Dioxolanones as Synthetic Intermediates. Part 2.† Synthesis of Tetronic Acids and Pulvinones

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The utility of 1,3-dioxolan-4-ones as intermediates in the synthesis of tetronic acids is examined. The reaction of dioxolanone (**1**) with lithium enolates of 2-substituted methyl or t-butyl acetates at −78 °C in tetrahydrofuran afforded a general synthesis of 2-substituted tetronic acids (**3**)—(**8**). Treatment of (**1**) with the anions of 2-substituted acetonitriles led to formation of the corresponding 3-substituted-2-aminofuran-4(5*H*)-ones (**13**) and (**14**).

A route to unsymmetrically substituted pulvinones by reaction of 5-arylidene-2,2-pentamethylene-1,3-dioxolan-4-ones [5′-arylidenecyclohexanespiro-2′(1′,3′-dioxolan)-4′-ones] with appropriately substituted phenylacetic ester anions has been devised. Thus, the preparation of the naturally occurring pigment 3′,4′,4-trihydroxypulvinone (**18**) was achieved *via* an intermediate in which the phenolic groups were protected as benzyl ethers. The dioxolanone (**26**) has been used in the preparation of 2-acyl-4-benzylidenetetronic acids.

Tetronic acids have been prepared by a host of methods,[1] varying widely in their general synthetic use, since the first synthesis of 2-methyltetronic acid (**3**) by Demarcay in 1879.[1a]

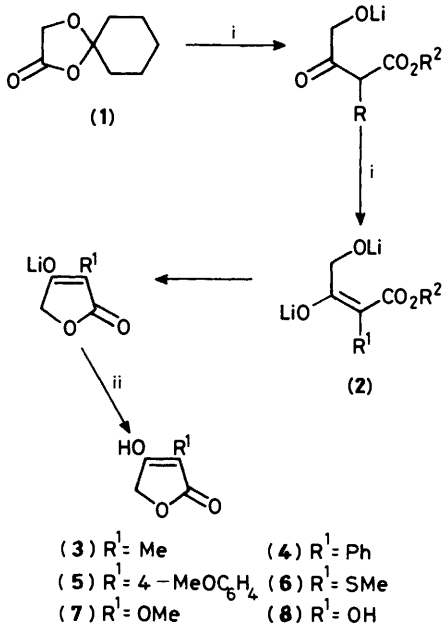
We now report that 2,2-pentamethylene-1,3-dioxolan-4-one [cyclohexanespiro-2′-(1′,3′-dioxolan)-4′-one] (**1**)[2] can be used as a readily available starting material for the synthesis of a wide range of tetronic acids. For example, nucleophilic attack on (**1**) by α-lithioacetic esters, generated using lithium di-isopropylamide (LDA), afforded a series of 2-substituted tetronic acids (**3**)—(**7**), presumably *via* the intermediate (**2**) and with the extrusion of cyclohexanone (Scheme 1). The reactions were carried out in tetrahydrofuran (THF); removal of the solvent and partition of the residue between ether and water followed by acidification of the aqueous layer gave the substituted tetronic acid which was isolated by filtration or extraction. Two equivalents of the ester anion are required in the reaction (Scheme 1), the first to provide initial nucleophilic attack on (**1**), and the second to furnish the intermediate dianion (**2**). In practice the use of 2.5 equivalents of ester anion gave the highest yields and it was shown that methyl (R^2 = Me) and t-butyl (R^2 = Bu^t) esters could be used with equal facility (see Table). Generation of the lithium enolate of (**1**) followed by addition of a solution of (**1**) in THF gave, after the usual work-up, 2-hydroxytetronic acid (**8**) in 40% yield. All the 2-substituted tetronic acids prepared in this way gave satisfactory analytical and spectral data and the acid (**5**) was further characterised by preparation of the known[3] methyl ether (**9**) using the method reported by Boll and co-workers.[4] The crude product from this reaction contained approximately 5% of the isomeric methylation product (**10**).

It was thought that reaction of the dioxolanone (**1**) with the anion of a 2-substituted acetonitrile (**11**) would give the corresponding 2-substituted tetronic acid after hydrolysis of the intermediate imine (**12**). However, addition of the dioxolanone (**1**) to a THF solution containing 2.5 equivalents of the anion of phenylacetonitrile (**11**; R = Ph) gave, in 80% yield, the known 2-amino-3-phenylfuran-4(5*H*)-one (**13**).[5] In similar fashion, the furanone (**14**) was prepared in 53% yield from propionitrile. The

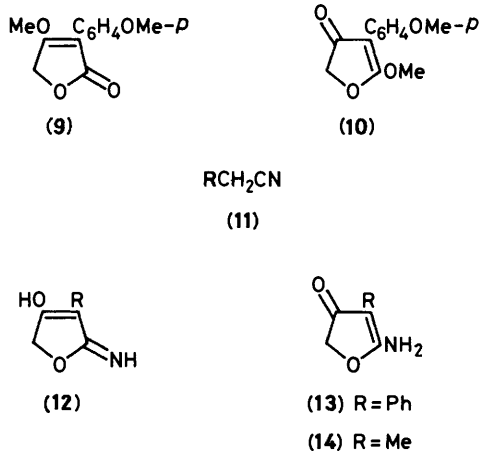
† Part 1, preceding paper.

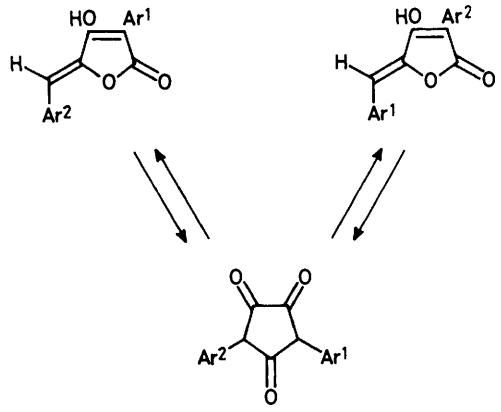
Table.

Tetronic acid	R^1	R^2	Yield (%)
(**3**)	Me	Me	48
(**3**)	Me	Bu^t	48
(**4**)	Ph	Me	54
(**4**)	Ph	Bu^t	57
(**5**)	4-$MeOC_6H_4$	Me	52
(**5**)	4-$MeOC_6H_4$	Bu^t	63
(**6**)	SMe	Me	43
(**7**)	OMe	Me	35
(**8**)	OH		40



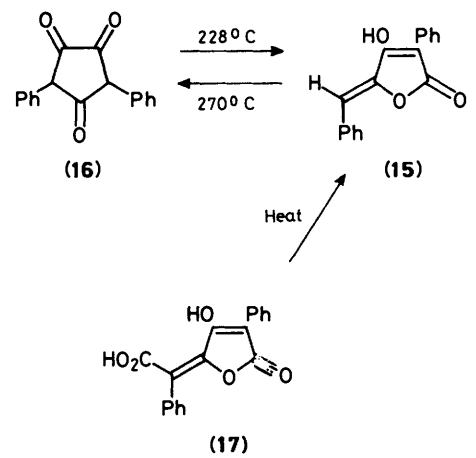
Scheme 1. *Reagents:* i, $R^1CH(Li)CO_2R^2$; ii, H^+/H_2O





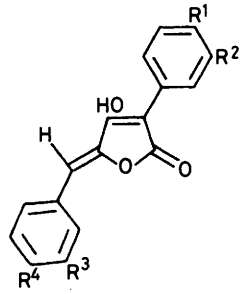
Scheme 2.

above methodology for tetronic acid synthesis has been extended to include preparation of 2-aryl-4-arylidenetetronic acids[6] (pulvinones) using the previously described[2] 5-arylidene-2,2-pentamethylene-1,3-dioxolan-4-ones. The first preparation of pulvinone (**15**) was reported in 1895 by Claisen and Ewan.[7] Condensation of dibenzyl ketone with diethyl oxalate gave the trione (**16**), and this when heated to *ca.* 228 °C was thermally rearranged to (**15**). Schonberg and Sina later showed that (**15**) and (**16**) existed in thermal equilibrium and that if the temperature was raised above 270 °C the equilibrium was displaced towards (**16**) as a result of its removal by sublimation.[8] These authors also showed that pulvinic acid (**17**), on being heated with copper chromite in quinoline, underwent decarboxylation to give pulvinone (**15**).



In 1973 Edwards and Gill reported the isolation of 3′,4′,4-trihydroxypulvinone (**18**) from the common larch mushroom *Suillus grevillei* (*Boletus elegans*),[9] and in the same year Seto and co-workers disclosed that extraction of a culture filtrate of *Aspergillus terreus* led to the isolation of seven pulvinones (aspulvinones A-G).[10] The simplest of these, aspulvinone E, was shown to be 4,4′-dihydroxypulvinone (**19**) and the structures of the other aspulvinones were later assigned on the basis of their spectral properties and products of alkaline degradation.[11] However, these degradation studies were unreliable owing to the presence of an equilibrium between isomeric pulvinones[6] *via* an intermediate trione (Scheme 2) and thus an unambiguous synthesis of unsymmetrical pulvinones was desirable for structure assignment. One such route to permethylated derivatives of unsymmetrical pulvinones, developed by Pattenden and Knight,[12] has proved of great value in structure elucidation. By a combination of synthetic, spectral, and *X*-ray studies Pattenden demonstrated that several of the aspulvinone structures assigned by Seto were erroneous.[13]

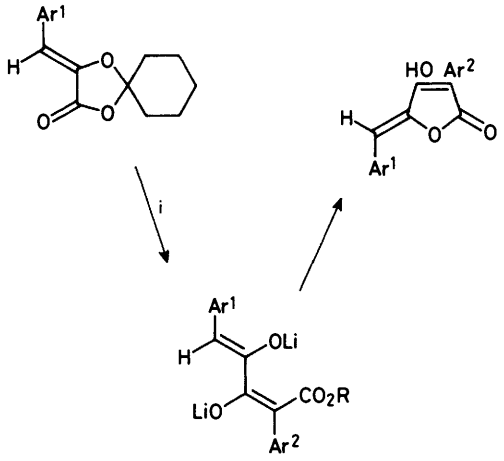
Our route to pulvinones (Scheme 3) has led to the first unambiguous synthesis of pulvinones containing free phenolic groups. Thus, treatment of the (*Z*)-dioxolanone (**26**)[2] in THF with 2.5 equivalents of the lithium enolate of methyl or t-butyl phenylacetate gave pulvinone (**15**) in yields greater than 90%. There was no evidence for the alternative mode of cyclisation of the intermediate dianion (**25**; $Ar^1 = Ar^2 = Ph$) whereby the trione (**16**) could be formed, and u.v. studies of the reaction showed that cyclisation of the intermediate dianion (**25**; $Ar^1 = Ar^2 = Ph$, R = Me) proceeded more rapidly than cyclisation of the corresponding t-butyl ester (**25**; $Ar^1 = Ar^2 = Ph$, R = Bu^t). This rate difference has proved extremely valuable in the unambiguous synthesis of unsymmetrically substituted pulvinic acids which is discussed in a succeeding paper.



(**18**) $R^1 = R^3 = R^4 = OH$; $R^2 = H$
(**19**) $R^1 = R^4 = OH$; $R^2 = R^3 = H$
(**20**) $R^1 = R^3 = R^4 = OCH_2Ph$; $R^2 = H$
(**21**) $R^1 = OCH_2Ph$; $R^2 = R^3 = R^4 = H$
(**22**) $R^1 = R^2 = R^4 = OH$; $R^3 = H$
(**23**) $R^4 = OCH_2Ph$; $R^1 = R^2 = R^3 = H$
(**24**) $R^1 = OH$; $R^2 = R^3 = R^4 = H$

Attention was turned to preparation of the naturally occurring 3′,4′,4-trihydroxypulvinone (**18**) *via* an intermediate (**20**) in which the phenolic groups were protected as benzyl ethers. This synthesis required as synthons methyl 4-benzyloxyphenylacetate (**28**) and the dioxolanone (**29**). 4-Benzyloxyphenylacetic acid (**27**) was obtained in 76% yield by the method of Barton and Kirby[14] and was converted into its methyl ester (**28**) using diazomethane.

Treatment of 3,4-dihydroxybenzaldehyde with benzyl chlor-

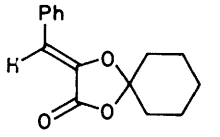


(25)

Scheme 3. *Reagents:* i, $Ar^2CH(Li)CO_2R$ (2.5 equiv.)

ide in K_2CO_3–DMF at 75 °C gave 3,4-dibenzyloxybenzaldehyde (**30**) in excellent yield, and reaction of (**30**) with the phosphorane (**31**)[2] afforded the required dioxolanone (**29**) in 80% yield after chromatography and recrystallisation. The dioxolanone (**29**) was added to a slurry of the lithium enolate of the ester (**28**) in THF at −78 °C, and on removal of the solvent followed by addition of ether and water a bright yellow solid was obtained. From spectral data this appeared to be a hydrate of the uncyclised acid (**32**), which could not be fully characterised owing to its facile conversion into the pulvinone (**20**) on attempted purification. Recrystallisation of (**32**), from either ethanol or aqueous acetic acid, gave the required pulvinone (**20**). The Nujol mull i.r. spectrum of (**20**) showed the lactone absorption at 1 700 cm^{-1}, and a shift to 1 765 cm^{-1}, characteristic of pulvinones, was observed on measurement of the spectrum in dioxane. The ^1H n.m.r. spectrum showed a singlet at δ 6.57 due to the vinylic proton but a mass spectrum could not be obtained due to decomposition of the product at the high temperature required to sublime it at the probe.

It therefore appeared that cyclisation of the intermediate (**25**) was retarded when the aromatic rings carried benzyloxy substituents. This was borne out when the preparation of 4-benzyloxypulvinone (**21**) was attempted from the dioxolanone (**26**) and the anion of the methyl ester (**28**). The customary work-up procedure gave only a moderate (30%) yield of (**21**); the main product was the amide (**34**) formed by reaction between diisopropylamine and the methyl ester of the intermediate (**33**). The cyclisation to form (**21**) was promoted by addition of water to the THF solution followed by a reflux period of 30 min; this procedure gave a 71% yield of (**21**) with only a trace of the amide (**34**).



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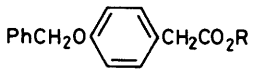
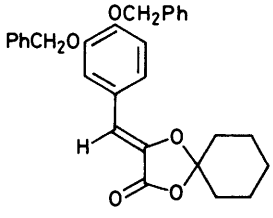


(27) R = H

(28) R = Me



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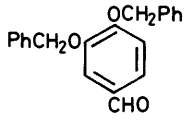

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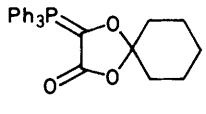

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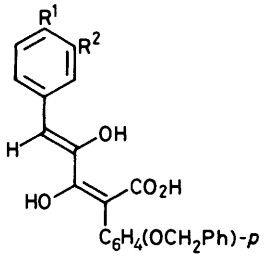
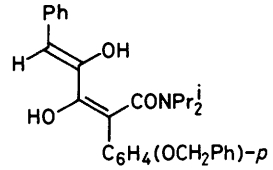


(32) $R^1 = R^2 = OCH_2Ph$

(33) $R^1 = R^2 = H$



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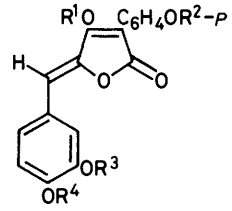


(35) R^{1-4} = Me

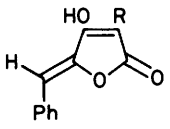
(36) R^{1-4} = Ac

Removal of the benzyl groups from the tribenzyloxypulvinone (**20**) using HBr in glacial acetic acid gave two products as shown by ^1H n.m.r. spectroscopy and t.l.c. (ratio *ca.* 9:1). Purification was carried out by preparative t.l.c. and the major product was identical (^1H n.m.r. and t.l.c.) with an authentic sample of 3′,4′,4-trihydroxypulvinone (**18**). The minor product was tentatively assigned the structure of the previously unreported 3,4,4′-trihydroxypulvinone (**22**). Acid-catalysed nucleophilic attack of the solvent at the lactone carbonyl of (**18**) would lead to isomerisation to (**22**) *via* an intermediate trione (Scheme 2).

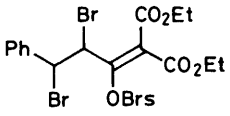
Hydrogenolysis has frequently been used as a method for cleavage of benzyl ether groups.[15] When the monobenzyloxypulvinone (**21**) was hydrogenated for 30 min in methanol containing a few drops of concentrated HCl, with 10% palladium on charcoal as catalyst, there was no apparent debenzylation but the ^1H n.m.r. spectrum showed two vinylic signals and two benzylic methylene groups. It was concluded that an acid-catalysed nucleophilic ring-opening had again taken place leading to formation of the isomeric pulvinone (**23**). The hydrogenolysis of (**21**) proved to be solvent dependent in that use of the non-nucleophilic solvent DMF containing a small amount of concentrated HCl with 10% palladium on charcoal as catalyst gave the required 4-hydroxypulvinone (**24**) but even after several hours some (**21**) remained and some reduction of the exocyclic double bond had occurred. However, hydrogenation for 18 h under these conditions led to complete disappearance of (**21**) and 4-hydroxypulvinone (**24**) was isolated in 68% yield after chromatography and recrystallisation to remove over-reduced products. Surprisingly, complete deprotection of the tribenzyloxypulvinone (**20**) was achieved in 1 h under these conditions with no double-bond reduction and 3′,4′,4-trihydroxypulvinone (**18**) was isolated in 96% yield after

chromatography. The product was identical (^{1}H n.m.r. and t.l.c.) with a natural sample isolated from *Suillus grevillei* and showed all the other spectral properties reported[9] for (**18**). Methylation using diazomethane gave the tetramethyl ether (**35**) and acetylation gave the tetra-acetate (**36**). Both of these derivatives exhibited the reported[9] spectral properties.

The benzylidenedioxolanone (**26**) has also been used to prepare the 2-acyl-4-benzylidenetetronic acids (**37**) and (**38**). In 1963 Fleming and Harley-Mason[16] reported the preparation of 4-benzylidene-2-ethoxycarbonyltetronic acid (**37**) by treatment of the dibromide (**39**) with alkali. In accord with the strategy outlined in Scheme 3, reaction of (**26**) with diethyl sodiomalonate in DMF gave the required acid (**37**) in 48% yield after recrystallisation. In similar fashion, 2-acetyl-4-benzylidenetetronic acid (**38**) was prepared in 51% yield from ethyl acetoacetate.



(**37**) R = CO_2Et
(**38**) R = Ac



(**39**)

Brs = *p*-$BrC_6H_4SO_2$

Experimental

I.r. spectra, calibrated against polystyrene film at 1 603 cm^{-1}, were recorded on a Perkin-Elmer 197 spectrophotometer. 60 MHz ^{1}H N.m.r. spectra were recorded on Perkin-Elmer R12 and R20A spectrometers, 80 MHz on a Bruker WP80, 90 MHz on a Perkin-Elmer R32, 220 MHz on a Perkin-Elmer R34 and 300 MHz on a Varian SC300 spectrometer; chemical shifts are relative to internal $SiMe_4$ at 0.00 p.p.m. ^{13}C N.m.r. spectra were recorded at 21.1 MHz on a Bruker WP80; chemical shifts are relative to $^{13}CDCl_3$ at 76.9 p.p.m. or $(^{13}CD_3)_2CO$ at 29.2 p.p.m. U.v. spectra were recorded on a Varian Cary 118X or Pye Unicam SP8-100 spectrophotometer. Mass spectra were recorded on A.E.I. MS 902 and Kratos MS 45 spectrometers with an ionisation potential of 70 eV. Microanalyses were made on a Perkin-Elmer 240 Elemental Analyser. Melting points were determined on a Buchi 510 or a Kofler hot-stage microscope and are uncorrected as are boiling points. T.l.c. was carried out on silica gel (Fluka GF 254) and examined by u.v. light at 254 and 366 nm or by staining in iodine vapour. Preparative chromatography was performed on silica gel 60 (70—230 mesh ASTM) (Merck). Flash column chromatography was carried out on Kieselgel 60H (Merck). Unless stated otherwise all reactions were carried out at room temperature (18—24 °C). Commercially available solvents were dried by standard procedures and distilled prior to use. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl immediately before use. Petroleum refers to the fraction boiling in the range 40—60 °C. Nitrogen was purified by passing it successively through Fieser's solution, saturated aqueous lead(II) acetate, concentrated sulphuric acid, and potassium hydroxide pellets.

Preparation of Tetronic Acids: General Procedure.—Solutions of lithium di-isopropylamide (LDA) were prepared at −78 °C under nitrogen by addition of a solution of Bu^{n}Li (1 equiv.) in hexane to a solution of di-isopropylamine (1.05 equiv.) in THF (*ca.* 1 mmol/ml). This solution was kept at −78 °C for 25 min before generation of the lithium enolates of esters by addition of the appropriate ester (1 equiv.) in THF (*ca.* 1 mmol/ml). The enolates were kept at −78 °C for 25 min before addition of the required dioxolanone in THF. The reaction mixture was allowed to attain room temperature gradually (overnight stirring) before evaporation of the solvent and partition of the residue between ether and water. The ethereal layer was washed with water; acidification of the combined aqueous layers to *ca.* pH 1 with concentrated HCl gave the tetronic acid which was isolated by filtration or extraction.

3-*Methylfuran*-2,4(3H,5H)-*dione* (2-*Methyltetronic Acid*) (**3**).—By the general procedure dioxolanone (**1**)[2] (3.91 g, 25 mmol) was treated with the lithium enolate of methyl propionate (62.5 mmol). To the acidified aqueous layer from work-up was added sodium chloride and the solution was subjected to continuous ether extraction for 16 h. Evaporation under reduced pressure gave a yellow solid which was triturated with ether to give the acid (**3**) (1.35 g, 48%), m.p. 186—190 °C (from ethyl acetate–petroleum) (lit.,[17] 190—191 °C) (Found: C, 52.6; H, 5.3. Calc. for $C_5H_6O_3$: C, 52.6; H, 5.3%); $\lambda_{max.}$(EtOH) 228 (ε 8 900) and 256 nm (6 000); $\lambda_{max.}$(EtOH) + 1 drop 2M-NaOH) 256nm (ε 18 400); $\nu_{max.}$(Nujol) 3 000—2 300m, 1 720m, 1 600s, and 1 540m cm^{-1}; $\nu_{max.}$(dioxane) 1 755s and 1 675m cm^{-1}; δ_H [220MHz, $(CD_3)_2SO$] 11.7 (1 H, s, OH), 4.54 (2 H, q, *J* 1 Hz, CH_2), and 1.57 (3 H, t, *J* 1 Hz, Me); *m/z* 114 (M^+).

3-*Phenylfuran*-2,4(3H,5H)-*dione* (2-*Phenyltetronic Acid*) (**4**).—By the general procedure dioxolanone (**1**) (3.90 g, 25 mmol) was treated with the lithium enolate of t-butyl phenylacetate (62.5 mmol). Acidification gave the crude product which was filtered, dried, and recrystallised (MeOH–H_2O) to give acid (**4**) (2.51 g, 57%), m.p. 258—263.5 °C (lit.,[18] 256—257 °C) (Found: C, 68.3; H, 4.5. Calc. for $C_{10}H_8O_3$: C, 68.15; H, 4.6%); $\lambda_{max.}$(EtOH) 260nm (ε 19 800); $\lambda_{max.}$ (EtOH + 1 drop 2M-NaOH) 260nm (ε 21 500); $\nu_{max.}$(Nujol) 2 900—2 300m, 1 690m, and 1 600s cm^{-1}; $\nu_{max.}$(dioxane) 1 755s and 1 670m cm^{-1}; δ_H [220 MHz, $(CD_3)_2SO$] 7.95 (2 H, d), 7.20—7.45 (3 H, m), and 4.77 (2 H, s, CH_2); *m/z* 176 (M^+, 100%).

3-(4-*Methoxyphenyl*)*furan*-2,4(3H,5H)-*dione* [2-(4-*Methoxyphenyl*)*tetronic Acid*] (**5**).—By the general procedure the dioxolanone (**1**) (3.90 g, 25 mmol) was treated with the lithium enolate of methyl 4-methoxyphenylacetate (62.5 mmol). Acidification gave the crude product which was filtered off, dried, and recrystallised (ethyl acetate) to give the *acid* (**5**) (2.66 g, 52%), m.p. 228—230 °C (Found: C, 64.4; H, 5.2. $C_{11}H_{10}O_4$ requires C, 64.1; H, 4.9%); $\lambda_{max.}$(EtOH) 260 (ε 14 900) and 276 (infl.) nm (13 700); $\nu_{max.}$(Nujol) 2 675m, 1 690m, 1 640s, and 1 610s cm^{-1}; $\nu_{max.}$(dioxane) 1 755s and 1 680m cm^{-1}; δ_H [90 MHz, $(CD_3)_2SO$–$CDCl_3$] 7.90 (2 H, d, *J* 9 Hz), 6.89 (2 H, d, *J* 9 Hz), 4.66 (2 H, s, CH_2), and 3.76 (3 H, s, OMe); *m/z* 206 (M^+, 100%).

3-*Methylthiofuran*-2,4(3H,5H)-*dione* (2-*Methylthiotetronic Acid*) (**6**).—By the general procedure the dioxolanone (**1**) (1.18 g, 7.4 mmol) was treated with the lithium enolate of methyl methylthioacetate (18.8 mmol). The acidified aqueous layer was continuously extracted with ether (18 h); the ether extracts were dried, filtered, and evaporated under reduced pressure to give an orange semi-solid. Trituration with dichloromethane gave an off-white solid (0.6 g) which was purified by chromatography on silica gel (30 g) with benzene–ethyl acetate–acetic acid (50:49:1) as eluant and recrystallisation from ethyl acetate–petroleum to give the *acid* (**6**) as white crystals (0.48 g, 43%), m.p. 170.5—171.5 °C (Found: C, 41.1; H, 4.1; S, 21.7. $C_5H_6O_3S$ requires C, 41.1; H, 4.1; S, 21.9%); $\lambda_{max.}$(EtOH) 228 (ε 8 100) and 258nm (6 550); $\lambda_{max.}$(EtOH + 1 drop 2M-NaOH) 252nm (ε 13 950); $\nu_{max.}$(dioxane) 1 765s and 1 625s cm^{-1}; δ_H [220 MHz,

$(CD_3)_2CO$] 4.70 (2 H, s, CH_2) and 2.20 (3 H, s, SMe); *m/z* 146 (M^+, 100%).

3-*Methoxyfuran*-2,4(3H,5H)-*dione* (2-*Methoxytetronic Acid*) (**7**).—By the general procedure, the dioxolanone (**1**) (7.87 g, 50.5 mmol) was treated with the lithium enolate of methyl methoxyacetate (125 mmol). The acidified aqueous layer was continuously extracted (72 h) with ether; the ether extracts were dried, filtered, and evaporated under reduced pressure to give a brown semi-solid. Trituration with ethyl acetate gave an off-white solid which was purified by chromatography on silica gel (60 g) with benzene–ethyl acetate–acetic acid (50:49:1) as eluant and recrystallisation from ethyl acetate–petroleum to give the *acid* (**7**) (2.29 g, 35%), m.p. 145—145.5 °C (Found: C, 46.4; H, 4.7. $C_5H_6O_4$ requires C, 46.1; H, 4.65%); $\lambda_{max.}$(EtOH) 237nm (ε 10 650); $\lambda_{max.}$(EtOH + 1 drop 2M-NaOH) 260nm (ε 20 200); $\nu_{max.}$(dioxane) 1 765s and 1 685s cm^{-1}; δ_H [220 MHz, $(CD_3)_2CO$] 4.65 (2 H, s, CH_2) and 3.80 (3 H, s, OMe); *m/z* 130 (M^+, 100%).

3-*Hydroxyfuran*-2,4(3H,5H)-*dione* (2-*Hydroxytetronic Acid*) (**8**).—To the lithium enolate of dioxolanone (**1**) (37.6 mmol) in THF (40 ml) at −78 °C was added a solution of (**1**) (2.37 g, 15.2 mmol) in THF (10 ml). The solution was kept at −78 °C for 2 h and allowed to attain room temperature. The reaction was worked up as usual; the acidified aqueous layer was continuously extracted with ether for 40 h. Trituration of the dried ether extracts with dichloromethane gave a yellow solid which was purified by flash chromatography on silica gel (20 g) with benzene–ethyl acetate–acetic acid (50:49:1) as eluant and recrystallisation from ether–petroleum (b.p. 60—80 °C) to give the acid (**8**) as white crystals (0.7 g, 40%), m.p. 153—154 °C (lit.,[19] 153 °C) (Found: C, 41.6; H, 3.7. Calc. for $C_4H_4O_4$: C, 41.4; H, 3.5%); $\lambda_{max.}$(EtOH) 244 nm (ε 11 200); $\nu_{max.}$(dioxane) 1 770s and 1 700s cm^{-1}; δ_H [220 MHz, $(CD_3)_2SO$] 10.9—11.6 (1 H, br s, OH), 8.2—8.9 (1 H, br s, OH), and 4.70 (2 H, s, CH_2); *m/z* 116 (M^+, 94%).

4-*Methoxy*-3-(p-*methoxyphenyl*)*furan*-2(5H)-*one* [*Methyl* 2-(4-*Methoxyphenyl*)*tetronate*] (**9**).—This compound was prepared from the acid (**5**) by the method of Boll and co-workers.[4] The product was separated from approximately 5% of the isomeric compound (**10**) by chromatography on silica gel using chloroform as eluant; it had m.p. 109—113 °C (MeOH) (lit.,[3] 111.5—112 °C) (Found: C, 65.3; H, 5.4. Calc. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.5%); $\lambda_{max.}$($CHCl_3$) 275nm (ε 19 800); $\nu_{max.}$(Nujol) 1 730s and 1 640s cm^{-1}; δ_H [60 MHz, $(CD_3)_2CO$] 7.86 (2 H, d, *J* 9 Hz), 6.90 (2 H, d, *J* 9 Hz), 4.99 (2 H, s, CH_2), 4.05 (3 H, s, OMe), and 3.78 (3 H, s, OMe); *m/z* 220 (M^+, 81%).

5-*Amino*-4-*phenylfuran*-3(2H)-*one* (**13**).—To LDA (8 mmol) in THF (10 ml) at −78 °C under N_2 was added phenylacetonitrile (1.178 g, 9.98 mmol) in THF (40 ml). After 10 min dioxolanone (**1**) (0.63 g, 4 mmol) in THF (16 ml) was added. The solution was kept at −78 °C for 1.5 h and allowed to attain room temperature before removal of the solvent and partition of the residue between ether and water. The aqueous layer was acidified with concentrated HCl and the resulting precipitate was filtered off and dried to give the furanone (**13**) (0.57 g, 80%), m.p. 223—226 °C (EtOH) (lit.,[5] 224—226 °C) (Found: C, 68.5; H, 5.3; N, 8.0. Calc. for $C_{10}H_9NO_2$: C, 68.55; H, 5.2; N, 8.0%); $\lambda_{max.}$(EtOH) 268 nm (ε 18 100); $\nu_{max.}$(Nujol) 1 620s and 1 380s cm^{-1}; δ_H [90 MHz, $(CD_3)_2CO$–$CDCl_3$] 7.9 (2 H, s, NH_2, exchanges with D_2O), 7.04—7.60 (5 H, m), and 4.53 (2 H, s, CH_2); *m/z* 175 (M^+, 100%).

5-*Amino*-4-*methylfuran*-3(2H)-*one* (**14**).—To LDA (19.6 mmol) in THF (22 ml) at −78 °C under N_2 was added propiononitrile (1.1 g, 20 mmol) in THF (20 ml). After 10 min the dioxolanone (**1**) (1.56 g, 10 mmol) in THF (12 ml) was added. The solution was kept at −78 °C for 1.5 h and allowed to attain room temperature before removal of the solvent and partition of the residue between ether and water. The aqueous layer was acidified with concentrated HCl and subjected to continuous extraction with ethyl acetate. The extracts were dried and evaporated to give the *furanone* (**14**) (0.59 g, 53%), m.p. 210—213 °C (acetone) (Found: C, 52.8; H, 6.2; N, 12.2. $C_5H_7NO_2$ requires C, 53.1; H, 6.2; N, 12.4%); $\lambda_{max.}$(EtOH) 268nm (ε 9 000); $\nu_{max.}$(Nujol) 1 640m and 1 530s cm^{-1}; δ_H [90 MHz, $(CD_3)_2SO$–$CDCl_3$] 7.51 (2 H, s, NH_2, exchanges with D_2O), 4.34 (2 H, s, CH_2), and 1.52 (3 H, s, CH_3); *m/z* 113 (M^+, 100%).

(*Z*)-5-*Benzylidene*-3-*phenylfuran*-2,4(3H,5H)-*dione* [(*Z*)-4-*Benzylidene*-2-*phenyltetronic Acid: Pulvinone*] (**15**).—By the general procedure the (*Z*)-benzylidenedioxolanone (**26**) (0.98 g, 4.02 mmol) in THF (4 ml) was treated with the lithium enolate of methyl phenylacetate (10 mmol). Acidification of the aqueous layer from the work-up procedure gave a pale yellow precipitate of pulvinone (**15**) (0.99 g, 94%), m.p. 243—247 °C (acetic acid) (lit.,[7] 248—249 °C) (Found: C, 77.4; H, 4.8. Calc. for $C_{17}H_{12}O_3$: C, 77.3; H, 4.6%); $\lambda_{max.}$(EtOH) 358nm (ε 9 300); $\lambda_{max.}$(EtOH + 1 drop 2M-NaOH) 368nm (ε 8 500); $\nu_{max.}$(Nujol) 2 650w and 1 700s cm^{-1}; $\nu_{max.}$(dioxane) 1 765s cm^{-1}; δ_H [220 MHz, $(CD_3)_2SO$] 7.96 (2 H, d), 7.77 (2 H, d), 7.26—7.62 (6 H, m), and 6.73 (1 H, s, PhCH=); *m/z* 264 (M^+, 75%).

Methyl 4-*Benzyloxyphenylacetate* (**28**).—This compound was prepared in 96% yield after recrystallisation by treatment of the acid (**27**)[14] with an ethereal solution of diazomethane; it had m.p. 58—59 °C (MeOH) (lit.,[20] 58.5—59 °C).

3,4-*Dibenzyloxybenzaldehyde* (**30**).—A mixture of 3,4-dihydroxybenzaldehyde (13.81 g, 0.1 mol), benzyl chloride (31.6 g, 0.25 mol), and anhydrous K_2CO_3 (69 g, 0.5 mol) in DMF (200 ml) was heated at 75 °C for 4 h. The mixture was filtered and the filtrate was evaporated under reduced pressure to leave a brown oil. Trituration with water gave a yellow solid which was filtered off and dried *in vacuo* at 60 °C. The crude product was chromatographed on silica gel (200 g) with chloroform as eluant and recrystallised from ethanol to give the aldehyde (**30**) (28.1 g, 88%), m.p. 89—90 °C (lit.,[21] 90—92 °C); $\nu_{max.}$(Nujol) 1 680s cm^{-1}; δ_H (60 MHz, $CDCl_3$) 9.78 (1 H, s, CHO), 6.90—7.55 (13 H, m), 5.18 (2 H, s, OCH_2Ph), and 5.16 (2 H, s, OCH_2Ph).

(*Z*)-5′-(3,4-*Dibenzyloxybenzylidene*)*cyclohexanespiro*-2′-(1′,3′-*dioxolan*)-4′-*one* (**29**).—To a solution of the phosphorane (**31**) (40 mmol) (see General procedure in preceding paper[2]) in toluene (40 ml) at 70 °C under N_2 was added the aldehyde (**30**) (9.54 g, 30 mmol) in toluene (90 ml). After 4 h the reaction mixture was allowed to cool and then filtered. Evaporation gave the crude product (23 g) which was purified by chromatography on silica gel (320 g) with chloroform as eluant and recrystallisation from ethanol to give the *dioxolanone* (**29**) (10.96 g, 80%), m.p. 97—98 °C (Found: C, 76.5; H, 6.3. $C_{29}H_{28}O_5$ requires C, 76.3; H, 6.2%); $\lambda_{max.}$(EtOH) 306infl (ε 17 500) and 324nm (23 600); $\nu_{max.}$($CHCl_3$) 1 775s and 1 665w cm^{-1}; δ_H (220 MHz, $CDCl_3$) 6.92—7.53 (13 H, m), 6.38 (1 H, s, ArCH=), 5.20 (4 H, s, 2 × OCH_2Ph), and 1.44—1.90 (10 H, m); *m/z* 456 (M^+, 8%) and 91 (100%).

(*Z*)-3-(4-*Benzyloxyphenyl*)-5-(3,4-*dibenzyloxybenzylidene*)-*furan*-2,4(3H,5H)-*dione* [(*Z*)-2-(4-*Benzyloxyphenyl*)-4-(3,4-*dibenzyloxybenzylidene*)*tetronic Acid: 3′,4′,4-Tribenzyloxypulvinone*] (**20**).—By the general procedure the dioxolanone (**29**) (4.56 g, 10 mmol) in THF (20 ml) was treated with the lithium

enolate of methyl 4-benzyloxyphenylacetate (**28**) (25.0 mmol). The solvent was removed under reduced pressure and to the resulting oil were added ether and water. A yellow precipitate appeared immediately and this was filtered off and dried. The filtrate was allowed to stand for a few minutes whereupon a second crop of the same yellow solid appeared; this was filtered off and dried. Recrystallisation of (**32**) from glacial acetic acid–water gave 3′,4′,4-*tribenzyloxypulvinone* (**20**) (4.55 g, 78%), m.p. 181.5—182 °C (Found: C, 78.0; H, 5.0. $C_{38}H_{30}O_6$ requires C, 78.3; H, 5.2%); $\lambda_{max.}$(EtOH) 257 (ε 12 300), 304 (13 500), 324 (14 600), and 372nm (9 350); $\nu_{max.}$(Nujol) 2 650w, 1 700s, 1 660w, and 1 610s cm^{-1}; $\nu_{max.}$(dioxane) 3 575m, 3 520m, 1 765s, and 1 610s cm^{-1}; δ_H [80 MHz, $(CD_3)_2CO$] 8.02 (2 H, d, *J* 8 Hz), 7.35—7.85 (17 H, m), 7.22 (1 H, d, *J* 8 Hz), 7.13 (2 H, d, *J* 8 Hz), 6.57 (1 H, s, ArCH=), 5.32 (4 H, s, 2 × OCH_2Ph), and 5.29 (2 H, s, OCH_2Ph).

(*Z*)-5-*Benzylidene*-3-(4-*benzyloxyphenyl*)*furan*-2,4(3H,5H)-*dione* [(Z)-4-*Benzylidene*-2-(4-*benzyloxyphenyl*)*tetronic Acid*: 4-*Benzyloxypulvinone*] (**21**).—By the general procedure the dioxolanone (**26**) (0.73 g, 3 mmol) in THF (3 ml) was treated with the lithium enolate of methyl 4-benzyloxyphenylacetate (**28**) (7.5 mmol) at −78 °C. The reaction mixture was allowed to attain room temperature before it was diluted with water (5 ml) and refluxed for 0.5 h. The solvent was evaporated and to the residue were added ether and water. The ethereal layer was washed with water whereupon the amide (**34**) (0.23 g) precipitated. The combined aqueous layers were acidified with concentrated HCl and the precipitate which appeared was filtered off and dried to give a mixture of the pulvinone (**21**) and 4-benzyloxyphenylacetic acid (1.86 g). This was stirred with chloroform and filtered to give 4-*benzyloxypulvinone* (**21**) (0.78 g, 71%). Evaporation of the filtrate gave 4-benzyloxyphenylacetic acid (1.08 g). 4-Benzyloxypulvinone (**21**) had m.p. 235—237 °C (EtOH) (Found: C, 77.8; H, 4.6. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%); $\lambda_{max.}$(EtOH) 300 (ε 18 200) and 380nm (6 000); $\nu_{max.}$(Nujol) 2 650w, 1 690s, and 1 660w cm^{-1}; $\nu_{max.}$(dioxane) 1 765s cm^{-1}; δ_H [80 MHz, $(CD_3)_2CO$] 8.00 (2 H, d, *J* 8 Hz), 7.35—7.87 (10 H, m), 7.17 (2 H, d, *J* 8 Hz), 6.67 (1 H, s, ArCH=), and 5.25 (2 H, s, OCH_2Ph); *m/z* 370 (M^+, 10%) and 91 (100%).

N,N-Di-isopropyl-2-(4-benzyloxyphenyl)-3,4-dihydroxy-5-phenylpenta-2,4-dien-1-oic acid amide (**34**), m.p. 201—205 °C (EtOH–H_2O) (Found: C, 76.5; H, 6.9; N, 2.8. $C_{30}H_{33}NO_4$ requires C, 76.4; H, 7.05; N, 2.95%); $\lambda_{max.}$(EtOH) 300 (ε 25 500) and 382 nm (8 250); $\nu_{max.}$(Nujol) 3 100—2 600w, 1 690s, 1 570s, and 1 555s cm^{-1}; δ_H [220 MHz, $(CD_3)_2SO$] 8.23 (2 H, d, *J* 8 Hz), 7.12—7.80 (10 H, m), 6.88 (2 H, d, *J* 8 Hz), 5.98 (1 H, s, PhCH=), 5.07 (2 H, s, OCH_2Ph), 3.30 (2 H, septet, 2 × CH), and 1.23 (12 H, d, *J* 6 Hz, 2 × $CHMe_2$); *m/z* 370 [M^+ − $HN(CHMe_2)_2$, 30%] and 91 (100%).

Deprotection of (Z)-3-(4-*Benzyloxyphenyl*)-5-(3,4-*dibenzyloxybenzylidene*)*furan*-2,4(3H,5H)-*dione* (**20**) *using* HBr.—The pulvinone (**20**) (0.583 g, 1.0 mmol) was stirred in 48% HBr in acetic acid (10 ml) for 16 h. Evaporation of the solvent revealed a yellow solid. A small portion of the product was purified by preparative t.l.c. on silica gel using benzene–ethyl acetate–acetic acid (50 : 49 : 1) as eluant. The lower R_F (major) component was identical (^1H n.m.r. and t.l.c.) with a sample of natural 3′,4′,4-trihydroxypulvinone (**18**) from *Suillus grevillei*.

(*Z*)-5-*Benzylidene*-3-(4-*hydroxyphenyl*)*furan*-2,4(3H,5H)-*dione* [(Z)-4-*Benzylidene*-2-(4-*hydroxyphenyl*)*tetronic Acid*: 4-*Hydroxypulvinone*] (**24**).—To a solution of 4-benzyloxypulvinone (**21**) (186.5 mg, 0.5 mmol) in DMF (20 ml) was added 10% Pd-C (40 mg) and concentrated HCl (5 drops) and the mixture was stirred under hydrogen for 18 h. The catalyst was filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in acetone (1 ml) and purified by chromatography on silica gel (40 g) using benzene–ethyl acetate–acetic acid (50:49:1) as eluant. Recrystallisation gave 4-*hydroxypulvinone* (**24**) (95 mg, 68%), m.p. 258—263 °C (Pr^iOH–petroleum) (Found: C, 72.6; H, 4.0. $C_{17}H_{12}O_4$ requires C, 72.85; H, 4.3%); $\lambda_{max.}$(EtOH) 300 (ε 38 200) and 380 nm (11 200); $\nu_{max.}$(Nujol) 3 360w, 2 625w, and 1 700s cm^{-1}; $\nu_{max.}$(dioxane) 3 300s and 1 765s cm^{-1}; δ_H [80 MHz, $(CD_3)_2CO$] 7.90 (2 H, d, *J* 8 Hz), 7.37—7.98 (5 H, m), 6.95 (2 H, d, *J* 8 Hz), and 6.62 (1 H, s, PhCH=); *m/z* 280 (M^+, 100%).

(*Z*)-5-(3,4-*Dihydroxybenzylidene*)-3-(4-*hydroxyphenyl*)*furan*-2,4(3H,5H)-*dione* [(Z)-4-(3,4-*Dihydroxybenzylidene*)-2-(4-*hydroxyphenyl*)*tetronic Acid*: 3′,4′,4-*Trihydroxypulvinone*] (**18**).—A solution of the tribenzyloxypulvinone (**20**) (0.553 g, 1.0 mmol) in dimethylformamide (40 ml) containing 10% Pd-C (0.24 g) and concentrated HCl (10 drops) was stirred under hydrogen for 1 h. The catalyst was removed by filtration and the filtrate was evaporated under reduced pressure to give a bright yellow solid. This was dissolved in acetone (2 ml) and chromatographed on silica gel (90 g). Elution with benzene–ethyl acetate–acetic acid (50:49:1) gave 3′,4′,4-trihydroxypulvinone (**18**) (0.298 g, 96%), m.p. 289—291 °C (Pr^iOH–light petroleum) (lit.,[9] 291 °C) (Found: C, 65.3; H, 3.9. Calc. for $C_{17}H_{12}O_6$: C, 65.4; H, 3.85%); $\lambda_{max.}$(EtOH) 242 (ε 20 050) and 381nm (30 100); $\lambda_{max.}$(10% EtOH) 252 and 335nm; $\lambda_{max.}$(10% EtOH + 2 drops 2M-NH_4OH after 2 min) 259 and 386nm; $\nu_{max.}$(Nujol) 3 350s, 2 650w, 1 695s, 1 665w, 1 620s, and 1 610s cm^{-1}; $\nu_{max.}$(dioxane) 1 755s cm^{-1}; δ_H [80 MHz, $(CD_3)_2CO$] 7.95 (2 H, d, *J* 8 Hz), 7.54 (1 H, d, *J* 2 Hz), 7.16 (1 H, dd, *J* 8, 2 Hz), 6.95 (2 H, d, *J* 8 Hz), 6.93 (1 H, d, *J* 8 Hz), and 6.52 (1 H, s, ArCH=); *m/z* 312 (M^+, 47%). The product was identical (^1H n.m.r. and t.l.c.) with a natural sample of 3′,4′,4-trihydroxypulvinone from *Suillus grevillei*.

5-(3,4-*Dimethoxyphenyl*)-3-(4-*methoxyphenyl*)-4-*methoxyfuran*-2(5H)-*one* (3′,4′,4-*Trimethoxy*-O-*methylpulvinone*) (**35**).—Methylation of trihydroxypulvinone (**18**) with an excess of ethereal diazomethane and removal of the solvent under reduced pressure gave (**35**), m.p. 152.5—153.5 °C (EtOH) (lit.,[9] 153—155 °C) (Found: C, 68.6; H, 5.5. Calc. for $C_{21}H_{20}O_6$: C, 68.45; H, 5.5%); $\nu_{max.}$(Nujol) 1 745s and 1 655m cm^{-1}; $\nu_{max.}$($CHCl_3$) 1 755s and 1 635m cm^{-1}; δ_H (80 MHz, $CDCl_3$) 6.83—7.82 (7 H, m), 6.25 (1 H, s, ArCH=), 3.96 (3 H, s, OMe), 3.93 (3 H, s, OMe), and 3.87 (6 H, s, 2 × OMe); *m/z* 368 (M^+, 100%).

5-(3,4-*Diacetoxyphenyl*)-3-(4-*acetoxyphenyl*)-4-*acetoxyfuran*-2(5H)-*one* (3′,4′,4-*Triacetoxy*-O-*acetylpulvinone*) (**36**).—3′,4′,4-Trihydroxypulvinone (**18**) was acetylated as described by Edwards[9] to give the tetra-acetate (**36**), m.p. 198—199 °C (from glacial acetic acid) (lit.,[9] 200—203 °C); $\nu_{max.}$(Nujol) 1 755s cm^{-1}; δ_H (80 MHz, $CDCl_3$) 7.08—7.90 (7 H, m), 6.00 (1 H, s, ArCH), 2.43 (3 H, s, COMe), 2.34 (3 H, s, COMe), 2.33 (3 H, s, COMe), and 2.32 (3 H, s, COMe); *m/z* 480 (M^+, 6%).

5-*Benzylidene*-3-*ethoxycarbonylfuran*-2,4(3H,5H)-*dione* (4-*Benzylidene*-2-*ethoxycarbonyltetronic Acid*) (**37**).—Diethyl malonate (2.21 g, 13.8 mmol) in DMF (5 ml) was added dropwise to a slurry of sodium hydride (0.33 g, 13.8 mmol) in DMF cooled to 0 °C under N_2. The suspension was warmed to room temperature before addition of the dioxolanone (**26**) (1.08 g, 4.4 mmol) in DMF (8 ml) and the mixture was heated to 100 °C for 3 h, cooled, and evaporated to give a brown oil which was partitioned between water (100 ml) and ether (100 ml). Acidification (pH 1) of the aqueous layer gave a white solid which was filtered off, dried, and recrystallised from dichloromethane–petroleum (b.p. 60—80 °C) to afford the acid (**37**) (0.55 g, 48%), m.p. 199—200 °C (lit.,[16] 196 °C) (Found: C, 64.6;

H, 4.4. Calc. for $C_{14}H_{12}O_5$: C, 64.6; H, 4.65%); $\lambda_{max.}$(EtOH) 305nm (ε 31 700); $\nu_{max.}$(CH_2Cl_2) 1 790s, 1 670s, 1 610s, and 1 350m cm^{-1}; δ_H (220 MHz, $CDCl_3$) 7.75—7.85 (2 H, m), 7.35—7.50 (3 H, m), 6.55 (1 H, s, PhCH=), 4.42 (2 H, q, OCH_2Me), and 1.38 (3 H, t, OCH_2Me); *m/z* 260 (M^+, 8%).

(3-*Acetyl*-5-*benzylidenefuran*-2,4(3H,5H)-*dione* (2-*Acetyl*-4-*benzylidenetetronic Acid*) (**38**).—Ethyl acetoacetate (1.16 g, 12.3 mmol) in DMF (5 ml) was added to a slurry of NaH (0.29 g, 12 mmol) in DMF (10 ml) at 0 °C under N_2. The mixture was warmed to room temperature before addition of the dioxolanone (**26**) (1.0 g, 4.1 mmol) in DMF (7 ml) and the mixture was heated to 100 °C for 3 h; it was then cooled and evaporated to give a brown oil which was partitioned between water (75 ml) and ether (100 ml). Acidification (pH 1) of the aqueous layer gave a yellow solid which was filtered off, dried, and recrystallised from CH_2Cl_2–$CHCl_3$–petroleum (b.p. 60—80 °C) to afford the *acid* (**38**) as yellow needles (0.48 g, 51%), m.p. 162.5—163 °C (Found: C, 68.0; H, 4.1. $C_{13}H_{10}O_4$ requires C, 67.8; H, 4.4%); $\lambda_{max.}$(EtOH) 307nm (ε 35 400); $\lambda_{max.}$(EtOH + 1 drop 2M-NaOH) 329nm (ε 26 400); $\nu_{max.}$(CH_2Cl_2) 1 780s, 1 680w, 1 660m, and 1 645s cm^{-1}; δ_H (220 MHz, $CDCl_3$) 7.8—7.9 (2 H, m), 7.4—7.5 (3 H, m), 6.67 (1 H, s, PhCH=), and 2.60 (3 H, s, COMe); *m/z* 230 (M^+, 68%).

Acknowledgements

We thank Dr. R. L. Edwards (Bradford) and Dr. J. Harley-Mason (Cambridge) for the provision of authentic samples, and the S.E.R.C. for generous support (G. J. G., F. E. S., and J. N. A. S.).

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Received 10*th October* 1983; *Paper* 3/1783