In addition, a small amount (14%) of the primary alcohol (10) was isolated.



SCHEME 1

Hydrogenation of the carboxylic ester (7a) was next undertaken, since it was thought that cyclisation of its dihydro-derivative (5b) might result in the 2,3-dihydro-derivative of the phenalenone (8a). It was hoped that elaboration of the side-chain in the dihydrophenalenone



SCHEME 2

would be less subject to complications arising by vinylogous addition to the conjugated carbonyl group, followed by elimination. In the event, the trisubstituted olefinic double bond of the ester (7a) was resistant to hydrogenation at atmospheric pressure in ethanol at 60° (5% palladised charcoal as catalyst), and in dioxan at atmospheric pressure and room temperature (platinum oxide or Raney nickel as catalyst). Hydrogenation in dioxan solution at room temperature, under a pressure of 2 atm (10% palladised charcoal as catalyst) gave the tetralin (6a), which was esterified with diazomethane to facilitate purification. The n.m.r. spectrum of the methyl ester (6b) thus obtained showed it to be a 2 : 1 mixture of diastereoisomers. The acid (6a) was also obtained when hydrogenation was carried out, using the same catalyst, in glacial acetic acid solution at room temperature and atmospheric pressure. The required naphthalene (5a) was readily obtained, in an overall yield of 100% from the olefin (7a), by treatment of the tetralin (6b) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) at room temperature in benzene solution. Cyclisation of the diester (5a) with polyphosphoric acid, however, resulted also in dehydrogenation of the initially formed dihydrophenalenone, and only the phenalenone (8a) was isolated. It was not possible to investigate cyclisation of the derived dicarboxylic acid under milder conditions, since saponification of the diester (5a) using excess of potassium hydroxide gave only the monocarboxylic acid (5b).

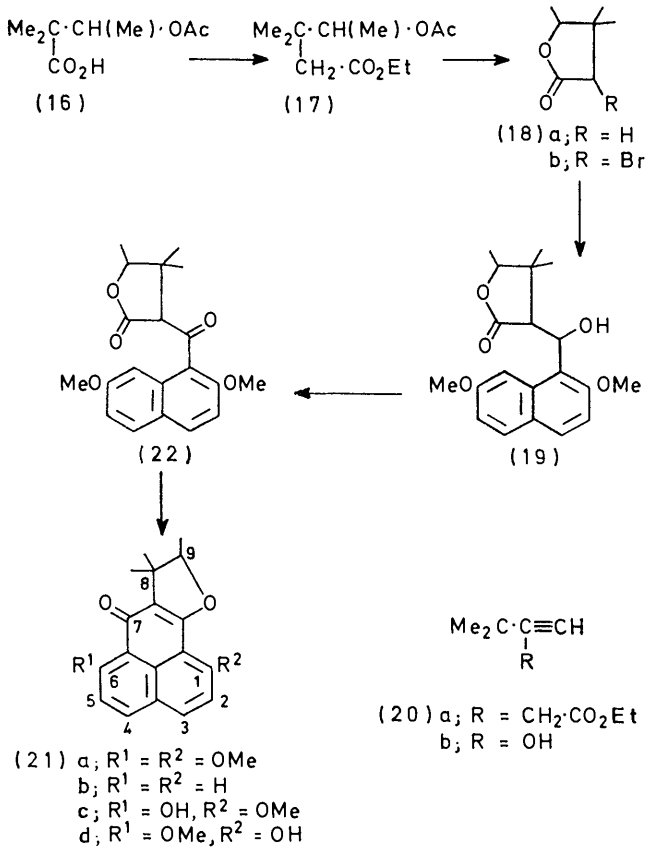
The alcohol (14a) was finally obtained from the unsaturated ester (7a) by a route which involved construction of the required side-chain *before* cyclisation to produce the phenalenone system. Treatment of the carboxylic acid (7a) successively with oxalyl chloride and diazomethane gave the diazo-ketone (7b), which was converted almost quantitatively into the chloromethyl ketone (7c) by treatment with dry hydrogen chloride gas, and thence into the methyl ketone (7d) by reduction with zinc dust and acetic acid. Attempted cyclisation of the compound (7d) with polyphosphoric acid, which proceeded very smoothly in the case of the analogous ester (7a), gave none of the required phenalenone (13a), however. Conversion into the phenalenone (13a) was achieved by first saponifying the ester (7d) to give, after acidification, the hydroxy-lactone (9a), which was then treated with polyphosphoric acid; the low yield (15%) of the phenalenone (13a) obtained in this way was improved (to 51%) by proceeding *via* the acid chloride (7e), which was cyclised by treatment with stannic chloride in carbon disulphide solution. The acid chloride (7e) was prepared from the lactone (9a) by treatment of the derived sodium salt (7f) with oxalyl chloride.

Attempts to reduce the ketone (13a) to the alcohol (14a) using aluminium isopropoxide in propan-2-ol or in toluene resulted only in the replacement of one of the methoxy-groups with isopropoxy. By analogy with other similar addition–elimination reactions at the 9-position of the phenalenone system (see above) the product is assigned structure (13b). Selective reduction of the phenalenone (13a) to the carbinol (14a) was achieved using a large excess of lithium aluminium hydride in tetrahydrofuran solution at −78°.

A number of unsuccessful attempts were made to bring about cyclisation of the carbinol (14a) to yield, after dehydrogenation, the phenalenone (21a). These involved heating the carbinol or the derived alkoxide in benzene or tetrahydrofuran in the presence of air or DDQ, and also treatment of the carbinol with perchloric acid or boron trifluoride–ether, again employing air or DDQ as a dehydrogenating agent. The only product isolated from these reactions was the ketone (13a), obtained by heating a solution of the alcohol (14a), or the derived alkoxide, in benzene solution with DDQ. The oxidation of saturated alcohols with this reagent is unusual but not unknown.[12]

In a further attempt to utilise the unsaturated lactone (9a) it was converted into the vinyl bromide (9b; configuration of the olefinic double bond not established) by adding bromine to the olefinic double bond, and dehydrobrominating the initially formed dibromide by heating a solution of it in benzene. Since it was not possible to

[12] D. Walker and J. D. Hiebert, *Chem. Rev.*, 1967, **67**, 153.



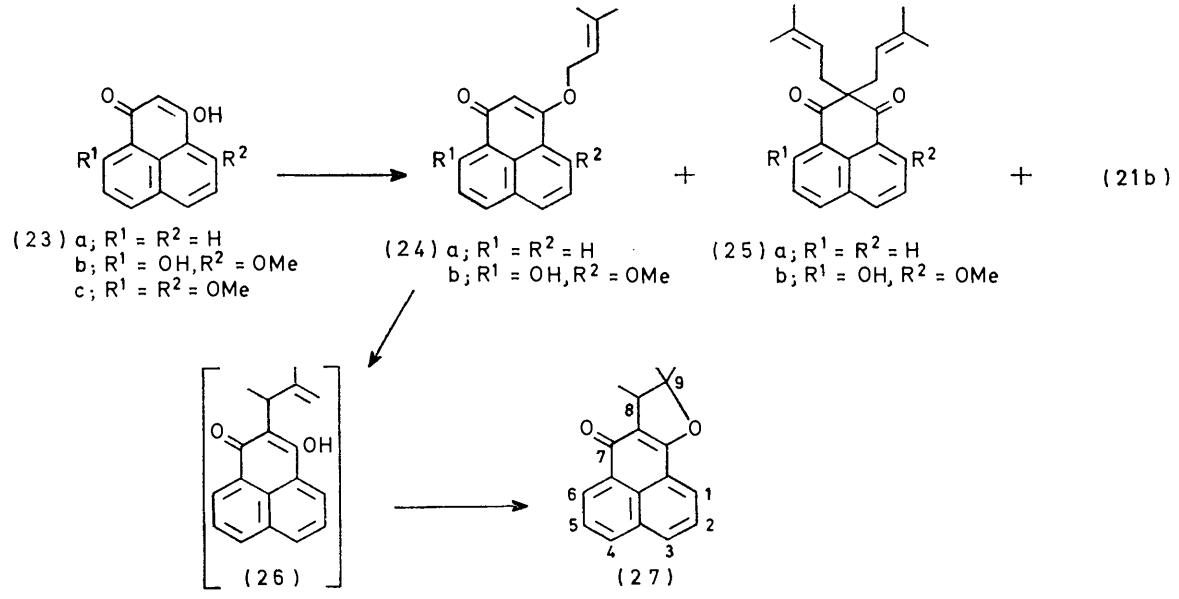
isolate a pure sample of the bromophenalenone (13c) by treatment of the bromide (9b) with polyphosphoric acid by conjugate addition of the hydroxy-group to the enone system followed by elimination of hydrogen bromide to give the phenalenone (21a).

A successful preparation of the phenalenone (21a) was achieved utilising as an intermediate the hydroxy-lactone (19), which was prepared in high yield (95%) by Reformatsky reaction between 2,7-dimethoxy-1-naphthaldehyde (3) and 2-bromo-3,3-dimethylpentan-4-olide (18b). A mixture of the diastereoisomeric bromolactones (18b), in a ratio of 2 : 1 as judged by n.m.r. spectroscopy, was obtained in a yield of 73% by bromination of the substituted valerolactone (18a) with bromine and red phosphorus. The mixture of diastereoisomers was used without separation.

The lactone (18a) has been reported [13] as the end product, in an overall yield of 26%, of a four-step sequence from the acetylenic ester (20a); the latter is obtainable from 2-methylbut-3-yn-2-ol (20b) in two steps in a yield of 15%.[14] In the present work the lactone (18a) was prepared from the readily accessible 3-acetoxy-2,2-dimethylbutyric acid (16) [15] in an overall yield of 59% by saponification of the ester (17) formed by Arndt–Eistert homologation.

Oxidation of the alcohol (19) was accomplished (75% yield) by treatment with a mixture of dimethyl sulphoxide and acetic anhydride,[16] and the ketone (22) thus obtained was cyclised to the phenalenone (21a) (79% yield) with polyphosphoric acid.

An alternative method for the preparation of compounds of the general structure (21), in which substitution of the ethereal side chain into the phenalenone nucleus is achieved by a Claisen rearrangement, was also



we were unable to prepare the derived alcohol (14b) which might be expected to undergo acid-catalysed cyclisation realised. Treatment of 3-hydroxyphenalenone (23a) with 3-methylbut-2-enyl bromide and potassium carbon-

[13] N. R. Easton and R. D. Dillard, *J. Org. Chem.*, 1962, **27**, 3602.

[14] O. K. Behrens, J. Corse, D. E. Huff, R. G. Jones, Q. F. Soper, and C. W. Whitehead, *J. Biol. Chem.*, 1948, **175**, 771.

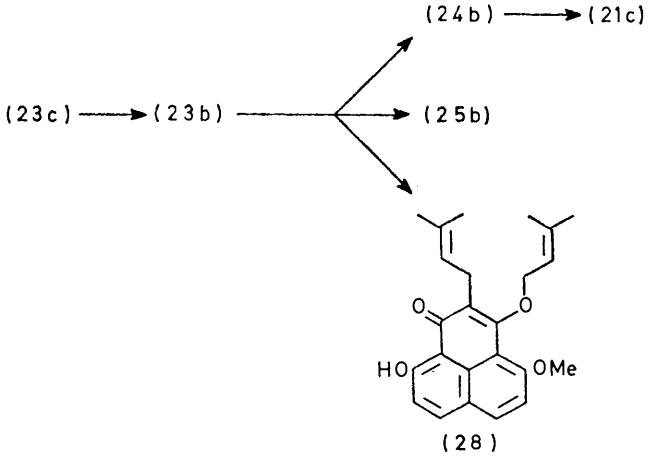
[15] M. A. Courtot, *Bull. Soc. chim. France*, 1906, **35**, 111.

[16] J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, 1967, **89**, 2416.

ate in acetone under reflux gave, in addition to the required 3-methylbut-2-enyl ether (24a), the product (25a) of bis-*C*-alkylation, and the cyclic ether (21b). All three compounds were obtained in low yield, the last-named arising presumably by cyclisation of the product formed by Claisen rearrangement of the ether (24a). In the hope of trapping as its butyrate the initial phenol formed by Claisen rearrangement, the ether (24a) was heated for 8 h at 185° in a mixture of *NN*-diethylaniline and butyric anhydride.[17] The only material isolated, however, in a yield of 74%, was 8,9-dihydro-8,9,9-trimethylphenaleno[1,2-*b*]furan-7-one (27), formed by cyclisation of the compound (26) arising by an abnormal Claisen rearrangement.[18]

The cyclic ethers (21b) and (27) were readily distinguished by their n.m.r. spectra. The quartet assigned to the furan methine proton appeared at τ 5·36 in the former and at 6·72 in the latter in accord with observations on similar systems.[19]

Application of the Claisen rearrangement was further explored using 3,9-dihydroxy-4-methoxyphenalenone (23b) as starting material. This compound was readily prepared by a Friedel–Crafts reaction between 2,7-dimethoxynaphthalene and malonyl chloride in nitrobenzene in the presence of aluminium chloride. It could also be obtained by hydrolysis with dilute hydrochloric acid of the dimethyl ether (23c), which is formed by the action of malonic acid on 2,7-dimethoxynaphthalene in the presence of polyphosphoric acid.



(28)

Treatment of the dihydroxyphenalenone (23b) with 3-methylbut-2-enyl bromide and potassium carbonate in acetone gave the required 3-methylbut-2-enyl ether (24b) as the major product (41%), together with smaller amounts of the dialkylated compounds (25b) (22%) and (28) (19%). When the ether (24b) was heated at 155° in dimethylformamide the phenalenone (21c) was obtained in a yield of 72%. The structure of the product followed from its n.m.r. spectrum; it exhibited the furan methine quartet at τ 5·30 (indicating that the Claisen rearrangement had followed the normal course) and the phenolic hydroxy-signal at τ −7·40, which implies a strong intramolecular hydrogen bond between the carbonyl and hydroxy-groups and excludes the other possible cyclic ether structure (21d).

EXPERIMENTAL

M.p.s were measured on a Kofler hot-stage apparatus. I.r. spectra were recorded on a Unicam SP 200 or 1000 G spectrophotometer or on a Perkin-Elmer 125 instrument and refer to KCl discs unless stated otherwise. U.v. spectra were recorded on a Unicam SP 800 spectrophotometer (95% ethanol as solvent). N.m.r. spectra were recorded on a Varian A60A instrument with deuteriochloroform as solvent, unless specified otherwise. Mass spectra were recorded on an A.E.I. MS 902 spectrometer. T.l.c. was carried out using plates coated with Merck Kieselgel G or GF_{254}. Light petroleum refers to the fraction of boiling range 60—80°. Solutions in organic solvents were dried with anhydrous sodium sulphate or magnesium sulphate.

4-(2,7-*Dimethoxy*-1-*naphthyl*)-3-*ethoxycarbonyl*-2,2-*dimethylbutan*-4-*olide* (4).—Zinc wool (1 g) was added to a solution of diethyl α-bromo-ββ-dimethylsuccinate (2·81 g) and 2,7-dimethoxy-1-naphthaldehyde (3) (2·16 g) in dry benzene (10 ml), and the mixture was stirred and heated under reflux for 3 h, cooled, and decomposed with dilute sulphuric acid. The organic layer was separated, washed with water, dried, and evaporated *in vacuo*. The residue was crystallised from benzene–light petroleum to give the *lactone* (4) (2·57 g, 69%) as crystals, m.p. 132—133° (Found: C, 67·7; H, 6·3. $C_{21}H_{24}O_6$ requires C, 67·75; H, 6·5%), $\lambda_{max.}$ 238, 279, 315, 322, and 331 nm (log ε 4·49, 3·80, 3·30, 3·15, and 3·26); $\nu_{max.}$ 1730 and 1763 cm^{-1}; τ 2·2—3·4 (5H, m, ArH), 5·7—6·3 (4H, m, 3-H, 4-H, and $CO_2{\cdot}CH_2{\cdot}CH_3$), 6·06 and 6·10 (each 3H, s, OMe), 8·42 and 8·66 (each 3H, s, CMe_2), and 8·79 (3H, t, *J* 7 Hz, $CO_2{\cdot}CH_2{\cdot}CH_3$).

4-(2,7-*Dimethoxy*-1-*naphthyl*)-3-*ethoxycarbonyl*-2,2-*dimethylbut*-3-*enoic Acid* (7a).—To a solution of potassium t-butoxide, prepared by dissolving potassium (2·15 g) in t-butyl alcohol (45 ml), were added 2,7-dimethoxy-1-naphthaldehyde (3) (10·8 g) and diethyl αα-dimethylsuccinate (15·15 g) and the mixture was heated under reflux in an atmosphere of nitrogen for 30 min, then acidified with 6N-hydrochloric acid and extracted with ether. The extract was washed several times with dilute sodium carbonate solution then with water, dried, and evaporated under reduced pressure to give the *acid* (7a) (14·6 g, 79%), which crystallised from benzene–light petroleum, m.p. 145—146° (Found: C, 67·6; H, 6·35. $C_{21}H_{24}O_6$ requires C, 67·75; H, 6·5%), $\lambda_{max.}$ 215, 239, 308, 318, and 331 nm (log ε 4·36, 4·81, 2·72, 2·73, and 2·72); $\nu_{max.}$ 1634, 1712, and 1740 cm^{-1}; τ 2·3—3·2 (6H, m, 5 × ArH and olefinic proton), 6·12 and 6·18 (each 3H, s, OMe), 6·36 (2H, q, *J* 7 Hz, $CO_2{\cdot}CH_2{\cdot}CH_3$), 8·38 (6H, s, CMe_2), and 9·57 (3H, t, *J* 7 Hz, $CO_2{\cdot}CH_2{\cdot}CH_3$).

2-(4,9-*Dimethoxy*-1-*oxophenalen*-2-*yl*)-2-*methylpropionic Acid* (8a).—(*a*) The lactone ester (4) (200 mg) was stirred with polyphosphoric acid (5 g) at 100°; further additions of

[17] *Cf.* A. Jefferson and F. Scheinmann, *J. Chem. Soc.* (*C*), 1969, 243; R. D. H. Murray and M. M. Ballantyne, *Tetrahedron*, 1970, **26**, 4667.

[18] H. J. Shine, 'Aromatic Rearrangements,' Elsevier, London, 1967, pp. 89—123.

[19] T. R. Chamberlain and M. F. Grundon, *J. Chem. Soc.* (*C*), 1971, 910.

polyphosphoric acid (2 g) were made after 30 mm and after 1 h. The mixture was heated at 100° for 16 h, then hydrolysed with water and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo* to give the *keto-acid* (8a) (145 mg, 83%) as a yellow powder, which crystallised from ethanol as yellow prisms, m.p. 234—235° (Found: C, 69·35; H, 5·65%; M^+, 326·1167. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·55%; M, 326·1154), $\lambda_{max.}$ 208, 230, 264, 384, and 419 nm (log ε 4·41, 4·14, 4·35, 4·22, and 4·04); $\nu_{max.}$ (Nujol) 1631 and 1731 cm^{-1}.

The derived *methyl ester* (8b) was obtained, by treatment with ethereal diazomethane, as yellow crystals (from chloroform–light petroleum), m.p. 224—225° (Found: C, 70·3; H, 5·8. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%), $\lambda_{max.}$ 204, 230, 264. 270infl, 280infl, 315, 384, 420, and 441 nm (log ε 4·49, 4·08, 4·21, 4·18, 3·91, 3·28, 4·23, 4·04, and 3·81); $\nu_{max.}$ 1625 and 1727 cm^{-1}; *m/e* 340 (20%, M^+), 325 (15, M^+ — Me), 309 (8, M^+ — OMe), and 281 (100, M^+ — CO_2Me).

The *phenyl ester* (8f) was prepared as follows. Boron trifluoride–ether (0·8 ml) was added to a solution of the acid (8a) (600 mg) and phenol (4 g) in benzene (20 ml), and the mixture was stirred at room temperature for 6 h. More boron trifluoride–ether (0·5 ml), phenol (2 g), and benzene (10 ml) were added and the mixture was left at room temperature for a further 16 h. Water (300 ml) was added and the organic phase was separated, washed successively with dilute sodium hydroxide solution and water, dried, and evaporated under reduced pressure. Recrystallisation of the residue from benzene–light petroleum gave the phenyl ester (8f) (560 mg, 76%) as yellow crystals, m.p. 202—204° (Found: C, 74·75; H, 5·5. $C_{25}H_{22}O_5$ requires C, 74·6; H, 5·5%), $\lambda_{max.}$ 264, 322, 417infl, and 435 nm (log ε 4·44, 3·69, 4·12, and 4·17); $\nu_{max.}$ 1632 and 1760 cm^{-1}; τ 1·52 (1H, s, 3-H), 1·78 and 1·95 (each 1H, d, *J* 9 Hz, 6- and 7-H), 2·5—3·1 (7H, m, CO_2Ph, 5-H, and 8-H), 5·83 and 5·85 (each 3H, s, OMe), and 8·23 (6H, s, CMe_2).

(*b*) The αβ-unsaturated ester (7a) (4 g) was stirred with polyphosphoric acid (50 g) at 100° for 5 min, then a further portion (30 g) of polyphosphoric acid was added and heating was continued for a further 1 h. The reaction was worked up as described in (*a*) to give the keto-acid (8a) (3·3 g, 94%), identical with material obtained as described in (*a*).

(*c*) A mixture of the diester (5a) (46 mg) and polyphosphoric acid (3·5 ml) was heated at 70° under nitrogen with occasional stirring for 4 h. The mixture was cooled in ice and hydrolysed with water, and the products (shown by t.l.c. to contain one major and several minor components) were extracted with chloroform. The major component was isolated by preparative t.l.c. and shown to be the phenalenone (8a) by comparison with authentic material.

Methyl 2-(4-Methoxy-9-methylsulphinylmethyl-1-oxophenalen-2-yl)-2-methylpropionate (8d).—Sodium hydride (715 mg) and dimethyl sulphoxide (20 ml) were stirred at 70—75° for 1 h. Tetrahydrofuran (20 ml) was added to the cooled solution which was then further cooled to 0°, and a solution of the methyl ester (8b) (1 g) in tetrahydrofuran (30 ml) was added dropwise. The deep-red mixture was stirred at room temperature for 30 min, poured into water (200 ml), acidified with dilute hydrochloric acid, and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on a column of Kieselgel G (100 g) (chloroform as eluant) to give unchanged starting material (240 mg) and the *sulphoxide* (8d) (490 mg) as yellow crystals, m.p. 94—96° (from benzene–light petroleum) (Found: S, 8·15. $C_{21}H_{22}O_5S$ requires S, 8·3%), $\lambda_{max.}$ 208, 268, 324, 380, 417, and 437 nm (log ε 4·47, 4·45, 3·61, 3·77, 3·98, and 4·01); $\nu_{max.}$ 1620 and 1730 cm^{-1}; τ 1·59 (1H, s, 3-H), 1·76 (1H, d, *J* 8 Hz, 6- or 7-H), 1·83 (1H, d, *J* 9 Hz, 6- or 7-H), 2·31 (1H, d, *J* 8 Hz, 5- or 8-H), 2·52 (1H, d, *J* 9 Hz, 5- or 8-H), 4·58 and 5·38 (each 1H, d, *J* 12 Hz, CH_2·SOMe), 5·80 (3H, s, OMe), 6·33 (3H, s, CO_2Me), 7·27 (3H, s, SOMe), and 8·42 (6H, s, CMe_2); *m/e* 386 (1%, M^+) and 323 (100, M^+ — SOMe).

Methyl 2-(4-Methoxy-9-methyl-1-oxophenalen-2-yl)-2-methylpropionate (8e).—A solution of the sulphoxide (8d) (150 mg) in ethanol (10 ml) was shaken for 10 min with Raney nickel (1 g), filtered, and evaporated under reduced pressure. The residue was taken up in chloroform and the solution was washed with water, dried, and evaporated. The product was chromatographed on alumina (10 g; grade 3) (benzene as eluant) to afford the *ester* (8e) (117 mg, 93%) as bright yellow crystals, m.p. 170—171° (from benzene–light petroleum) (Found: C, 74·2; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%), $\lambda_{max.}$ 207, 264, 319, 374, 402, and 421 nm (log ε 4·56, 4·50, 3·67, 3·95, 4·15, and 4·19); $\nu_{max.}$ 1622 and 1734 cm^{-1}; τ 1·57 (1H, s, 3-H), 1·88 (1H, d, *J* 9 Hz, 6- or 7-H), 1·88 (1H, d, *J* 8 Hz, 6- or 7-H), 2·44 (1H, d, *J* 8 Hz, 5- or 8-H), 2·57 (1H, d, *J* 9 Hz, 5- or 8-H), 5·83 (3H, s, OMe), 6·28 (3H, s, CO_2Me), 6·97 (3H, s, ArMe), and 8·38 (6H, s, CMe_2).

Reduction of the Methyl Ester (8e).—A solution of the ester (8e) (350 mg) and lithium aluminium hydride (200 mg) in ether (70 ml) was kept at −78° for 1 h, a further portion (200 mg) of lithium aluminium hydride was added, and the mixture was kept at −78° for a further 2 h. It was then allowed to warm to room temperature, and water was added, followed by dilute hydrochloric acid. The mixture was extracted with chloroform, and the extract was washed with water, dried, and evaporated *in vacuo*. Chromatography of the residue on a column of Kieselgel G (50 g) (30% ether–70% benzene as eluant) gave, in addition to unchanged starting material (70 mg), two reduction products.

The product of higher R_F value was recrystallised from benzene–light petroleum to give 2-(2-hydroxy-1,1-dimethylethyl)-4-methoxy-9-methylphenalen-1-one (12a) (130 mg) as yellow crystals, m.p. 175—176° (Found: M^+, 269. $C_{19}H_{20}O_3$ requires M, 269), $\lambda_{max.}$ 265, 322, 377infl, 403infl, and 422 nm (log ε 4·40, 3·30, 3·77, 3·94, and 3·96); $\nu_{max.}$ 1586, 1600, 1620, and 3400 cm^{-1}; τ 1·55 (1H, s, 3-H), 1·91 (1H, d, *J* 9·5 Hz, 6- or 7-H), 1·92 (1H, d, *J* 8·5 Hz, 6- or 7-H), 2·45 (1H, d, *J* 8·5 Hz, 5- or 8-H), 2·63 (1H, d, *J* 9·5 Hz, 5- or 8-H), 5·84 (3H, s, OMe), 6·08 (2H, s, CH_2·OH), 6·1br (1H, s, exchangeable with D_2O, OH), 6·98 (3H, s, Ar*Me*), and 8·52 (6H, s, CMe_2). Treatment with acetic anhydride and pyridine overnight at room temperature gave the *acetate* (12b), which crystallised from benzene–light petroleum; m.p. 137—138° (Found: C, 74·0; H, 6·65. $C_{21}H_{22}O_4$ requires C, 74·5; H, 6·55%), $\lambda_{max.}$ 264, 335, and 418 nm (log ε 4·48, 3·83, and 4·15); $\nu_{max.}$ 1585, 1600, 1615, and 1720 cm^{-1}; τ 1·64 (1H, s, 3-H), 1·93 (1H, d, *J* 9·5 Hz, 6- or 7-H), 1·95 (1H, d, *J* 8·5 Hz, 6- or 7-H), 2·47 (1H, d, *J* 8·5 Hz, 5- or 8-H), 2·63 (1H, d, *J* 9·5 Hz, 5- or 8-H), 5·33 (2H, s, CH_2·OAc), 5·83 (3H, s, OMe), 6·96 (3H, s, Ar*Me*), 8·01 (3H, s, O·CO·CH_3), and 8·48 (6H, s, CMe_2).

The product of lower R_F value was recrystallised from benzene–petroleum to give 8-(2-*hydroxy*-1,1-*dimethylethyl*)-6-*methylphenalen*-1-*one* (11) (38 mg) as yellow crystals, m.p. 178—179° (Found: C, 81·15; H, 6·75. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·7%), $\lambda_{max.}$ 257, 267, 321, 375infl, and 400 nm

(log ε 4·49, 4·48, 3·70, 4·10, and 4·11); $\nu_{max.}$ 1570, 1582, 1610, 1628, and 3300 cm^{-1}; τ 1·14 (1H, d, *J* 2 Hz, 9-H), 1·45 (1H, d, *J* 2 Hz, 7-H), 2·30 (1H, d, *J* 10 Hz, 3-H), 2·32 (1H, d, *J* 7 Hz, 4- or 5-H), 2·53 (1H, d, *J* 7 Hz, 4- or 5-H), 3·36 (1H, d, *J* 10 Hz, 2-H), 6·13 (2H, s, CH_2·OH), 7·17 (3H, s, Ar*Me*), 7·90br (s, exchangeable with D_2O, OH), and 8·46 (6H, s, CMe_2); *m/e* 266 (13%, M^+) and 235 (100, $M^+ - CH_2$·OH).

8,9-*Dihydro*-1,8,8-*trimethylphenaleno*[1,2-b]*furan*-6-*one* (15).—Dilute hydrochloric acid (4 ml; 2N) was added to a solution of the alcohol (12a) (38 mg) in dioxan (4 ml), and the clear solution was left at room temperature for 24 h. Water (100 ml) was added, and the mixture was extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo*; the residue was purified by preparative t.l.c. (p.l.c.) [20 × 20 cm plate, 0·5 mm coating of Kieselgel G; 2% methanol–98% chloroform as eluant] to give the *phenalenofuran* (15) (30 mg), which crystallised from benzene–light petroleum as yellow crystals, m.p. 160—161° (Found: C, 81·0; H, 6·0. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%), $\lambda_{max.}$ 264infl, 271, 338, and 430 nm (log ε 4·45, 4·53, 3·92, and 4·29); $\nu_{max.}$ (Nujol) 1575, 1612, and 1630 cm^{-1}; τ 1·32 (1H, s, 7-H), 2·24 (1H, d, *J* 10 Hz, 4-H), 2·28 (1H, d, *J* 7·5 Hz, 3-H), 2·63 (1H, dq, *J* 7·5 and 1 Hz, 2-H), 3·21 (1H, d, *J* 10 Hz, 5-H), 5·40 (2H, s, 9-H), 7·08br (3H, s, Ar*Me*), and 8·52 (6H, s, CMe_2); *m/e* 264 (56%, M^+) and 249 (100, M^+ — Me).

Phenyl 2-(4-*Methoxy*-1-*oxophenalen*-2-*yl*)-2-*methylpropionate* (8g).—A solution of the phenyl ester (8f) (201 mg) in tetrahydrofuran (4 ml) was stirred under nitrogen at room temperature for 24 h with lithium tri-t-butoxyaluminium hydride (127 mg), more tetrahydrofuran was then added to dissolve precipitated material, and stirring was continued for a further 24 h. After the addition of a second portion (127 mg) of lithium tri-t-butoxyaluminium hydride the mixture was stirred for a third period of 24 h, then poured into water, acidified with dilute hydrochloric acid, and extracted with chloroform. The extract was washed with water, dried, and evaporated under reduced pressure. From the residue was obtained by preparative t.l.c. (20 × 20 cm plate, coated with 16 g of Kieselgel G; chloroform as eluant) unchanged starting material (164 mg) and the *phenyl ester* (8 g) (30 mg), which gave yellow crystals, m.p. 159—160° (from benzene–light petroleum) (Found: C, 77·5; H, 5·55. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%), $\lambda_{max.}$ 210, 264, 310, 321, 417, and 435 nm (log ε 4·45, 4·44, 3·62, 3·69, 4·12, and 4·17); $\nu_{max.}$ 1632 and 1760 cm^{-1}; τ 1·14 (1H, dd, *J* 7·5 and 1·5 Hz, 9-H), 1·61 (1H, s, 3-H), 1·80 (1H, dd, *J* 7·5 and 1·5 Hz, 7-H), 1·90 (1H, d, *J* 9 Hz, 6-H), 2·28 (1H, t, *J* 7·5 Hz, 8-H), 2·5—2·8 (6H, m, CO_2Ph and 5-H), 5·89 (3H, s, OMe), and 8·26 (6H, s, CMe_2).

Reduction of the Methyl Ester (8b).—The ester (8b) (710 mg) and lithium aluminium hydride (42 mg) in tetrahydrofuran (20 ml) were stirred at 0° for 20 min and then at room temperature for 1·5 h. The mixture was poured into water, acidified (dilute hydrochloric acid), and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on a column of Kieselgel G (70 g) (chloroform as eluant) to give unchanged starting material (212 mg) and two reduction products. The material of higher R_F value was the *keto-ester* (8h) (280 mg), which gave yellow crystals, m.p. 170—171° (from benzene–light petroleum) (Found: C, 73·6; H, 6·0. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·85%), $\lambda_{max.}$ 206, 265, 309infl, 321, 417infl, and 436 nm (log ε 4·49, 4·45, 3·55, 3·66, 4·11, and 4·16); $\nu_{max.}$ 1626 and 1727 cm^{-1}; τ 1·18 (1H, dd, *J* 7·5 and 1·5 Hz, 9-H), 1·61 (1H, s, 3-H), 1·76 (1H, dd, *J* 7·5 and 1·5 Hz, 7-H), 1·86 (1H, d, *J* 9·5 Hz, 6-H), 2·25 (1H, t, *J* 7·5 Hz, 8-H), 2·58 (1H, d, *J* 9·5 Hz, 5-H), 5·83 (3H, s, OMe), 6·25 (3H, s, CO_2Me), and 8·36 (3H, s, CMe_2).

The material of lower R_F value (70 mg) was recrystallised from benzene–light petroleum to give 2-(2-*hydroxy*-1,1-*dimethylethyl*)-4-*methoxyphenalen*-1-*one* (10) (70 mg) as yellow crystals, m.p. 164—166° (Found: C, 76·7; H, 6·55. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%), $\lambda_{max.}$ 208, 266, 322, 418, and 436 nm (log ε 4·42, 4·44, 3·65, 4·03, and 4·06); $\nu_{max.}$ 1630 and 3390 cm^{-1}; τ 1·15 (1H, dd, *J* 7·5 and 1·5 Hz, 9-H), 1·55 (1H, s, 3-H), 1·80 (1H, dd, *J* 8 and 1·5 Hz, 7-H), 1·89 (1H, d, *J* 9 Hz, 6-H), 2·28 (1H, dd, *J* 7·5 and 8 Hz, 8-H), 2·59 (1H, d, *J* 9 Hz, 5-H), 5·83 (3H, s, OMe), 6·08 (2H, s, OCH_2), and 8·54 (6H, s, CMe_2).

Methyl 3-*Ethoxycarbonyl*-2,2-*dimethyl*-4-(5,6,7,8-*tetrahydro*-2,7-*dimethoxy*-1-*naphthyl*)*butyrate* (6b).—(*a*) A solution of the unsaturated ester (7a) (2 g) in dioxan (100 ml) was hydrogenated over 10% palladised charcoal (2 g) at 2 atm for 44 h to give an oil, which was dissolved in chloroform (25 ml) and methylated with ethereal diazomethane. Removal of solvent gave the *diester* (6b) (2 g, 95%), b.p. 160° at 0·1 mmHg. This material, although chromatographically homogeneous, was a 2 : 1 mixture of diastereoisomers, as judged by its n.m.r. spectrum; (Found: C, 67·65; H, 8·25. $C_{23}H_{32}O_6$ requires C, 67·3; H, 8·2%); $\nu_{max.}$ (liquid film) 1731 and 1736 cm^{-1}; τ 2·93 and 3·24 (each 1H, d, *J* 8·5 Hz, ArH), 6·00 and 6·03 (total 2H, 2q, ratio 2 : 1, *J* 7 Hz, CO_2·CH_2Me), 6·16 (3H, s, ArO*Me*), 6·25 and 6·23 (total 3H, 2s, ratio 2 : 1, 7-OMe), 6·50 (3H, s, CO_2Me), 6·7—7·5 (6H, m, benzylic CH_2), 7·8—8·4 (2H, m, 6-CH_2), 8·58 and 8·63 (each 3H, s, CMe_2), and 8·97 and 9·00 (total 3H, 2t, ratio 2 : 1, *J* 7 Hz, CO_2·CH_2*Me*).

(*b*) A solution of the unsaturated ester (7a) (140 mg) in glacial acetic acid (10 ml) was hydrogenated over 10% palladised charcoal at room temperature and pressure for 72 h to give the tetralin (6a) (142 mg, 100%), which was characterised as its methyl ester (6b), identical with material obtained as described in (*a*).

Methyl 4-(2,7-*Dimethoxy*-1-*naphthyl*)-3-*ethoxycarbonyl*-2,2-*dimethylbutyrate* (5a).—A solution of the tetralin (6b) (840 mg) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (1·02 g) in benzene (20 ml) was stirred for 4 h at room temperature. The mixture was passed through a short column of alumina (grade 3) (benzene as eluant) to give the *diester* (5a) (832 mg, 100%), which afforded white crystals, m.p. 101—102° (from light petroleum) (Found: C, 68·15; H, 7·1. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·25%); $\nu_{max.}$ (Nujol) 1715 and 1740 cm^{-1}; τ 2·24 (2H, d, *J* 9 Hz, 4- and 5-ArH), 2·56 (1H, d, *J* 3 Hz, 8-ArH), 2·82 (1H, d, *J* 9 Hz, 3-ArH), 2·90 (1H, dd, *J* 3 and 9 Hz, 6-ArH), 5·99 and 6·04 (each 3H, s, ArO*Me*), 6·28 (3H, s, CO_2Me), 6·1—7·0 (5H, m, CO_2·CH_2Me, CH, and CH_2), 8·51 and 8·57 (each 3H, s, CMe_2), and 9·23 (3H, t, CO_2·CH_2*Me*); *m/e* 388 (27%, M^+) and 201 (100, $ArCH_2^+$).

4-(2,7-*Dimethoxy*-1-*naphthyl*)-3-*ethoxycarbonyl*-2,2-*dimethylbutyric Acid* (5b).—A solution of the diester (5a) (700 mg) and potassium hydroxide (1 g) in ethanol (20 ml) and water (10 ml) was heated under reflux for 4 h, most of the ethanol was distilled off under reduced pressure, and the aqueous solution was acidified (dilute hydrochloric acid) and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo* to afford the *acid* (5b) (620 mg, 92%), which gave white crystals, m.p.

145—146° (from benzene–light petroleum) (Found: C, 67·7; H, 7·0. $C_{21}H_{26}O_6$ requires C, 67·4; H, 7·0%); $\nu_{max.}$ 1695 and 1726 cm^{-1}; τ 0·55br (1H, s, exchangeable with D_2O, CO_2H), 2·43 (2H, d, *J* 9 Hz, 4- and 5-ArH), 2·80 (1H, d, *J* 2·5 Hz, 8-ArH), 3·01 (1H, d, *J* 9 Hz, 3-ArH), 3·10 (1H, dd, *J* 9 and 2·5 Hz, 6-ArH), 6·12 and 6·14 (each 3H, s, ArO*Me*), 6·0—7·1 (5H, m, $CO_2{\cdot}CH_2Me$, CH, and CH_2), 8·55 (6H, s, CMe_2), and 9·31 (3H, t, *J* 7 Hz, $CO_2{\cdot}CH_2Me$); *m/e* 374 (35%, M^+) and 201 (100, $ArCH_2^+$).

Ethyl 5-Chloro-2-(2,7-dimethoxy-1-naphthylmethylene)-3,3-dimethyl-4-oxovalerate (7c).—A solution of the acid (7a) (2·2 g) and oxalyl chloride (15 ml) in dry benzene (15 ml) was stirred at room temperature for 20 min, excess of oxalyl chloride and benzene were removed under reduced pressure, and a solution of the residual acid chloride in benzene (20 ml) was added to a stirred ethereal solution of diazomethane (0·018 mol) at 0°. The mixture was stirred at room temp. for 20 min, then evaporated at 30° under reduced pressure. The residual diazo-ketone (7b) ($\nu_{max.}$ 2130 cm^{-1}) was dissolved in ether (30 ml) and dry hydrogen chloride gas was passed through the stirred solution for 30 min at 0°. Removal of solvent afforded a pale yellow oil which was chromatographed on a column of Kieselgel G (70 g) (chloroform as eluant) to give the *chloro-keto-ester* (7c) (2 g, 84%) as white crystals, m.p. 125—126° (from benzene–light petroleum) (Found: C, 65·4; H, 6·25; Cl, 8·75. $C_{22}H_{25}ClO_5$ requires C, 65·25; H, 6·2; Cl, 8·75%), $\lambda_{max.}$ 239 and 325—330 nm (log ε 4·70 and 3·80); $\nu_{max.}$ 1619, 1700, and 1730 cm^{-1}; τ 2·27 (1H, d, *J* 9 Hz, 4- or 5-ArH), 2·32 (1H, d, *J* 9·5 Hz, 4- or 5-ArH), 2·85—3·10 (4H, m, 3-, 6-, and 8-ArH, and olefinic H), 5·35 (2H, s, CH_2Cl), 6·12 and 6·13 (each 3H, s, OMe), 6·23 (2H, q, $CO_2{\cdot}CH_2Me$), 8·48 (6H, s, CMe_2), and 9·40 (3H, t, *J* 7 Hz, $CO_2{\cdot}CH_2Me$).

Ethyl 2-(2,7-Dimethoxy-1-naphthylmethylene)-3,3-dimethyl-4-oxovalerate (7d).—A solution of the chloro-ketone (7c) (7 g) in glacial acetic acid (80 ml) was shaken at room temp. for 1 h with zinc dust (30 g) and potassium iodide (7 g). Water (20 ml) was added and the mixture was shaken for a further 2 min and filtered; the residue was washed with chloroform. The chloroform solution was washed with water and dried, and evaporated under reduced pressure to afford the *keto-ester* (7d) (6·4 g, 100%), which gave white crystals, m.p. 78—79° (from benzene–light petroleum) (Found: C, 71·6; H, 7·0. $C_{22}H_{26}O_5$ requires C, 71·35; H, 7·1%), $\lambda_{max.}$ 238 nm (log ε 4·77); $\nu_{max.}$ 1620, 1693, and 1712 cm^{-1}; τ 2·30 and 2·33 (each 1H, d, *J* 9 Hz, 4- and 5-ArH), 2·86—3·12 (4H, m, 3-, 6-, and 8-ArH, and olefinic H), 6·12 (6H, s, OMe), 6·27 (2H, q, *J* 7 Hz, $CO_2{\cdot}CH_2Me$), 7·64 (3H, s, MeCO), 8·53 (6H, s, CMe_2), and 9·43 (3H, t, *J* 7 Hz, $CO_2{\cdot}CH_2Me$); *m/e* 370 (20%, M^+), 355 (10, M^+ — Me), 327 (50, M^+ — MeCO), and 281 (100).

2-(2,7-Dimethoxy-1-naphthylmethylene)-4-hydroxy-3,3-dimethylpentan-4-olide (9a).—A solution of the methyl ketone (7d) (6·4 g) in ethanol (70 ml) and aqueous sodium hydroxide (60 ml; 2N) was left at room temp. for 30 min, then diluted with water, acidified (dilute hydrochloric acid), and extracted with chloroform. The extract was washed with water, dried, and evaporated under reduced pressure to yield the *hydroxy-lactone* (9a) (5·91 g, 100%), which gave white crystals, m.p. 166—167° (from benzene) (Found: C, 70·35; H, 6·55. $C_{20}H_{22}O_5$ requires C, 70·15; H, 6·5%), $\lambda_{max.}$ 238 nm (log ε 4·76); $\nu_{max.}$ 1625, 1739, and 3350 cm^{-1}; τ 2·29 (1H, d, *J* 9 Hz, 4- or 5-ArH), 2·36 (1H, d, *J* 10 Hz, 4- or 5-ArH), 2·87—3·14 (4H, m, 3-, 6-, and 8-ArH, and olefinic H), 6·11 and 6·18 (each 3H, s, OMe), 8·56 (6H, s, CMe_2), and 8·86 [3H, s, *Me*C(OH)O–], *m/e* 342 (53%), M^+) and 299 (100, M^+ —MeCO).

2-(1,1-Dimethyl-2-oxopropyl)-4,9-dimethoxyphenalen-1-one (13a).—(*a*) A solution of the hydroxy-lactone (9a) (513 mg) in aqueous sodium hydroxide (15 ml; 0·1N) was evaporated under reduced pressure. Benzene (15 ml) and oxalyl chloride (4 ml) were added to the residue and the mixture was stirred for 20 min at room temp, then filtered and evaporated *in vacuo*. A solution of the residue in carbon disulphide (20 ml) was heated under reflux for 30 min with tin(IV) chloride (4 ml), and the solvent was removed *in vacuo*. Water (30 ml) was added, the mixture was made alkaline with dilute sodium hydroxide solution, then warmed to dissolve the red precipitate, and extracted with chloroform. The extract was washed with water, dried, and evaporated under reduced pressure. Chromatography of the residue on alumina (grade 3) [benzene as eluant initially, gradually changing to benzene–chloroform (6 : 4)] gave the *diketone* (13a) (248 mg, 51%), which crystallised from benzene–light petroleum as yellow prisms, m.p. 223—224° (Found: C, 73·95; H, 6·15. $C_{20}H_{20}O_4$ requires C, 74·05; H, 6·2%), $\lambda_{max.}$ 228, 263, 389, 424, and 451 nm (log ε 4·31, 4·33, 4·33, 4·16, and 3·96); $\nu_{max.}$ (Nujol) 1632 and 1700 cm^{-1}; τ 1·74 (1H, s, 3-ArH), 1·91 and 2·07 (each 1H, d, *J* 9 Hz, 6- and 7-ArH), 2·72 and 2·82 (each 1H, d, *J* 9 Hz, 5- and 8-ArH), 5·88 and 5·92 (each 3H, s, OMe), 7·87 (3H, s, MeCO), and 8·52 (6H, s, CMe_2); *m/e* 324 (15%, M^+), 309 (3, M^+ — Me), and 281 (100, M^+ — MeCO).

(*b*) A mixture of the hydroxy-lactone (9a) (150 mg) and polyphosphoric acid (10 ml) was stirred at 70° for 30 min, then cooled, hydrolysed with water, and extracted with chloroform. The extract was washed with water, dried, and evaporated under reduced pressure. P.l.c. [20 × 20 cm plate, 0·5 mm coating of Kieselgel G; chloroform–methanol (19 : 1) as eluant] gave the diketone (13a) (21 mg, 15%), identical with material obtained as described in (*a*).

(*c*) A solution of the alcohol (14a) (26 mg) and DDQ (20 mg) in benzene (2 ml) was heated under reflux for 2 h, then filtered through a column of alumina (grade 3). P.l.c. afforded the diketone (7 mg), identical with material obtained in (*a*) and (*b*). A similar result was obtained when a solution of the alcohol (14a) (26 mg) in tetrahydrofuran (2 ml) was treated with lithium tri-t-butoxyaluminium hydride (20 mg) and DDQ (19 mg), and the resulting deep red mixture was stirred at room temp. for 20 h.

2-(1,1-Dimethyl-2-oxopropyl)-9-isopropoxy-4-methoxyphenalen-1-one (13b).—A solution of the methyl ketone (13a) (70 mg) and aluminium isopropoxide (2 g) in propan-2-ol (10 ml) was distilled slowly, with more propan-2-ol being added to maintain the volume above 6 ml. After 1 h, the solvent was removed under reduced pressure, and dilute hydrochloric acid was added. The aqueous solution was then made alkaline with dilute aqueous sodium hydroxide, and extracted with chloroform. The extract was washed with water dried, and evaporated *in vacuo*. P.l.c. [20 × 20 cm plate, 16 g Kieselgel G; chloroform–methanol (95 : 5) as eluant] afforded the *diketone* (13b) (75 mg, 99%), which gave yellow crystals, m.p. 155—157° (from benzene–light petroleum) (Found: *m/e* 352·1672. $C_{22}H_{24}O_4$ requires *M*, 352·1674), $\lambda_{max.}$ 212, 230, 265, 389, 420, and 445 nm (log ε 4·30, 4·23, 4·27, 4·27, 4·09, and 3·85); $\nu_{max.}$ (Nujol) 1615, 1629, and 1698 cm^{-1}; τ 1·75 (1H, s, 3-ArH), 1·99 and 2·10 (each 1H, d, *J* 9 Hz, 6- and 7-ArH), 2·76 and 2·85 (each 1H, d, *J* 9 Hz, 5- and 8-ArH), 5·19 (1H, septet, *J* 6 Hz, $O{\cdot}CHMe_2$),

5·94 (3H, s, OMe), 7·95 (3H, s, MeCO), 8·54 (6H, s, MeCO·CMe_2), and 8·54 (6H, d, J 6 Hz, O·CHMe_2); *m/e* 352 (11%, M^+), 347 (2, M^+ − Me), 309 (17, M^+ − MeCO), and 267 (100, M^+ − $CH_3CO{\cdot}CMe_2$).

The same product was obtained when the methyl ketone (13a) (28 mg) was heated under reflux in toluene (10 ml) with aluminium isopropoxide (2 g).

2-(2-*Hydroxy*-1,1-*dimethylpropyl*)-4,9-*dimethoxyphenalen*-1-*one* (14a).—Lithium aluminium hydride was added in five portions (each 30 mg) at hourly intervals to a stirred solution of the methyl ketone (13a) in tetrahydrofuran (10 ml) at −78°. The mixture was stirred at −78° for a further 2 h, then water was added; the mixture was acidified with dilute hydrochloric acid, then made alkaline with dilute aqueous sodium hydroxide, and extracted with chloroform. The extract was washed with water, dried, and evaporated under reduced pressure. P.l.c. [20 × 20 cm plate, 16 g Kieselgel G; chloroform–methanol (19 : 1) as eluant] gave the *hydroxy-ketone* (14a) (27 mg, 77%) as yellow crystals, m.p. 195—196° (from benzene–light petroleum) (Found: C, 73·5; H, 6·75. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%), $\lambda_{max.}$ 211, 229, 265, 388, 425, and 450 nm (log ε 4·45, 4·23, 4·25, 4·21, 4·05, and 3·84); $\nu_{max.}$ (chloroform) 1625 and 3280 cm^{-1}; τ 1·73 (1H, s, 3-ArH), 1·92 and 2·06 (each 1H, d, J 9 Hz, 6- and 7-ArH), 2·70 and 2·81 (each 1H, d, J 9 Hz, 5- and 8-ArH), 4·85br (1H, s, exchangeable with D_2O, OH), 5·84 and 5·91 (each 3H, s, OMe), 6·00 (1H, broad; on addition of D_2O sharpens to q, J 6·5 Hz, CH·OH), 8·51 and 8·56 (each 3H, s, CMe_2), and 8·95 (3H, d, J 6·5 Hz, *Me*CH·OH).

2-[*Bromo*-(2,7-*dimethoxy*-1-*naphthyl*)*methylene*]-4-*hydroxy*-3,3-*dimethylpentan*-4-*olide* (9b).—The hydroxy-lactone (9a) (68 mg) was dissolved in a solution of bromine in glacial acetic acid (4·1 ml; 0·1N). The colour faded immediately, and after 5 min the mixture was poured into water and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo*. The resulting product, homogeneous by t.l.c., was taken up in benzene (10 ml) and heated under reflux for 10 min; removal of the solvent then gave the *bromo-lactone* (9b) (84 mg, 100%), m.p. 192—199° (Found: C, 57·1; H, 4·95; Br, 18·9. $C_{20}H_{21}BrO_5$ requires C, 57·0; H, 5·0; Br, 19·0%); $\nu_{max.}$ (Nujol) 1610, 1660, 1726, and 3340 cm^{-1}; τ 2·29 (2H, d, J 9 Hz, 4- and 5-ArH), 2·53br (1H, s, 8-ArH), 2·89br (1H, d, J 9 Hz, 6-ArH), 2·92 (1H, d, J 9 Hz, 3-ArH), 6·07 and 6·20 (each 3H, s, OMe), 6·86br (1H, s, exchangeable with D_2O, OH), and 8·49, 8·60, and 8·71 (each 3H, s, CMe); *m/e* 422 [0·5%, $M^+(^{81}Br)$], 420 [0·5, $M^+(^{79}Br)$], and 341 (100, M^+ − Br).

Ethyl 4-*Acetoxy*-3,3-*dimethylvalerate* (17).—Thionyl chloride (15 ml) was added to 3-acetoxy-2,2-dimethylbutyric acid (4·3 g); the mixture was left at room temp. for 20 min, then heated under reflux for 1 h, and excess of thionyl chloride was removed under reduced pressure. The residual acid chloride was dissolved in ether (50 ml) and added slowly to ethereal diazomethane (0·06 mol) at 0°. The mixture was stirred at room temp. for 2 h, and the solvent was removed under reduced pressure, at room temp. The diazo-ketone thus obtained was dissolved in dry ethanol (35 ml) at 50°, and silver oxide [half of the amount produced by treating aqueous silver nitrate (30 ml; 10%) with aqueous 2N-sodium hydroxide, washing with water, then with ethanol, and drying at 100°] was added as a slurry in ethanol. After stirring at 60° for 30 min the remaining silver oxide was added in six portions at 5 min intervals, and the mixture was heated under reflux for 2·5 h, then filtered. Ethanol was removed under reduced pressure and the residual oil was distilled (60°; 0·3 mmHg) to give the *ethyl ester* (17) (3·34 g, 63%) (Found: C, 61·15; H, 9·2. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%); $\nu_{max.}$ (film) 1733 cm^{-1}; τ 5·24 [1H, q, J 6·5 Hz, CH(Me)OAc], 5·92 (2H, q, J 7 Hz, $CO_2{\cdot}CH_2Me$), 7·77br (2H, s, $CH_2{\cdot}CO_2Et$), 7·98 (3H, s, OAc), 8·80 (3H, t, J 7 Hz, $CO_2{\cdot}CH_2Me$), 8·85 [3H, d, J 6·5 Hz, CH(*Me*)OAc], and 8·98 (6H, s, CMe_2).

3,3-*Dimethylpentan*-4-*olide* (18a).—Aqueous sodium hydroxide (30 ml; 2N) was added to a solution of ethyl 4-acetoxy-3,3-dimethylvalerate (3·6 g) in ethanol (30 ml), and the reaction vessel was flushed with nitrogen, stoppered, and left overnight at room temp. The solution was acidified and extracted with chloroform; the extract was washed with water, dried, and the solvent was removed *in vacuo* to give, after distillation, the lactone (18a) (2 g, 94%), b.p. 70° at 1 mmHg (lit.,[13] 50° at 0·5 mmHg) (Found: C, 65·15; H, 9·55. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·45%); $\nu_{max.}$ (film) 1780 cm^{-1}; τ 5·76 [1H, q, J 6·5 Hz, CH(Me)O·CO], 7·66 (2H, s, CH_2), 8·75 [3H, d, J 6·5 Hz, CH(*Me*)O·CO], and 8·85 and 8·96 (each 3H, s, CMe_2).

2-*Bromo*-3,3-*dimethylpentan*-4-*olide* (18b).—Bromine (860 mg) was added dropwise to a mixture of red phosphorus (62 mg) and the lactone (18a) (600 mg) at 0°. The mixture was heated to 70°, and more bromine (860 mg) was added dropwise. The mixture was heated at 80° for 3 h. Nitrogen was blown through the cooled mixture until excess of bromine and hydrogen bromide had been removed (1 h), the mixture was again warmed to 80°, and water (0·12 ml) was added. After 5 min, more water (1·3 ml) was added and the mixture was heated under reflux for 4 h. The product was extracted with ether, and the extract washed with water and dried. Removal of solvent gave a light brown oil which was chromatographed on silica gel (50 g, 100—200 mesh) [benzene–chloroform (1 : 1) as eluant] to give a mixture of the diastereoisomeric *bromo-lactones* (18b) (704 mg 73%) (Found: C, 40·25; H, 5·45; Br, 38·3. $C_7H_{11}BrO_2$ requires C, 40·6; H, 5·35; Br, 38·6%); $\nu_{max.}$ (film) 1783 cm^{-1}; the n.m.r. spectrum showed the presence of a pair of diastereoisomers in the approximate ratio 2 : 1, τ (major isomer) 5·54 (1H, s, CHBr), 5·67 [1H, q, J 6·5 Hz, CH(Me)O·CO], 8·62 [3H, d, J 6·5 Hz, CH(*Me*)O·CO], and 8·83 and 8·95 (each 3H, s, CMe_2); the corresponding peaks exhibited by the minor isomer appeared at τ 5·88, 5·51, 8·65, 8·76, and 8·86.

2-[*Hydroxy*-(2,7-*dimethoxy*-1-*naphthyl*)*methyl*]-3,3-*dimethylpentan*-4-*olide* (19).—Zinc wool (46 mg) and a crystal of iodine were added to a solution of 2,7-dimethoxy-1-naphthaldehyde (127 mg) and a mixture of the diastereoisomeric bromo-lactones (18b) (123 mg) in benzene (2 ml) and toluene (2 ml). The mixture was stirred and heated under reflux for 4 h, then cooled, acidified with dilute sulphuric acid, and extracted with benzene. The extract was washed with water, dried, and evaporated *in vacuo* to leave a pale brown oil which was chromatographed on silica gel (20 g, 100—200 mesh) [benzene–chloroform (1 : 1) as eluant] to give the *hydroxy-lactone* (19) (190 mg, 94%) as white crystals, m.p. 145—146° (from benzene–light petroleum) (Found: C, 69·9; H, 7·0. $C_{20}H_{24}O_5$ requires C, 69·75; H, 7·0%), $\lambda_{max.}$ 238 and 278infl nm (log ε 4·17 and 3·50); $\nu_{max.}$ 1740 and 3460 cm^{-1}; τ 2·29 and 2·33 (each 1H, d, J 9 Hz, 4- and 5-ArH), 2·39 (1H, d, J 2·5 Hz, 8-ArH), 2·94 (1H, d, J 9 Hz, 3-ArH), 3·00 (1H, dd, J 9 and 2·5 Hz, 6-ArH), 4·10 (1H, dd, J 8·5 and 4 Hz, collapses to d, J 8·5 Hz, upon shaking with D_2O, CH·OH), 5·07 (1H, d, J 4 Hz,

exchangeable with D_2O, OH), 5·72 [1H, q, *J* 7 Hz, C*H*(Me)-O·CO], 6·07 and 6·12 (each 3H, s, OMe), 6·57 (1H, d, *J* 8·5 Hz, O·CO·C*H*), 8·82 [3H, d, *J* 7 Hz, CH(*Me*)O·CO], and 8·89 and 9·60 (each 3H, s, CMe_2); *m/e* 344 (12%, M^+) and 217 (100, $Ar\overset{+}{C}HOH$).

2-(2,7-*Dimethoxy*-1-*naphthoyl*)-3,3-*dimethylpentan*-4-*olide* (22).—A solution of the hydroxy-lactone (19) (100 mg) in dimethyl sulphoxide (3 ml) and acetic anhydride (1 ml) was left at room temp for 6 h, then poured into ice–water, made alkaline with concentrated ammonium hydroxide, and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo* to yield the *keto-lactone* (22) (75 mg, 75%) as an oil which could not be crystallised (Found: *m/e* 342·1451. $C_{20}H_{22}O_5$ requires *M*, 342·1467); $\nu_{max.}$ 1626, 1684, and 1760 cm^{-1}.

8,9-*Dihydro*-1,6-*dimethoxy*-8,8,9-*trimethylphenaleno*[1,2-b]-*furan*-7-*one* (21a).—The keto-lactone (22) (64 mg) was stirred with polyphosphoric acid (4 ml) at 60° for 20 min; the mixture was cooled, hydrolysed with ice–water, and made alkaline by dropwise addition of concentrated aqueous ammonium hydroxide. The alkaline solution was extracted with chloroform, and the extract was washed with water and dried. Removal of solvent *in vacuo*, followed by p.l.c., [20 × 20 cm plate, 16 g Kieselgel G; chloroform–methanol (97 : 3) as eluant] afforded the *phenalenofuranone* (21a) (48 mg, 79%) which gave yellow crystals, m.p. 227—228° (from benzene–light petroleum) (Found: C, 73·9; H, 6·25. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·15%), $\lambda_{max.}$ 215, 253, 269, 279, 374, and 422 nm (log ε 4·87, 4·74, 4·47, 4·34, 4·73, and 4·13); $\nu_{max.}$ (Nujol) 1610 and 1626 cm^{-1}; τ 2·02 and 2·07 (each 1H, d, *J* 9 Hz, 3- and 4-H), 2·72 and 2·84 (each 1H, d, *J* 9 Hz, 2- and 5-H), 5·46 (1H, q, *J* 6·5 Hz, 9-H), 5·87 and 5·93 (each 3H, s, OMe), 8·44 and 8·67 (each 3H, s, CMe_2), and 8·53 (3H, d, *J* 6·5 Hz, 9-Me).

Alkylation of 3-*Hydroxyphenalenone* (23a) *with* 3-*Methylbut*-2-*enyl Bromide*.—3-Methylbut-2-enyl bromide (270 mg) was added to a suspension of 3-hydroxyphenalenone (23a) (204 mg) and potassium carbonate (196 mg) in acetone (50 ml), and the mixture was heated under reflux for 1 week. More 3-methylbut-2-enyl bromide (100 mg) was then added, and heating was continued for a further 3 weeks. The solvent was removed under reduced pressure and the residue was acidified with dilute hydrochloric acid. The aqueous mixture was extracted with chloroform, and the extract was washed with water, dried, and evaporated *in vacuo* to give a yellow gum, from which three compounds were isolated by p.l.c. (two 20 × 20 cm plates, 16 g Kieselgel G spread on each; chloroform as eluant). From the band of highest R_F, 2,2-*bis*-(3-*methylbut*-2-*enyl*)*phenalene*-1,3(2H)-*dione* (25a) (40 mg, 12%) was obtained as an oil (Found: *m/e* 332·1771. $C_{23}H_{24}O_2$ requires *M*, 332·1776); $\nu_{max.}$ (film) 1620, 1663, and 1687 cm^{-1}; τ 1·55 (2H, dd, *J* 7 and 1·5 Hz, 4- and 9-ArH or 6- and 7-ArH), 1·81 (2H, dd, *J* 8 and 1·5 Hz, 4- and 9-ArH or 6- and 7-ArH), 2·28 (2H, dd, *J* 7 and 8 Hz, 5- and 8-ArH), 5·14br (2H, t, *J* 8 Hz, olefinic H), 7·28 (4H, d, *J* 8 Hz, CH_2), and 8·44br and 8·59br (each 6H, s, CMe_2).

The yellow band of intermediate R_F afforded 8,9-*dihydro*-8,8,9-*trimethylphenaleno*[1,2-b]*furan*-7-*one* (21b) (12 mg, 4%), which crystallised from benzene–light petroleum as yellow needles, m.p. 160—162° (Found: *m/e*, 264·1154. $C_{18}H_{16}O_2$ requires *M*, 264·1150), $\lambda_{max.}$ 213, 235, 256infl, 339, 356infl, and 428 nm (log ε 4·32, 4·41, 3·92, 4·03, 3·91, and 3·34); $\nu_{max.}$ (chloroform) 1633 and 1645 cm^{-1}; τ 1·39 (1H, dd, *J* 2 and 7 Hz, 6-H), 1·7—2·5 (5H, m, remaining ArH), 5·36 (1H, q, *J* 6·5 Hz, 9-H), 8·57 (3H, d, *J* 6·5 Hz, 9-Me), and 8·45 and 8·66 (each 3H, s, CMe_2); *m/e* 264 (40%, M^+) and 249 (100, M^+ − Me).

The yellow band of lowest R_F yielded 3-(3-*methylbut*-2-*enyloxy*)*phenalen*-1-*one* (24a) (22 mg, 8%), which crystallised from benzene–light petroleum as yellow prisms, m.p. 117—118° (Found: *m/e* 264·1148. $C_{18}H_{16}O_2$ requires *M*, 264·1150), $\lambda_{max.}$ 226, 245, 327, 352, and 394infl (log ε 4·32, 4·32, 4·09, 4·06, and 3·75); $\nu_{max.}$ (Nujol) 1622 and 1640 cm^{-1}; τ 1·36 (1H, dd, *J* 2 and 7·5 Hz, 9-ArH), 1·7—2·6 (5H, m, ArH), 3·89 (1H, s, 2-ArH), 4·44br (1H, t, *J* 6·5 Hz, olefinic H), 5·33 (2H, d, *J* 6·5 Hz, CH_2), and 9·0br (6H, CMe_2).

8,9-*Dihydro*-8,9,9-*trimethylphenaleno*[1,2-b]*furan*-7-*one* (27).—A solution of the allyl ether (24a) (27 mg) in *NN*-diethylaniline and n-butyric anhydride (0·15 ml) was heated at 185° for 8 h in an atmosphere of nitrogen, then diluted with ice–water and left overnight. The organic material was extracted with ethyl acetate, and the extract was washed with water, dried, and evaporated *in vacuo*. The residue was purified by p.l.c. (20 × 20 cm plate, 0·5 mm coating of Kieselgel G; chloroform as eluant), then crystallised from benzene–light petroleum, to give the *phenalenofuranone* (27) (20 mg, 74%) as yellow plates, m.p. 130—131° (Found: *m/e* 264·1150. $C_{18}H_{16}O_2$ requires *M*, 264·1150), $\lambda_{max.}$ 214, 235, 258infl, 340, and 356infl nm (log ε 4·32, 4·42, 3·80, 4·07, and 3·96); $\nu_{max.}$ (chloroform) 1634 and 1645 cm^{-1}; τ 1·44 (1H, dd, *J* 7·5 and 1·5 Hz, 6-H), 1·8—3·0 (5H, m, remaining ArH), 6·72 (1H, q, *J* 7 Hz, 8-H), 8·48 (6H, s, CMe_2), and 8·67 (3H, d, *J* 7 Hz, 8-Me); *m/e* 264 (50%, M^+) and 249 (100, M^+ − Me).

3-*Hydroxy*-4,9-*dimethoxyphenalen*-1-*one* (23c).—A mixture of 2,7-dimethoxynaphthalene (5 g), malonic acid (10 g), and polyphosphoric acid (40 ml) was stirred at 100° for 5 min, more polyphosphoric acid (40 ml) was added, and the mixture was kept at 100° for a further 18 h. The cooled mixture was hydrolysed with water, made alkaline with sodium hydrogen carbonate, and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo* to yield a residue which was chromatographed on a column of Kieselgel G (300 g) (chloroform as eluant) to give 3-*hydroxy*-4,9-*dimethoxyphenalenone* (23c) (1·35 g, 20%), which crystallised from chloroform as yellow prisms, m.p. 155—156° (Found: *m/e*, 256·0740. $C_{15}H_{12}O_4$ requires *M*, 256·0736); τ 2·11 (2H, d, *J* 9 Hz, 6- and 7-H), 2·81 (2H, d, *J* 9 Hz, 5- and 8-H), 3·85 (1H, s, 2-H), and 5·86 (6H, s, OMe).

3,9-*Dihydroxy*-4-*methoxyphenalen*-1-*one* (23b).—(*a*) A solution of 2,7-dimethoxynaphthalene (1·88 g) and malonyl chloride (1·5 g) in nitrobenzene (25 ml) was stirred with aluminium chloride (2·7 g) for 1 h at 70°, dilute hydrochloric acid was added, the nitrobenzene was removed by steam-distillation, and the residual aqueous mixture was extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo*. Chromatography of the residue on a column of Kieselgel G (50 g) (chloroform as eluant) gave 3,9-*dihydroxy*-4-*methoxyphenalen*-1-*one* (23b) (1·23 g, 51%), which crystallised from ethanol as yellow rosettes, m.p. 242—243° (Found: C, 69·6; H, 4·5%; *m/e* 242·0575. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·15%; *M*, 242·0579), $\lambda_{max.}$ 212, 254, 276, 286, 372, 416, and 431 nm (log ε 4·53, 4·10, 4·01, 3·91, 4·07, 4·07, and 3·90); τ (CF_3CO_2H) 1·30 and 1·45 (each 1H, d, *J* 7·5 Hz, 6- and 7-H), 2·30 and 2·45 (each 1H, d, *J* 7·5 Hz, 5- and 8-H), 2·98 (1H, s, 2-H), and 5·45 (3H, s, OMe).

(*b*) A solution of 3-hydroxy-4,9-dimethoxyphenalen-1-one (900 mg) in ethanol (40 ml) acidified with aqueous hydrochloric acid (40 ml; 6N) was heated under reflux for 2 h. The mixture was cooled, basified with aqueous 2N-sodium hydroxide, re-acidified with acetic acid, and extracted with chloroform. The extract was washed, dried, and evaporated *in vacuo* to yield 3,9-dihydroxy-4-methoxyphenalen-1-one (650 mg 77%), identical with material obtained as described in (*a*).

Alkylation of 3,9-*Dihydroxy*-4-*methoxyphenalen*-1-*one* (23b) *with* 3-*Methylbut*-2-*enyl Bromide*.—Potassium carbonate (690 mg) and 3-methylbut-2-enyl bromide (1·19 g) were added to a solution of 3,9-dihydroxy-4-methoxyphenalen-1-one (23b) (1·21 g) in acetone (200 ml) and the mixture was stirred and heated under reflux for 15 h. The acetone was removed under reduced pressure, water was added, and the aqueous mixture was acidified with dilute hydrochloric acid and extracted with chloroform. The extract was washed with water, dried, and evaporated *in vacuo* to leave a residue from which three products were isolated by chromatography on a column of Kieselgel G (100 g) (chloroform as eluant).

From the band of highest R_F was obtained 4-*hydroxy*-9-*methoxy*-2,2-*bis*-(3-*methylbut*-2-*enyl*)*phenalene*-1,3(2H)-*dione* (25b) (419 mg, 22%), which crystallised from methanol as needles, m.p. 100—102° (Found: C, 76·0; H, 6·8. $C_{24}H_{26}O_4$ requires C, 76·15; H, 6·95%), $\lambda_{max.}$ 208, 248, 325infl, 353, and 364 nm (log ε 4·39, 4·50, 3·97, 4·10, and 4·10); $\nu_{max.}$ (Nujol) 1623 and 1692 cm^{-1}; τ −4·19 (1H, s, exchangeable with D_2O, OH), 2·09 and 2·12 (each 1H, d, *J* 9 Hz, 6- and 7-ArH), 2·82 and 2·96 (each 1H, d, *J* 9 Hz, 5- and 8-ArH), 5·06br (2H, t, *J* 7 Hz, olefinic H), 5·92 (3H, s, OMe), 7·27 (4H, d, *J* 7 Hz, CH_2), and 8·42br and 8·50br (total 12H, each s, CMe_2).

The yellow band of intermediate R_F yielded 9-*hydroxy*-4-*methoxy*-2-(3-*methylbut*-2-*enyl*)-3-(3-*methylbut*-2-*enyloxy*)-*phenalen*-1-*one* (28) (363 mg, 19%), which crystallised from benzene–light petroleum as yellow needles, m.p. 125—126° (Found: C, 75·9; H, 6·95. $C_{24}H_{26}O_4$ requires C, 76·15; H, 6·95%), $\lambda_{max.}$ 216, 233infl, 277, 285, 380, 410, and 431 nm (log ε 4·50, 4·35, 4·00, 3·91, 4·20, 4·18, and 4·11); $\nu_{max.}$ (Nujol) 1624 cm^{-1}; τ −7·40 (1H, s, exchangeable with D_2O, OH), 2·14 (2H, d, *J* 9 Hz, 6- and 7-ArH), 2·95 and 3·03 (each 1H, d, *J* 9 Hz, 5- and 8-ArH), 4·36br and 4·70br (each 1H, t, *J* 7 Hz, olefinic H), 5·54 (2H, d, *J* 7 Hz, $ArOCH_2CH$), 5·91 (3H, s, OMe), 6·44 (2H, d, *J* 7 Hz, $ArCH_2{\cdot}CH$), and 8·16br and 8·30br (total 12H, each s, CMe_2).

The band of lowest R_F afforded 9-*hydroxy*-4-*methoxy*-3-(3-*methylbut*-2-*enyloxy*)*phenalen*-1-*one* (24b) (630 mg, 41%), which crystallised from benzene–light petroleum as yellow rosettes, m.p. 131—133° (Found: C, 73·6; H, 5·9. $C_{19}H_{18}O_4$ requires C, 73·55; H, 5·85%), $\lambda_{max.}$ 215, 236infl, 254infl, 273, 283, 383, 400, and 428 nm (log ε 4·44, 4·35, 4·12, 3·93, 3·87, 4·19, 4·17, and 4·03); $\nu_{max.}$ (Nujol) 1630 and 3270 cm^{-1}; τ −7·15 (1H, s, exchangeable with D_2O, OH), 2·12 and 2·14 (each 1H, d, *J* 9 Hz, 6- and 7-ArH), 2·94 and 3·01 (each 1H, d, *J* 9 Hz, 5- and 8-ArH), 3·58 (1H, s, 2-ArH), 4·42br (1H, t, *J* 7 Hz, olefinic H), 5·27 (2H, d, *J* 7 Hz, CH_2), 5·97 (3H, s, OMe), and 8·20br (6H, s, CMe_2).

8,9-*Dihydro*-6-*hydroxy*-1-*methoxy*-8,8,9-*trimethylphenaleno*-[1,2-b]*furan*-7-*one* (21c).—A solution of the allyl ether (24b) (50 mg) in dimethylformamide (2 ml) was heated under reflux for 5 h. The solvent was removed under reduced pressure, and the residue was purified by p.l.c. [20 × 20 cm plate, 16 g Kieselgel G; ether–benzene (1 : 4) as eluant] to give the *hydroxy-phenalenofuranone* (21c) (36 mg, 72%), which crystallised from benzene–light petroleum as yellow needles, m.p. 167—168° (Found: C, 73·8; H, 5·8. $C_{19}H_{18}O_4$ requires C, 73·55; H, 5·85%), $\lambda_{max.}$ 215, 252, 275, 285, 358, 385, 405, and 434 nm (log ε 4·50, 4·15, 4·12, 4·15, 4·04, 4·15, 4·18, and 4·20); $\nu_{max.}$ (Nujol) 1625 cm^{-1}; τ −7·40 (1H, s, exchangeable with D_2O, OH), 2·08 and 2·14 (each 1H, 3- and 4-H), 2·96 and 3·01 (each 1H, d, *J* 9 Hz, 2- and 5-H), 5·30 (1H, q, *J* 6·5 Hz, 9-H), 5·91 (3H, s, OMe), 8·48 (3H, d, *J* 6·5 Hz, 9-Me), and 8·40 and 8·63 (each 3H, s, CMe_2); *m/e* 310 (25%, M^+) and 295 (100, M^+ − Me).

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