

Novel Conversions and Coupling Reactions of Chalcones and their Epoxides

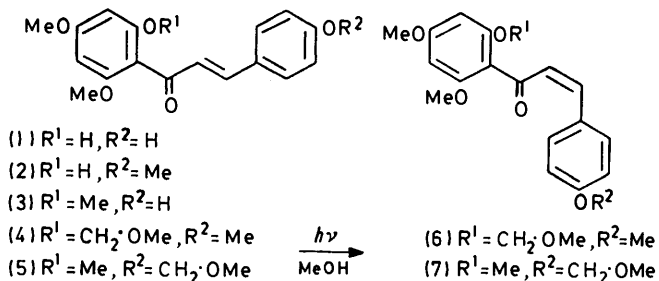
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Chalcones undergo photoisomerization from *trans*- to the hitherto unknown *cis*-forms only when available phenolic hydroxy-functions are fully substituted. The *cis*-chalcones are metastable and revert immediately to *trans*-isomers during acidic hydrolysis of protective acetal groups.

Both *trans*- and *cis*-isomers of fully *O*-substituted chalcones form stable *trans*-epoxides with alkaline hydrogen peroxide. These can serve as synthetic intermediates, as in the synthesis of a pair of 2-hydroxy-3-methoxy-3-phenylpropiofenone racemates by acidic hydrolysis in methanol (S_N1 mechanism) and of α -hydroxychalcones (alkaline hydrolysis).

Stereoselective β -addition of phenolic nuclei *via* unstable epoxide intermediates (S_N2 mechanism) occurs with alkaline peroxide when a 4-hydroxy-function is present in the chalcone, giving structural isomers of 3,3-diaryl-2-hydroxypropiofenones.

ALTHOUGH *trans* \rightarrow *cis* photoisomerization of α -methoxychalcones occurs with relative ease,^{1,2} the possible natural existence and synthetic availability of 'conventional' *cis*-chalcones have remained a matter for conjecture. Our initial attempts to effect *trans* \rightarrow *cis* conversions of 2'-hydroxy-4,4',6'-trimethoxy- and 4-hydroxy-2',4',6'-trimethoxy-*trans*-chalcones (2) and (3) by similar means (350 and 300 nm; MeOH) were unsuccessful, but their *O*-methoxymethyl derivatives (4) and (5) underwent the desired isomerizations, *cis*-chalcones being distinguished from the *trans*-forms by their smaller coupling constants (J 12.0 and 16.0 Hz, respectively). At ambient temperatures these fully *O*-substituted *cis*-chalcones (6) and (7) slowly revert to



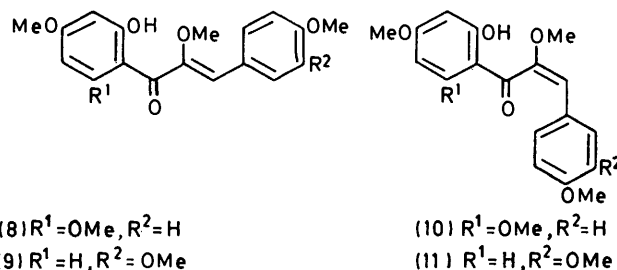
the thermodynamically more stable *trans*-isomers (ca. 50% conversion over 6 months). The 2'-hydroxy- α -methoxy-*cis*-chalcones (10) and (11) are relatively stable.^{1,2} These observations are consistent with the anticipated larger energy difference between *trans*- and *cis*-forms of 'conventional' chalcones (4) and (5), and (6) and (7) as compared with the corresponding α -methoxychalcones (8) and (9), and (10) and (11), as is evident from space-filling models. On this basis it is anticipated that the free phenolic forms of 'conventional' *cis*-chalcones do not exist in nature, nor could they be synthesised.

Removal of the protective methoxymethyl groups of the *cis*-chalcones (6) and (7) by acidic hydrolysis leads to the hydroxy-*trans*-chalcones (2) and (3), inversion being presumably catalysed by protonation of the

¹ F. du R. Volsteedt, G. J. H. Rall, and D. G. Roux, *Tetrahedron Letters*, 1973, 1001.

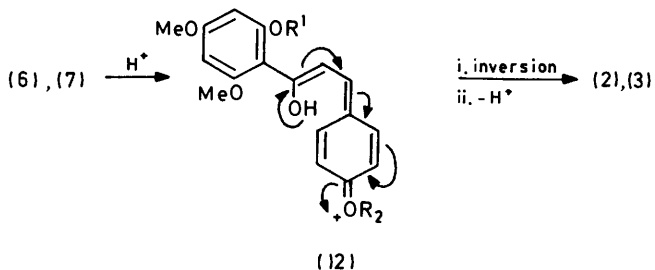
² D. Ferreira, E. V. Brandt, F. du R. Volsteedt, and D. G. Roux, *J.C.S. Perkin I*, 1975, 1437.

carbonyl group and electron-release by the 4-hydroxy- or 4-methoxy-substituents, *i.e.* (6), (7) \rightarrow (12) \rightarrow (2), (3).



In alkaline peroxide³ the fully *O*-substituted pairs of *trans*- and *cis*-chalcones (4) and (6), and (5) and (7) both form *trans*-epoxides (14) and (15), which can be stored unchanged for at least 6 months. For the *cis*-chalcones (6) and (7) this observation is consistent with the mechanism (6), (7) \rightarrow (13) \rightarrow (14), (15) (*cf.* ref. 4) in which the intermediate (13), as before, reverts to the lower-energy *trans*-form.

Treatment of the fully *O*-substituted *trans*-chalcones (4) and (5) under identical conditions, but in the presence of 3,5-dimethoxyphenol (17) with a view to β -coupling, again results in the *trans*-epoxide analogues (14) and (15), but no evidence was obtained for participation by

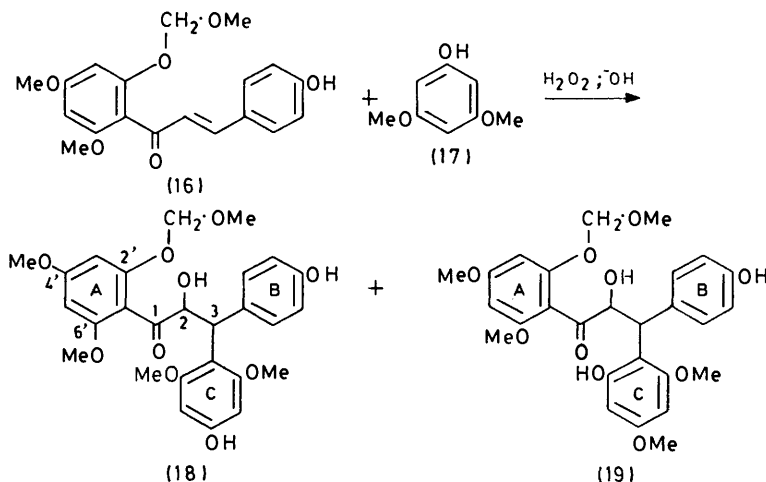
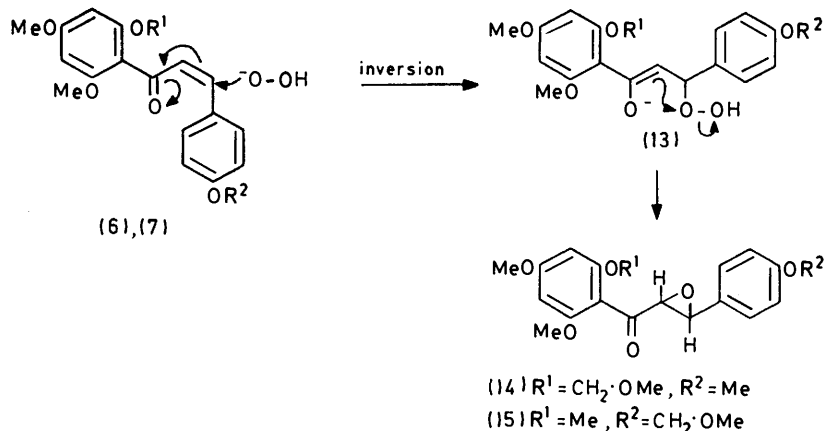


the phenol. Potential coupling reactions were accordingly further examined by selecting a number of variously hydroxylated chalcones which we considered would participate in coupling *via* unstable epoxide intermediates. Treatment of the 2',4'-dihydroxychalcone (1) and 3,5-dimethoxyphenol (17) with alkaline hydrogen peroxide (1% NaOH; 6% H_2O_2) at ambient tem-

³ H. Jörländer, *Ber.*, 1917, 50, 406.

⁴ C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 1949, 665.

peratures gave a single product, 3,4'-dihydroxy-5,7-dimethoxy-2,3-*trans*-flavanone (36% yield). However, its 2'-*O*-methoxymethyl derivative (16) under the same conditions, but at lower temperature, gave a mixture of racemic 2-hydroxy-3-(4-hydroxy-2,6-dimethoxyphenyl)-3-(4-hydroxyphenyl)-4',6'-dimethoxy-2'-methoxymethoxypropiofenone (18) (44%) and its structural isomer (19) (22%), resulting from β -coupling with the 4- and 2-positions of the phenol. By contrast, the 4-*O*-methyl derivative (2) of the same chalcone (1) affords 3-hydroxy-4',5,7-trimethoxyflavone (23%), (\pm)-3-hydroxy-4',5,7-trimethoxy-2,3-*trans*-flavanone (13%),



and 4,4',6-trimethoxyaurone (11%), again in the presence of the phenol.

The above reactions with alkaline peroxides and hydroxychalcones at ambient or lower temperatures are apparently all mediated by unstable epoxides, despite previous opinion (affecting the formation of certain hydroxyflavanones) to the contrary.⁵ On this assumption, when a 2'-hydroxy-function is present in the chalcone, intramolecular cyclization (mainly at the β -position) with opening of the epoxide ring occurs to the exclusion of β -addition by the phenol, whereas when

* This argument is not necessarily conclusive, since only natural and synthetic 3-methoxy-*cis*- and -*trans*-flavanones are known,⁷ and *cis*-hydroxyflavanones could conceivably readily invert to give their *trans*-stereoisomers.

the 2'-hydroxy-group is substituted, but a 4-hydroxy-function is available, coupling is the exclusive reaction. Fully *O*-substituted chalcones, on the other hand, furnish stable epoxides, again with exclusion of coupling. During intramolecular β -cyclization the 2'-phenoxy-function acts as nucleophile when attacking the epoxide ring in a stereoselective⁶ S_N2 reaction, giving only racemic 3-hydroxy-2,3-*trans*-flavanones.* Where the 3,5-dimethoxyphenolate ion acts as nucleophile (remarkably at positions *para* and *ortho* to the hydroxy-group), the now intermolecular reaction is similarly stereoselective, leading to single racemates for each of the

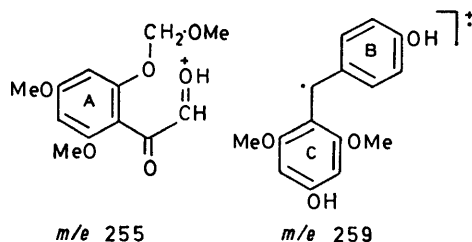
isomeric 2-hydroxy-3,3-diphenylpropiophenones (18) and (19), as found. A surprising feature of the coupling is that no phenyl ether link is formed. The mechanism of peroxide-induced β -coupling of 3,5-dimethoxyphenol with the chalcone differs from that previously observed by us^{2,7} under conditions [K₃Fe(CN)₆; OH⁻] which promote formation of free radicals; in the latter instance a mixture of four diastereoisomers (two racemates) was formed.

⁵ F. M. Dean and V. Podimuang, *J. Chem. Soc.*, 1965, 3978; T. R. Gormley and W. I. O'Sullivan, *Tetrahedron*, 1973, **29**, 369.

⁶ G. Natta and M. Farina, 'Stereochemistry,' Longmans, London, 1972, pp. 130-131.

⁷ F. du R. Volsteedt, D. Ferreira, and D. G. Roux, *J.C.S. Chem. Comm.*, 1975, 217.

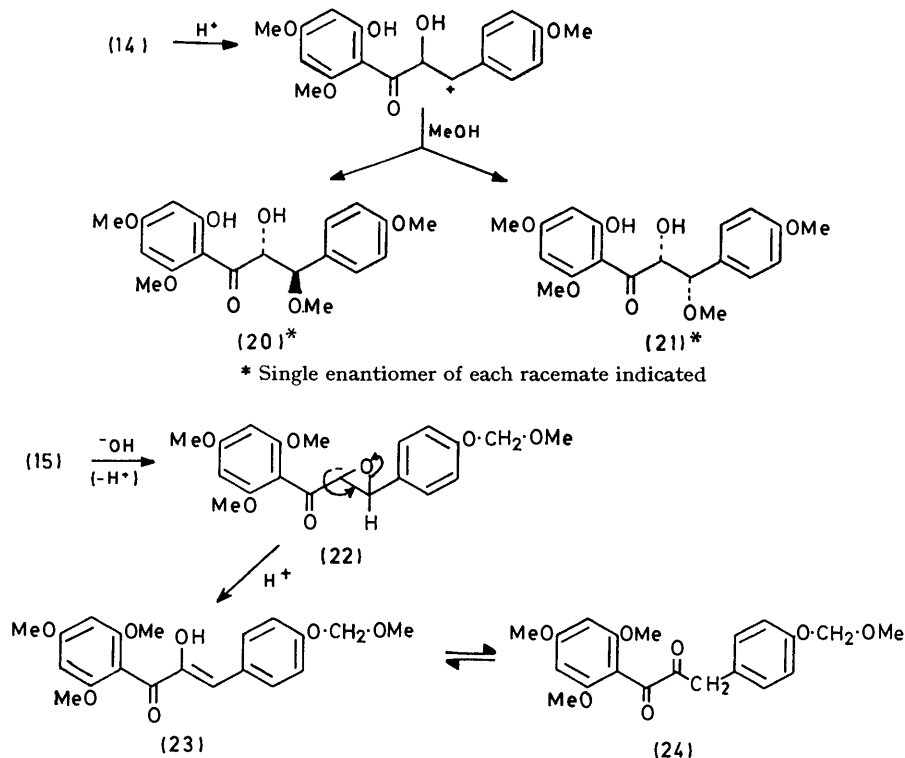
The isomeric 2-hydroxy-3,3-diphenylpropiophenones, R_F 0.13 (18) and 0.32 (19) in benzene-acetone (7 : 3 v/v), and their triacetates show identical mass spectra (M^+



514 and 640), featuring prominent loss of acetic acid in the latter instance, but differ in their ^1H n.m.r. spectra. Notable is the magnetic non-equivalence of the aromatic 3- and 5-protons on ring c of (19) as opposed to

consistent with the structural assignments. Final proof of the structural relationship between (18) and (19) was provided by methylation with diazomethane, which gave identical fully methylated α -ketols.

Stable epoxides of fully *O*-substituted chalcones are potentially useful as synthetic intermediates. For example, acidic hydrolysis in methanol of the *trans*-epoxide (14) proceeds with simultaneous removal of the methoxymethyl group and solvolytic ring opening to yield a pair of enantiomeric 3-aryl-2-hydroxy-3-methoxypropiophenones (20) and (21). This is to be anticipated from benzylium-ion-mediated (S_N1) reactions which result in the creation of chiral centres at C-2 and C-3 in the products. A feature of these α -ketols (20) and (21) is the abnormally large *HC-OH* coupling constant (J 9.4 Hz). The above finding differs from those of



their equivalence in (18); the difference in coupling constants of the 2- and 3-protons of (18) and (19) (J 9.5 and 4 Hz, respectively); and the sharpening and deshielding of the broad 2-proton resonances on acetylation ($\Delta\tau$ -1.27 and -1.18). The remarkable difference in coupling constants may be attributed to the effect of intramolecular hydrogen bonding between the 2-hydroxy-group on ring c and the carbonyl group in (19) [τ 0.37 and 2.00 (broad s, $2 \times \text{OH}$)], as compared with its absence in (18) [τ 2.07 (broad s, $2 \times \text{OH}$)], on the dihedral angle. The triacetates exhibit similar coupling constants (J 11.8 and 11.2 respectively).

The significant fragments m/e 255 (10.0%) and 259 (11.7%) in the mass spectra of both racemates are

⁸ C. Enebäck, *Soc. Sci. Fennica, Commentationes phys.-math.*, 1963, **28**, 1.

Enebäck (*cf. ref. 8*, p. 71) who claimed formation of 3-hydroxyflavanones from a number of 2'-methoxy-methoxychalcone epoxides under identical conditions by intramolecular β -addition.

Base-catalysed hydrolysis of the stable *trans*-chalcone epoxide (15) which has both the 2'- and the 4-hydroxy-group protected affords an α -diketone (24), thus providing an alternative route (*cf. ref. 9*) to the α -hydroxy-chalcone (enolic form of α -diketone) (23). Although this represents a known³ reaction, its mechanistic course *via* a putative carbanion intermediate (22) was not postulated previously. N.m.r. spectra of the α -hydroxy-chalcone again provide evidence of a keto-enol equilibrium, (24) \rightleftharpoons (23) (*cf. ref. 9*).

⁹ T. G. Fourie, D. Ferreira, and D. G. Roux, *J.C.S. Chem. Comm.*, 1974, 760; *J.C.S. Perkin I*, 1976, preceding paper.

EXPERIMENTAL

Irradiation of chalcones was carried out in methanolic solution in a quartz vessel with a Rayonet photochemical reactor (Southern New England Ultra-Violet Company). T.l.c. was performed on Kieselgel PF254 (0.25 mm); for preparative scale separations (p.l.c.) the same material (1 mm) was used. Plates were air-dried and unactivated, and were sprayed with H_2SO_4 -40% HCHO (40:1). Acetylations were carried out with acetic anhydride-pyridine, and methylation with an excess of diazomethane in methanol-diethyl ether at -15°C for 48 h. Mass spectral data (including accurate mass measurements) were recorded with A.E.I. MS9 and Varian CH-5 spectrometers, and n.m.r. data with a Varian T-60 spectrometer (OH resonances were identified by exchange with D_2O). Mass spectral fragmentations were in accord with the proposed structures in each instance.

Synthesis of Chalcones.—4,4',6'-Trimethoxy-2'-methoxymethoxy-trans-chalcone (4). 4',6'-Dimethoxy-2'-methoxymethoxyacetophenone (2.4 g) (prepared from the potassium salt of 2'-hydroxy-4',6'-dimethoxyacetophenone and chloromethyl methyl ether in the presence of 18-crown-6 ether¹⁰) and anisaldehyde (1.8 g) in ethanol (50 ml) and 50% (w/v) potassium hydroxide (20 ml) were stirred for 6 h at ambient temperature. The mixture was poured on to an excess of ice, carefully acidified (3N-HCl) and extracted with ether. The resultant solids were purified by p.l.c. in benzene-acetone (23:2 v/v) and isolated as a yellow oil (2.63 g; R_F 0.48) (Found: M^+ , 358.141. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires M , 358.142), τ (CDCl_3) 2.47 (d, 2- + 6-H, J 8.5 Hz), 2.58 (d, α -H, J 16 Hz), 3.06 (d, 3- + 5-H, J 8.5 Hz), 3.13 (d, β -H, J 16 Hz), 3.55 and 3.70 (dd, 3'- + 5'-H, J 2.0 Hz), 4.83 (s, CH_2), and 6.15, 6.18, 6.23, and 6.59 (each s, 4 \times OMe).

2',4',6'-Trimethoxy-4-methoxymethoxy-trans-chalcone (5). 2',4',6'-Trimethoxyacetophenone (6.1 g) and *p*-methoxymethoxybenzaldehyde (5.81 g) dissolved in ethanol (30 ml) and 50% potassium hydroxide (w/v) (30 ml) were refluxed for 2.5 h and the product was worked up as above to give yellow needles, m.p. 101° (from ethanol) (7.27 g; R_F 0.51) (Found: M^+ , 358.144. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires M , 358.142), τ (CDCl_3) 2.45 (d, 2- + 6-H, J 8.5 Hz), 2.57 (d, α -H, J 16 Hz), 2.91 (d, 3- + 5-H, J 8.5 Hz), 3.10 (d, β -H, J 16 Hz), 3.75 (s, 3'- + 5'-H), 4.77 (s, CH_2), 6.10 (s, OMe), 6.19 (s, 2 \times OMe), and 6.50 (s, OMe).

Photoreactions of Chalcones.—4,4',6'-Trimethoxy-2'-methoxymethoxy-cis-chalcone (6). The *trans*-chalcone (4) (400 mg) in methanol (500 ml) was irradiated for 3 h at 350 nm under nitrogen. Removal of the solvent followed by p.l.c. in benzene-acetone (19:1 v/v) gave both *trans*- (230 mg; R_F 0.32) and *cis*-chalcones (160 mg; R_F 0.38), the latter as a yellow oil after two developments (Found: M^+ , 358.141. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires M , 358.142), τ (CDCl_3) 2.20 (d, 2- + 6-H, J 8.5 Hz), 3.17 (d, 3- + 5-H), 3.22 (d, α -H, J 12.0 Hz), 3.62 (d, β -H, J 12.0 Hz), 3.67 and 3.86 (dd, 3'- + 5'-H, J ca. 2.0 Hz), 4.87 (s, CH_2), 6.23 (s, 3 \times OMe), and 6.55 (s, OMe).

2',4',6'-Trimethoxy-4-methoxymethoxy-cis-chalcone (7). The *trans*-chalcone (5) was irradiated under identical conditions but for 4 h. The product was separated by p.l.c. [two successive developments in 1,2-dichloroethane-acetone (19:1 v/v)] into *trans*- (237 mg; R_F 0.52) and *cis*- (142 mg; R_F 0.45) isomers, the latter as yellow

needles, m.p. 105° (from ethanol) (Found: M^+ , 358.143. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires M , 358.142), τ (CDCl_3) 2.30 (d, 2- + 6-H, J 8.5 Hz), 3.06 (d, 3- + 5-H, J 8.5 Hz), 3.20 (d, α -H, J 12.0 Hz), 3.63 (d, β -H, J 12.0 Hz), 3.91 (s, 3'- + 5'-H), 4.80 (s, CH_2), 6.20 (s, OMe), 6.22 (s, 2 \times OMe), and 6.59 (s, OMe).

Epoxidation of Chalcones.—The chalcones (4)–(7) (300 mg each) were individually stirred in methanol (100 ml), *n*-sodium hydroxide (1.5 ml), and 6% (v/v) hydrogen peroxide (5.0 ml) for 4 h at room temperature. The solutions were added to an excess of water and extracted with ether. The ether layers were washed free of alkali with water, dried (Na_2SO_4), and evaporated. The *trans*- and *cis*-chalcones (4) and (6) gave the same *trans*-epoxide (14) (307 and 309 mg respectively) as an oil (Found: M^+ , 374.136. $\text{C}_{20}\text{H}_{22}\text{O}_7$ requires M , 374.137), τ (C_6H_6) 2.80 (d, 2- + 6-H, J 8.5 Hz), 3.22 (d, 3- + 5-H, J 8.5 Hz), 3.49 and 3.87 (dd, 3'- + 5'-H, J 2.5 Hz), 5.04 (s, CH_2), 5.80br (d, β -H, J 1.6 Hz), 5.88 (d, α -H, J 1.6 Hz), and 6.52, 6.57, 6.60, and 6.77 (each s, 4 \times OMe). The *trans*- and *cis*-chalcones (5) and (7) gave the same *trans*-epoxide (15) (310 and 309 mg, respectively) as white needles (from ethanol), m.p. 101.5° (Found: M^+ , 374.137. $\text{C}_{20}\text{H}_{22}\text{O}_7$ requires M , 374.137), τ (C_6D_6) 2.81 (d, 2- + 6-H, J 8.5 Hz), 3.0 (d, 3- + 5-H, J 8.5 Hz), 3.93 (s, 3'- + 5'-H), 5.13 (s, CH_2), 5.82 (d, β -H, J 1.6 Hz), 6.0 (d, α -H, J 1.6 Hz), 6.57 (s, OMe), 6.67 (s, 2 \times OMe), and 6.82 (s, OMe). Coupling constants of the oxiran ring protons (J 1.6 Hz) in both chalcones indicate a *trans*-configuration.¹¹

Coupling Reactions.—Attempted coupling of fully *o*-substituted *trans*-chalcones with 3,5-dimethoxyphenol. The *trans*-chalcones (4) and (5) give the same *trans*-epoxides (14) and (15) in the presence of 3,5-dimethoxyphenol (16) under the above conditions. No evidence of coupling was obtained.

2-Hydroxy-3-(4-hydroxy-2,6-dimethoxyphenyl)-3-(4-hydroxyphenyl)-4',6'-dimethoxy-2'-methoxymethoxypropio-phenone (18) and its 3-(2-hydroxy-4,6-dimethoxyphenyl) isomer (19). 4-Hydroxy-4',6'-dimethoxy-2'-methoxymethoxy-trans-chalcone (4) (1.25 g) and 3,5-dimethoxyphenol (16) (2.15 g) in *n*-sodium hydroxide (40 ml) were cooled in ice. Ice-cold 6% hydrogen peroxide (5.4 ml) was added and the mixture stirred for 30 min at 0°C . After acidification (3N-HCl) the mixture was extracted with ethyl acetate (2 \times); the extract was washed with water (5 \times) until acid-free, dried (Na_2SO_4) and evaporated. The residual solids were separated by p.l.c. in benzene-acetone (7:3 v/v), giving two bands, R_F 0.13 and 0.32 (816 and 403 mg, respectively). The major product (18), R_F 0.13, gave white platelets (from ethanol), m.p. 195° (Found: C, 63.1; H, 6.1. $\text{C}_{27}\text{H}_{30}\text{O}_{10}$ requires C, 63.0; H, 5.9%), M^+ 514. The minor product (19), R_F 0.32, gave a white amorphous solid (Found: C, 63.0; H, 6.0. $\text{C}_{27}\text{H}_{30}\text{O}_{10}$ requires C, 63.0; H, 5.9%), M^+ 514, τ [$(\text{CD}_3)_2\text{CO}$] [for (18) and (19), respectively] 2.07vbr (s, 2 \times OH) and 0.37, 2.0 (both br, s, 2 \times OH), 2.85 and 2.83 (d, aromatic 2- + 6-H, J 8.0 Hz), 3.52 and 3.15 (d, aromatic 3- + 5-H, J 8.0 Hz), 3.88 (s) and 4.02, 4.15 (dd, J 2.5 Hz) (aromatic 3- + 5-H), 3.77 and 3.63 (d, 3'-H, J 2.5 Hz), 3.95 and 3.73 (d, 5'-H, J 2.5 Hz), 4.20 (dd, J 7.9 and 9.5 Hz) and 4.25br (d, $J_{1,2}$ 4.0 Hz, sharpened by D_2O -exch.) (2-H), 5.18 (d, $J_{1,2}$ 9.5 Hz) and 4.68 (s, $J_{1,2}$ 4.0 Hz) (3-H), 4.93 (s) and 4.93, 5.10

¹⁰ G. J. H. Rall, M. E. Oberholzer, D. Ferreira, and D. G. Roux, *Tetrahedron Letters*, 1976, 1033.

¹¹ J. M. Lehn and J. J. Riehl, *Mol. Phys.*, 1964, 8, 33; J. J. Riehl, J. M. Lehn, and F. Hemmert, *Bull. Soc. chim France*, 1963, 224.

(dd, J 7.4 Hz, CH_2), 6.13 (d, J 7.9 Hz) and 7.05br (s) (OH), 6.28, 6.31 (6 H), 6.36 and 6.16, 6.30, 6.35, 6.65 (s, $4 \times \text{OMe}$), and 6.55 and 6.70 (s, $\text{CH}_2 \cdot \text{OMe}$).

The two propiophenones formed differing white amorphous *triacetates*, M^+ 640, τ $[(\text{CD}_3)_2\text{CO}]$ 2.93 and 3.07 (d, 2-H, $J_{2,3}$ 11.8 and 11.2 Hz), 4.61 and 4.92 (d, 3-H, $J_{2,3}$ 11.8 and 11.2 Hz), 7.81 (6 H), 8.32 and 7.67, 7.78, and 8.28 (s, 3 Ac).

2-Hydroxy-4',6'-dimethoxy-3-(4-methoxyphenyl)-2'-methoxymethoxy-3-(2,4,6-trimethoxyphenyl)propiophenone.

Methylation of the propiophenones (18) and (19) with an excess of diazomethane in methanol gave the same methyl ether as an amorphous white *solid* after p.l.c. in benzene-acetone (9:1 v/v) (Found: C, 64.0; H, 6.4. $\text{C}_{29}\text{H}_{34}\text{O}_{10}$ requires C, 64.2; H, 6.3%), τ $[(\text{CD}_3)_2\text{CO}]$ 2.75 (d, aromatic 2- + 6-H), 3.45 (d aromatic 3- + 5-H), 3.82 (s, aromatic 3- + 5-H), 3.80 and 3.97 (dd, 3' + 5'-H, J 2.5 Hz), 4.17 (dd, 2-H, J 10.5 and 7.5 Hz), 4.93 (s, CH_2), 5.20 (d, 3-H, J 10.5 Hz), 6.22 (s, $2 \times \text{OMe}$), 6.27 (s, $2 \times \text{OMe}$), and 6.35, 6.38, and 6.53 (s, $3 \times \text{OMe}$).

Attempted coupling of 3,5-dimethoxyphenol with 2'-hydroxy- and 2',4-dihydroxy-trans-chalcones. 2',4-Dihydroxy-4',6'-dimethoxy-*trans*-chalcone (1) (150 mg) and 3,5-dimethoxyphenol (154 mg) were stirred in alkaline hydrogen peroxide [N-NaOH (4.3 ml) and 6% H_2O_2 (2.5 ml)] for 6 h as above. 3,4'-Dihydroxy-5,7-dimethoxy-2,3-*trans*-flavanone (91 mg) was isolated as the sole product. Structural confirmation was obtained by n.m.r. ($J_{2,3}$ 12.0 Hz) and mass spectrometry.

2'-Hydroxy-4,4',6'-trimethoxy-*trans*-chalcone (2) (157 mg) and 3,5-dimethoxyphenol (154 mg) stirred with alkaline hydrogen peroxide [N-NaOH (4.6 ml) and 6% H_2O_2 (2.6 ml)] for 5 h gave 3-hydroxy-4',5,7-trimethoxy-2,3-*trans*-flavanone (19 mg), 3-hydroxy-4',5,7-trimethoxyflavone (34 mg), and 4,4',6-trimethoxyaurone (17 mg). Structural assignments were made by n.m.r. and mass spectrometry (*cf. ref. 2*).

Acidic Hydrolysis of a trans-Chalcone Epoxide.—2,2'-Dihydroxy-3,4',6'-trimethoxy-3-(4-methoxyphenyl)propiophenones (20) and (21). The *trans*-epoxide (14) (200 mg) in methanol (20 ml) and 2*N*-sulphuric acid (2 ml) was refluxed for 30 min. After extraction with ether the product was separated by p.l.c. in benzene-acetone (17:3 v/v) into two bands, R_F 0.49 and 0.60. The R_F 0.60 band gave white *needles* (83 mg), m.p. 144° (from ethanol) (Found: C, 62.9;

H, 6.3. $\text{C}_{19}\text{H}_{22}\text{O}_7$ requires C, 63.0; H, 6.1%), τ (CDCl_3 - C_6D_6 , 1:1 v/v) -3.51 (s, OH), 2.63 (d, aromatic 2- + 6-H, J 8.5 Hz), 3.15 (d, aromatic 3- + 5-H, J 8.5 Hz), 3.90 and 4.15 (dd, 3' + 5'-H, J 2.5 Hz), 4.73 (dd, 2-H, J 1.7 and 9.4 Hz), 5.59 (d, 3-H, J 1.7 Hz), 6.00 (d, OH, J 9.4 Hz), 6.42 (s, OMe), 6.48 (s, $2 \times \text{OMe}$), and 7.00 (s, 3-OMe). Deuterium exchange removes the sharp doublet at τ 6.00 and decouples the doublet of doublets at 4.73 to a doublet, J 1.7 Hz. Acetylation similarly removes the high-field doublet and causes deshielding ($\Delta\tau$ -1.19) of 2-H: τ (CDCl_3) 3.58 (d, 2-H, J 2.6 Hz), 5.30 (d, 3-H, J 2.6 Hz), and 7.72 and 7.93 (s, $2 \times \text{Ac}$).

The R_F 0.49 band gave a pale yellow *oil* (50 mg) (Found: C, 63.0; H, 6.2%), τ (CDCl_3 - C_6D_6 , 1:1 v/v) -3.05 (s, OH), 2.93 (d, aromatic 2- + 6-H, J 8.5 Hz), 3.27 (d, aromatic 3- + 5-H), 3.92 and 4.16 (dd, 3' + 5'-H), 4.32 (dd, 2-H, J 2.4 and 9.2 Hz), 5.57 (d, 3-H, J 2.4 Hz), 6.43 (s, $3 \times \text{OMe}$), 6.55 (d, OH, J 9.2 Hz), and 6.76 (s, 1-OMe). The diacetate, τ 3.67 (d, 2-H, J 5.5 Hz), 5.42 (d, 3-H, J 5.5 Hz), and 7.80 and 8.00 (s, $2 \times \text{Ac}$), showed similar deshielding ($\Delta\tau$ -0.65) of the 2-H.

Alkaline Hydrolysis of a trans-Chalcone Epoxide.— α -Hydroxy-2',4',6'-trimethoxy-4-methoxymethoxychalcone (23) and its α -diketone tautomer (24). 2',4',6'-Trimethoxy-4-methoxymethoxy-*trans*-chalcone epoxide (15) (300 mg) in ethanol (5 ml) and *n*-sodium hydroxide (1.5 ml) was refluxed for 1 h. The solution was added to ice and extracted with ether. The ether-soluble product was purified by p.l.c. in benzene-acetone (9:1 v/v) (R_F 0.59) and was obtained as a pale yellow *oil* (117 mg) (Found: M^+ , 374.137. $\text{C}_{20}\text{H}_{22}\text{O}_7$ requires M , 374.137), τ (CDCl_3) 2.20 (d, 2- + 6-H, J 8.5 Hz), 2.50br (s, α -OH), 2.95 (d, 3- + 5-H), 3.77 (s, broadened at base, β - + 3'- + 5'-H), 4.80 (s, OCH_2O), 6.13 (s, OMe), 6.17 (s, CH_2 of diketone form), 6.27 (s, $2 \times \text{OMe}$), and 6.53 (s, OMe). The compound consists of *ca.* 70% of the (presumably *trans*) enolic form, with evidence (τ 6.17) of the presence of the α -diketone.

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