New Routes to Phenalenones from 2,7-Dihydroxynaphthalene. *X*-Ray Crystal Structure of 4-(α-Hydroxybenzyl)-2-phenyl-6*H*-phenaleno-[1,9-*bc*]pyran-6-one

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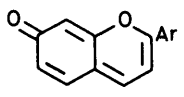
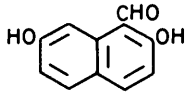
9-Aryl-6-hydroxy-1*H*-phenalen-1-ones and 2-aryl-4-aroyl-6*H*-phenaleno[1,9-*bc*]pyran-6-ones can be obtained by the reaction of 2,7-dihydroxynaphthalene-1-carbaldehyde with acetophenones and by condensation of aroylacetaldehydes with 2,7-dihydroxynaphthalene under acid conditions. Aroylacetaldehydes may be involved in the former reaction also, arising by transfer of the formyl group from the naphthaldehyde to the acetophenone. 2,7-Dihydroxynaphthalene-1-carbaldehyde reacts with 2-hydroxyacetophenone to form 1*H*-naphtho[2,1,8-*mna*]xanthen-1-one.

Interaction of naphthalene-2,7-dioxybismagnesium dibromide with cinnamaldehydes affords 4-benzyl-2-phenyl-6*H*-phenaleno[1,9-*bc*]pyran-6-ones.

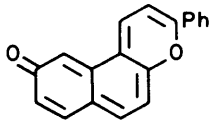
Quinone methides of type (1) can be obtained [1] by the condensation of 2,4-dihydroxybenzaldehydes with acetophenones under acid conditions, followed by treatment with base, and by analogy a similar reaction of the dihydroxy aldehyde (2) should afford the extended quinone methide (3). In practice when a mixture of acetophenone and the aldehyde (2) in acetic acid was treated with hydrogen chloride a crystalline, water-soluble product was obtained which was not the expected flavylium salt. On basification, two compounds, red and orange, were obtained, the latter being alkali-soluble.



(1)

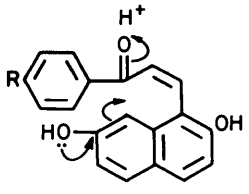


(2)

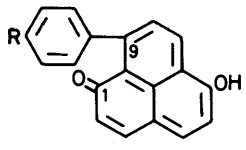


(3)

The orange compound, $C_{19}H_{12}O_2$, was recognised from its spectroscopic properties, notably the strong $(M - 1)^+$ peak in the mass spectrum,[2] as the phenalenone (5; R = H); this assignment was confirmed by comparison with an authentic sample.[3] Evidently the chalcone which was formed initially cyclised onto the adjacent *peri* position as indicated in structure (4). The *p*-methoxy derivative (5; R = OMe) was similarly prepared (together with another red compound) from *p*-methoxyacetophenone, both phenalenones being obtained in *ca.* 50% yield when the solvent was changed to ethanol (the yields of the corresponding *p*-bromo products from *p*-bromoacetophenone were lower). As several natural phenalenones [2] carry a phenyl group at C(9), and an hydroxy group at C(6), there has been considerable interest [3,4] in the synthesis of phenalenones of this type starting from 2,7-dihydroxy- or 2,7-dimethoxy-naphthalene, but overall yields are well below 50%.



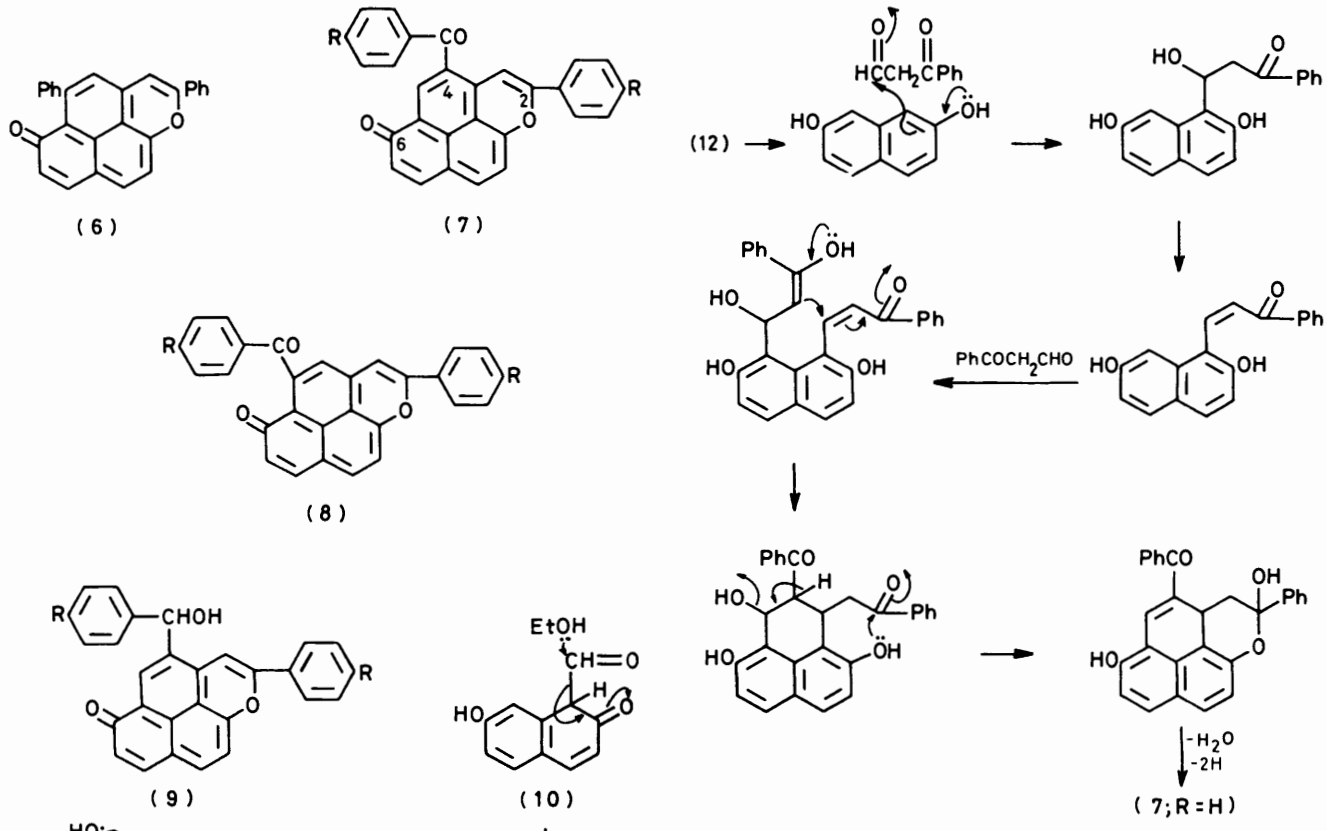
(4)



(5)

The red compound formed together with the phenalenone (5; R = H) had the molecular formula $C_{28}H_{16}O_3$ and showed a broad carbonyl absorption at 1 645 cm^{-1}. It is possible to formulate a mechanistic scheme involving the condensation of the aldehyde (2) with 2 mol of acetophenone leading to the formation of a phenalenone such as (6), but the molecular formula of compound (6), $C_{27}H_{16}O_2$, falls short of that found by one atom each of carbon and oxygen. As the red compounds derived from the reaction of the aldehyde (2) with either *p*-methoxy- or *p*-bromo-acetophenone each showed two distinct i.r. carbonyl bands, at 1 645 and 1 638, and 1 656 and 1 642 cm^{-1}, respectively, it seemed that the 'extra' atoms might contribute an additional carbonyl group. Furthermore the mass spectrum of the original red compound ($C_{28}H_{16}O_3$) includes a significant peak at $(M - 105)^+$, suggesting the presence of a benzoyl group, and this was supported by reduction of the red compound with sodium borohydride to give a secondary alcohol which showed (in $[^2H_6]Me_2SO$ solution) two one-proton doublets at δ 6.58 (*J* 3 Hz, C*H*OH) and 6.35 (*J* 3 Hz, CHO*H*). Thus, structures (7 or 8; R = H) could be tentatively assigned to the red compound, structure (7; R = H) being preferred since a singlet in the n.m.r. spectrum at δ 8.82 was consistent [2] with a proton at C(5). The absence of an $(M - 1)^+$ peak in the mass spectrum excluded structures carrying the phenyl group at C(5), adjacent to the carbonyl group. This assignment (7; R = H) was confirmed by an *X*-ray crystallographic analysis of the derived secondary alcohol which established its structure as (9; R = H). The original red compound is therefore the pyranophenalenone (7; R = H), the analogues mentioned previously being (7; R = OMe and Br).

Having established that the red phenalenone obtained from the reaction of 2,7-dihydroxynaphthalene-1-carbaldehyde (2) and acetophenone is compound (7; R = H), what then is the origin of the 'extra' carbonyl group? It is not the solvent, since the same compound was obtained when the reaction was conducted in ethyl acetate, diethyl ether, or ethanol. A more likely source is the formyl group of compound (2), and indeed

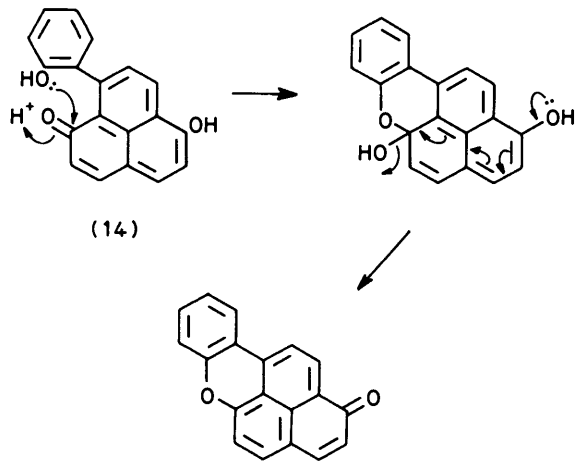


Scheme 1.

when hydrogen chloride was passed through a solution of the aldehyde (2) in ethanol, 2,7-dihydroxynaphthalene (11) was rapidly formed in high yield; the formyl group was probably removed by solvolysis as shown in (10). In the reaction leading to the pyranophenalenone (7; R = H), deformylation could be effected by acetophenone, leading [see (12)] to the formation of benzoylacetaldehyde and 2,7-dihydroxynaphthalene. Further speculation then suggested that benzoylacetaldehyde might condense with acetophenone to form the diketone (13) which in turn could condense with the aldehyde (2) to yield the red compound (7; R = H). In practice all attempts to react compound (13) with the aldehyde (2) gave complex mixtures which did not contain the expected pyranophenalenone (7). However, when 2,7-dihydroxynaphthalene (11) was allowed to react with benzoylacetaldehyde in ethanolic hydrogen chloride a crystalline product formed almost immediately which, on basification, gave the red pyranophenalenone (7; R = H) (27%) as well as a small amount of the orange phenalenone (5; R = H). A similar reaction with 4-methoxybenzoylacetaldehyde gave the compounds (7; R = OMe) and (5; R = OMe) in lower yield. The origin of the red compound (7; R = H) is therefore clear and a possible pathway is outlined in Scheme 1. The orange phenalenone (5; R = H) must arise by *peri*-cyclisation of the chalcone (4) as previously indicated. In the original synthesis the chalcone (4) could be formed either by aldol condensation of the aldehyde (2) with acetophenone or from 2,7-dihydroxynaphthalene (11) and benzoylacetaldehyde (Scheme 1), and it is likely that both routes operate. This also applies to the formation of the red compound (7; R = H). When the condensation with acetophenone was repeated with 8-bromo-2,7-dihydroxynaphthalene-1-carbaldehyde (to prevent *peri*-cyclisation) the same orange (5; R = H) and red (7; R = H) compounds were obtained with elimination of bromine, and when the same reaction was repeated with 2,7-dihydroxy-8-methylnaphthalene-1-carbaldehyde, complex mixtures resulted which contained 2,7-dihydroxy-1-methylnaphthalene.

The reaction of the aldehyde (2) with 2-hydroxyacetophenone gave an alkali-insoluble orange compound (32%) which was shown to be the naphthoxanthenone (15), presumably formed by way of the *o*-hydroxyphenylphenalenone (14) (Scheme 2). Compound (15) has been prepared previously, but in several steps and in lower overall yield.[4a]

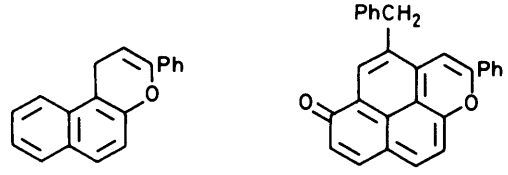
It has been reported [5] that the reaction of 2-naphthoxymagnesium bromide with cinnamaldehyde yields the pyran (16) and its double-bond isomer. This suggested that a similar reaction starting from 2,7-dihydroxynaphthalene (11) might provide a route to the quinone methide (3). In the light of our results reported above that now seems unlikely and, in fact, reaction occurred again at the 1,8-positions. Treatment of the product from compound (11) and ethylmagnesium bromide (1 mol equiv.) with cinnamaldehyde gave a red compound,



(14)

(15)

Scheme 2.



(16) (17)

$C_{28}H_{18}O_2$, showing that two molecules of the aldehyde had reacted with one of the diol and suggesting a close relationship of the product with compound (7; R = H) ($C_{28}H_{16}O_3$). Important spectroscopic features of the new compound were its carbonyl absorption at 1 644 cm^{-1}, a methylene singlet at δ 4.34 and a one-proton singlet at δ 8.73 in the ^1H n.m.r. spectrum, and (significantly) the very close similarity of the visible spectrum with that of the pyranophenalenone (7; R = H). These data indicated the benzylic structure (17) which was confirmed by an alternative synthesis from the alcohol (9; R = H) by reduction of the tosylate (toluene-*p*-sulphonate) with lithium aluminium hydride. It is difficult in this case to write a convincing mechanism for the formation of (17), although it is not a minor product since, by modification of the conditions, the yield could be increased to 44%. A similar compound was obtained using 2-nitrocinnamaldehyde as starting material.

X-Ray Crystal Structure Determination of the Secondary Alcohol (9; R = H).—An *X*-ray analysis of the alcohol produced by reduction of the red compound (7; R = H) established its structure as (9; R = H). The molecular structure is shown in the Figure and the atomic co-ordinates, bond lengths, valency angles, and torsion angles are listed in Table 1—4, respectively

The aromatic C–C bonds in rings E and F vary from 1.351(9) to 1.395(7) Å whereas in the pyranophenalenone nucleus the C–C bonds vary from 1.330(6) to 1.469(6) Å. The long C=O bond [1.249(7) Å] is due to the presence of intermolecular hydrogen bonding between the carbonyl and hydroxy group oxygens of adjacent molecules. The geometry of the hydrogen bonding is shown in Table 5. The O(3′) · · · O(2) * distance of 2.423(14) Å is very short and such separations are normally

* Asterisk defined in footnote to Table 5.

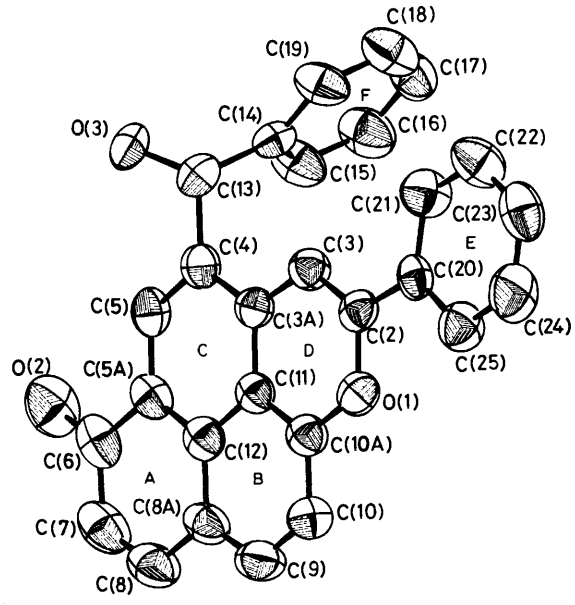


Figure. The molecular structure and crystallographic numbering scheme for compound (9; R = H) [O(3′) omitted]

associated with ' symmetrical ' H bonds as found in some acid salts of carboxylic acids. However, the standard deviation associated with this separation may be underestimated.

The valency angles C(3)–C(2)–C(20) 126.6(4)° and C(20)–C(2)–O(1) 112.3(3)° are considerably distorted from their ideal values. This in-plane bending relieves unfavourable *peri* interaction between H(3) and H(21) which are separated by 1.94(6) Å. Out-of-plane bending here is minimal as the torsion angles centred on C(2)–C(20) are close to the ideal values for co-planar rings D and E. The dihedral angle between the pyranophenalenone nucleus (ABCD) and ring E is 2.22°; similarly the ABCD/F dihedral angle is 95.92°. Other dihedral angles are given in Table 6.

All the 6-membered rings in the molecule are virtually planar—the most-nearly-planar ring is ring D ($\Sigma\Delta^2$ 4.3 × 10^{-5} Å) and the least planar is ring C ($\Sigma\Delta^2$ 2.56 × 10^{-4} Å). Displacements of atoms from various planes are shown in Table 7. The planarity of the pyranophenalenone nucleus is also a feature of the corresponding carba ' derivative ' pyrene.[6]

The crystal structure of compound (9; R = H) is disordered as the enantiomers do not uniquely occupy their respective positions *x*, *y*, *z* and $\bar{x}$, $\bar{y}$, $\bar{z}$ but are distributed over both sites. The *X*-ray study revealed the average atom positions of the superimposed enantiomers. The only asymmetric centre in the molecule is C(13) and since the molecules of the racemate are closely superimposable it is only the atoms in the 13(H) and 13(OH) groups that give rise to twin peaks. An almost identical packing disorder was found in the crystals of 1-(*p*-bromophenylsulphonyloxymethyl)-5-methylbicyclo[3.3.1]nonan-9-ol.[7] Accordingly, the primed atoms in Table 1 indicate the 13(H), 13(OH) atoms associated with the lower occupation factor.

Experimental

N.m.r. spectra were measured for solutions in deuteriochloroform, and i.r. spectra for KBr discs, unless otherwise stated. Merck Kieselgel 100 (70—230 mesh) was used for dry column chromatography, and GF_{254} for p.l.c. (preparative layer chromatography).

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s (in parentheses) and equivalent values of the anisotropic temperature factor coefficients ($\times 10^3$)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$$

	x/a	y/b	z/c	U_{eq}
O(1)	7 399(3)	9 832(2)	10 409(2)	54
O(2)	10 840(5)	13 865(3)	8 347(2)	87
O(3)	8 276(7)	10 792(4)	7 125(3)	57
O(3′)	8 129(21)	9 361(8)	7 750(7)	80
C(2)	6 788(5)	9 285(3)	9 807(2)	46
C(3)	7 020(5)	9 632(3)	9 163(2)	50
C(3A)	7 915(4)	10 591(3)	9 059(2)	45
C(4)	8 211(5)	10 983(3)	8 393(2)	47
C(5)	9 094(5)	11 924(3)	8 376(3)	51
C(5A)	9 697(5)	12 488(3)	8 985(2)	52
C(6)	10 600(6)	13 485(4)	8 935(3)	64
C(7)	11 179(6)	13 991(4)	9 599(3)	72
C(8)	10 922(6)	13 588(4)	10 232(3)	70
C(8A)	10 034(5)	12 626(3)	10 298(3)	56
C(9)	9 726(6)	12 187(4)	10 942(3)	65
C(10)	8 863(6)	11 260(4)	10 984(3)	63
C(10A)	8 274(5)	10 746(3)	10 357(2)	49
C(11)	8 536(4)	11 141(3)	9 687(2)	43
C(12)	9 442(5)	12 092(3)	9 655(2)	48
C(13)	7 562(5)	10 417(3)	7 714(2)	51
C(14)	5 731(5)	10 512(3)	7 549(2)	48
C(15)	5 002(6)	11 493(4)	7 506(3)	70
C(16)	3 350(7)	11 606(5)	7 366(3)	80
C(17)	2 379(6)	10 707(5)	7 259(3)	75
C(18)	3 082(8)	9 735(5)	7 292(3)	84
C(19)	4 742(7)	9 635(4)	7 442(3)	69
C(20)	5 925(5)	8 320(3)	9 971(2)	48
C(21)	5 179(6)	7 665(4)	9 432(3)	67
C(22)	4 399(7)	6 747(4)	9 580(3)	77
C(23)	4 303(7)	6 451(5)	10 266(4)	76
C(24)	4 999(7)	7 092(5)	10 800(3)	83
C(25)	5 801(6)	8 016(4)	10 666(3)	65
*H*O(3)	8 690(76)	10 140(34)	6 909(31)	
*H*O(3′)	8 444(142)	9 222(56)	7 263(29)	
H(3)	6 527(53)	9 188(34)	9 757(19)	
H(5)	9 362(48)	12 187(31)	7 909(14)	
H(7)	11 833(62)	14 657(30)	9 577(32)	
H(8)	11 351(52)	13 984(34)	10 662(17)	
H(9)	10 205(51)	12 512(34)	11 400(15)	
H(10)	8 624(68)	10 887(42)	11 426(20)	
H(13)	7 863(126)	9 645(23)	7 724(37)	
H(13′)	8 000(198)	10 691(42)	7 280(58)	
H(15)	5 619(54)	12 145(27)	7 650(26)	
H(16)	2 868(60)	12 336(23)	7 319(28)	
H(17)	1 186(26)	10 843(37)	7 208(24)	
H(18)	2 440(71)	9 069(33)	7 182(36)	
H(19)	5 320(59)	8 936(26)	7 464(28)	
H(21)	5 245(58)	7 948(37)	8 934(14)	
H(22)	3 762(53)	6 328(35)	9 192(21)	
H(23)	3 716(53)	5 813(27)	10 400(26)	
H(24)	5 069(62)	6 800(39)	11 287(14)	
H(25)	6 425(61)	8 467(39)	11 043(23)	

Table 2. Bond lengths (Å) with e.s.d.s (in parentheses)

O(1)–C(2)	1.373(5)	C(8A)–C(12)	1.423(6)
O(1)–C(10A)	1.369(5)	C(9)–C(10)	1.375(7)
O(2)–C(6)	1.249(7)	C(10)–C(10A)	1.386(6)
O(3)–C(13)	1.407(7)	C(10A)–C(11)	1.403(6)
O(3′)–C(13)	1.405(11)	C(11)–C(12)	1.417(5)
C(2)–C(3)	1.330(6)	C(13)–C(14)	1.524(6)
C(2)–C(20)	1.461(6)	C(14)–C(15)	1.370(7)
C(3)–C(3A)	1.442(6)	C(14)–C(19)	1.375(7)
C(3A)–C(4)	1.402(6)	C(15)–C(16)	1.377(8)
C(3A)–C(11)	1.416(6)	C(16)–C(17)	1.388(8)
C(4)–C(5)	1.393(6)	C(17)–C(18)	1.351(9)
C(4)–C(13)	1.509(6)	C(18)–C(19)	1.383(8)
C(5)–C(5A)	1.392(6)	C(20)–C(21)	1.395(7)
C(5A)–C(6)	1.469(6)	C(20)–C(25)	1.385(7)
C(5A)–C(12)	1.402(6)	C(21)–C(22)	1.368(8)
C(6)–C(7)	1.437(8)	C(22)–C(23)	1.362(9)
C(7)–C(8)	1.341(9)	C(23)–C(24)	1.364(9)
C(8)–C(8A)	1.429(7)	C(24)–C(25)	1.377(8)
C(8A)–C(9)	1.389(7)		
O(3)–HO(3)	1.00(5)	C(15)–H(15)	0.99(4)
O(3′)–HO(3′)	1.00(7)	C(16)–H(16)	1.00(3)
C(3)–H(3)	1.00(4)	C(17)–H(17)	1.00(2)
C(5)–H(5)	0.99(3)	C(18)–H(18)	1.00(5)
C(7)–H(7)	1.00(4)	C(19)–H(19)	1.00(4)
C(8)–H(8)	0.98(4)	C(21)–H(21)	1.01(3)
C(9)–H(9)	1.00(3)	C(22)–H(22)	1.00(4)
C(10)–H(10)	1.00(4)	C(23)–H(23)	0.99(4)
C(13)–H(13)	1.00(4)	C(24)–H(24)	0.99(3)
C(13)–H(13′)	1.00(12)	C(25)–H(25)	1.00(5)

Table 3. Valency angles (°) with e.s.d.s (in parentheses)

C(10A)–O(1)–C(2)	120.4(3)	C(3)–C(2)–O(1)	121.0(4)
C(20)–C(2)–O(1)	112.3(3)	C(10)–C(10A)–O(1)	117.7(4)
C(11)–C(10A)–O(1)	120.3(4)	C(5A)–C(6)–O(2)	121.5(5)
C(7)–C(6)–O(2)	122.5(5)	C(14)–C(13)–O(3)	108.8(4)
C(4)–C(13)–O(3)	112.0(4)	C(14)–C(13)–O(3′)	113.9(7)
C(4)–C(13)–O(3′)	108.6(6)	C(3A)–C(3)–C(2)	122.3(4)
C(20)–C(2)–C(3)	126.6(4)	C(25)–C(20)–C(2)	121.7(4)
C(21)–C(20)–C(2)	121.3(4)	C(11)–C(3A)–C(3)	115.7(3)
C(4)–C(3A)–C(3)	124.5(4)	C(5)–C(4)–C(3A)	118.0(4)
C(11)–C(3A)–C(4)	119.8(4)	C(10A)–C(11)–C(3A)	120.3(4)
C(13)–C(4)–C(3A)	121.0(4)	C(13)–C(4)–C(5)	120.9(4)
C(12)–C(11)–C(3A)	121.1(4)	C(14)–C(13)–C(4)	112.5(3)
C(5A)–C(5)–C(4)	123.3(4)	C(12)–C(5A)–C(5)	119.3(4)
C(6)–C(5A)–C(5)	121.0(4)	C(7)–C(6)–C(5A)	116.1(5)
C(12)–C(5A)–C(6)	119.7(4)	C(11)–C(12)–C(5A)	118.5(4)
C(8A)–C(12)–C(5A)	122.1(4)	C(8A)–C(8)–C(7)	122.5(5)
C(8)–C(7)–C(6)	122.7(5)	C(12)–C(8A)–C(8)	116.9(4)
C(9)–C(8A)–C(8)	124.4(5)	C(10)–C(9)–C(8A)	122.7(5)
C(12)–C(8A)–C(9)	118.8(4)	C(10A)–C(10)–C(9)	118.5(4)
C(11)–C(12)–C(8A)	119.4(4)	C(12)–C(11)–C(10A)	118.6(4)
C(11)–C(10A)–C(10)	122.1(4)	C(19)–C(14)–C(13)	122.3(4)
C(15)–C(14)–C(13)	120.5(4)	C(16)–C(15)–C(14)	122.0(5)
C(19)–C(14)–C(15)	117.2(4)	C(17)–C(16)–C(15)	119.7(5)
C(18)–C(19)–C(14)	121.6(5)	C(19)–C(18)–C(17)	120.6(5)
C(18)–C(17)–C(16)	119.0(5)	C(22)–C(21)–C(20)	121.8(5)
C(25)–C(20)–C(21)	117.0(4)	C(23)–C(22)–C(21)	120.6(6)
C(24)–C(25)–C(20)	120.1(5)	C(25)–C(24)–(23)	122.1(6)
C(24)–C(23)–C(22)	118.4(5)		

Reaction of 2,7-Dihydroxynaphthalene-1-carbaldehyde (2) *with Acetophenone.*—(a) 2,7-Dihydroxynaphthalene-1-carbaldehyde (2) (0.94 g, 5.0 mmol) and acetophenone (2.4 g, 20.0 mol) were dissolved in acetic acid (10 ml) and dry hydrogen chloride was passed through the mixture for 4 h at room temperature. After 15 h the black crystals were collected by filtration, washed in turn with acetic acid (5 ml) and diethyl ether (30 ml), and dissolved in a mixture of water (15 ml) and ethanol (25 ml) containing sodium carbonate (2.0 g). The mixture was boiled under reflux for 1 h, cooled, and diluted with water (250 ml). The red solid (A) was collected by filtration and the filtrate was acidified with hydrochloric acid to precipitate an orange compound (B).

The orange product (B) was crystallised from benzene–methanol (4 : 1) to give 6-hydroxy-9-phenyl-1*H*-phenalen-1-one (5; R = H) as orange plates (0.28 g, 20.6%), m.p. 284—285 °C (lit.,[3] 282—284 °C) (Found: C, 83.8; H, 4.4%. Calc. for $C_{19}H_{12}O_2$: C, 83.8; H, 4.4%); *m/z* 272 (M^+, 100%), 271 (18),

Table 4. Torsion angles (°) with e.s.d.s (in parentheses)

C(10A)–O(1)–C(2)–C(3)	−0.5(6)	C(10A)–O(1)–C(2)–C(20)	178.6(3)
C(2)–O(1)–C(10A)–C(10)	−179.8(4)	C(2)–O(1)–C(10A)–C(11)	0.9(6)
O(1)–C(2)–C(3)–C(3A)	−0.0(6)	C(20)–C(2)–C(3)–C(3A)	−179.0(4)
O(1)–C(2)–C(20)–C(21)	178.4(4)	O(1)–C(2)–C(20)–C(25)	−1.2(6)
C(3)–C(2)–C(20)–C(21)	−2.5(7)	C(3)–C(2)–C(20)–C(25)	177.9(4)
C(2)–C(3)–C(3A)–C(4)	179.1(4)	C(2)–C(3)–C(3A)–C(11)	0.1(6)
C(3)–C(3A)–C(4)–C(5)	179.8(4)	C(3)–C(3A)–C(4)–C(13)	1.2(6)
C(11)–C(3A)–C(4)–C(5)	−1.2(6)	C(11)–C(3A)–C(4)–C(13)	−179.8(4)
C(3)–C(3A)–C(11)–C(10A)	0.3(6)	C(3)–C(3A)–C(11)–C(12)	179.8(4)
C(4)–C(3A)–C(11)–C(10A)	−178.8(4)	C(4)–C(3A)–C(11)–C(12)	0.7(6)
C(3A)–C(4)–C(5)–C(5A)	0.2(6)	C(13)–C(4)–C(5)–C(5A)	178.9(4)
C(3A)–C(4)–C(13)–O(3)	−166.9(4)	C(3A)–C(4)–C(13)–O(3′)	−56.7(7)
C(3A)–C(4)–C(13)–C(14)	70.2(5)	C(5)–C(4)–C(13)–O(3)	14.5(6)
C(5)–C(4)–C(13)–O(3′)	124.5(7)	C(5)–C(4)–C(13)–C(14)	−108.4(4)
C(4)–C(5)–C(5A)–C(6)	−179.1(4)	C(4)–C(5)–C(5A)–C(12)	1.2(7)
C(5)–C(5A)–C(6)–O(2)	0.8(7)	C(5)–C(5A)–C(6)–C(7)	−179.3(4)
C(12)–C(5A)–C(6)–O(2)	−179.5(5)	C(12)–C(5A)–C(6)–C(7)	0.3(7)
C(5)–C(5A)–C(12)–C(8A)	179.6(4)	C(5)–C(5A)–C(12)–C(11)	−1.7(6)
C(6)–C(5A)–C(12)–C(8A)	−0.1(6)	C(6)–C(5A)–C(12)–C(11)	178.6(4)
O(2)–C(6)–C(7)–C(8)	179.8(5)	C(5A)–C(6)–C(7)–C(8)	0.0(8)
C(6)–C(7)–C(8)–C(8A)	−0.7(9)	C(7)–C(8)–C(8A)–C(9)	−179.3(5)
C(7)–C(8)–C(8A)–C(12)	1.0(8)	C(8)–C(8A)–C(9)–C(10)	179.9(5)
C(12)–C(8A)–C(9)–C(10)	−0.4(7)	C(8)–C(8A)–C(12)–C(5A)	−0.6(6)
C(8)–C(8A)–C(12)–C(11)	−179.2(4)	C(9)–C(8A)–C(12)–C(5A)	179.7(4)
C(9)–C(8A)–C(12)–C(11)	1.0(6)	C(8A)–C(9)–C(10)–C(10A)	−0.2(8)
C(9)–C(10)–C(10A)–O(1)	−179.1(4)	C(9)–C(10)–C(10A)–C(11)	0.2(7)
O(1)–C(10A)–C(11)–C(3A)	−0.8(6)	O(1)–C(10A)–C(11)–C(12)	179.7(4)
C(10)–C(10A)–C(11)–C(3A)	179.9(4)	C(10)–C(10A)–C(11)–C(12)	0.4(6)
C(3A)–C(11)–C(12)–C(5A)	0.8(6)	C(3A)–C(11)–C(12)–C(8A)	179.5(4)
C(10A)–C(11)–C(12)–C(5A)	−179.7(4)	C(10A)–C(11)–C(12)–C(8A)	−1.0(6)
O(3)–C(13)–C(14)–C(15)	−69.7(5)	O(3)–C(13)–C(14)–C(19)	110.7(5)
O(3′)–C(13)–C(14)–C(15)	179.2(7)	O(3′)–C(13)–C(14)–C(19)	−0.4(8)
C(4)–C(13)–C(14)–C(15)	55.0(5)	C(4)–C(13)–C(14)–C(19)	−124.6(4)
C(13)–C(14)–C(15)–C(16)	−179.2(5)	C(19)–C(14)–C(15)–C(16)	0.4(7)
C(13)–C(14)–C(19)–C(18)	−179.9(5)	C(15)–C(14)–C(19)–C(18)	0.5(7)
C(14)–C(15)–C(16)–C(17)	−0.5(8)	C(15)–C(16)–C(17)–C(18)	−0.3(9)
C(16)–C(17)–C(18)–C(19)	1.1(9)	C(17)–C(18)–C(19)–C(14)	−1.2(9)
C(2)–C(20)–C(21)–C(22)	178.5(5)	C(25)–C(20)–C(21)–C(22)	−1.8(7)
C(2)–C(20)–C(25)–C(24)	−179.0(5)	C(21)–C(20)–C(25)–C(24)	1.4(7)
C(20)–C(21)–C(22)–C(23)	1.1(9)	C(21)–C(22)–C(23)–C(24)	0.1(9)
C(22)–C(23)–C(24)–C(25)	−0.6(9)	C(23)–C(24)–C(25)–C(20)	−0.2(9)

Table 5. Geometry of hydrogen bonding

Donor (D) Acceptor (A)	Distance (Å)	D–H (Å)	H ··· A (Å)	∠D–H ··· A (°)
O(3) ··· O(2) *	2.710(6)	1.00(5)	1.73(5)	168(5)
O(3′) ··· O(2) *	2.423(14)	1.00(7)	1.43(8)	167(9)

* Co-ordinates transformed by $2 - x$, $0.5 + y$, $1.5 - z$.

Table 6. Dihedral angles (°) between ring planes

ABCD/E	2.22	ABCD/F	95.92	A/B	−0.66	A/C	−0.88
A/D	0.93	B/C	0.36	B/D	−0.27	C/D	0.37

243 (5.5), and 215 (7); the product was identical (u.v., n.m.r., m.s.) with an authentic sample.

The red solid (A) was crystallised from benzene to give 4-*benzoyl*-2-*phenyl*-6H-*phenaleno*[1,9-bc]*pyran*-6-*one* (7; R = H) as red needles (0.31 g, 15.5%), m.p. 283—284 °C [Found: C, 83.8; H, 4.3%; $(M - C_7H_5O)^+$, 295.0797. $C_{28}H_{16}O_3$ requires C, 84.0; H, 4.0%; $(M - C_7H_5O)$, 295.0759]; $\lambda_{max.}$ ($CHCl_3$) 276, 320, 364, 482sh, 510, and 544 nm (log ε 4.57, 3.95, 3.97, 4.18, 4.34, and 4.19); $\nu_{max.}$ 1 656sh and 1 645 cm^{-1}; δ 6.88 (1 H, d, *J* 9.5 Hz, =CH), 7.40—7.70 (7 H, m, Ph + 2 × =CH), 7.80—8.03 (7 H, m, Ph + 2 × =CH), and 8.82 (1 H, s, =CH); *m/z* 400 (M^+, 100%), 371 (11), 323 (9), and 295 (10).

(b) Compound (2) (0.94 g, 5.0 mmol) and acetophenone (0.66 g, 5.5 mmol) were dissolved in ethanol (25 ml) and dry hydrogen chloride was passed through the mixture for 2 h. After 8 h the crystalline product was collected by filtration, washed with ethanol, and treated as in (a) above to give compounds (5; R = H) (0.65 g, 47.8%) and (7; R = H) (0.12 g, 5.8%).

(c) Repetition of the reaction described in (a) above, but with 8-bromo-2,7-dihydroxynaphthalene-1-carbaldehyde, gave compounds (5; R = H) (20%) and (7; R = H) (18%).

Reaction of 2,7*Dihydroxynaphthalene*-1-*carbaldehyde* (2) *with* 4-*Methoxyacetophenone*.—The aldehyde (2) (0.376 g, 2.0 mmol) and 4-methoxyacetophenone (0.165 g, 1.1 mmol)

Table 7. Displacement (Å) of atoms from various planes

(i)	O(1) −0.01, C(2) −0.01, C(3) −0.01, C(3A) 0.00, C(4) 0.01, C(5) 0.01, C(5A) 0.00, C(6) −0.02, C(7) −0.02, C(8) 0.00, C(8A) 0.00, C(9) 0.01, C(10) 0.01, C(10A) 0.01, C(11) 0.00, C(12) 0.01, *O(2)* −0.04, *C(13)* 0.00, *O(3)* 0.32, *O(3')* 1.11, *C(20)* 0.00, *C(21)* −0.03, *C(25)* 0.05
(ii)	C(14) 0.00, C(15) 0.00, C(16) 0.00, C(17) 0.00, C(18) −0.01, C(19) 0.00, *C(13)* 0.01, *O(3)* −1.23, *O(3')* 0.03
(ii)	C(20) 0.01, C(21) −0.01, C(22) 0.00, C(23) 0.01, C(24) 0.00, C(25) −0.01, *C(2)* 0.03, *O(1)* 0.06, *C(3)* 0.08

Atoms in italics were not included in the derivation of the plane

were dissolved in ethanol (25 ml) and the solution was treated with dry hydrogen chloride for 2 h. The crystalline phenalenium salts were collected by filtration and worked up as above. The alkali-soluble fraction was crystallised from benzene–methanol (4 : 1) to give 6-hydroxy-9-(4-methoxyphenyl)-1*H*-phenalen-1-one (5; R = OMe) as orange needles (0.32 g, 53.0%), m.p. 278—279 °C (lit.,[4d] 281—282 °C) (Found: C, 80.2; H, 4.5%. Calc. for $C_{20}H_{14}O_3$: C, 80.5; H, 4.7%); $\lambda_{max.}$ ($CHCl_3$) 277 and 445 nm (log ε 4.28 and 4.03); $\nu_{max.}$ (1 630 cm^{-1}; δ ([$^2H_6$]Me_2SO) 3.83 (3 H, s, OMe), 6.46 (1 H, d, *J* 9.0 Hz, =CH), 6.97 (3 H, d, *J* 8.0 Hz, 2 × ArH + =CH), 7.28 (2 H, d, *J* 8.0 Hz, 2 × ArH), 7.53 (1 H, d, *J* 8.0 Hz, =CH), 7.80 (1 H, d, *J* 9.0 Hz, =CH), 7.85 (1 H, d, *J* 8.0 Hz, =CH), and 8.54 (1 H, d, *J* 8.0 Hz, =CH); *m/z* 302 (M^+, 100%), 301 (8), 271 (4), 259 (5), 258 (5), 242 (5), 229 (3.5), and 203 (8).

The alkali-insoluble compound, 4-(4-*methoxybenzoyl*)-2-(4-*methoxyphenyl*)-6H-*phenaleno*[1,9-bc]*pyran*-6-*one* (7; R = OMe) formed red needles (from benzene) (0.3 g, 32.6%), m.p. >300 °C (Found: C, 78.1; H, 4.7%. $C_{30}H_{20}O_5$ requires C, 78.2; H, 4.4%); $\lambda_{max.}$ ($CHCl_3$) 283, 386, 482sh, 511, and 546 nm (log ε 4.56, 4.01, 4.20, 4.41, and 4.32); $\nu_{max.}$ 1 645 and 1 638 cm^{-1}; δ 3.88 and 3.90 (each 3 H, s, OMe), 6.91 (1 H, d, *J* 9.5 Hz, =CH), 6.99 (3 H, d, *J* 8 Hz, 2 × ArH + =CH), 7.35 (1 H, s, =CH), 7.43 (1 H, d, *J* 8.5 Hz, =CH), 7.80—7.95 (6 H, m, 6 × ArH), 8.00 (1 H, d, *J* 8.5 Hz, =CH), and 8.86 (1 H, s, =CH); *m/z* 460 (M^+, 100%).

Reaction of 2,7-*Dihydroxynaphthalene*-1-*carbaldehyde* (2) *with* 4-*Bromoacetophenone*.—Dry hydrogen chloride was passed through a solution of the aldehyde (2) (0.94 g, 5.0 mmol) and the ketone (3.98 g, 20.0 mmol) in ethanol (20 ml) for 3 h. After 24 h the solvent was removed and the residue was treated with sodium carbonate and worked up as before. The alkali-soluble product, 9-(4-*bromophenyl*)-6-*hydroxy*-1H-*phenalen*-1-*one* (5; R = Br), was crystallised from benzene–methanol (4 : 1) in orange needles (0.27 g, 15.3%), m.p. >300 °C (Found: C, 65.0; H, 3.2; Br, 23.1%. $C_{19}H_{11}BrO_2$ requires C, 65.0; H, 3.2; Br, 22.8%); $\lambda_{max.}$ (C_5H_5N) 318, 360, and 446 nm (log ε 3.96, 3.70, and 4.04); $\nu_{max.}$ 1 630 cm^{-1}; δ ([$^2H_6$]Me_2SO) 6.48 (1 H, d, *J* 9.0 Hz, =CH), 6.89 (1 H, d, *J* 9.0 Hz, =CH), 7.28 (2 H, d, *J* 9.5 Hz, 2 × ArH), 7.52 (1 H, d, *J* 9.0 Hz, =CH), 7.58 (2 H, d, *J* 9.5 Hz, 2 × ArH), 7.82 (1 H, d, *J* 9.0 Hz, =CH), 7.87 (1 H, d, *J* 9.0 Hz, =CH), and 8.57 (1 H, d, *J* 9.0 Hz, =CH); *m/z* 350 (M^+ with ^{79}Br, 89%), 349 (32), 281 (14), 271 (100), 242 (28), 213 (14), 198 (13), and 167 (18).

The red compound, 4-(4-*bromobenzoyl*)-2-(4-*bromophenyl*)-6H-*phenaleno*[1,9-bc]*pyran*-6-*one* (7; R = Br), formed dark red needles (from ethoxyethanol) (0.41 g, 14.7%), m.p. >300 °C (Found: C, 59.9; H, 2.8; Br, 28.3%. $C_{28}H_{14}Br_2O_3$ requires C, 60.2; H, 2.5; Br, 28.6%); $\lambda_{max.}$ (C_5H_5N) 325, 358, 419, 484sh, 510, and 543sh nm (log ε 4.04, 4.10, 3.85, 4.24, 4.33, and 4.16); $\nu_{max.}$ 1 656 and 1 642 cm^{-1}; δ (CF_3CO_2D) 7.79 (6 H, m, 6 × ArH), 8.04 (1 H, d, *J* 9.0 Hz, =CH), 8.19 (2 H, d, *J* 9.0 Hz, 2 × ArH), 8.45 (1 H, d, *J* 9.5 Hz, =CH), 8.99 (2 H, m, =CH), 9.12 (1 H, d, *J* 9.5 Hz, =CH), and 9.68 (1 H, s, =CH); *m/z* 556 (M^+ with ^{79}Br, 100%), 528 (5), 478 (5), 401 (10), 373 (14), and 237 (5.5).

Reduction of 4-*Benzoyl*-2-*phenyl*-6H-*phenaleno*[1,9-bc]-*pyran*-6-*one* (7; R = H).—Sodium borohydride (38 mg) was added to a solution of the ketone (7; R = H) (200 mg) in dioxan (25 ml) and the mixture was stirred for 14 h, during which time a red solid precipitated. Crystallisation from ethoxyethanol to give 4-(α-*hydroxybenzyl*)-2-*phenyl*-6H-*phenaleno*[1,9-bc]*pyran*-6-*one* (9; R = H) as dark-red needles with a green metallic reflex (0.13 g, 65%), m.p. 285—286 °C (Found: C, 83.9; H, 4.7%. $C_{28}H_{18}O_3$ requires C, 83.6; H, 4.5%); $\lambda_{max.}$ [$CHCl_3$–MeOH (9 : 1)] 276, 308, 345, 374, 486, 511, and 544 nm (log ε 4.55, 3.96, 3.87, 3.83, 4.18, 4.38, and 4.32); $\nu_{max.}$ 3 350br and 1 641 cm^{-1}; δ ([$^2H_6$]Me_2SO) 6.35 (1 H, d, *J* 3 Hz, CHO*H*, exchangeable with D_2O), 6.58 (1 H, d, *J* 3 Hz, C*H*OH, collapses to a singlet at δ 6.55 on D_2O exchange), 6.77 (1 H, d, *J* 9.5 Hz, =CH), 7.20—7.71 (9 H, m, ArH + =CH), 7.85 (1 H, s, =CH), 8.05—8.25 (4 H, m, ArH + =CH), and 8.80 (1 H, s, =CH); *m/z* 402 (M^+, 100%), 386 (28), 385 (16), 325 (14), 297 (8), 281 (5), and 239 (6).

Reduction of 4-(4-*Methoxybenzoyl*)-2-(4-*methoxyphenyl*)-6H-*phenaleno*[1,9-bc]*pyran*-6-*one* (7; R = OMe).—Sodium borohydride (380 mg) was added to the ketone (7; R = OMe) (115 mg) partially dissolved in dimethylformamide (10 ml), and the mixture was stirred for 16 h. The deep-red solution was poured into water (100 ml) to give the product (9; R = OMe) which was collected by filtration and purified by p.l.c. with chloroform–methanol (19 : 1) as developer, followed by crystallisation from nitromethane to give the *alcohol* (9; R = OMe) as dark-red needles (70 mg, 60.6%), m.p. 236—237 °C (Found: C, 77.8; H, 5.0%. $C_{30}H_{22}O_3$ requires C, 77.9; H, 4.8%); $\lambda_{max.}$ [$CHCl_3$–MeOH (9 : 1)] 282, 310sh, 486sh, 514, and 549 nm (log ε 4.63, 4.07, 4.15, 4.40, and 4.39); $\nu_{max.}$ 3 350 and 1 640 cm^{-1}; δ ([$^2H_6$]Me_2SO) 3.70 and 3.86 (each 3 H, s, OMe), 6.17 (1 H, d, *J* 4 Hz, CHO*H* exchangeable), 6.46 (1 H, d, *J* 4 Hz, C*H*OH, collapses to a singlet at δ 6.44 on D_2O exchange), 6.76 (1 H, d, *J* 8.5 Hz, =CH), 6.91 (2 H, d, *J* 8.0 Hz, 2 × ArH), 7.13 (2 H, d, *J* 8.0 Hz, 2 × ArH), 7.41 (2 H, d, *J* 8.0 Hz, 2 × ArH), 7.52 (1 H, d, *J* 8.5 Hz, =CH), 7.66 (1 H, s, =CH), 8.06 (3 H, (3 H, m, 2 × ArH + =CH), 8.15 (1 H, d, *J* 8.5 Hz, =CH), and 8.79 (1 H, s, =CH); *m/z* 462 (M^+, 100%), 445 (71), 355 (4), 327 (7), and 310 (6).

Deformylation of 2,7-*Dihydroxynaphthalene*-1-*carbaldehyde* (2).—Dry hydrogen chloride was passed through a solution of the aldehyde (2) (188 mg) in ethanol (10 ml) for 30 min. After evaporation the product was purified by p.l.c. with chloroform–ethyl acetate (9 : 1) as developer, followed by crystallisation from benzene to give 2,7-dihydroxynaphthalene (11) as needles (130 mg, 82%), m.p. and mixed m.p. 189 °C.

8-*Bromo*-2,7-*dihydroxynaphthalene*-1-*carbaldehyde*.—To a stirred solution of compound (2) (3.76 g, 20.0 mmol) in pyridine (100 ml) was added a solution of bromine (4.8 g, 30.0 mmol) in the same solvent (50 ml) during 1 h. The mixture was stirred for a further 1 h, the volume was then reduced to 30 ml, and the residual mixture was poured into ice–water (250 ml) containing concentrated hydrochloric acid (75 ml). The precipitate was crystallised from chloroform as plates (2.9 g, 52%), m.p. 159—160 °C (Found: C, 49.3; H, 2.9; Br, 30.1%. $C_{11}H_7BrO_3$ requires C, 49.3; H, 2.6; Br, 29.9%); $\nu_{max.}$ 3 240, 1 618sh, and 1 612 cm^{-1}; δ ([$^2H_6$]Me_2CO) 6.98, 7.26, 7.83,

and 8.02 (each 1 H, d, *J* 8.5 Hz, ArH); *m/z* 266 (M^+ with ^{79}Br, 7%) and 187 (100).

Debromination of 8-*Bromo*-2,7-*dihydroxynaphthalene*-1-*carbaldehyde*.—Dry hydrogen chloride was passed through a solution of the bromo compound (134 mg) in ethanol (25 ml) for 30 min. After evaporation the residue was purified by preparative h.p.l.c. with chloroform–ethyl acetate (4 : 1) as eluant to give 2,7-dihydroxynaphthalene-1-carbaldehyde (2) (35%) and 2,7-dihydroxynaphthalene (11) (20%).

2,7-*Dihydroxy*-8-*methylnaphthalene*-1-*carbaldehyde*.—Dry hydrogen chloride was passed through a suspension of 2,7-dihydroxy-1-methylnaphthalene [8] (1.74 g, 10.0 mmol) and zinc cyanide (1.29 g, 11.0 mmol) in dry diethyl ether (50 ml) for 4 h. The insoluble solid was collected by filtration, washed with diethyl ether, and was then stirred in water (100 ml) on a steam-bath for 1 h. The mixture was filtered and the residue was crystallised from toluene to give the *title aldehyde* as needles, m.p. 129 °C (1.4 g, 69%) (Found: C, 71.2; H, 4.5%. $C_{12}H_{10}O_3$ requires C, 71.3; H, 5.0%); $\lambda_{max.}$ 3 240 and 1 605 cm^{-1}; δ 2.62 (3 H, s, Me), 5.34 [1 H, s, 7(OH), exchangeable], 6.96, 6.98, 7.58, and 7.84 (each 1 H, d, *J* 9.0 Hz, ArH), 10.30 (1 H, s, CHO), and 13.38 [1 H, s, 2(OH), exchangeable]; *m/z* 202 (M^+, 40%), 184 (100), 156 (11), 128 (11), and 115 (10).

Reaction of Benzoylacetaldehyde with 2,7-*Dihydroxynaphthalene* (11).—Benzoylacetaldehyde (as sodium salt [9]) (8.5 g, 50 mmol) was added to a solution of 2,7-dihydroxynaphthalene (11) (0.8 g, 5 mmol) in ethanol (50 ml), and dry hydrogen chloride was passed through the resultant suspension for 3 h. The solvent was then evaporated off and the residue was boiled under reflux with a mixture of water (30 ml), ethanol (50 ml), and sodium carbonate (5.0 g) for 1 h; the mixture was then diluted with water (250 ml) and extracted with diethyl ether. Evaporation and p.l.c. with chloroform–ethyl acetate (9 : 1) as eluant gave an orange and a red compound. The former was crystallised from benzene–methanol (4 : 1) as orange plates (68 mg, 5.0%), m.p. 285 °C, identical with compound (5; R = H) described above, while the latter separated out from ethoxyethanol as dark-red needles (550 mg, 27.5%), m.p. 283 °C, identical with compound (7; R = H) described above.

Reaction of 4-*Methoxybenzoylacetaldehyde with* 2,7-*Dihydroxynaphthalene* (11).—Dry hydrogen chloride was passed through a suspension of 2,7-dihydroxynaphthalene (11) (1.6 g, 10 mmol) and 4-methoxybenzoylacetaldehyde (as sodium salt) (20.1 g, 100.0 mmol) in ethanol (50 ml) for 6 h. The solvent was removed and the residue was worked up as before to give compound (5; R = OMe) as orange plates (90 mg, 3.5%), m.p. 280 °C and compound (7; R = OMe) as dark-red needles (640 mg, 16%), m.p. >300 °C, both identical with the products described above.

1H-*Naphtho*[2,1,8-mna]*xanthen*-1-*one* (15).—Dry hydrogen chloride was passed through a solution of the aldehyde (2) (0.94 g, 5 mmol) and 2-hydroxyacetophenone (0.75 g, 5.5 mmol) in ethanol (50 ml) for 4 h. After evaporation the residue was boiled under reflux with a mixture of water (15 ml), ethanol (25 ml), and sodium carbonate (2.0 g) for 1 h and the mixture was then diluted with water (250 ml). The precipitate was purified by dry column chromatography with chloroform–ethyl acetate (9 : 1) as eluant, followed by crystallisation from benzene to give the xanthenone (15) as small, red plates (0.44 g, 32.5%), m.p. 222—224 °C (lit.,[4b] 226 °C) (Found: C, 84.2; H, 4.0%. Calc. for $C_{19}N_{20}O_2$: C, 84.4; H, 3.7%), identical (t.l.c., u.v., m.s.) with an authentic sample.

4-*Benzyl*-2-*phenyl*-6H-*phenaleno*[1,9-bc]*pyran*-6-*one* (17).—(a) Ethyl bromide (1.2 g, 11.0 mmol) was added dropwise to a stirred suspension of magnesium (0.26 g, 11.0 mg-atom) in dry diethyl ether (50 ml) under nitrogen during 30 min. After being stirred for a further 1 h the solution was added dropwise to a solution of 2,7-dihydroxynaphthalene (11) (1.6 g, 10 mmol) in diethyl ether (50 ml) during 15 min. After being stirred for a further 15 min the solution was evaporated to dryness and the residue was suspended and stirred in benzene (50 ml) to which a solution of cinnamaldehyde (2.64 g, 20.0 mmol) in benzene (50 ml) was added during 2 h. The red solid precipitate was collected by filtration, washed with benzene, and was then stirred for 1 h in water (225 ml) containing concentrated hydrochloric acid (25 ml). The resulting red oil was extracted into chloroform, and the extract was washed with water, dried ($MgSO_4$), and purified by dry column chromatography with chloroform–ethyl acetate (9 : 1) as eluant, followed by crystallisation from toluene to give the *title ketone* as dark-red needles (0.52 g, 13.5%), m.p. 169—171 °C (Found: C, 87.2; H, 4.9%. $C_{28}H_{18}O_2$ requires C, 87.0; H, 4.7%); $\lambda_{max.}$ ($CHCl_3$) 263, 344, 378, 484, 509, and 542 nm (log ε 4.34, 3.65, 3.51, 3.98, 4.12, and 3.98); $\nu_{max.}$ 1 644 cm^{-1}; δ 4.34 (2 H, s, CH_2), 6.74 (1 H, s, =CH), 6.95—7.92 (14 H, m, 2 × Ph + 4 × =CH), and 8.73 (1 H, s, =CH); *m/z* 386 (M^+, 100%), 309 (6), and 250 (5). Reducing the amount of ethyl bromide or cinnamaldehyde used only reduced the yield of compound (17).

(b) A solution of the alcohol (9; R = H) (0.4 g, 1.0 mmol) in dioxan (50 ml) was stirred at 50 °C for 1 h with toluene-4-sulphonyl chloride (0.18 g, 1.0 mmol) and anhydrous sodium acetate (80 mg, 1.0 mmol). After the mixture had cooled, lithium aluminium hydride (0.15 g, 4.0 mmol) was added and the mixture was stirred for 2 h at room temperature, and for 2 h at 80 °C. Filtration and evaporation left a red solid which, after p.l.c. (chloroform as eluant) and crystallisation from toluene, gave red needles of compound (17) (20 mg, 5%), m.p. 169 °C, identical with a sample obtained in (a) above.

4-(2-*Nitrobenzyl*)-2-(2-*nitrophenyl*)-6H-*phenaleno*[1,9-bc]-*pyran*-6-*one*.—The above reaction (a) was repeated but with the cinnamaldehyde replaced by 2-nitrocinnamaldehyde (2.68 g, 15.0 mmol). The same work-up afforded dark-red needles of the *title compound* (0.4 g, 8.5%), m.p. 289—290 °C (from ethoxyethanol) (Found: C, 70.7; H, 3.6; N, 5.7%. $C_{28}H_{16}N_2O_6$ requires C, 70.6; H, 3.4; N, 5.9%); $\lambda_{max.}$ 269, 362. 5, 485, 510, and 543 nm (log ε 4.57, 3.94, 4.18, 4.22, and 3.99); $\nu_{max.}$ 1 645, 1 619, 1 563, 1 525, 1 379, and 1 345 cm^{-1}; δ ([$^2H_6$]-Me_2SO) 4.73 (2 H, s, CH_2), 6.76 (1 H, d, *J* 9.5 Hz, =CH), 7.57—8.64 (12 H, m, 8 × ArH + 4 × =CH), and 8.88 (1 H, s, =CH); *m/z* 476 (M^+, 100%) and 446 (16).

Crystal Structure Determination of 4-(α-*Hydroxybenzyl*)-2-*phenyl*-6H-*phenaleno*[1,9-bc]*pyran*-6-*one* (9; R = H)—*Crystal data*. $C_{28}H_{18}O_3$, M = 402.1 monoclinic, a = 8.332(3), b = 12.545(5), c = 18.917(14) Å, β = 97.04(5)°, U = 1 962 Å^3, D_c = 1.36 g cm^{-3}, Z = 4, F(000) 840, space group $P2_1/c$. Mo-K_α radiation, λ = 0.7107 Å, μ = 0.49 cm^{-1}.

Final values of the cell dimensions, for a dark-red crystal, were determined from angular measurements on a Nicolet P3 automatic diffractometer. Reflections in the range θ < 25° were surveyed and the intensities of 1 947 independent reflections with $I > 2.5\sigma(I)$ were obtained.

The crystal structure was elucidated by direct methods using the programme MULTAN.[10] The C- and O-atom positions were located from the *E*-map and the remaining H-atom positions were observed on Fourier difference maps obtained at intermediate stages of least-squares refinement. The SHELX [11] suite of programmes was employed.

The oxygen atom of the hydroxy group appeared in the electron-density distribution as two distinct peaks, one in each of the stereochemically acceptable sites. Accordingly, the occupation factors of the 13(H) and 13(OH) atoms were refined and converged at 0.67 and 0.33. During the least-squares calculations equivalent bond lengths involving the 13(H) and 13(OH) atoms were constrained to be equal.

With the adoption of anisotropic thermal parameters for the C and O atoms, and isotropic thermal parameters for the H atoms, convergence was reached at R 5.8%. The weighting scheme used in the final calculations is given by $[w = 0.1557/\sigma^2(F_o) + 0.0012F_o^2]$. Observed and calculated structure amplitudes and the thermal parameters of the atoms are listed in Supplementary Publication No. 23556 (15 pp.).*

* For details of the Supplementary publications scheme, see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

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