# Synthetic Studies on *O*-Heterocycles *via* Cycloadditions. Part 1. Photochemical (Electron Transfer Sensitised) C-C Cleavage of Diaryloxiranes

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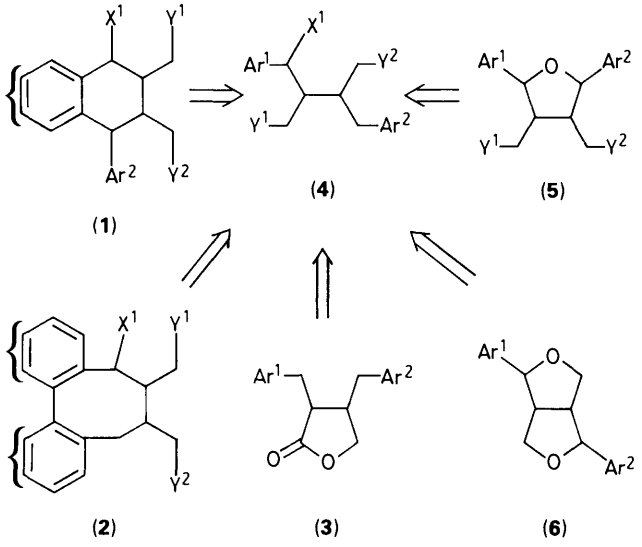
Irradiation of *trans*-stilbene oxide with naphthalene-1,4-dicarbonitrile as sensitiser in the presence of electron deficient dipolarophiles leads, *via* a presumed carbonyl ylide, to various dihydro- and tetrahydro-furans. This chemistry is extended, for the first time, to an example with both aryl rings oxygenated, 2,3-bis(*p*-methoxyphenyl)oxirane, using anthracene-9,10-dicarbonitrile as sensitiser; in contrast to stilbene oxide, in this case direct irradiation, triplet sensitisation, or thermal activation lead to C–O bond cleavage. The bis(*p*-methoxyphenyl) adducts, of interest in the lignan area, are formed with a lack of stereoselectivity suggestive of diradical intermediates.

The lignans are a major group of natural products stemming from the shikimate pathway. A steady flow of new examples continues, with increasing structural diversity.[1] In recent years attention has been paid to the biological activity of lignans, which are remarkably varied.[2] Most importantly, at present, significant antitumour activity is observed in several sub-groups. Derivatives of podophyllotoxin, an aryl tetralin (**1**), are currently of use in the clinic, while bisbenzocyclo-octadienes (**2**), *e.g.* steganone, and bisbenzyl-lactones (**3**), *e.g.* burseran, are also of interest. These groups have attracted considerable synthetic attention.

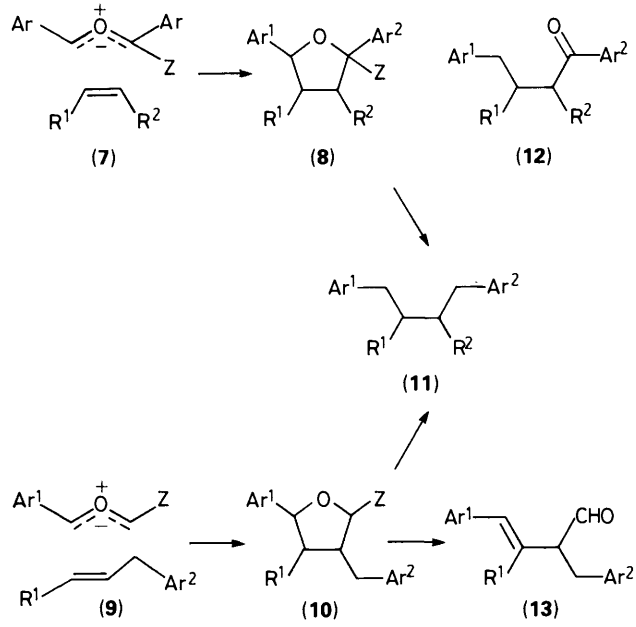
In a number of successful synthetic strategies intermediates of type (**4**) occupy pivotal positions (Scheme 1). Thus suitable




**Scheme 1.**

bisarylbutanes (**4**) can lead to tetralins (**1**), *via* aromatic substitution by a benzyl cation, to bisbenzocyclo-octadienes (**2**) by aryl coupling, and to lactones (**4**), substituted tetrahydrofurans (**5**), or bisaryldioxabicyclo-octanes (**6**), by appropriate functional group transformations. Compounds (**4**) are likely biosynthetic intermediates to a number of the natural lignans.

We were attracted to the use of carbonyl ylides as a means of synthetic entry to this area (Scheme 2). Thus an ylide (**7**), generated from a readily available stilbene oxide, would

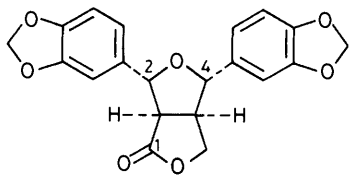



**Scheme 2.**

undergo dipolar cycloaddition to a 2,5-bisaryltetrahydrofuran (**8**), while the parallel reaction of the ylide (**9**) would yield the isomeric tetrahydrofuran (**10**); in both cases stereo- and regio-control might be achieved. Both (**8**) and (**10**) could be subject to benzylic hydrogenolysis to bisarylbutane (**11**) with defined stereochemistry, or to fragmentation to (**12**) or (**13**), specifically functionalised relatives of (**11**). The tetrahydrofuran structure (**8**) is the framework of many lignans, while the isomer (**10**) is the core of more unusual types, *e.g.* magnostellin A[3] and magnolenin C.[4] A useful range of the products, (**8**)–(**13**), thus appeared conveniently available from carbonyl ylide cycloadditions, offering a varied base from which to reach natural products. We set out to explore the viability of this approach, bearing in mind such specific targets as the lactone (**14**), the structure proposed for aptosimon[5] at the outset of our work,† and veraguensin (**15**), an antibacterial tetrahydrofuran.[7]

The generation and 1,3-dipolar cycloadditions of carbonyl ylides have been thoroughly investigated from various

† The structure of aptosimon has subsequently been revised.[6]



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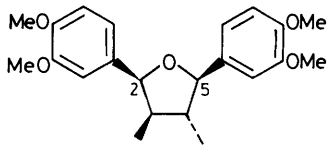

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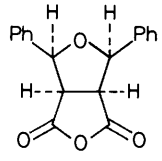

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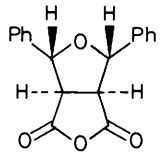

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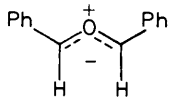

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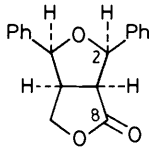

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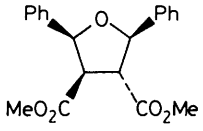
mechanistic viewpoints. Much published work treats symmetrical ylides and dipolarophiles but less attention has been paid to permitted variations in aromatic substituents, to ylides with strongly differentiated termini, and to unsymmetrical dipolarophiles. It was necessary to investigate some of these aspects of the reaction.

We first examined the reaction of *trans*-stilbene oxide with maleic anhydride. It has been reported[8] that a mixture of stereoisomeric adducts was obtained on direct irradiation (medium-pressure mercury lamp) of these reagents. We were unable to verify these results and turned to the recently introduced method of electron-transfer photosensitisation to induce oxirane ring opening.[9] Irradiation of maleic anhydride and *trans*-stilbene oxide in degassed acetonitrile in the presence of naphthalene-1,4-dicarbonitrile gave to our satisfaction the *cis*-fused bicyclic adduct (**16**) (63%). The stereochemistry was assigned by $^1$H NMR comparisons with known 2,5-diaryltetrahydrofurans including the isomer (**17**) synthesised by Lavie and co-workers.[10]* The stereochemistry shown, (**16**), results from the expected *endo*-cyclisation of a carbonyl ylide in an extended (*exo-exo*) conformation (**18**). Under similar conditions *trans*-stilbene oxide also reacted smoothly with butenolide to give the lactone (**19**) in essentially quantitative yield. The chemical shifts of 2-H and 4-H accord with a *cis*-2,4-diphenyl stereochemistry and 1-H and 5-H do not show the upfield shifts characteristic of protons *cis* to phenyl substituents in such systems; stereochemistry (**19**) is thus proposed. In agreement, the lactone (**19**) could be obtained from borohydride reduction of the anhydride (**16**) in isopropyl alcohol.

Butenolide and *trans*-stilbene oxide also reacted photochemically using triplet sensitisation (acetone) to yield the adduct (**19**) but in reduced yield (43%), and other stereoisomers were detected by NMR in the total reaction product.

The value of electron transfer photosensitisation was further confirmed by trapping of the ylide from stilbene oxide with dimethyl fumarate, dimethyl acetylenedicarboxylate, and ethyl propiolate, in turn, with naphthalene-1,4-dicarbonitrile as sensitiser. The respective products were the tetrahydrofuran (**20**) (63%), a mixture (8:5) of the dihydrofurans (**21**) and (**22**) (47%), and the dihydrofuran (**23**) (53%). The last product was smoothly dehydrogenated (81%) with dichlorodicyanobenzoquinone (DDQ) to the diphenylfuran carboxylate (**24**).



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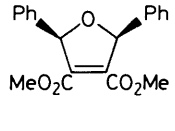

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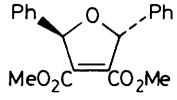

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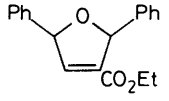

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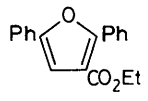

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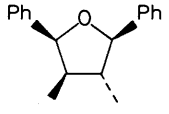

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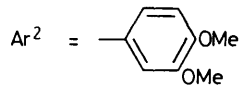
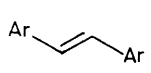
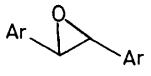
The adduct (**20**) was readily transformed, by lithium aluminium hydride (LAH) reduction, tosylation of the product diol, and a second LAH reduction, to the stereoisomer (**25**) of 3,4-dimethyl-2,5-diphenyltetrahydrofuran. At this stage we had easy access to the lactone (**19**), epimeric at C-2 and C-4 with the target (**14**) and lacking the aryl oxygenation, and the tetrahydrofuran (**25**) with the stereochemistry of veraguensin (**15**), but again lacking the appropriate aromatic substitutents. Since *p*-oxygenated aryl substituents $\alpha$ to tetahydrofuran oxygens are known, in natural lignans, to epimerise readily in dilute acid,[11] we projected that the 3,4-methylenedioxy analogue of (**16**) would epimerise under mild conditions to the more stable stereochemistry of the target (**14**). We thus set out to investigate the crucial question of the effects of aryl oxygen substitution on the ring-opening reactions of stilbene oxides. The *trans* bis-(4-methoxy)-, bis-(3,4-dimethoxy)-, and bis(3,4-methylenedioxy)-stilbenes (**26**), (**27**), and (**28**) were prepared using appropriate benzylic phosphonates and converted into the corresponding *trans*-oxiranes (**29**), (**30**), and (**31**) using buffered *m*-chloroperbenzoic acid. The oxirane (**29**) and naphthalene-1,4-dicarbonitrile were irradiated with an excess of methyl acrylate, and with an excess of butenolide. However, the product proved, on NMR examination, to be a mixture of the diarylacetaldehyde (**32**) and the deoxybenzoin (**33**). Similar products (**34**) and (**35**) were isolated from treatment of the

* In a six-step non-stereoselective synthesis.

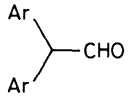


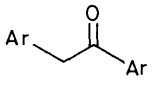




(26) Ar = $Ar^1$
(27) Ar = $Ar^2$
(28) Ar = $Ar^3$

(29) Ar = $Ar^1$
(30) Ar = $Ar^2$
(31) Ar = $Ar^3$



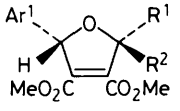


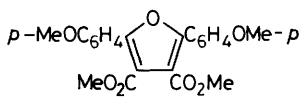
(32) Ar = $Ar^1$
(34) Ar = $Ar^3$

(33) Ar = $Ar^1$
(35) Ar = $Ar^3$

epoxide (**31**) under the same conditions, 15 and 42% respectively. The reactions took a similar course using irradiation with acetone and acetophenone as triplet sensitisers, on direct irradiation, and on heating (150 °C).

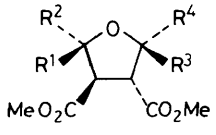
However since we considered that, when using naphthalene-1,4-dicarbonitrile, any electron transfer reactions might have been overwhelmed by the direct irradiation processes, we investigated a sensitiser absorbing at longer wavelength, *i.e.* anthracene-9,10-dicarbonitrile (ADC). The radiation was filtered through a solution of phenanthrene in toluene to screen the oxirane. Under these conditions bis(*p*-methoxyphenyl)-oxirane (**29**) reacted cleanly, although slowly, with dimethyl acetylenedicarboxylate to yield the adducts (**36**) and (**37**) (54%, 9:7) characterised by dihydrofuran ring protons at δ 6.08, 6.32 ($CDCl_3$). Dehydrogenation of the mixture of (**36**) and (**37**) afforded the crystalline furan (**38**) (60%). A similar experiment with dimethyl fumarate gave the tetrahydrofurans (**39**), (**40**), and (**41**) (38%; 4:2:1).





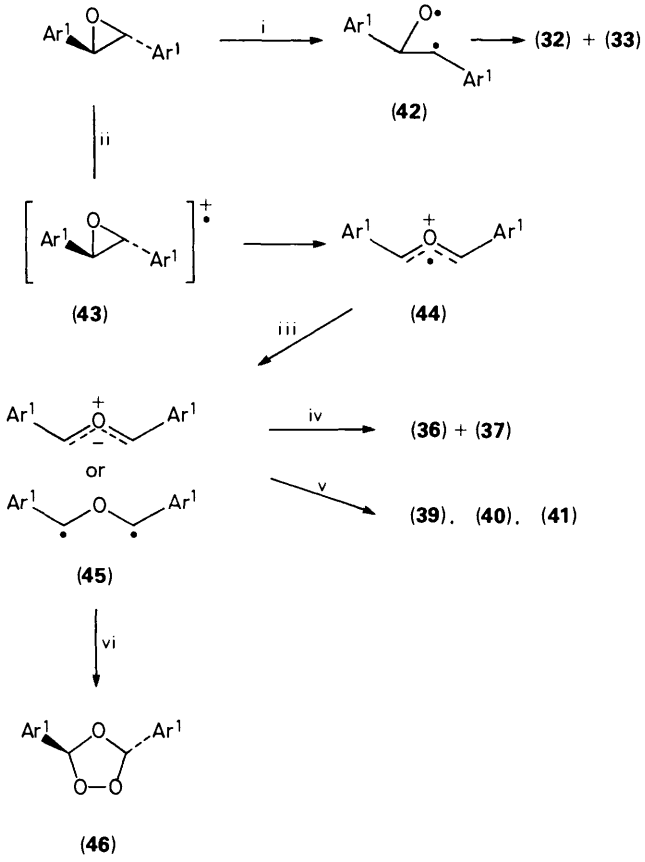
(36) $R^1$ = H, $R^2$ = $Ar^1$
(37) $R^1$ = $Ar^1$, $R^2$ = H

(38)



(39) $R^1$ = $R^2$ = $Ar^1$, $R^2$ = $R^4$ = H
(40) $R^1$ = $R^4$ = $Ar^1$, $R^2$ = $R^3$ = H
(41) $R^2$ = $R^3$ = $Ar^1$, $R^1$ = $R^4$ = H

The mechanistic aspects of these reactions are summarised in Scheme 3. It is apparent that irradiation of the bisaryloxirane



**Scheme 3.** i, *hν*, or *hν*,PhCOMe, or heat; ii, *hν*,DCA; iii, $ADC^{\cdot-}$; iv, $MeO_2CC{\equiv}CCO_2Me$; v, $MeO_2C{\pm}CO_2Me$; vi, $O_2$.

(**29**) with or without triplet sensitisers leads to a C–O bond-cleaved species (**42**)—presumably a diradical—which then rearranges with either hydrogen or aryl migration to the carbonyl compounds (**32**) and (**33**). The thermal reaction takes a similar course. In contrast, the abstraction of an electron, by an excited anthracenedicarbonitrile species, yields the radical cation (**43**) which may then open by C–C cleavage to (**44**); electron return from the sensitiser generates species (**45**) which reacts with an electron deficient bond to give the observed products. The intermediate (**45**) might be viewed as either a carbonyl ylide or a diradical. The lack of stereospecificity observed in the two reactions reported suggests to us that the diradical formulation is the more reasonable. This accords with the report[12] that the intermediate (**45**) reacts with oxygen to product *trans*-ozonide (**46**) through, in part at least, a diradical stage.

From a synthetic viewpoint these reactions are somewhat disappointing; the C–C ring cleavage of (**26**) can be accomplished, and the resulting intermediate trapped by two electrophiles. However the reactions are sluggish and importantly, non-stereospecific. It is true that the diarylfuran (**38**) can be readily reached. This furan or its analogues might perhaps be of use, *e.g.* the bis(methylenedioxy) analogue would serve as a base to prepare the lactone (**14**) following the reaction scheme employed by Lavie and co-workers[10] to prepare the lactone (**17**) from dimethyl 2,5-diphenylfuran-3,4-dicarboxylate. However such approaches would be limited by the lack of regioselectivity which would certainly be seen in the chemistry of oxiranes substituted by two aryls carrying different oxygenation patterns. Thus the problems of regiochemical control in this situation must be addressed in future work.

## Experimental

*Generalisations.*—UV spectra were recorded in ethanol; log ε follows $\lambda_{max}$ in parenthesis. Mass spectra were measured using electron impact on a double focussing spectrometer at 70 eV. NMR spectra were obtained using deuteriochloroform solutions with tetramethylsilane as internal standard. Observed splittings (*J*) are given in Hz. 'Drying' means drying over anhydrous magnesium sulphate, and 'evaporation' implies the use of reduced pressure. Photochemical experiments used a Hanovia 450W medium-pressure mercury lamp with a quartz cooling jacket, or, where specified, a Rayonet reactor fitted with 2 537, 3 000, or 3 500 Å emission lamps. Solutions for irradiation were degassed by purging with argon for 30 min, and photochemical reactions were carried out in 15 $cm^3$ quartz or Pyrex test-tubes. A 'phenanthrene filter' was a 1 cm thick solution of phenanthrene in toluene (1 g per 100 $cm^3$). Thin layer chromatography (TLC) used silica $HF_{254}$; 0.8 mm thick layers were employed preparatively. 'Light petroleum' is the fraction b.p. 40–60 °C.

(1) 2,5-*Diphenyltetrahydrofuran*-3,4-*dicarboxylic Acid Anhydride.*—*trans*-Stilbene oxide (0.196 g), maleic anhydride (0.196 g), and naphthalene-1,4-dicarbonitrile (0.036 g) in dry acetonitrile (10 $cm^3$) were irradiated in a Pyrex tube at *ca.* 8 °C for 3 h, using a medium-pressure mercury arc. After evaporation of the solvent the products were eluted through a neutral alumina column (2 × 10 cm) with methylene dichloride. The product crystallised on evaporation of the eluate; recrystallisation from chloroform afforded the *title anhydride* (**16**) (0.186 g, 63%), m.p. 252–253 °C (Found: C, 72.95; H, 4.95%; *m/z* 294.089. $C_{18}H_{14}O_4$ requires C, 73.45; H, 4.8%; $M^+$, 294.089); $\nu_{max}$ (KBr) 1 860 and 1 796 $cm^{-1}$; $\lambda_{max}$ 205 nm (4.20); δ 3.94 (2 H, m, 1-H, 5-H), 5.35 (2 H, m, 2-H, 4-H) and 7.27–7.49 (10 H, ArH).

(2) 2,4-*Diphenyl*-3,7-*dioxabicyclo*[3.3.0]*octan*-8-*one.*—(i) *trans*-Stilbene oxide (0.392 g) and but-2-enolide (0.34 g) in dry benzene (10 $cm^3$) with dry acetone (2 $cm^3$) was irradiated as in expt. 1 for 6 h. After evaporation, the residues were separated by preparative TLC (chloroform–acetone, 9:1). The major fraction was recrystallised from methanol to give the *stereoisomer* (**19**) of the title lactone (0.24 g, 43%), m.p. 167–169 °C (Found: C, 76.8; H, 5.7%; *m/z* 280.109. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.9%; $M^+$, 280.110); $\nu_{max}$(KBr) 3 010, 1 764, 1 168, and 1 026 $cm^{-1}$; $\lambda_{max}$ 207 (4.25), 213 (4.15), and 216 nm (4.03); $\delta_H$ 3.5 (1 H, t, *J* 9, 1-H), 3.61 (1 H, m, 5-H), 3.88 (1 H, dd, *J* 6, 9, 6-$H_a$), 4.01 (1 H, dd, *J* 9, 9, 6-$H_b$), 5.23 (1 H, d, *J* 4, 4-H), 5.27 (1 H, d, *J* 9, 2-H), and 7.2–7.5 (10 H, ArH).

(ii) *trans*-Stilbene oxide (0.196 g) and but-2-enolide (0.17 g) in dry acetonitrile (10 $cm^3$) with naphthalene-1,4-dicarbonitrile (0.036 g) were irradiated as in expt. 1. Product isolation as in expt. 2 (ii) gave the lactone (**19**) (0.257 g, 92%), identical with the above sample.

(3) *Dimethyl* 2,5-*Diphenyltetrahydrofuran*-3,4-*dicarboxylate.*—*trans*-Stilbene oxide (0.294 g), dimethyl fumarate (0.576 g), and naphthalene-1,4-dicarbonitrile (0.036 g) in dry acetonitrile (10 $cm^3$) were irradiated as in expt. 1 for 3 h. After evaporation, the residue was separated by preparative TLC (chloroform–light petroleum, 3:2) to yield a mixture (0.32 g, 63%) of stereoisomers of the ester (**20**). Further TLC (alumina, hexane–ethyl acetate, 3:1) gave the *stereoisomer* (**20**) of the title diester as an oil (Found: *m/z* 340.132. $C_{20}H_{20}O_5$ requires $M^+$, 340.131); $\nu_{max}$($CHCl_3$) 1 738 and 1 715 $cm^{-1}$; $\lambda_{max}$ 207 (4.23), 213 (4.15), and 217 nm (4.03); δ 3.06 and 3.60 (each 3 H, s, OMe), 3.7–4.04 (2 H, m, 3-H, 4-H), 5.1 (1 H, d, *J* 8, 2-H), 5.36 (1 H, d, *J* 5-H), and 7.2–7.5 (10 H, ArH).

(4) 3,4-*Dimethyl*-2,5-*diphenyltetrahydrofuran.*—The diester (**2**) (0.1 g, 0.3 mmol) in dry tetrahydrofuran (15 $cm^3$) was treated with lithium aluminium hydride (3 mmol) for 24 h at room temperature. The mixture was diluted with ethyl acetate and washed with water. The dried organic phase was evaporated and the residual diol treated with toluene-*p*-sulphonyl chloride (0.6 mmol) in dry pyridine (5 $cm^3$) at −8 °C for 20 h. The crude tosylate was reduced with lithium aluminium hydride (3 mmol) in dry tetrahydrofuran (10 $cm^3$). Product isolation as above gave an oil which on elution with chloroform from a silica column afforded the *title tetrahydrofuran*, stereoisomer (**25**), as an oil (0.22 g, 28%) (Found: *m/z* 252.153. $C_{18}H_{20}O$ requires $M^+$, 252.151); $\lambda_{max}$ 210 nm (3.75); δ 1.0–1.16 (6 H, 2 × d, 3-Me, 4-Me), 3.32 (2 H, m, 3-H, 4-H), 4.44 and 5.16 (each 1 H, dd, *J* 2, 8, 2-H, 5-H), and 7.26–7.44 (10 H, ArH).

(5) *Dimethyl* 2,5-*Diphenyl*-2,5-*dihydrofuran*-3,4-*dicarboxylate.*—*trans*-Stilbene oxide (0.294 g), dimethyl acetylenedicarboxylate (0.295 g), and naphthalene-1,4-dicarbonitrile (0.036 g) in dry acetonitrile (10 $cm^3$) were irradiated for 2 h as in expt. 1. Evaporation and preparative TLC (alumina, chloroform) of the residue gave a mixture of the adducts (**21**) and (**22**) (0.24 g, 47%). Stereoisomer (**22**) of the *title dihydrofuran* was isolated by further TLC (alumina, chloroform–light petroleum, 3:1) as an oil (Found: *m/z* 338.117. $C_{20}H_{18}O_5$ requires $M^+$, 338.115); $\lambda_{max}$ 215 (4.16), 228 (3.95), and 291 nm (3.88); $\nu_{max}$($CHCl_3$) 1 725 and 1 665 $cm^{-1}$; δ 3.7 (6 H, s, OMe), 6.1 (2 H, s, 2-H, 5-H), and 7.3–7.46 (10 H, ArH).

(6) *Ethyl* 2,5-*Diphenylfuran*-3-*carboxylate.*—*trans*-Stilbene oxide (0.29 g), ethyl propiolate (0.39 g), and naphthalene-1,4-dicarbonitrile (0.036 g) in dry acetonitrile (10 $cm^{-3}$) was irradiated for 2 h as in expt. 1. Evaporation of the solvent and preparative TLC (alumina, chloroform–light petroleum, 2:1) afforded the dihydrofurans (**23**) (0.24 g, 53%) (Found: *m/z* 294.128. $C_{19}H_{18}O_3$ requires $M^+$, 294.126); $\nu_{max}$($CHCl_3$) 1 722, 1 652, and 1 602 $cm^{-1}$; δ 1.25–1.39 (3 H, Me), 3.98–4.38 (2 H, $OCH_2$) 5.99–6.12 (1 H, 5-H), 6.99–7.02 (1 H, 2-H), and 7.21–7.47 (10 H, ArH). The dihydrofuran mixture (0.2 g) was stirred in dry benzene (15 $cm^3$) with 2,3-dichloro-5,6-dicyanobenzoquinone (0.5 g) for 20 h at room temperature. The product mixture was filtered and eluted through a short alumina column with chloroform. Evaporation of the eluate gave a solid which on recrystallisation from chloroform–light petroleum afforded the *title furan* (**24**) (0.17 g, 81%), m.p. 79–80 °C (Found: C, 78.2; H, 5.45%; *m/z* 292.109. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5%; $M^+$, 292.110); $\lambda_{max}$ 220 (4.24) and 303 nm (4.16); $\nu_{max}$ 3 220, 2 970, and 1 705 $cm^{-1}$.

(7) trans-2,3-*Bis*(3,4-*methylenedioxyphenyl*)*oxirane.*—3,4; 3′,4′-Bismethylenedioxystilbene[13] (0.536 g) was suspended in methylene dichloride (200 $cm^3$) in contact with aqueous sodium hydrogen carbonate (0.5M; 60 $cm^3$). The mixture was vigorously stirred and *m*-chloroperbenzoic acid (0.8 g) was added in portions over 30 min. The mixture was stirred at room temperature for 24 h after which the organic layer was separated and washed with aqueous sodium sulphite, aqueous sodium hydroxide (0.1M), and water. The dried solution was evaporated and the product chromatographed (alumina, chloroform) to yield the trans-*oxirane* (**31**) (0.42 g, 74%), m.p. 100–100.5 °C from chloroform–light petroleum (Found: C, 67.15; H, 4.1% *m/z* 284.067. $C_{16}H_{12}O_5$ requires C, 67.6; H, 4.4%; $M^+$, 284.068); δ 3.72 (2 H, s, CH), 5.94 (4 H, s, $OCH_2O$), and 6.78–6.82 (6 H, ArH).

(8) C–O *Bond Cleavage of* 2,3-*Bis*(3,4-*methylenedioxy*)-*oxirane.*—(i) The title oxirane (1 mmol) was irradiated in dry acetonitrile (10 $cm^3$) with but-2-enolide (2.5 mmol) and naphthalene-1,4-carbonitrile (0.2 mmol) at 10 °C, through

Pyrex, using a medium-pressure mercury lamp. After 10 h, the solvent was evaporated and the residue was separated by preparative TLC, to afford (a) 3,4-methylenedioxybenzyl 3,4-methylenedioxyphenyl ketone (**35**) (42%), m.p. 113 °C (Found: *m/z* 284. $C_{16}H_{12}O_5$ requires $M^+$, 284); δ 4.08 (2 H, s, $CH_2$), 5.88 (2 H, s, $OCH_2O$), 6.0 (2 H, s, $OCH_2O$), 6.72–6.84 (3 H, ArH), and 7.44–7.62 (3 H, ArH), and (b) bis(3,4-methylenedioxy)-acetaldehyde (**34**) (15%) as an oil (Found: *m/z* 284); $\nu_{max}$($CHCl_3$) 1 715 $cm^{-1}$; δ 4.7 (1 H, d, *J* 2, CH), 5.96 (4 H, s, $OCH_2O$), 6.56–6.87 (6 H, ArH), and 9.8 (1 H, d, *J* 2, CHO).

(ii) The same reaction products were detected by NMR and TLC when the oxirane was irradiated with (a) methyl acrylate and naphthalene-1,4-dicarbonitrile (b) but-2-enolide in benzene–acetone, and when the oxirane was heated at 150 °C (20 h) with neat but-2-enolide.

(9) *Dimethyl* 2,5-*Bis*(4-*methoxyphenyl*)-2,5-*dihydrofuran*-3,4-*dicarboxylate*.—*trans*-2,3-Bis(4-methoxyphenyl)oxirane* (0.05 g), dimethyl acetylenedicarboxylate (0.1 g), and anthracene-9,10-dicarbonitrile (0.5 mg) in deuteriochloroform (0.5 $cm^3$) in a Pyrex NMR tube were irradiated through a phenanthrene filter for 26 h, using a medium-pressure mercury lamp. After evaporation, the residue was purifed by preparative TLC to give the *title compound* as a mixture of isomers (**36**) and (**37**) (0.042 g, 54%) (Found: C, 65.9; H, 5.55%; *m/z* 398.137. $C_{22}H_{22}O_7$ requires C, 66.3; H, 5.6%; $M^+$, 398.137); $\nu_{max}$ 1 725, 1 670, and 1 615 $cm^{-1}$; isomer (**36**) had $\delta_H$ 3.73 (6 H, s, $CO_2Me$), 3.84 (6 H, s, ArOMe), 6.32 (2 H, s, 2-H, 5-H), 6.98 (4 H, d, *J* 9, Ar*H*), and 7.42 (4 H, d, *J* 9, ArH); isomer (**37**) had $\delta_H$ 3.73 (6 H, s, $CO_2Me$), 3.84 (6 H, s, ArOMe), 6.08 (2 H, s, 2-H, 5-H), 6.98 (4 H, d, *J* 9, Ar*H*), and 7.44 (4 H, d, *J* 9, ArH).

(10) *Dimethyl* 2,5-*Bis*(4-*methoxyphenyl*)*furan*-3,4-*dicarboxylate*.—A mixture of the dihydrofurans (**36**) and (**37**) (0.05 g) in dry benzene (5 $cm^3$) was stirred at room temperature with 2,3-dichloro-5,6-dicyanobenzoquinone (0.1 g) for 5 h. The product was filtered through a short alumina column, eluting with chloroform. Evaporation of the eluate gave a solid which on recrystallisation from ether–hexane gave the *title furan* (**38**) (0.03 g, 60%), m.p. 92–93 °C (Found: C, 66.7; H, 5.25%; *m/z* 396.118. $C_{22}H_{20}O_7$ requires C, 66.5; H, 5.1%; $M^+$, 396.121); $\lambda_{max}$ 230 infl. (4.18), 273 infl. (4.15), 293 infl. (4.29), and 310 nm (4.31); $\nu_{max}$($CHCl_3$) 1 725, 1 610, and 1 580 $cm^{-1}$; δ 3.89 (12 H, s, OMe), 7.01 (4 H, d, *J* 8, ArH), and 7.87 (4 H, d, *J* 8, ArH).

(11) *Dimethyl* 2,5-*Bis*(4-*methoxyphenyl*)*tetrahydrofuran*-3,4-*dicarboxylate*.—The oxirane (**29**) (0.05 g), dimethyl fumarate (0.1 g), and naphthalene-1,4-dicarbonitrile (0.5 mg) in deuteriochloroform were irradiated as described in expt. 9, and the products similarly isolated. Purification by TLC (light petroleum–ethyl acetate, 4:1) (two elutions) gave the isomers (**39**), (**40**), and (**41**) as a mixture (38%) (Found: *m/z* 400.156. $C_{22}H_{24}O_7$ requires $M^+$, 400.152); $\nu_{max}$($CHCl_3$) 1 730, 1 610, and 1 585 $cm^{-1}$. Isomer (**39**) had δ 3.21 (3 H, s, $CO_2Me$), 3.69 (3 H, s, $CO_2Me$), 3.80 (6 H, s, ArOMe), 5.0 (1 H, d, *J* 9, 2-H), and 5.30 (1 H, d, *J* 9, 5 H). Isomer (**40**) showed δ 3.33 (6 H, s, $CO_2Me$) and isomer (**41**) had δ 3.70 (6 H, s, $CO_2Me$).

* Prepared from 4,4′-dimethoxystilbene and *m*-chloroperbenzoic acid, m.p. 132–133 °C; m.p. 112–113 °C is recorded [14] for a sample prepared by a different route, and for which no stereochemistry is reported.

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