Synthetic Studies on O-Heterocycles *via* Cycloadditions. Part 2. Adducts from Styrene Oxides

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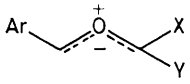
The styrene oxides (**14**) and (**15**), bearing electron-withdrawing functions, readily undergo thermal and photochemical (triplet sensitised) dipolar cycloadditions with simple electron-deficient olefins, regioselectively in the case of methyl acrylate. However, cycloadditions with 5-arylbutenolides as dipolarophiles, required for lignan synthesis, could not be effected in significant yield. A new short route to 5-arylbut-2-enolides was devised. The dihydro- and tetrahydro-furan adducts (**18d**), (**19d**), and (**20d**) all fragment in base to the dienol nitrile (**25**).

In the preceding paper [1] we pointed out that while the chemistry of carbonyl ylides has received a good deal of mechanistic attention, little work has been directed towards the utilisation of this chemistry for natural product synthesis, and we sketched out synthetic strategies towards various lignans dependent upon carbonyl ylide cycloadditions. These included the additions of ylides of type (**1**) with electron deficient olefins (**2**). The *Z*-configuration of (**2**) would ensure 3,4-*cis*-geometry in the adduct (**3**) which has the correct carbon skeleton for transformation to lignans of types (**4**) and (**5**). These classes of natural *O*-heterocycle include a number with interesting biological activity,[2] and surprisingly few synthetic methods have been devised for their construction.[3]

We thus embarked on examination of the reactions of substituted styrene oxides, under thermal and photochemical conditions, and we selected the arylbutenolides (**6**) as potentially suitable partners in cycloadditions. Considerable interest has been expressed in the synthesis of furan-2(5*H*)-ones since such lactones occur in Nature and are valuable intermediates in synthesis. Early methods of preparation have been reviewed[4] and many new procedures have been reported.[5] However few 5-arylfuranones (**6**) are known; their synthesis is complicated by ready isomerisation (acid or base catalysed) to the more stable β,γ-unsaturated isomers (**7**). Available methods were either poor-yielding, or over-sophisticated for such modest goals, and we devised the simple chemistry of Scheme 1 as an alternative. Aldol condensation of aryl aldehydes with pyruvic acid[6] gave 2-oxo-4-arylbut-3-enoic acids (**8**) (60–70%). Borohyride treatment of the potassium salts[7] lead only to 1,2-reduction (50–65%). The allylic alcohols (**9**) were then dissolved in trifluoroacetic acid (TFA) with trifluoroacetic anhydride (1 equiv), to afford the desired lactones (**6**), presumably *via* cations (**10**). The yields were fair (40–45%) and the product lactones were obtained free of the isomers (**7**). Isomerisation to the β,γ-forms occurred during chromatography, on storage, and in chloroform solution. The lack of isomerisation under preparative conditions indicates that the protonated lactones (**11**) are the major form in solution in TFA. As an alternative, the (*E*)-4-oxo-4-arylbut-2-enoic acids (**12**), obtained by acylation of arenes with maleic anhydride,[8] were reduced to the allylic alcohols (**13**). These alcohols also cyclised to the desired lactones in TFA; the *transoid* intermediate cations (**10**) must stereomutate before cyclisation.

The required epoxides (**14**) and (**15**) were prepared by epoxidation using t-butyl hydroperoxide or sodium hypochlorite at pH 8, of the appropriate arylidenemalonitrile or (*E*)-cyanoacetate. The bis-sulphone (**16**) was also prepared by aldol condensation; since it decomposed on attempted purification, it was directly oxidised to the epoxybis(sulphone) (**17**).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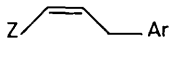
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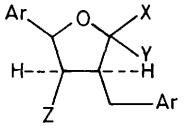
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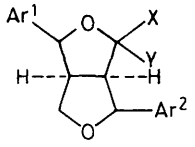
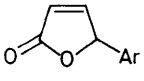
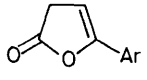
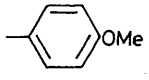
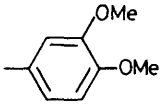

(4) X = Y = H
(5) X,Y = O

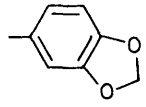

(6)


(7)

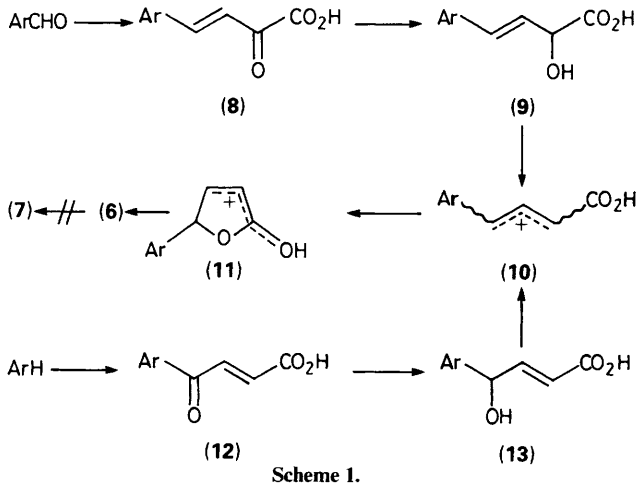
a; Ar = Ph

b; Ar = 

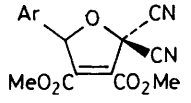
c; Ar = 

d; Ar = 

Several cycloadditions of these epoxides with symmetrical dipolarophiles were investigated. Thus (**14d**) when heated with dimethyl acetylenedicarboxylate (DMAD) at 110 °C smoothly afforded the dihydrofuran (**18d**) (71%). Irradiation of (**15b**) with DMAD using acetophenone as sensitiser provided (53%) both isomers (*ca.* 1:1) of the dihydrofuran (**19b**); (**15d**) similarly gave (**19d**) (68%). Both thermal and photochemical activation were also successful with dimethyl fumarate; (**14d**) gave the 5α- and

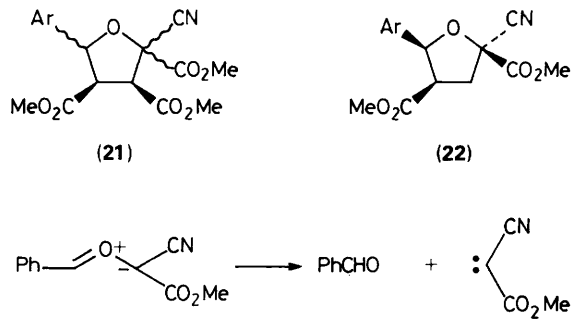


Scheme 1.

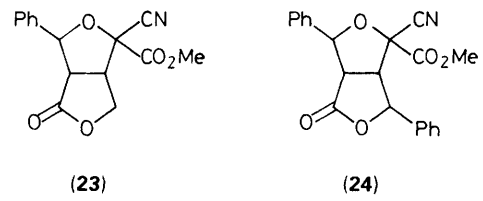


5β-isomers of (**20d**) with retention of dipolarophile geometry, and (**15d**) reacted thermally with dimethyl maleate to yield three stereoisomers of the adduct (**21**). With an unsymmetrical dipolarophile, methyl acrylate, the thermal cycloaddition with (**14d**) was regiospecific and stereospecific, with (**22d**) the only adduct isolated (*endo* preference). A number of experiments attempted to trap an ylide from the epoxy sulphone (**17**), using both thermal and photochemical methods, but no traces of any adducts with DMAD or dimethyl fumarate were found.

Attention was then turned to the butenolides (**6**) as dipolarophile. In view of the thermal instability of these lactones, photochemical generation of the carbonyl ylides was chosen, and epoxide (**15a**) was irradiated with but-2-enolide, and with the lactone (**6a**) in benzene, using acetophenone as triplet sensitiser. Although the ylide was certainly generated under these conditions (see below) its reactions with these olefins were slow. N.m.r. monitoring indicated that benzaldehyde was formed, *i.e.* the ylide fragments as in Scheme 2; fragmentation is faster than trapping since only trace quantities of adducts (**23**)



Scheme 2.



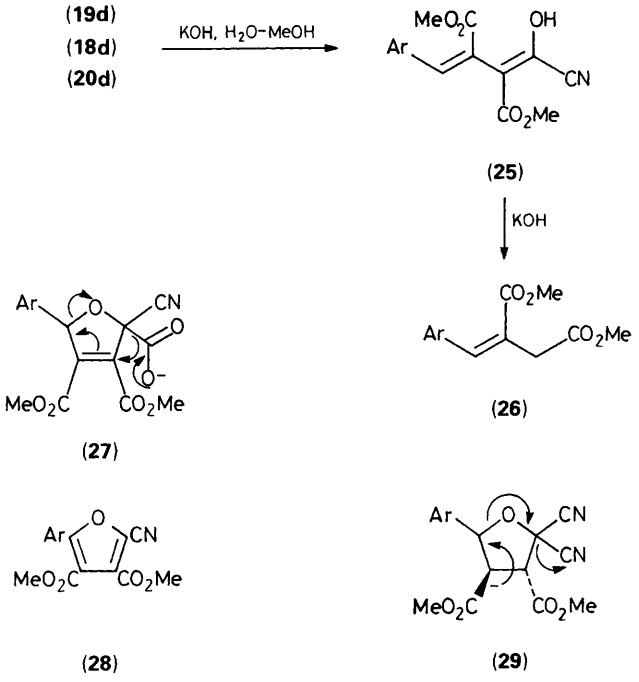
and (**24**) were obtained, characterised only by their mass spectra; that for (**23**) shows *m/z* 287.078 ($C_{15}H_{13}NO_5$ requires M^+, 287.079), and that for (**24**) shows *m/z* 363.112 ($C_{21}H_{17}NO_5$ requires M^+, 363.111). Since the yields of these assumed adducts were so low, and we could not improve them, this approach to lignan skeletons was frustrated.

Finally we examined some chemistry of certain of the above adducts, expecting the manipulation of products such as the elusive (**24**). Thus the dihydrofuran (**19d**) was treated with aqueous potassium hydroxide in methanol. Reaction took place at ambient temperature and a crystalline acidic product (69%) was isolated. However, this did not result from simple ester hydrolysis, since from the ^1H and ^{13}C NMR spectral results (see Experimental section) it could be assigned the enolic structure (**25**). It gave a methyl ether on treatment with diazoethane, and when heated with aqueous base underwent retro-Claisen cleavage to the diester (**26**) (identified as dimethyl piperonylidenesuccinate by comparison with an authentic sample obtained through Stobbe condensation). Thus hydrolysis of the non-conjugated ester in (**19d**) must be followed by decarboxylation and ring-opening as shown in (**27**). A similar reaction ensued when the bisnitrile (**18d**) was treated with potassium hydroxide in dimethyl sulphoxide; the enol (**25**) was again obtained, with the furan (**28**) as a minor product, from dehydrocyanation. Finally, the enol (**25**) was also obtained by treating the tetrahydrofuran (**20d**) with potassium hydroxide–dimethyl sulphoxide. Fragmentation as in (**29**) is the simplest mechanistic rationalisation.

Experimental

For generalisations, see Part 1.[1]

(1) *Reduction of 2-Oxo-4-arylbut-3-enoic and 4-Oxo-4-arylbut-2-enoic Acids.*—The appropriate acid (10 ml) was dissolved in saturated aqueous potassium hydrogen carbonate (30 cm^3) and potassium borohydride (10–20 mmol) was added. The solution was stirred at ambient temperature for 24 h, and then acidified to pH 1. The products were isolated through collection in ether, in the usual manner, and crystallised. In this way were obtained: 2-hydroxy-4-(3,4-methylenedioxyphenyl)but-3-enoic acid (**9d**), m.p. 118 °C (from acetone–light petroleum) (Found: C, 59.65; H, 4.8%; *m/z*, 222.053. $C_{11}H_{10}O_5$ requires C, 59.5; H, 4.5%; *M*, 222.054); λ_{max}(EtOH) 266, (4 200) and 305 nm (2 650); δ([$^2H_6$]acetone)



4.74 (1 H, dd, *J* 2, 6 Hz, 2 H), 5.96 (2 H, s, OCH_2O), 6.16 (1 H, dd, *J* 6, 16 Hz, 3-H), and 6.6–7 (4 H, ArH, 4-H): 2-hydroxy-4-phenylbut-3-enoic acid (**9a**), m.p. 137 °C (lit.,[7] m.p. 137 °C): 2-hydroxy-4-(4-methoxyphenyl)but-3-enoic acid (**9b**), m.p. 144 °C (lit.,[7] m.p. 145 °C): 4-hydroxy-4-(3,4-dimethoxyphenyl)-but-2-enoic acid (**13c**), m.p. 100 °C from chloroform–light petroleum (Found: C, 60.6; H, 5.8%; *m/z*, 238.086. $C_{12}H_{14}O_5$ requires C, 60.50; H, 5.9%; *M*, 238.084); λ_{max}(EtOH) 280 nm (7 600), δ([$^2H_6$]acetone) 3.92 (6 H, s, 2 × OMe), 5.38 (1 H, dd, *J* 2, 4 Hz, 4-H), 6.1 (1 H, dd, *J* 2, 16 Hz, 2 H), and 6.9–7.2 (4 H, ArH, 3 H): 4-hydroxy-4-(4-methoxyphenyl)but-2-enoic acid (**13b**), m.p. 92 °C from chloroform–light petroleum (Found: C, 63.0; H, 5.95%; *m/z* 208.076. $C_{11}H_{12}O_4$ requires C, 63.45; H, 5.75; *M*, 208.074), λ_{max}(EtOH) 268 nm (15 200); δ([$^2H_6$]acetone) 3.84 (3 H, s, OMe), 5.34 (1 H, dd, *J* 2, 4 Hz, 4-H), 6.12 (1 H, dd, *J* 2, 16 Hz, 2-H), 6.72 (2 H, d, *J* 8 Hz, ArH), 7.0 (1 H, dd, *J* 4, 16 Hz, 3-H), and 7.34 (2 H, d, *J* 8 Hz, ArH): and 4-hydroxy-4-phenylbut-2-enoic acid, m.p. 90 °C (lit.,[9] m.p. 91 °C).

(2) *Cyclisation of the* trans-*Acids* (**9a**, **b**, **d**), (**13a**, **b**, **c**) *to* 5-*Arylfuran*-2(5H)-*ones* (**6a**, **b**, **c**, **d**).—The acid (1 mmol) was dissolved in trifluoroacetic acid (99%; 10 cm^3) with trifluoroacetic anhydride (1 mmol). The solution was stirred at ambient temperature for 24 h and evaporated under reduced pressure. The residue was dissolved in chloroform, washed with aqueous sodium hydrogen carbonate and water, and dried. Evaporation of the organic solvent yielded the appropriate lactone as a clear oil (40–45%) in which no contaminants could be detected by spectroscopic methods. No optimisation of yield was attempted. In this way were obtained: 5-(3,4-methylenedioxyphenyl)furan-2(5*H*)-one (**6d**) (Found: *m/z* 204.043, $C_{11}H_8O_4$ requires *M*, 204.043); ν_{max}($CHCl_3$) 1 786 and 1 758 cm^{-1}; δ($CDCl_3$) 6.04–6.14 (3 H, OCH_2O, 5-H), 6.32 (1 H, dd, *J* 2, 4 Hz, 3-H), 6.6–6.75 (3 H, ArH), and 7.68 (1 H, dd, *J* 2, 4 Hz, 4-H): 5-(3,4-dimethoxyphenyl)furan-2(5*H*)-one (**6c**) (Found: *m/z* 220.074. $C_{12}H_{12}O_4$ requires *M*, 220.074; ν_{max}($CHCl_3$) 1 795 and 1 758 cm^{-1}; δ($CDCl_3$) 3.86 (6 H, s, 2 × OMe), 5.92 (1 H, t, *J* 2 Hz, 5-H), 6.18 (1 H, dd, *J* 2, 4 Hz, 3-H), 6.68–6.82 (3 H, m, ArH), and 7.68 (1 H, dd, *J* 2, 4 Hz, 4-H): 5-(4-methoxyphenyl)furan-2(5*H*)-one[5] (**6b**) (Found: *m/z* 190.064. $C_{11}H_{10}O_4$ requires *M*, 190.063); ν_{max}($CHCl_3$) 1 797 and 1 759 cm^{-1}; δ($CDCl_3$) 3.72 (3 H, s, OMe), 5.84 (1 H, t, *J* 2 Hz, 5 H), 6.06 (1 H, dd, *J* 2, 4 Hz, 3-H), 6.74 (2 H, *J* 8 Hz, ArH), 7.02 (2 H, d, *J* 8 Hz, ArH), and 7.34 (1 H, dd, *J* 2, 4 Hz, 4-H): and 5-phenylfuran-2(5*H*)one[10] (**6a**) (Found: *m/z* 160.054. $C_{10}H_8O_2$ requires *M*, 160.053); ν_{max}-($CHCl_3$) 1 790 and 1 757 cm^{-1}; δ($CDCl_3$) 5.88 (1 H, t, *J* 2 Hz, 5-H), 6.06 (1 H, dd, *J* 2, 6 Hz, 3 H), 7.0–7.3 (5 H, ArH), and 7.36 (1 H, dd, *J* 2, 6 Hz, 4 H).

(3) 3,4-*bismethoxycarbonyl*-5-(3,4-*methylenedioxyphenyl*)-2,5-*dihydrofuran*-2,2-*dicarbonitrile*.—3-(3,4-Methylenedioxyphenyl)oxirane-2,2-dicarbonitrile (1.0 g), dimethyl acetylene dicarboxylate (1.5 g), and dry toluene (10 cm^3) were refluxed together under nitrogen for 24 h. The residue from evaporation was separated on a silica column (light petroleum–ethyl acetate, 3:1); the main fraction afforded the *title dihydrofuran* (**18d**) (1.18 g, 71%), m.p. 159.5–161 °C (Found: C, 57.3; H, 3.37; N, 7.7%; *m/z* 356.063. $C_{17}H_{12}N_2O_7$ requires C, 57.3; H, 3.37; N, 7.85%; M^+ 356.064); δ_H($CDCl_3$) 3.76 and 3.96 (both 3 H, s, OMe), 6.05 (2 H, s, OCH_2O), 6.28 (1 H, s, 5-H), and 6.38 (3 H, m, ArH).

(4) 2,3,4-*Trismethoxycarbonyl*-5-(4-*methoxyphenyl*)-2,5-*dihydrofuran*-2-*carbonitrile*.—(*E*)-2-Methoxycarbonyl-3-(4-methoxycarbonyl)oxirane-2-carbonitrile (0.46 g), dimethyl acetylenedicarboxylate (0.57 g), and acetophenone (0.48 g), in dry benzene (10 cm^3) were deaerated with argon over 40 min, and then irradiated (450 W mercury medium-pressure lamp) for 36 h at room temperature. Evaporation and chromatography as in expt. 3 gave the *title dihydrofuran* (**19b**) (0.4 g, 53%) as a mixture of stereoisomers. Repeated crystallisation from chloroform–light petroleum gave a single isomer, m.p. 115–116 °C (Found: C, 57.8; H, 4.5: *N*, 3.6%; *m/z* 375.097. $C_{18}H_{17}NO_8$ requires, C, 57.6; H, 4.5; N, 3.7%; M^+, 375.095); δ_H 3.68, 3.80, 3.88, and 3.96 (each 3 H, s, OMe), 6.18 (1 H, s, 5-H), and 6.82 and 7.28 (both 2 H, d, *J* 8, ArH).

(5) 2,3,4-*Trismethoxycarbonyl*-5-(3,4-*methylenedioxyphenyl*)-2,5-*dihydrofuran*-2-*carbonitrile*.—(a) (*E*)-2-Methoxycarbonyl-3-(3,4-methylenedioxyphenyl)oxirane-2-carbonitrile[11] (0.6 g), dimethyl acetylenedicarboxylate (0.7 g), and acetophenone (0.48 g) were irradiated in dry benzene (10 cm^3) as in expt. 4, and the products were similarly isolated to yield the title dihydrofuran (**19d**) (0.65 g, 68%) as a mixture of two isomers. Crystallisation from chloroform–light petroleum gave one isomer, m.p. 134–135 °C (Found: *m/z* 389.074. $C_{18}H_{15}NO_9$ requires 389.075); δ_H(CCl_4) 3.92, 4.04, and 4.14 (each 3 H, s, OMe), 6.16 (2 H, s, OCH_2O), 6.42 (1 H, s, 5-H), and 6.92–7.16 (3 H, m, ArH).

(b) The reagents above were refluxed together in toluene for 24 h. Isolation of the product as before, and several recrystallisations from ethanol, gave the isomer isolated in expt. (5a), m.p. 135 °C (38%).

(6) 3,4-*Bismethoxycarbonyl*-5-(3,4-*methylenedioxyphenyl*)-*tetrahydrofuran*-2,2-*dicarbonitrile*.—(*a*) 3-(3,4-methylenedioxyphenyl)oxirane-2,2-dicarbonitrile (0.5 g), dimethyl fumarate (1.0 g), and dry toluene (10 cm^3) were heated at 110 °C under nitrogen for 24 h. Evaporation and chromatography as in expt. (3) gave the *title tetrahydrofuran* (**20d**) as a crystalline mixture of two stereoisomers (Found: C, 57.05; H, 4.0; N, 7.65%; *m/z* 358.081. $C_{17}H_{14}N_2O_7$ requires C, 57.0; H, 3.9; N, 7.8%; M^+, 358.080). Isomer A (3,4-*trans*, 4,5-*cis*) had δ_H(C_6D_6) 2.88 and 3.20 (both 3 H, s, OMe), 3.80 (1 H, dd, *J* 9.5, 4-H), 4.37 (1 H, d, *J* 9.5, 3-H), 5.02 (1 H, d, *J* 9.5, 5-H), 5.22 (2 H, s, OCH_2O), and 6.50 (3 H, m, ArH); δ_H($CDCl_3$) 3.40 and 3.95 (both 3 H, s, OMe). Isomer B (3,4-*trans*, 4,5-*trans*) had δ_H(C_6D_6) 3.10 and 3.20 (both 3 H, s, OMe), 3.70 (1 H, dd, *J* 10, 10.5, 4-H), 4.23 (1 H, d, *J* 10.5, 3-H), 4.81 (1 H, d, *J* 10, 5-H), 5.21 (2 H, s, OCH_2O), and 6.50 (3 H, m, ArH); δ_H($CDCl_3$) 3.76 and 3.95 (both 3 H, s, OMe).

(b) Irradiation of the same reagents with acetophenone in benzene as in expt. 4 gave a similar mixture (42%).

(7) 2,3,4-*Trismethoxycarbonyl*-5-(3,4-*methylenedioxyphenyl*)-*tetrahydrofuran*-2-*carbonitrile*.—(*E*)-2-Methoxycarbonyl-3-(3,4-methylenedioxyphenyl)oxirane-2-carbonitrile (1.5 g), dimethyl maleate (2.0 g) and dry toluene (20 cm^3) were refluxed together for 48 h under nitrogen. Product isolation as in expt. 3 (light petroleum–ethyl acetate, 1:1) gave the *title compound* (**21d**) as a mixture (2.03 g, 86%) of three stereoisomers. Fractional crystallisation from ethanol afforded the 3,4-*cis*,4,5-*cis*-isomer, m.p. 134–136 °C (Found: C, 55.2; H, 4.0; N, 3.4%; *m/z* 391.091. $C_{18}H_{17}NO_9$ requires C, 55.25; H, 4.35; N 3.6%; M^+, 391.090); $\delta_H(CDCl_3)$ 3.46 (3 H, s, 4-CO_2Me), 3.70 (1 H, m, 4-H), 3.80 (3 H, s, 3-CO_2Me), 3.96 (3 H, s, 2-CO_2Me), 4.40 (1 H, d, *J* 7, 3-H), 5.44 (1 H, d, *J* 6, 5-H), 5.95 (2 H, s, OCH_2O), and 6.82 (3 H, m, ArH).

(8) 4-*Methoxycarbonyl*-5-(3,4-*methylenedioxyphenyl*)*tetrahydrofuran*-2,2-*dicarbonitrile*.—3-(3,4-Methylenedioxyphenyl)-oxirane-2,2-dicarbonitrile (2.0 g), methyl acrylate (2.5 g), and toluene (20 cm^3) were refluxed for 18 h under nitrogen. Product isolation as in expt. 7 gave the *title tetrahydrofuran* (**22d**) (0.61 g, 22%), m.p. 117–118 °C from ethanol–light petroleum (Found: C, 60.1; H, 4.25; N, 9.2%; *m/z* 300.073. $C_{15}H_{12}N_2O_5$ requires C, 60.0; H, 4.0; N, 9.33%; M^+, 300.076); $\delta_H(CDCl_3)$ 2.98 (1 H, dd, *J* 8, 14, 3-H_a), 3.32 (1 H, dd, *J* 7, 14, 3-H_b), 3.43 (3 H, s, CO_2Me), 3.66 (1 H, m, 4-H), 5.48 (1 H, d, *J* 8, 5-H), 6.00 (2 H, s, OCH_2O), and 6.81 (3 H, m, ArH).

(9) (1*E*,3*Z*)-2,3-*Bismethoxycarbonyl*-1-*hydroxy*-4-(3,4-*methylenedioxyphenyl*)*buta*-1,3-*diene*-1-*carbonitrile*.—(*a*) The dihydrofuran (**19d**) (0.85 g), suspended in methanol (30 cm^3) was treated with aqueous potassium hydroxide (4M), with stirring, the pH being kept at 8–9. When the pH no longer returned to 7, the addition of alkali was stopped, and the mixture was stirred for 1 h. The solution was washed with ether, and acidified. The products were collected with ether. Drying and evaporation gave the *title enol* (**25**) (0.5 g, 69%), m.p. 152–153 °C from ethanol (Found: C, 58.4; H, 3.95; N, 4.05%; *m/z* 331.069. $C_{16}H_{13}NO_7$ requires C, 58.0; H, 3.95; N, 4.25%; M^+, 331.069); ν_{max}(KBr) 3 300–3 000 (OH), 2 245 (CN), 1 705, 1 675, 1 615, and 1 595 cm^{-1}; λ_{max} 220 (4.2), 237 (4.15), 271 (4.26), and 327 nm (3.99); $\delta_H(CDCl_3)$ 3.82 (6 H, s, CO_2Me), 6.00 (2 H, s, OCH_2O), 6.84 (3 H, m, ArH), 7.88 (1 H, s, 4-H), and 12.01 (1 H, s, OH); $\delta_c(CDCl_3)$ 52.63 (q), 53.28 (q), 101.74 (t), 108.82 (d), 108.88 (d), 126.44 (d), 111.35 (s), 112.15 (s), 119.44 (s), 127.82 (s), 148.26 (s), 149.61 (s), 143.76 (s), 145.73 (d), 166.57 (s), and 171.04 (s).

The same product was isolated on treatment of dihydrofuran (**18d**) in a similar fashion.

(*b*) 3,4-Bismethoxycarbonyl-5-(3,4-methylenedioxyphenyl)-tetrahydrofuran-2,2-dicarbonitrile (**20d**) (0.2 g) in dimethyl sulphoxide (1 cm^3) was treated dropwise with sodium methoxide in methanol (0.1 g sodium in 5 cm^3 methanol) the pH being kept at *ca.* 8. When the pH ceased to fall below 8, the solution was set aside for 30 min and diluted with water. Product isolation as in the previous experiment gave the title enol (0.093 g, 50%), identical with the previous sample.

(10) *Dimethyl* (*Z*)-3-(3,4-*Methylenedioxyphenyl*)*prop*-2-*ene*-1,2-*dicarboxylate*.—The enol (**25**) (0.3 g) was suspended in water (6 cm^3), and aqueous potassium hydroxide (4M) added until the solid had dissolved. The pH was adjusted to 9, and the mixture was heated on steam for 1 h. On cooling, the mixture was extracted with ethyl acetate to yield the title ester (**26**) with i.r., ^1H NMR, and MS data indistinguishable from a sample prepared from piperonylidenesuccinic acid [12] using diazomethane.

(11) 3,4-*Bismethoxycarbonyl*-5-(3,4-*methylenedioxyphenyl*)-*furan*-2-*carbonitrile*.—Expt. (**9b**) was repeated using the tetrahydrofuran adduct (**20d**) (0.1 g) in dimethyl sulphoxide (1 cm^3). When the mixture was diluted with water and set aside overnight, a precipitate formed, which was crystallised from ethanol to yield the *title furan* (**28**) (0.015 g, 16%) (Found: C, 58.85; H, 3.55; N, 4.15%; *m/z* 329.054. $C_{16}H_{11}NO_7$ requires C, 58.36; H, 3.34; N, 4.25%; M^+, 329.054); $\delta_H(CDCl_3)$ 3.94 and 3.98 (both 3 H, s, CO_2Me), 6.08 (2 H, s, OCH_2), 6.94 (1 H, d, *J* 8, ArH), 7.03 (1 H, d, *J* 2, ArH), and 7.39 (1 H, dd, *J* 2,8, ArH).

(12) 2,2-*Bisphenylsulphonyl*-3-*phenyloxirane*.—Bis(phenylsulphonyl)methane (1.0 g),[13] benzaldehyde (1.0 g), piperidine (0.2 cm^3), and triethylamine (0.2 cm^3) were dissolved in benzene (30 cm^3) and refluxed with azeotropic removal of water for 18 h. The solution was evaporated to dryness and the residue was dissolved in dioxane (10 cm^3). t-Butyl hydroperoxide (1.5 cm^3) was added and aqueous potassium carbonate was used to adjust the pH to 8. After 1 h, water (20 cm^3) was added and the mixture extracted with ether. The extracts on evaporation gave a solid, recrystallising from acetone–light petroleum to yield the *title oxirane* (**17**) (0.6 g, 45%), m.p. 139–140 °C (Found: C, 60.4; H, 4.2. $C_{20}H_{16}O_5S_2$ requires C, 60.0; H, 4.05%); δ_H 5.24 (1 H, s) and 7.2–8.3 (15 H, m, ArH).

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