Base-catalysed Acyloin Rearrangements: the First Synthesis of 4-Arylflavan-3-ones *via* Chalcone Epoxides

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3,3-Diaryl-2-hydroxypropiophenones are amenable to base-catalysed α-ketol rearrangements yielding isomeric 1-hydroxypropan-2-ones. These structural isomers exhibit marked differences in oxidation potential and serve as useful synthetic intermediates for novel 4-arylflavan-3-ones.

EPOXIDE-MEDIATED coupling reactions have recently been used by us to effect stereoselective β-addition of phenolic nuclei to 2′-(methoxymethoxy)-4-hydroxychalcones, thus leading to 3,3-diaryl-2-hydropropiophenones.[1] We now demonstrate the susceptibility of these propiophenones to alkaline-induced α-ketol rearrangements at elevated temperatures to give the corresponding 1,3,3-triaryl-1-hydroxypropan-2-ones, and the facile acid-catalysed conversion of the latter to structurally unique 4-arylflavan-3-ones.

RESULTS AND DISCUSSION

Treatment of the 4-hydroxychalcone (1) with alkaline hydrogen peroxide at 40 °C in the presence of 3,5-dimethoxyphenol gives, besides the previously described [1] propiophenones (2) and (3) (at 0 °C), also an α-diketone (12), a quinone methide (15), and racemates of each of the isomeric 1,3,3-triaryl-1-hydroxypropan-2-ones (6), (9), and (13). Similar treatment of propiophenone (3) but in the absence of hydrogen peroxide affords the propan-2-ones (9) and (13), the former being relatively unstable, converting partly into the more stable (13) *via* base-catalysed inversion at C-1. Prolonged reaction time leads to complete conversion of (9) to (13).

The propiophenone (2) on treatment with 1M-sodium hydroxide at 40 °C is subject to a similar transformation yielding (6), but without indication of a C-1 epimeric intermediate of type (9). The propan-2-one (6) is, however, accompanied by an oxygen-labile α-diketone (12) and the stable quinone methide (15), the latter originating from (12) by auto-oxidation. Formal oxidation of (6) with active manganese dioxide [2] also leads to (12) and (15), both in low yields. Formation of the latter compounds contrasts with the absence of related isomers from alkaline conversion of the propiophenone (3), presumably reflecting the higher oxidation potentials of the propan-2-ones (9) and (13) in comparison with that of (6).

The isomeric 1,3,3-triaryl-1-hydroxypropan-2-ones (6), (9), and (13), their dimethyl ethers (7) and (11), and triacetates (8), (10), and (14) exhibit similar mass-fragmentation patterns. Significant fragments, *m/e* 227 for the alcohols and *m/e* 269 for the triacetates, differentiate the rearranged α-ketols convincingly from the parent compounds (2) and (3), where the *m/e* 225 and 255 fragments predominate.[1] The prominent *m/e* 259 fragment is, of course, common to both groups of α-ketols. Daughter-ion analysis of the *m/e* 269 fragments confirms the original benzylic acetate groupings.

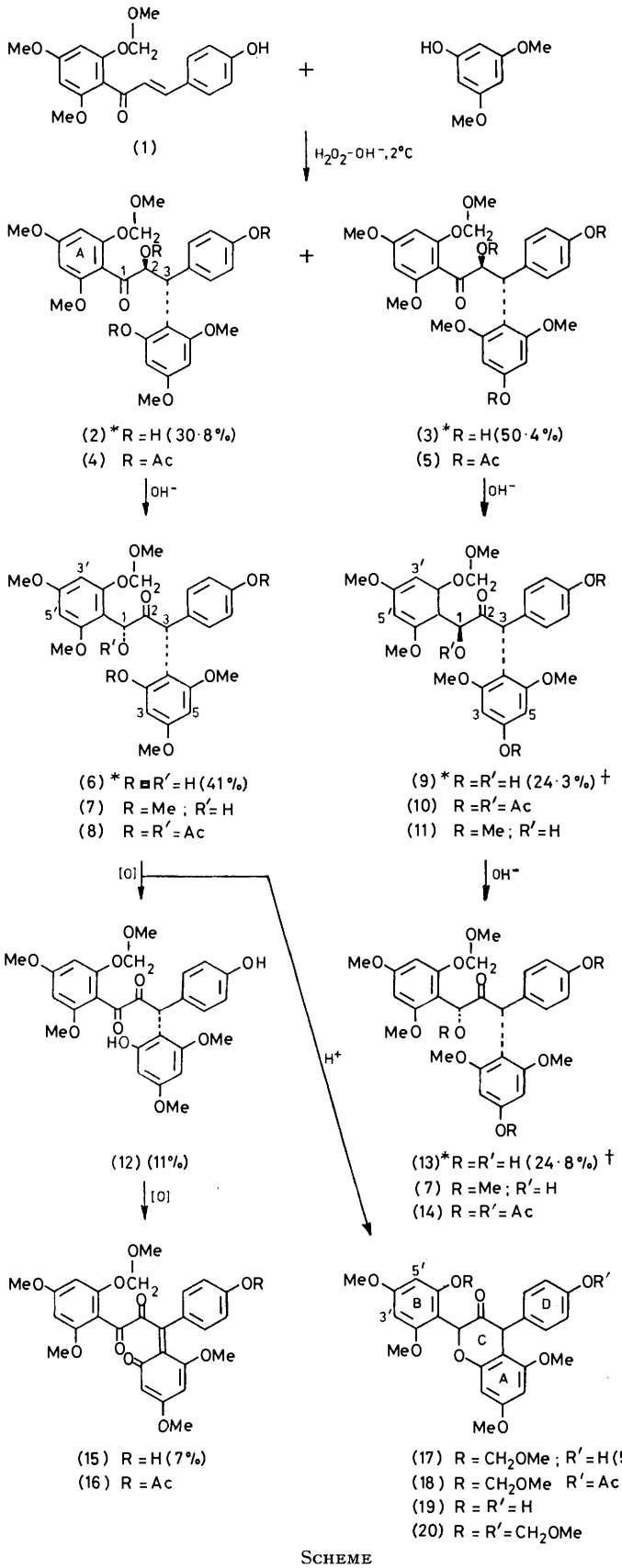
^{1}H N.m.r. spectra revealed marked differences between the two groups of α-ketols [(2), (3); and (6), (9), and (13)]. Whereas the spectra of the 2-hydroxypropiophenones (2) and (3) clearly show vicinal coupling of the 2- and 3-protons, the spectra of the 1-hydroxypropan-2-ones (6), (9), and (13) exhibit vicinal coupling between the 1- and C-1-hydroxy protons only (J 7.0, 4.5, and 5.0 Hz, respectively) and a slightly broadened singlet for 3-H due to benzylic or long-range coupling. Chemical shifts ($\Delta\tau$ 0.37) for one of the acetate signals in the spectra of triacetates (8) and (14) (τ 7.93) relative to those of the aliphatic acetates (τ 8.30) for (4) and (5), confirm the benzylic nature of the former. Notable is the abnormal high-field position of the C-1-acetate (τ 8.33) in (10) due to anisotropic shielding by ring C as is apparent from Dreiding models.

A carbonyl stretching absorption at 1 720—1 730 cm^{-1} for the 1-hydroxypropan-2-ones (6), (9), and (13) confirms the aliphatic nature of their C=O groups in contrast with absorption for (2) and (3) at 1 695—1 700 cm^{-1}, indicative of benzoyl C=O. I.r. data in conjunction with ^{1}H n.m.r. also define the α-diketone (12) and quinone methide (15); the C=O stretching band at 1 820 cm^{-1} being attributable to the quinone methide moiety in the latter instance.

Final proof of the structural relationship between (6) and (13) is provided by methylation with diazomethane, which gives the identical fully methylated α-ketol (7) in each instance. Considering the ease of formation of the enolic methyl ether [*e.g.* (22)] of conjugated α-hydroxychalcones [*e.g.* (21)] under similar conditions of methylation,[3] the absence of enolisation in the case of the 1-hydroxypropan-2-ones (6) and (13) may be ascribed to lack of conjugation in the anticipated products.

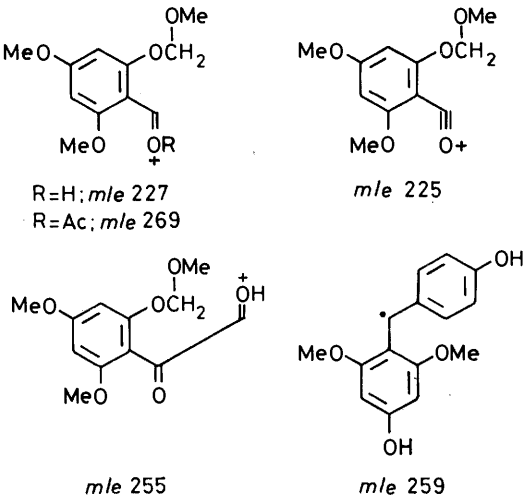
The alkaline-induced conversions of the propiophenones (2) and (3) may be rationalised in terms of aldol-type rearrangements, applicable to those sugars which are subject to significant changes in rotation under basic conditions.[4,5] Isomerisation [(2)→(6) and (3)→(9)] occurs *via* a 1,2-carbonyl shift [(23)→(24)→(25)] which appears unusual in that it entails loss of conjugation of the carbonyl group with ring A. Epimerisation of the 1-hydroxypropan-2-one (9) to (13) by inversion at C-1 is explicable on the same basis.

The benzylic nature of the hydroxy-group in (6) and

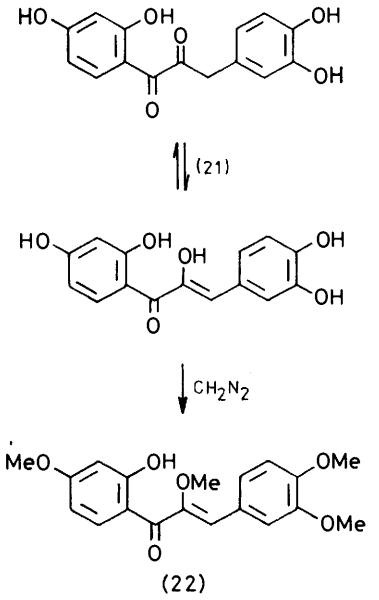


SCHEME

thus in (13) is established unambiguously by acid-catalysed conversion to the 4-arylflavan-3-ones (17), (19), and (20) *via* a carbocation-mediated cyclisation. The flavan-3-one (20) presumably originates from either (6)



or (17) by intermolecular migration of a methoxymethyl oxonium ion (CH_3–$\overset{+}{O}$=CH_2) liberated during the reaction. The structures of the flavan-3-ones were elucidated by means of ^{1}H n.m.r. (one-proton singlets for 2- and 4-H), i.r. (C=O absorption at 1 735 cm^{-1}), and mass



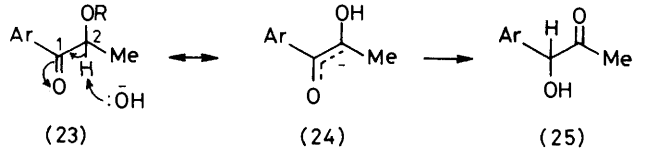
spectrometry (facile RDA fragmentation in each instance).

Since substitution of phloroglucinol or resorcinol for 3,5-dimethoxyphenol would ultimately lead to a single racemate of the 1-hydroxypropan-2-one type [*e.g.* (6)], the synthetic route, following cyclisation, offers the first

* Single enantiomer of each racemate indicated: stereochemistry based on relative chemical shifts of 1-H in preferred conformations.

† Combined yield from (3) totals 49%.

and general method of access to 4-arylflavan-3-ones, and one in which the functionalisation of the aromatic nuclei may be subject to selective variation. Yields are indicated in the Scheme.



(23) (24) (25)

EXPERIMENTAL

T.l.c. was performed on DC-Platikfolin Kieselgel 60 F_{254} (0.25 mm) and the plates sprayed with H_2SO_4–HCHO (40 : 1) after development. Preparative plates [Kieselgel PF_{254} (1.0 mm)] were air-dried and used without prior activation. Evaporations were carried out under reduced pressure with a water-bath temperature of 60 °C. Methylations were performed with an excess of diazomethane in methanol–diethyl ether at −15 °C for 48 h, while acetylations were carried out with acetic anhydride–pyridine. M.p.s were determined with a Reichert hot-stage apparatus. ^{1}H N.m.r. spectra were recorded on a Varian T-60 or Bruker WP-80 spectrometer with $SiMe_4$ as internal standard; mass-spectral data on a Varian CH-5 instrument; and i.r. data on a Unicam SP 1000 spectrophotometer for solutions in $CHCl_3$. Analyses (C and H) were performed by Analytische Laboratorien, Fritz-Pregl-Strasse 24, 5270 Gummersbach 1 Elbach, Germany.

Coupling and Conversion Reactions. 2-*Hydroxy*-3-(4-*hydroxy*-2,6-*dimethoxyphenyl*)-3-(4-*hydroxyphenyl*)-4′,6′-*dimethoxy*-2′-(*methoxymethoxy*)*propiophenone* (3) *and the* 3-(2-*Hydroxy*-4,6-*dimethoxyphenyl*) *Isomer* (2).—4-Hydroxy-4′,6′-dimethoxy-2′-(methoxymethoxy)-*trans*-chalcone (1) (1.2 g) and 3,5-dimethoxyphenol (2.15 g) in 1M-sodium hydroxide (36 ml) were cooled in ice. Hydrogen peroxide (6%, 20 ml) was added and the mixture stirred for 30 min at 2 °C. After acidification (3M-HCl) the mixture was extracted with ethyl acetate (3 × 100 ml); the extract was washed with water (6 × 100 ml), dried (Na_2SO_4) and evaporated. The residual solids were separated by p.l.c. in benzene–acetone (7 : 3 v/v) to give the two propiophenones (3) (R_F 0.22, 904 mg) and (2) (R_F 0.48, 552 mg). These propiophenones and their triacetates (5) and (4) were identical to those previously described.[1]

1-*Hydroxy*-1-[4,6-*dimethoxy*-2-(*methoxymethoxy*)*phenyl*-3-(4-*hydroxy*-2,6-*dimethoxyphenyl*)-3-(4-*hydroxyphenyl*)*propan*-2-*one* (9) *and the* C-1-*Epimer* (13).—Propiophenone (3) (200 mg) in 1M-sodium hydroxide (10 ml) was stirred under nitrogen for 1 h at 40 °C. Work-up and p.l.c. separation as above gave two bands, R_F 0.23 (48.5 mg) and R_F 0.20 (49.5 mg). Crystallisation of the former from ethanol afforded the propan-2-one (9) as *white platelets*, m.p. 201—202 °C (Found: C, 63.3; H, 5.9. $C_{27}H_{30}O_{10}$ requires C, 63.0; H, 5.9%). The latter fraction gave (13) as *white rods* (from ethanol), m.p. 217—218 °C (Found: C, 62.8; H, 5.7. $C_{27}H_{30}O_{10}$ requires C, 63.0; H, 5.9%); τ [$(CD_3)_2CO$] [for (9) and (13), respectively] 1.81 and 2.02, 1.76 and 2.07 (both br s, 2 × OH), 3.02 and 2.98 (d, aromatic, 2- + 6-H, *J* 8.5 Hz), 3.45 and 3.35 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.72 and 3.86, 3.68 and 3.83 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.84 and 3.93 (s, aromatic 3- and 5-H), 4.38 and 4.65 (d, 1-H, *J* 7.0 and 4.5 Hz), 4.64 and 4.92 (s, 3-H), 5.01 and 5.04 (s, CH_2), 5.87 and 5.97 (d, 1-OH, *J* 7.0 and 4.5 Hz), 6.23, 6.30 (6 H), 6.38 and 6.22, 6.41, 6.48 (6 H) (s, 4 × OMe), and 6.63 and 6.62 (s, CH_2OMe); M^+ [for (9) and (13) respectively] both 514 (0%), *m/e* 496 (5.6, 10.4%), 259 (25, 59), 255 (4.2, 14.3), 227 (100, 100), 225 (77, 61), 197 (60, 51), 195 (32, 61), 154 (52, 60), 153 (24, 59), and 107 (31, 60); $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1} for both (9) and (13).

The two propan-2-ones (9) and (13) formed differing *solid white amorphous triacetates* (10) and (14); τ [$(CD_3)_2CO$] [for (10) and (14), respectively] 2.77 and 2.75 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.13 and 3.08 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.14 and 3.21 (s, 1-H), 3.58 and 3.62 (s, aromatic 3- and 5-H), 3.77 and 3.84, 3.64 and 3.80 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 4.28 and 4.75 (s, 3-H), 4.87 and 4.94 (s, CH_2), 6.18 (6 H), 6.24 (6 H), and 6.18, 6.36 (9 H) (s, 4 × OMe), 6.55 and 6.58 (s, CH_2OMe), 7.78 and 7.81, 7.77 and 7.81 (s, 2 × OAc), and 8.33 and 7.98 (s, 1-OAc); M^+ [for (10) and (14) respectively] 640 (1.3%), *m/e* 343 (18.5, 17.6), 301 (17.3, 17.8), 269 (100, 100), 259 (19.5, 18.9), 227 (72, 75), and 209 (13.3, 15.1); $\nu_{max.}$ ($CHCl_3$) 1 735 and 1 760 cm^{-1} for both (10) and (14).

Methylation of the propan-2-ones (9) and (13) gave dimethyl ethers (11) and (7), the former of which was obtained as a *white amorphous solid*, while (7) crystallised from ethanol as *fine white platelets*, m.p. 145—146 °C; τ [$(CD_3)_2CO$] [for (11) and (7) respectively] 2.93 and 2.92 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.34 and 3.29 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.71 and 3.88, 3.71 and 3.87 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.77 and 3.87 (s, aromatic 3- and 5-H), 4.41 and 4.71 (d, 1-H, *J* 5.0 Hz), 4.58 and 4.91 (s, 3-H), 5.0 and 5.08 (s, CH_2), 5.96 and 6.10 (d, 1-OH, *J* 5.0 Hz), 6.22 (6 H), 6.23 (6 H), 6.31, 6.40, 6.60, and 6.21 (6 H), 6.23 (6 H), 6.31, 6.45, 6.65 (s, 7 × OMe), M^+ [for (11) and (7), respectively] 514 (0%), *m/e* 288 (17.4, 51%), 287 (40, 72), 228 (12.6, 35), 227 (100, 100), 225 (7.0, 4.8), 195 (15.0, 31), 181 (13.9, 27), 167 (66, 90), and 121 (59, 88); $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1} for (11) and (7).

Treatment of propan-2-one (9) with 1M-sodium hydroxide for 2 h at 40 °C led to complete conversion into (13).

1-*Hydroxy*-1-[4,6-*dimethoxy*-2-(*methoxymethoxy*)*phenyl*]-3-(2-*hydroxy*-4,6-*dimethoxyphenyl*)-3-(4-*hydroxyphenyl*)*propan*-2-*one* (6) *and Oxidation Products* (12) *and* (15).—The propiophenone (2) (200 mg) in 1M-sodium hydroxide (10 ml) was stirred under nitrogen for 2 h at 40 °C. Work-up and p.l.c. separation as for (3) afforded three fractions, R_F 0.43 (81.5 mg), 0.50 (22.3 mg), and 0.58 (13.6 mg). Crystallisation of the former from ethanol gave the propan-2-one (6) as *white needles*, m.p. 191—192 °C; τ [$(CD_3)_2CO$] 1.55, 2.04 (br s, 2 × OH), 2.91 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.34 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.68, 3.88 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.82, 4.0 (d, aromatic 3- and 5-H, *J* 2.5 Hz), 4.50 (d, 1-H, *J* 5.0 Hz), 4.86 (s, 3 H), 5.01 (s, CH_2), 5.93 (d, 1-OH, *J* 5.0 Hz), and 6.21, 6.26, 6.41, 6.49, and 6.62 (s, 5 × OMe); M^+ 514 (0%), *m/e* 496 (4.4), 259 (45), 255 (2.2), 227 (100), 225 (39), 197 (6.9), 195 (23), 154 (29), 153 (25), and 107 (15.1); $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1} (Found: C, 62.8; H, 5.8. $C_{27}H_{30}O_{10}$ requires C, 63.0; H, 5.9%).

Methylation of the propan-2-one (6) furnished a dimethyl ether (7) identical to that of (13).

Acetylation of the propanone (6) gave a *solid white amorphous triacetate* (8); τ [$(CD_3)_2CO$] 2.80 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.03 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.20 (s, 1-H), 3.40—3.78 (d, aromatic 3- and 5-H, 3′- and 5′-H, *J* 2.5 Hz), 4.80 (s, 3-H), 4.93 (s, CH_2), 6.15, 6.17, 6.37 (6 H), and 6.57 (s, 5 × OMe), and 7.79, 7.97 (6 H) (s, 3 × OAc); M^+ 640 (0%), *m/e* 581 (4.1%), 535 (2.5), 493

(5.4), 343 (66), 301 (68), 297 (3.8), 269 (100), 259 (69), 227 (99), and 209 (66); $\nu_{max.}$ ($CHCl_3$) 1 735 and 1 760 cm^{-1}.

The R_F 0.50 band gave the *α-diketone* (12) as a *yellow amorphous solid*; τ ($CDCl_3$) 1.69 (s, OH), 2.89 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.32 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.66 (s, 3-H), 3.72, 3.92 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.84, 3.99 (d, aromatic 3- and 5-H, *J* 2.5 Hz), 5.05 (s, CH_2), 6.23, 6.27, 6.32, 6.39 (s, 4 × OMe), and 6.66 (s, CH_2OMe); $\nu_{max.}$ ($CHCl_3$) 1 735 and 1 685 cm^{-1}.

The R_F 0.58 fraction afforded the *quinone methide* (15) as a *light brown amorphous solid*; τ ($CDCl_3$) 2.57 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.29 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.71, 3.94 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.81, 4.11 (d, aromatic 3- and 5-H, *J* 2.5 Hz), 5.06 (s, CH_2), 6.24, 6.28, 6.47, 6.51, 6.66 (s, 5 × OMe), and 3.71—4.11 (OH); M^+ 510 (0%), *m/e* 479 (5.1%), 285 (31), 257 (16.7), 225 (100), 195 (49), and 181 (31); $\nu_{max.}$ ($CHCl_3$) 1 640, 1 720, and 1 818 cm^{-1} (accurate mass on *m/e* 479; found 479.133 3; $C_{26}H_{23}O_9$ requires 479.134 2).

Acetylation of the quinone methide (15) gave the *light yellow amorphous solid monoacetate* (16); τ ($CDCl_3$) 2.43 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 2.56 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.71, 3.95 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.82, 4.11 (d, 3- and 5-H, *J* 2.5 Hz), 5.06 (s, CH_2), 6.22, 6.28, 6.46, 6.52, 6.63 (s, 5 × OMe), and 7.73 (s, OAc); M^+ 552 (0%), *m/e* 328 (1.3%), 286 (3.2), 285 (4.6), 257 (3.2), 225 (100), 195 (26), 193 (7.7), and 181 (5.5); $\nu_{max.}$ ($CHCl_3$) 1 640, 1 730, 1 770, and 1 820 cm^{-1}.

Treatment of the propan-2-one (6) (70 mg) in chloroform (5 ml) with manganese dioxide [2] (200 mg) at ambient temperature for 4 h followed by p.l.c. separation [dichloroethane–acetone (8 : 2 v/v)] also gave the α-diketone (12) (R_F 0.59, 28 mg) and quinone methide (15) (R_F 0.72, 16 mg).

Synthesis of 4-Arylflavan-3-ones.—The propan-2-one (6) (50 mg) and toluene-*p*-sulphonic acid (10 mg) in anhydrous benzene (10 ml) were refluxed for 15 min. The mixture was washed with water (5 × 50 ml), dried (Na_2SO_4), and evaporated. P.l.c. separation [dichloroethane–acetone (9 : 1 v/v)] gave three fractions: (*a*) 2-[4,6-*dimethoxy*-2-(*methoxymethoxy*)*phenyl*]-4-(4-*hydroxyphenyl*)-5,7-*dimethoxyflavan*-3-*one* (17) (13 mg), R_F 0.40, as a *light yellow amorphous solid*; τ ($CDCl_3$) 2.87 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.31 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.74, 3.93 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.89 (s, 6- and 8-H), 4.07 (s, 2-H), 5.04 (s, 4-H), 5.20 (s, CH_2), 6.28, 6.30, 6.32, 6.44 (s, 4 × OMe), and 6.81 (s, CH_2OMe); M^+ 496 (30%), *m/e* 468 (54), 423 (100), 271 (18.9), 270 (58), 257 (21), 238 (6.3), 197 (18.3), 193 (51), and 167 (65); $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1} (accurate mass on *m/e* 496: found 496.171 3; $C_{27}H_{28}O_9$ requires 496.173 3). Acetylation of flavan-3-one (17) gave a *white amorphous monoacetate* (18); τ ($CDCl_3$) 2.74 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.06 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.75, 3.95 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.91 (s, 6- and 8-H), 4.09 (s, 2-H), 4.99 (s, 4-H), 5.21 (dd, CH_2), 6.27, 6.29, 6.32, 6.43 (s, 4 × OMe), 6.80 (s, CH_2OMe), and 7.74 (s, OAc).

(*b*) 2-[4,6-*Dimethoxy*-2-(*methoxymethoxy*)*phenyl*-4-[4-(*methoxymethoxy*)*phenyl*]-5,7-*dimethoxyflavan*-3-*one* (20) (5 mg), R_F 0.60, as a *light pink solid*; τ ($CDCl_3$) 2.79 (d, aromatic 2- and 6-H, *J* 8.75 Hz), 3.09 (d, aromatic 3- and 5-H, *J* 8.75 Hz), 3.75, 3.93 (d, aromatic 3′- and 5′-H, *J* 2.5 Hz), 3.89 (s, 6- and 8-H), 4.08 (s, 2-H), 4.89 (s, CH_2), 5.02 (s, 4-H), 5.20 (dd, CH_2), and 6.26, 6.29, 6.31, 6.42, 6.56, 6.79 (s, 6 × OMe); M^+ 540 (33%), *m/e* 512 (71), 467 (100), 315 (18.1), 314 (47), 303 (22), 257 (16.3), 238 (5.4), 197 (11.6), and 193 (67); $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1} (accurate mass on *m/e* 540: found 540.199 4. $C_{29}H_{32}O_{10}$ requires 540.199 5).

(*c*) 2-(2-*Hydroxy*-4,6-*dimethoxyphenyl*)-4-(4-*hydroxyphenyl*)-5,7-*dimethoxyflavan*-3-*one* (19) (9 mg), R_F 0.27, as a *light yellow amorphous solid*; τ [$(CD_3)_2CO$] 2.75 (d, aromatic 2- and 6-H, *J* 8.5 Hz), 3.31 (d, aromatic 3- and 5-H, *J* 8.5 Hz), 3.92, 3.95, 4.04, 4.14 (d, aromatic 3′-, 5′-, 6-, and 8-H, *J* 2.5 Hz), 4.58 (s, 2-H), 5.29 (s, 4-H), 6.13, 6.29 (6 H), 6.31 (s, 4 × OMe); M^+ 452 (31%), *m/e* 299 (6.4), 298 (21), 259 (100), 258 (20), 194 (28), 167 (59), and 153 (32); $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1} (accurate mass on *m/e* 452: found 452.146 6; $C_{25}H_{24}O_8$ requires 452.147 1).

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