Oxidation of 2′-Hydroxy-α-phenylchalcones: Substituent Effects on the Course of the Algar–Flynn–Oyamada (AFO) Reaction

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In alkaline hydrogen peroxide, 2′-hydroxy-α-phenylchalcones with and without a 6′-methoxy-substituent cyclised preferentially at the β-carbon atom to give chromanones. Fusion of a benzene ring at the 5′- and 6′-positions in the chalcone affected the directive influence of the α-phenyl group, and AFO oxidation afforded a 1 : 1 mixture of α- and β-cyclisation products. Products of aerial oxidation of the chalcones were also studied.

THE AFO reaction [1] (oxidation of 2′-hydroxychalcones by alkaline hydrogen peroxide) affords a useful general synthesis of flavanoids.

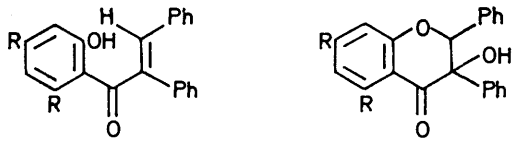
The preferential formation of derivatives of aurone [2-benzylidenebenzofuran-3(2*H*)-one] in the AFO oxidation of 2′-hydroxychalcones with a phloroglucinol-type ring A is due to the directive influence of the 6′-substituent.[2] This influence may be counteracted to some extent by the presence of a 2-[3] or 4-[4] hydroxy-group or by an increase in reaction temperature.[5]

As part of a programme to extend the scope of the AFO reaction, a series of experiments was carried out on 2′-hydroxychalcones containing an α-phenyl substituent. It was considered that coulombic repulsion of the α-phenyl group by the phenoxide ion would outweigh the steric effect of a 6′-methoxy-group and lead to preferential cyclisation at the β-carbon atom to give chromanones.

The chalcones (Ia and b) chosen for the initial studies were prepared by condensation of the corresponding deoxybenzoin and aldehyde, and were obtained as mixtures of *Z*- and *E*-isomers. The assignment of configuration to these chalcones is based on their u.v. and i.r. spectra. The chalcones assigned a *Z*-configuration exhibited larger ε values than the corresponding *E*-isomers and their ν_{CO} i.r. bands are at higher wavenumbers (10 cm^{-1}).[6] The *E*-isomer of the chalcone (Ia), which is the main condensation product, was used in the oxidation studies. The major oxidation products (IIa and b) have spectra (i.r. and n.m.r.) in accord with the chromanone structure. Mass spectra provided conclusive evidence for the heterocyclic structures.

[1] T. S. Wheeler, *Rec. Chem. Progr.*, 1957. **18**, 133.
[2] T. A. Geissman and D. K. Fukushima, *J. Amer. Chem. Soc.*, **70**, 1686.
[3] T. H. Simpson and W. B. Whalley, *J. Chem. Soc.*, 1955, 166.
[4] N. Anand, R. N. Iyer, and K. Venkataraman, *Proc. Indian Acad. Sci.*, 1949, **29***A*, 203.
[5] (*a*) J. Algar and J. P. Flynn, *Proc. Roy. Irish Acad.*, 1934, **42***B*, 1; (*b*) T. Oyamada, *J. Chem. Soc. Japan*, 1934, **55**, 1256.
[6] (*a*) R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' Wiley, New York, 1967; (*b*) W. B. Black and R. E. Lutz, *J. Amer. Chem. Soc.*, 1953, **75**, 5990; (*c*) W. F. Winecoff, tert., and D. W. Boykin, jun., *J. Org. Chem.*, 1972, **37**, 674; (*d*) P. J. Duke and D. W. Boykin, jun., *ibid.*, p. 1436.

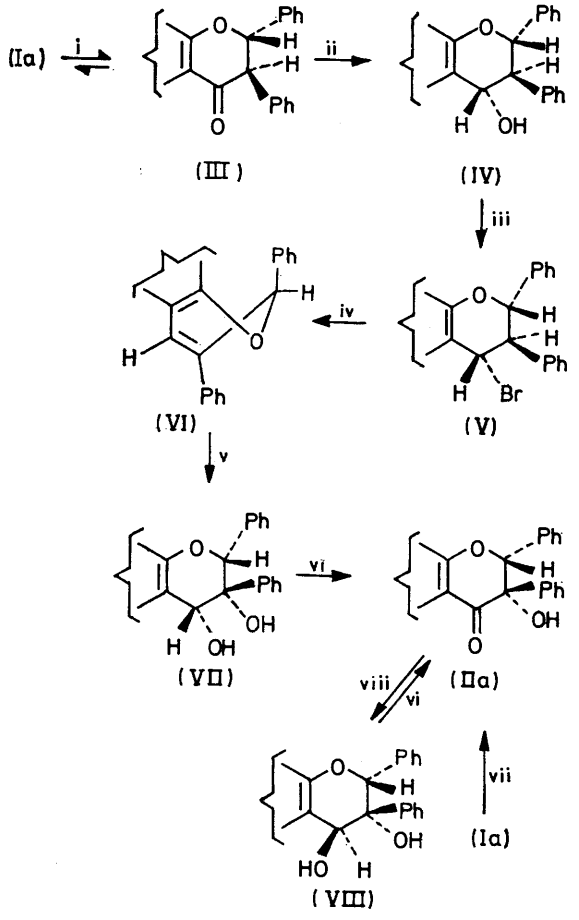
The evidence for the assignment of configuration of the substituents at C-3 was obtained from synthesis of 3-hydroxy-3-phenylflavanone (IIa) (see Scheme), from



(I) (II)

a; R = H
b; R = OMe

analysis of its n.m.r. spectrum, and from attempted dehydration experiments. In the synthesis, *t*-3-phenyl-(*r*-2-Ph)flavanone (III), the product of cyclisation with



SCHEME Reagents: i, OH^-, pH 10; ii, $NaBH_4$–MeOH; iii, PBr_3–Et_2O; iv, C_5H_5N, heat; v, OsO_4–C_6H_6; vi, CrO_3–AcOH; vii, O_2–^-OH or H_2O_2–^-OH; viii, $NaBH_4$–MeOH

base of the *E*-chalcone (Ia), was reduced by sodium borohydride in an aprotic solvent to give the *t*-3-phenyl-(*r*-2-Ph)flavan-*c*-4-ol (IV), which was thus designated on analytical, i.r., and n.m.r. evidence ($J_{2,3} = J_{3,4} = 11$ Hz). Bromination of the flavan-4-ol followed by dehydrobromination with pyridine [7] yielded 3-phenylflav-3-ene (VI). The olefinic proton signals in the n.m.r. spectrum of the flavene (VI) are masked in the aromatic region, and the stereochemical assignment is based on the similarity between its u.v. spectrum and that of the *E*-stilbene system. Thus the likely conformation is (VI). Stereospecific hydroxylation of 3-phenylflav-3-ene (VI) with osmium tetraoxide yielded the stable *cis*-diol (VII). Analogous *cis*-diols have been prepared from the flav-3-ene [7] and 3-methylflav-3-ene.[8] Oxidation of the diol (VII) afforded the flavanol (IIa) identical (m.p.; i.r., n.m.r., and mass spectra) with the AFO product. A second diol (VIII), the 4-epimer of the diol (VII), was prepared by reduction of the product (IIa) with sodium borohydride.

Comparable results were observed in the oxidation of 2′-hydroxy-2-methoxy-α-phenylchalcone and in the synthesis of 3-hydroxy-2′-methoxy-3-phenylflavanone. In the synthetic sequence, the formation of isomeric alcohols was observed in the reduction of the 2′-methoxy-*t*-3-phenyl(*r*-2-Ph)flavanone, the minor isomer is identified as 2′-methoxy-*c*-3-phenyl(*r*-2-Ar)flavan-*c*-4-ol ($J_{2,3} = J_{3,4} = 2.5$ Hz). 3-Hydroxy-3-phenylflavanone (IIa) remained unchanged when subjected to dehydrating conditions. Crombie and Godin [9] found that for isorotenolones A and B, the corresponding dehydration products are obtained by a *cis*- and a *trans*-elimination under acidic treatment; however, the 3-phenylflavanon-3-ol (IIa) is stable to acid and to heat. An explanation of this stability is the likely hindrance of the phenyl substituent to the alignment of the 3-OH and 2-H for a *cis*-elimination.

Oxidation of 1-(2-hydroxy-1-naphthyl)-2,3-diphenylprop-2-en-1-one (IX) was then undertaken, in an effort to determine the extent and limit of the influence exerted by a chalcone 6′-substituent on the course of the AFO reaction.[10] It was felt that the effect (+*I*) of the additional benzene ring might be sufficient to overcome the directive influence of the α-phenyl group.

The chalcone (IX) formed by condensation of 1-phenylacetyl-2-naphthol with benzaldehyde, was isolated as a monoacetate [τ 7.75 (2-OAc)] and was cyclised with sodium hydroxide to afford the corresponding *cis*-(major) and *trans*-flavanones. The presence in minor yield of a second chalcone isomer [τ 8.08 (2′-OAc)] was noted. AFO oxidation of the chalcone (IX) yielded a 1 : 1 mixture of 2,3-dihydro-2-hydroxy-2,3-diphenylnaphtho[2,1-*b*]pyran-1-one (X) and 2-(α-hydroxybenzyl)-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (XI) as shown by n.m.r. and mass spectral analyses. In the mass spectrum of the latter (XI) rupture occurs at the C(2)–CH bond with simultaneous hydrogen transfer.[8]

The susceptibility of the 3-phenylflavanone system

[7] (*a*) K. G. Marathe, E. M. Philbin, and T. S. Wheeler, *Chem. and Ind.*, 1962, 1793; (*b*) B. J. Bolger, K. G. Marathe, E. M. Philbin, T. S. Wheeler, and C. P. Lillya, *Tetrahedron*, 1967, **23**, 431; (*c*) J. W Clark-Lewis and D. C. Skingle, *Austral. J. Chem.*, 1967, **20**, 2169.

[8] W. P. Cullen, D. M. X. Donnelly, A. K. Keenan, T. P. Lavin, D. P. Melody, and E. M. Philbin, *J. Chem. Soc.*, 1971, 2848.

[9] L. Crombie and P. J. Godin, *J. Chem. Soc.*, 1961, 2861.

[10] M. G. Marathey, G. Athavale, and K. G. Gore, *J. Univ. Poona, Sci. and Technol.*, 1954, 87.

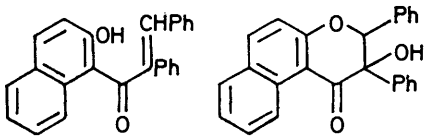
(isomeric with 2′-hydroxy-α-phenylchalcone) to autoxidation was recognised. It may occur subsequent to cyclisation of the chalcone and enolisation. Experiment demonstrated that treatment of the 2′-hydroxychalcone (Ia) with sodium hydroxide (1.5%) yielded only the isomeric *trans*-3-phenylflavanone (III); however, retention of the latter compound in solution by introduction of ethanol gave the product (IIa). Studies of this base-catalysed reaction under varying conditions (*e.g.* presence of air or oxygen; pH) showed yields akin to those observed in the AFO reaction. Results obtained by changing pH are summarised in Table 1. The pH in the AFO reactions is 13.2.

TABLE 1

Product dependence on pH (% yields)

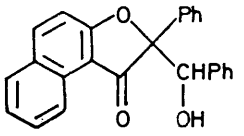
Product	pH 8	pH 9	pH 10	pH 11
2′-Hydroxy-α-phenylchalcone	84	60	0	14.5
t-3-Phenyl(*r*-2-Ph)flavanone	16	40	100	53.6
3-Hydroxy-3-phenylflavanone	0	0	0	31.9

Autoxidation at a benzylic position adjacent to a carbonyl group is recorded as a side reaction in the oxidation of indan-1-one [11] and in the alkylation of 2-acetyl-2-hydroxycoumaranone.[12] A further example is the conversion of (±)-deguelin into (±)-tephrosin and (±)-isotephrosin.[9]



(IX)

(X)



(XI)

EXPERIMENTAL

Unless otherwise stated, the following generalisations apply. M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were measured for KBr discs and 60 MHz n.m.r. spectra for solutions in deuteriochloroform (tetramethylsilane as internal reference). Merck Kieselgel HF_{254} and $PF_{254+366}$ were used for thin- and thick-layer chromatography. The chromatograms were examined under u.v. illumination and by spraying with chlorosulphuric acid in acetic acid followed by heating.

General Preparation of Chalcones.—Equimolar quantities of the appropriate 2′-hydroxydeoxybenzoin and aldehyde in ethanol were refluxed with aqueous potassium hydroxide (50%) for 1 h. The product was poured into an excess of ice–hydrochloric acid (3 : 1) to liberate the chalcones, which were mixtures of *E*- and *Z*-isomers. From preparative chromatography, the *E*-isomers of the chalcones (Ia and b) were obtained as crystalline solids. (*E*)-2′-Hydroxy-α-phenylchalcone (Ia) [13] had m.p. 130—132° (pale yellow plates from methanol). (E)-*2′-Hydroxy-2-methoxy-α-phenylchalcone* had m.p. 125—126° (yellow needles from methanol) (Found: C, 79.8; H, 5.4. $C_{22}H_{18}O_3$ requires C, 79.9; H, 5.5%); $\nu_{max.}$ 1 625 cm^{-1}; $\lambda_{max.}$ (MeOH) 343 nm (ε 15 400). (Z)-*2′-Hydroxy-2-methoxy-α-phenylchalcone* was an oil (Found: C, 79.8; H, 5.4%); $\nu_{max.}$ 1 632 cm^{-1}; $\lambda_{max.}$ (EtOH) 344 nm (ε 24 500). 2′-Hydroxy-4,6-dimethoxy-α-phenylchalcone (Ib) was a yellow oil showing a dark brown colouration with iron(III) chloride. Attempts at purification repeatedly caused cyclisation to *5,7-dimethoxy-t-3-phenyl*(r-2-Ph)*flavanone*, m.p. 140—151° (needles from methanol) (Found: C, 76.9; H, 5.8. $C_{23}H_{20}O_4$ requires C, 76.7; H, 5.6%); $\nu_{max.}$ 1 669 cm^{-1}; τ 4.5 (d, 2-H), 5.95 (d, 3-H) ($J_{2,3}$ 10.05 Hz). 1-(*2-Hydroxy-1-naphthyl*)-*2,3-diphenylprop-2-en-1-one* (IX) had m.p. 130—132° (yellow needles from methanol) (65% yield) (Found: C, 85.4; H, 5.05. $C_{25}H_{18}O_2$ requires C, 85.7; H, 5.1%); $\lambda_{max.}$ (MeOH) 290 nm (ε 22 000). Acetylation (pyridine–acetic anhydride) afforded an *acetate*, m.p. 110° (needles from n-hexane) (Found: C, 82.7; H, 5.3. $C_{27}H_{20}O_3$ requires C, 82.6; H, 5.1%); τ 7.75 (s, 2′-OAc).

Algar–Flynn–Oyamada Oxidation.—In general, the 2′-hydroxy-α-phenylchalcone (1.0 g) in a mixture of methanol (20 ml) and aqueous sodium hydroxide (10 ml; 10%) was kept at 0—5 °C during addition of hydrogen peroxide (2 ml; 30%) with stirring, which was continued for a further 72 h at 0 °C. The product was liberated by ice–hydrochloric acid and extracted with ether. Evaporation of the washed and dried extracts gave the 3-hydroxy-3-phenylflavanones. The results of the oxidation experiments are summarised in Table 2.

Autoxidation.—A mixture of the *E*-chalcone (Ia) [or the flavanone (III)] (0.3 g), ethanol (20 ml), and sodium hydroxide (10 ml; 1.5%) was stirred at room temperature during 24 h, then added to ice-cold hydrochloric acid and extracted with chloroform. Evaporation of the washed and dried extracts gave 3-hydroxy-3-phenylflavanone (IIa) and the corresponding flavanone (III). Repetition of the reactions in oxygen usually gave improved yields (see Table 2).

Autoxidation of 2′-Hydroxy-α-phenylchalcone (Ia) *at various* pH *Values.*—In each experiment a buffer solution (2.5 ml) of specified pH was added to a solution of the chalcone (Ia) in ethanol (5.5 ml). The mixture was stirred at room temperature for 24 h and added to ice-cold hydrochloric acid (10%). Extraction with chloroform and evaporated yielded a mixture which was separated by preparative t.l.c. [eluant chloroform–benzene (3 : 1)]. The eluted compounds were crystallised from methanol and identified by mixed m.p. and n.m.r. spectra (Table 1).

Synthesis of 3-Hydroxy-3-phenylflavanone (IIa).—t-3-*Phenyl*(r-2-Ph)*flavan*-c-4-*ol* (IV). *t*-3-Phenyl(*r*-2-Ph)-flavanone [13] (500 mg) was reduced with sodium borohydride (500 mg) in methanol (40 ml) at room temperature. The product was liberated by ice-cold acetic acid. Crystallisation of the solid from aqueous methanol gave the *flavan-4-ol* (400 mg) as plates, m.p. 127—128° (Found: C, 83.5; H, 6.1. $C_{21}H_{18}O_2$ requires C, 83.4; H, 6.0%); $\nu_{max.}$ 3 305 cm^{-1}; τ 4.66 (d, *J* 11.05 Hz, 2-H), 6.74 (m, *J* 11.05 Hz, 3-H), and 4.69 (d, *J* 11.05 Hz, 4-H). The *monoacetate* crystallised from methanol as needles, m.p. 116° (Found:

[11] D. W. Brown, C. Denman, and H. O'Donnell, *J. Chem. Soc.*, 1971, 3195.

[12] F. M. Dean and K. Manunapichu, *J. Chem. Soc.*, 1957, 3112.

[13] D. M. X. Donnelly, A. K. Keenan, T. Leahy, E. M. Philbin, G. Janzsó, F. Kállay, and I. Koczar, *Tetrahedron*, 1972, **28**. 2545.

TABLE 2
Results of oxidation experiments and relevant spectroscopic data

α-Phenylchalcone	Oxidation product [a] (3-phenylflavanone)	% Yield AFO	% Yield air	% Yield O_2	M.p. (°C) (solvent)	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H	$\nu_{max.}$/cm^{-1} OH	$\nu_{max.}$/cm^{-1} CO	τ Values (J/Hz) [b] 2-H	3-OH	5-H/OMe	6-H	7-OMe	2'-OMe
2'-Hydroxy- (Ia)	3-Hydroxy (IIa)	70	50	73	152—154 (MeOH)	79.6	5.3	79.75	5.1	3 450	1 684	4.47	5.81	1.8 (d) (9.5)	2.31 (d) (9.5)		
2'-Hydroxy-4',6'-dimethoxy- (Ib)	3-Hydroxy-5,7-dimethoxy- (IIb)	52			172—173 (EtOH)	73.8	5.7	73.4	5.4	3 445	1 668	4.61	5.52	6.1	3.8	6.1	
2'-Hydroxy-2-methoxy-	3-Hydroxy-2'-methoxy-	20	43	40	156—157 (MeOH)	75.9	5.4	76.2	5.25	3 445	1 688	3.76	5.95	1.8 (d) (8.5)			6.09
	2'-Methoxy-	21	10	47	139—140 (MeOH)	79.8	5.4	79.9	5.4		1 687	3.97(d) (11)	5.68(d) (11)				6.4

[a] Unchanged chalcone was recovered in each oxidation reaction. [b] Unless otherwise stated all signals are singlets.

C, 80.4; H, 5.9. $C_{23}H_{20}O_3$ requires C, 80.2; H, 5.9%); $\nu_{max.}$ 1 754 cm^{-1}, τ 3.37 (d, *J* 9.48 Hz, 4-H), 4.63 (d, *J* 10 Hz, 2-H), and 6.43 (m, *J* 10 and 9.48 Hz, 3-H).

3-Phenylflav-3-ene (VI). Phosphorus tribromide (630 mg) was added to a stirred solution of 3-phenylflavan-4-ol (500 mg) in anhydrous ether at 0 °C and the solution was kept at room temperature for 16 h. Evaporation of the washed and dried ethereal extract afforded *c*-4-bromo-*t*-3-phenyl(*r*-2-Ph)flavan (V) as an unstable solid (80—90%). The n.m.r. spectrum was recorded immediately [τ 5.02 (d, *J* 10.1 Hz, 2-H), 6.38 (m, 3-H), and 4.30 (d, *J* 9.8 Hz, 4-H)]. The bromoflavan (V) (450 mg) in anhydrous pyridine (20 ml) was refluxed for 18 h and then added to an excess of ice-cold dilute hydrochloric acid. The *3-phenylflavene* (VI) which separated crystallised from ethanol in needles (270 mg), m.p. 125—126° (Found: C, 88.5; H, 5.9. $C_{21}H_{16}O$ requires C, 88.7; H, 5.7%); $\nu_{max.}$ 1 629 cm^{-1}, τ 3.71 (s, 2-H).

3-Phenyl(r-2-Ph)*flavan*-c-3,c-4-*diol* (VII). A solution of 3-phenylflav-3-ene (450 mg) in anhydrous benzene was added to a solution of osmium tetraoxide (500 mg) in benzene (20 ml). Pyridine (0.5 ml) was added and the mixture kept (3 days) at room temperature. The red crystals which separated were redissolved in methylene chloride (50 ml). This solution was stirred (6 h) during the addition of potassium hydroxide (2 g), mannitol (2 g), and water (50 ml). The organic layer was separated and the aqueous layer further extracted with methylene chloride. The residue obtained by evaporation of the dried extracts was crystallised from benzene–light petroleum (b.p. 40—60°) to give the *diol* (290 mg) as plates, m.p. 110—112° (Found: C, 79.5; H, 6.0. $C_{21}H_{18}O_3$ requires C, 79.2; H, 5.7%); $\nu_{max.}$ 3 335 and 3 261 cm^{-1}, τ 4.78 (s, 2-H), 5.15 (s, 4-H), 6.53 (s, 3-OH), and 7.1 (s, 4-OH).

3-Phenyl(r-2-Ph)*flavan*-c-3,t-4-*diol* (VIII). Reduction of 3-hydroxy-3-phenylflavanone (0.4 mg) in methanol with sodium borohydride (0.4 g) gave the corresponding diol (80%), m.p. 172—173°, rhombs from benzene–light petroleum (Found: C, 79.5; H, 5.9. $C_{21}H_{18}O_3$ as above); $\nu_{max.}$ 3 490 cm^{-1}. The *monoacetate* had m.p. 109—110° (Found: C, 76.7; H, 5.7. $C_{23}H_{20}O_4$ requires C, 76.65; H, 5.6%); $\nu_{max.}$ 1 715 and 3 410 cm^{-1}; τ 8.11 (s, 4-OAc), 5.01 (s, 3-OH), 4.65 (s, 2-H), and 3.63 (s, 4-H).

3-Hydroxy-3-phenylflavanone. A solution of chromium trioxide (50 mg) in water (2 ml) and acetic acid (5 ml) was added with stirring to the diol (VII) (100 mg) in acetic acid (5 ml). The mixture was stirred for 3 h then diluted with water (200 ml) and extracted with chloroform. When purified from methanol, the oil gave the flavanone (IIa) as needles (20 mg), m.p. and mixed m.p. 153—154°.

Synthesis of 2'-Methoxy-3-phenyl(r-2-Ar)*flavan*-c-3,c-4-*diol.*—The procedure adopted was similar to the preceding example. For *2'-methoxy-t-3-phenyl*(r-2-Ar)*flavanones* see Table 2. *2'-Methoxy-t-3-phenyl*(r-2-Ar)*flavan*-c-4-*ol* had m.p. 125—126° (rhombs from methanol) (Found: C, 79.0; H, 6.0. $C_{22}H_{20}O_3$ requires C, 79.5; H, 6.05%); τ 4.14 (d, *J* 11.0 Hz, 2-H), 6.4 (m, *J* 11.0 Hz, 3-H), 4.72 (d, *J* 11.0 Hz, 4-H), and 6.45 (s, OMe). *2'-Methoxy*-c-3-*phenyl*-(r-2-Ar)*flavan*-c-4-*ol* had m.p. 132—133° (plates from methanol) (Found: C, 79.8; H, 5.9%); τ 4.02 (d, *J* 2.5 Hz, 2-H), 6.06 (m, *J* 2.5 Hz, 3-H), 4.51 (d, *J* 2.5 Hz, 4-H), and 6.06 (s, 2'-OMe). *2'-Methoxy-3-phenylflav-3-ene* had m.p. 106—107° (needles from ethanol) (Found: C, 84.3; H, 5.9. $C_{22}H_{18}O_2$ requires C, 84.05; H, 5.75%); $\nu_{max.}$ 1 601 cm^{-1}. *2'-Methoxy-3-phenyl*(r-2-Ar)*flavan*-c-3,t-4-*diol* had m.p. 111—112° [rhombs from benzene–light petroleum (b.p. 40—60°)] (Found: C, 75.8; H, 5.8. $C_{23}H_{20}O_4$ requires C, 75.8; H, 5.8%); τ 6.02 (s, 2'-OMe). *2'-Methoxy-3-phenyl*(r-2-Ar)*flavan*-c-3,c-4-*diol* had m.p. 145—146° [rhombs from benzene–light petroleum (b.p. 40—60°)] (Found: C, 75.8; H, 5.6%); τ 6.2 (s, 2'-OMe).

Attempted Dehydration of 3-Hydroxy-3-phenylflavanone.—The 3-hydroxyflavanone (IIa) was heated (78 °C) in methanolic sulphuric acid (3 ml; 10%) for 24 h, cooled, and poured into ice–water. The solid which separated was crystallised from methanol to give starting material.

Cyclisation and AFO Oxidation of 1-(2-Hydroxy-1-naphthyl)-2,3-diphenylprop-2-en-1-one (IX).—The chalcone (IX) (1 g) in ethanol (10 ml) was treated (12 h) with sodium hydroxide (100 ml; 1.5%) to afford 2,3-*dihydro*-cis-2,3-*diphenylnaphtho*[2,1-b]*pyran*-1-*one* as an amorphous solid, m.p. 154° (Found: C, 85.6; H, 5.0. $C_{25}H_{18}O_2$ requires C, 85.69; H, 5.8%); $\nu_{max.}$ 1 670 cm^{-1}; τ 5.99 (d, *J* 3.0 Hz, 2-H) and 4.08 (d, *J* 3.0 Hz, 3-H). Fractional crystallisation from ethanol–benzene yielded the trans-*isomer*, m.p. 170—172° (Found: C, 85.3; H, 5.3%); τ 5.72 (d, *J* 10.8 Hz, 2-H) and 4.26 (d, *J* 10 Hz, 3-H).

AFO Oxidation of the Chalcone (IX).—Hydrogen peroxide (7 ml; 30%) was added under reflux to a solution of the chalcone (IX) (1.5 g) in methanol (30 ml) and sodium hydroxide (25 ml; 10%). Purification of the product (1.2 g) afforded a mixture of 2,3-dihydro-2-hydroxy-2,3-diphenylnaphtho[2,1-*b*]pyran-1-one (X) and 2-(α-hydroxybenzyl)-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (XI). Attempted separation by t.l.c. proved unsuccessful. Analytical and spectroscopic (n.m.r., mass) analyses indicated that the two products were present (Found: C, 82.0; H, 5.3. $C_{25}H_{18}O_3$ requires C, 82.0; H, 5.0%); τ [compound (X)] 5.3 (s, 2-OH) and 3.2 (s, 3-H); τ [compound (XI)] 4.7 (d, α-OH) and 3.62 (d, α-H), $J_{H,OH}$ 5.8 Hz.

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