

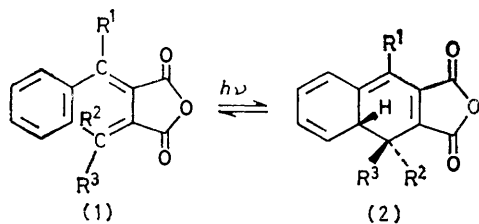
Photochromic Heterocyclic Fulgides. Part 1. Rearrangement Reactions of (*E*)- α -3-Furylethylidene(isopropylidene)succinic Anhydride

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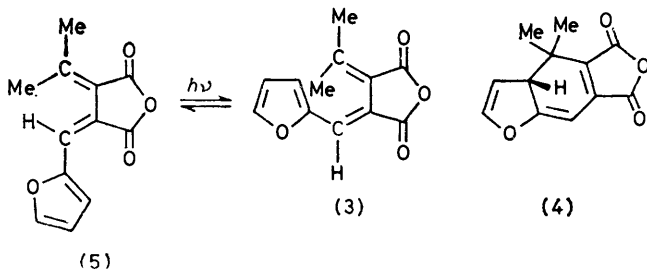
The title compound (6) undergoes photochemical conrotatory and thermal disrotatory ring-closure to give red 7,7a-dihydro-4,7,7-trimethylbenzo[*b*]furan-5,6-dicarboxylic anhydride (7,7a-DHBF) (8) in near quantitative yield. The latter ring-opens in a conrotatory mode to the title compound on exposure to white light, and shows a slow suprafacial 1,5-H shift on heating above 100 °C. The 7a-deuterio-derivative of (8) does not undergo a 1,5-D shift even at 140 °C. The 2,5-dideuterio-derivative of fulgide (6) shows a reversible intramolecular hydrogen-deuterium exchange at room temperature to give (*E,E*)- α -5-deuterio-3-furylethylidene(monodeuterioisopropylidene)succinic anhydride. The acid-catalysed reactions of fulgide (6) and 7,7a-DHBF (8) are described.

WE have shown that the photochromic properties of phenyl substituted fulgides (1) are due to conrotatory ring-closure to 1,8a-dihydronaphthalene-2,3-dicarboxylic anhydride derivatives (1,8a-DHNs) (2) which undergo the reverse process on exposure to white light, photochemical 1,7-H shifts, thermal disrotatory ring-opening, and thermal 1,5-H shifts.^{1,2}

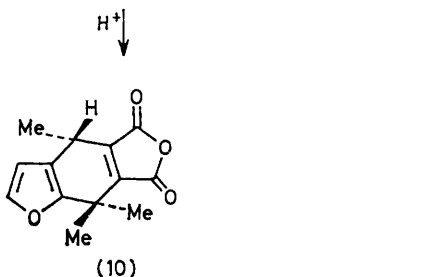
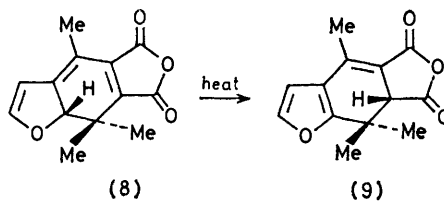
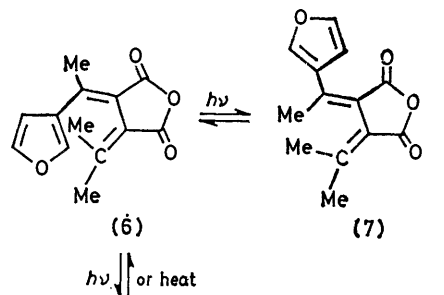
obtained as pale yellow crystals which turned red on warming, or on exposure to 366 nm radiation. The colour can be reversed on exposure to white light. Fulgide (6) shows photochromic and inverse photochromic properties in the solid, solution, and plastic



Stobbe reported the synthesis of 2-furylmethylene-(isopropylidene)succinic anhydride and a cursory study of its properties.^{3,4} A re-investigation of this compound, m.p. 63 °C, has shown that it is the (*E*)-isomer (3), that it is not photochromic, and that it undergoes only *E*—*Z* isomerization on irradiation at 366 nm in toluene. Application of the Chapman 'polar-state concept' for the photorearrangements $\alpha\beta$ -unsaturated carbonyl compounds⁵ leads to the prediction that photocyclisation onto the 2-position of an (*E*)-3-furyl fulgide [e.g. (6)] to give a resonance-stabilised 7,7a-dihydrobenzo[*b*]furan-5,6-dicarboxylic anhydride derivative (7,7a-DHBF) [e.g. (8)] would be a much more facile process than photocyclisation on to the 3-position of an (*E*)-2-furyl-fulgide [e.g. (3)] to give a 3a,4-DHBF [e.g. (4)].



(*E*)- α -3-Furylethylidene(isopropylidene)succinic anhydride (6), prepared *via* the Stobbe condensation of 3-acetylfuran with diethyl isopropylidenesuccinate, was



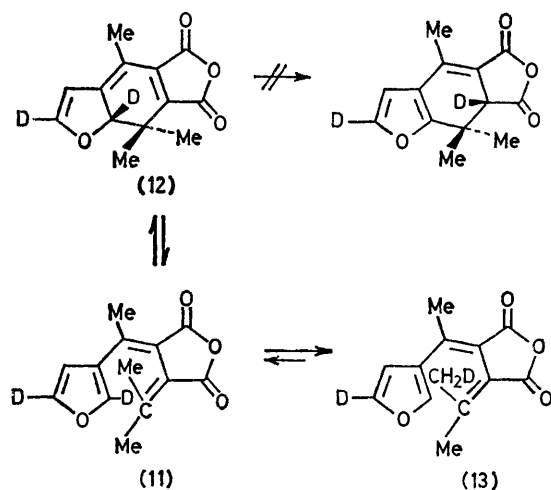
SCHEME 1

matrix [e.g. poly(methylmethacrylate), poly(ethylene orthophthalate), poly(allyldiglycol carbonate)]. A 0.2M solution of fulgide (6) in purified deuteriochloroform was converted nearly quantitatively into red 7,7a-DHBF (8) on heating in a sealed n.m.r. tube at 100 °C. Under these conditions, 7,7a-DHBF (8) underwent a slow 1,5-H shift to give 6,7-DHBF (9) in quantitative yield after heating for 400 h. A quantitative conversion

into 6,7-DHBF (9) was achieved within 4 h by heating fulgide (6) at 140 °C. When the reaction was repeated in deuteriochloroform containing 2% trichloroacetic acid, the 7,7a-DHBF (8) from the fulgide (6) underwent acid-catalysed rearrangement to give a *ca.* 3 : 2 mixture of 4,7-DHBF (10) and 6,7-DHBF (9) within 20 min (Scheme 1).

On irradiation at 366 nm, a 0.2M solution of fulgide (6) in deuteriochloroform gave a photostationary state consisting of 22% (*Z*)-fulgide (7), 33% (*E*)-fulgide (6), and 45% 7,7a-DHBF (8) within 10 h, which remained unchanged, with no evidence of other products, after irradiation for a further 120 h. Exposure of the red solution to white light caused complete colour reversal and the solution was shown to contain a 22 : 78 mixture of (*Z*)- and (*E*)-fulgides (7) and (6) (Scheme 1). These rearrangement reactions were monitored by n.m.r. spectroscopy, and the structural assignments of the DHBFs (which were not isolated) follow from their characteristic n.m.r. spectra.

In an attempt to improve the high resistance of the photochromic system to the thermal irreversible 1,5-H shift of the 7,7a-DHBF (8), deuterium was introduced into the 2-position of the 3-furyl group in fulgide (6) in the expectation that the rate of 1,5-D shift in the 7a-deuterio-7,7a-DHBF (12) would be an order of magnitude less than the rate of 1,5-H shift in 7,7a-DHBF (8) under similar conditions, because of the primary isotope effect.⁶ (*E*)-2,5-Dideuterio-3-furylfulgide (11) in deuteriochloroform, on heating at 140 °C for 4 h, gave 2,7a-dideuterio-7,7a-DHBF (12), which showed no 1,5-D shift. Non-deuteriated fulgide (6) rearranged completely to 6,7-DHBF (9) under similar conditions.

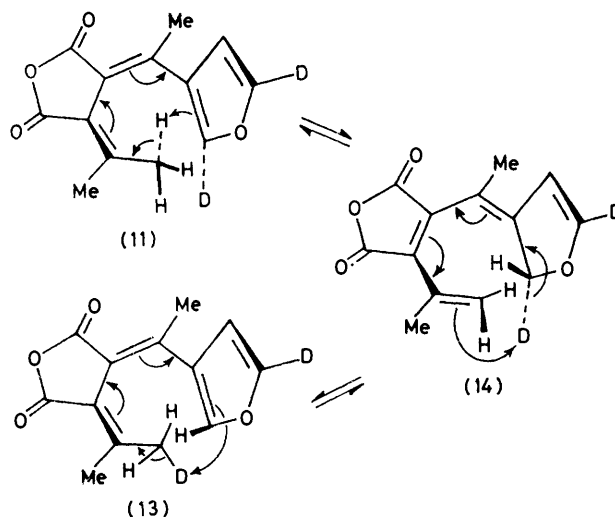


SCHEME 2

Under the above conditions, and even at 20 °C over a period of four weeks, 2,5-dideuterio-3-furylfulgide (11) underwent a reversible intramolecular hydrogen-deuterium exchange to give (*E*)-5-deuterio-3-furylfulgide (13), having one hydrogen of the methyl *trans* to the carbonyl replaced by deuterium (Scheme 2). The

reverse exchange process can be observed in (*E*)- α -3-furyl(hexadeuterioisopropylidene)succinic anhydride.

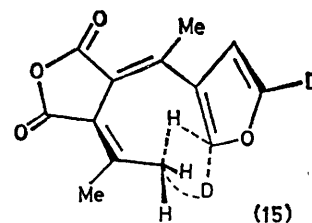
The mechanism of this remarkable hydrogen-deuterium exchange reaction has not been established. It is tempting to explain the exchange by postulating consecutive thermal 1,7-antarafacial shifts of hydrogen and deuterium in intermediate (14) as outlined in Scheme 3. If this mechanism is correct, we would



SCHEME 3

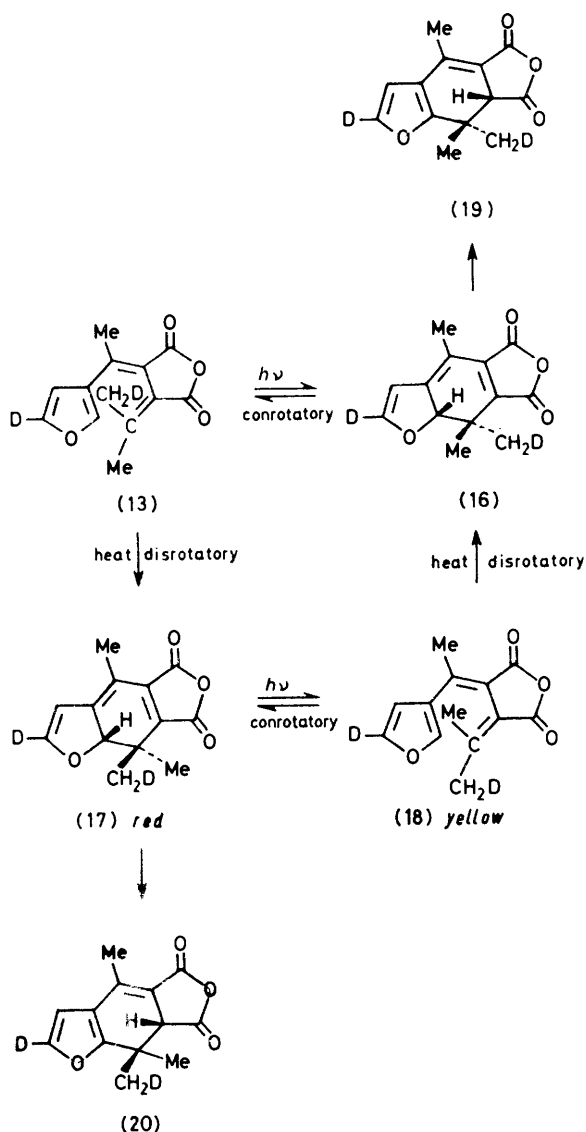
expect additional incorporation of deuterium into the methyl group *trans* to the carbonyl in 5-deuterio-3-furylfulgide (11), when the reaction is carried out in tetradeuterioacetic acid-deuteriochloroform (1 : 1). No additional incorporation of deuterium occurs on leaving the solution of fulgide (11) (2 weeks) at 37 °C.

An alternative mechanism, which we favour, is the unprecedented concerted 7,7-dyotropic process⁸ *via* transition state (15). The synthesis of (*E,E*)-5-deuterio-3-furylethylidene(monodeuterioisopropylidene)succinic anhydride (13) provided the means of establishing that



the photochemical and thermal ring-closures of fulgide (6) occurred by conrotatory and disrotatory modes, respectively, and that the resulting 7,7a-DHBF (8) ring-opened exclusively by a conrotatory mode on irradiation. 7,7a-DHBFs (16) and (17), formed in these reactions, slowly undergo a suprafacial 1,5-H shift to corresponding 6,7-DHBFs (19) and (20) on prolonged heating above 110 °C (Scheme 4). The stereospecificity of these pericyclic reactions is demonstrated by the relative intensities and the characteristic chemical shifts

of the deuteriomethyl and methyl groups in the fulgides (13) and (18), 7,7a-DHBFs (16) and (17), and 6,7-DHBFs (19) and (20). In the fulgides, the methyl



SCHEME 4

group of the isopropylidene group *cis* to a carbonyl gives a signal at lower field than in the *trans* arrangement, owing to the deshielding effect of the furyl group on the former and the shielding effect of the furyl group on the latter. In 7,7a- and 6,7-DHBFs, the equatorial 7-methyl group is deshielded by a carbonyl and gives a signal at lower field than the axial 7-methyl group. The 4-methyl groups in these DHBFs are also deshielded by a carbonyl but appear as doublets, J 3 Hz, being allylically coupled with the 7a- and 6-hydrogens, respectively. N.m.r. data are given in the Experimental section.

The hydrogen-deuterium exchange reaction, (11) \rightleftharpoons (13), is not acid-catalysed. Fulgide (6) rearranges to

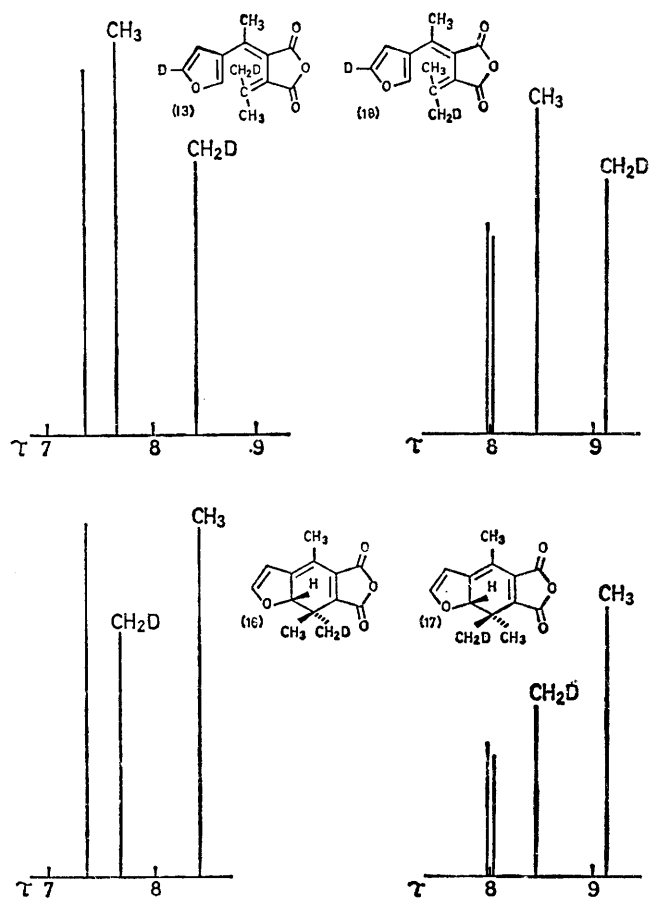
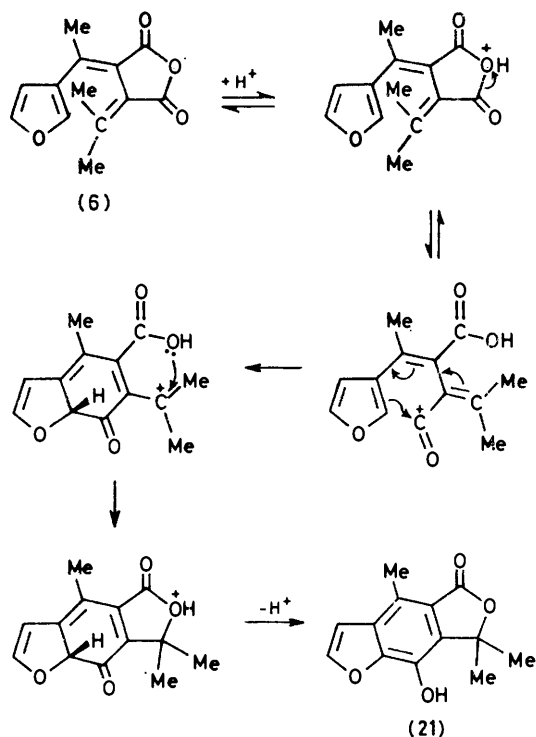
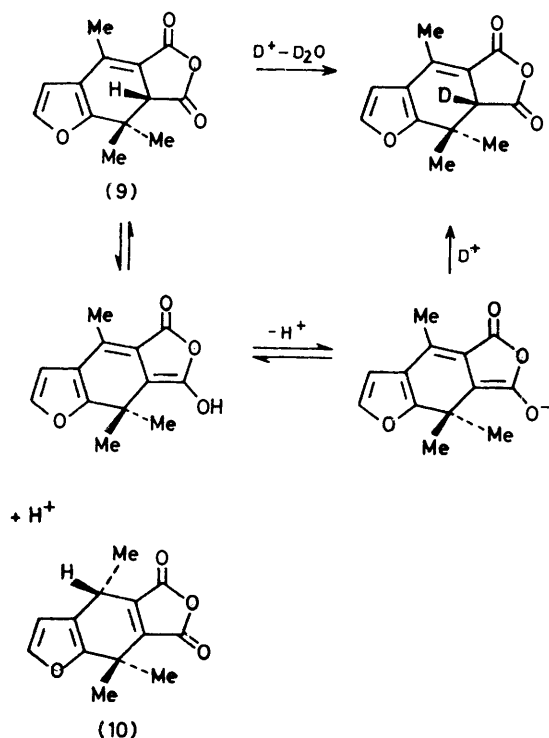


FIGURE N.m.r. spectra of deuterated fulgides (13) and (18), and 7,7a-DHBFs (16) and (17) (ca. 60% isotopic purity)



SCHEME 5

the lactone (21) on treatment with concentrated sulphuric acid (or with concentrated dideuteriosulphuric acid without incorporation of deuterium into the methyl groups), presumably by the mechanism shown in Scheme 5. On heating at 140 °C (20 h), 6,7-DHBF (9) in 10% v/v tetradeuterioacetic acid in deuteriochloroform exchanges the 6-hydrogen for deuterium, but does not rearrange to 4,7-DHBF (10). Under similar conditions, 4,7-DHBF (10) neither rearranges nor shows a hydrogen-deuterium exchange (Scheme 6), but fulgide (6) gives 7-



SCHEME 6

deuterio-6,7-DHBF and 4-deuterio-4,7-DHBF as the sole products. These experiments show that the rearrangements of 7,7a-DHBF (8) to 4,7-DHBF (10) is a non-concerted acid-catalysed process. That deuteration in these experiments was quantitative is indicated by the complete collapse to singlets of the 4-methyl doublets of the 6,7- and 4,7-DHBFs (9) and (10).

EXPERIMENTAL

U.v. spectra were measured in toluene on a Unicam SP1700B spectrometer; n.m.r. spectra were obtained with a Perkin-Elmer R32 (90 MHz) spectrometer (tetramethylsilane as internal standard except when monitoring thermal and photochemical reactions, for which an external standard was used). Photoreactions were carried out for ca. 50 mg reactant in 0.5 ml of deuteriochloroform in a sealed n.m.r. tube and exposed to irradiation (366 nm) from a 250-W mercury-discharge lamp (type ME/D, Thorn Lighting) with a filter (type OX1, Chance Pilkington) focused on to the solution, which was shaken occasionally. Thermal reactions were carried out in sealed n.m.r. tubes by immersion in the vapour of the appropriate boiling solvent (water

100 °C, toluene 110 °C, or xylene 140 °C). Deuteriochloroform (99.8%) was boiled with, and distilled from, anhydrous sodium carbonate before use. Petroleum refers to the fraction of b.p. 60–80 °C. Reagents and solvents were purified before use.

(E)- α -3-Furylethylidene(isopropylidene)succinic Anhydride (6).—A mixture of diethyl isopropylidenesuccinate (16 g)⁹ and 3-acetylfuran (8.3 g) was added dropwise to a stirred suspension of sodium hydride (14 g, 60% dispersion in oil) in toluene (200 ml). After 2 h, the mixture was poured into crushed ice and the aqueous layer separated and acidified with 5M HCl. The liberated half ester was hydrolysed with ethanolic KOH (8% w/v) to give a black oil after acidification, which was extracted with ether-petroleum (1 : 7). The extracted red oil (6.5 g) was boiled (1 h) with acetyl chloride (20 ml). Solvent was removed and the dark residual oil chromatographed on alumina using toluene-petroleum (1 : 1) as eluant. The yellow photochromic fraction gave the (E)-anhydride (6), pale yellow crystals from toluene-petroleum (1 : 1), m.p. 92–93 °C (Found: C, 67.1; H, 5.2. C₁₃H₁₂O₄ requires C, 67.2; H, 5.2%); λ_{max} 324 nm (log ϵ 3.89); τ 7.32 (3 H, s, Me), 7.64 (3 H, s, Me *cis* to C=O), and 8.37 (3 H, s, Me *trans* to C=O).

A second crop of crystals gave the (Z)-anhydride (7), yellow needles from toluene-petroleum, m.p. 105–106 °C (Found: C, 67.3; H, 5.2); λ_{max} 330 nm (log ϵ 3.96); τ 7.54, 7.80, and 7.98 (9 H, s, 3 \times Me).

(E)- α -2,5-Dideuterio-3-furylethylidene(isopropylidene)succinic Anhydride (11).—Small pieces of sodium (total weight 17 g) were dissolved in deuterium oxide (50 ml, 99.8% isotopic purity) and 3-furoic acid (30 g) in deuterium oxide (30 ml) was added. The mixture was heated (40 h) at 100 °C, cooled, the sodium salt filtered off, and the filtrate acidified, giving 2,5-dideuterio-3-furoic acid¹⁰ (75% isotopic purity) (26 g). The filtrate, on acidification, gave 2,5-dideuterio-3-furoic acid (98% isotopic purity) (3 g). The acid was converted into 2,5-dideuterio-3-acetylfuran by reaction with methyl-lithium in ether and reacted with diethyl isopropylidenesuccinate as described. (E)-2,5-Dideuteriofulgide (11) (60% isotopic purity) was obtained.

(E)-2-Furylmethylene(isopropylidene)succinic Anhydride (3).—This was prepared as described above, using furan-2-carbaldehyde (14 g) and diethyl isopropylidenesuccinate. The diacid (3 g), m.p. 213–216 °C (yellow crystals from ethanol) (lit.,³ 218 °C) was obtained from the black oil after hydrolysis by trituration with ether. The diacid (1 g) was treated with acetyl chloride (25 ml). After 1 h, solvent was removed and the residue crystallised from methanol, giving anhydride (3) (0.25 g), yellow plates, m.p. 66 °C (lit.,³ 63 °C); τ 2.62 (1 H, s, =CH), 7.50 (3 H, s, Me *cis* to C=O), and 8.02 (3 H, s, Me *trans* to C=O). On irradiation (366 nm) of the (E)-anhydride (3) (60 mg) in deuteriochloroform (24 h), a 1 : 1 mixture of (E)- and (Z)-anhydrides (3) and (5) was obtained. (Z)-Anhydride (5) crystallised from aqueous ethanol in yellow needles, m.p. 124–125 °C (Found: C, 66.1; H, 4.4%. C₁₂H₁₀O₄ requires C, 66.0; H, 4.6%); τ 2.68 (1 H, s, =CH), and 7.40 and 7.63 (6 H, s, 2 \times Me).

Rearrangement Reaction of Fulgide (6).—Fulgide (6) (100 mg) in chloroform (3 ml) was treated with 10 drops of concentrated H₂SO₄. The acid layer turned deep red. The two layers were shaken at intervals (over 20 min) and poured into water. The chloroform layer was

separated, washed, dried (MgSO_4), and the solvent removed. The residue crystallised from acetic acid giving 7-hydroxy-6-(2-hydroxyisopropyl)-4-methylbenzo[b]furan-5-carboxylic acid lactone (21) as colourless crystals, m.p. 254—255 °C (Found: C, 66.9; H, 5.3. $\text{C}_{13}\text{H}_{12}\text{O}_4$ requires C, 67.2; H, 5.3%); ν_{max} 3 520 cm^{-1} (OH) and 1 745 cm^{-1} (C=O of lactone); τ 2.29 and 3.06 (2 H, d, $J_{2,3}$ 2 Hz, 2- and 3-H), 7.19 (3 H, s, 4-Me), and 8.22 (6 H, s, 2 \times Me).

Fulgide (6) (50 mg) in deuteriochloroform (0.5 ml) after heating (10 h) at 100 °C gave a near-quantitative yield of 4,7,7-trimethyl-7,7a-dihydrobenzo[b]furan-5,6-dicarboxylic anhydride (8); τ 2.40 (1 H, d, $J_{2,3}$ 2.4 Hz, 2-H), 3.97 (1 H, d, $J_{2,3}$ 2.4 Hz, 3-H), 4.92 (1 H, q, J_{allylic} 3 Hz, 7a-H), 7.88 (3 H, d, J_{allylic} 3 Hz, 4-Me), 8.30 (3 H s, eq-7-Me), and 8.99 (3 H, s, ax-7-Me).

Fulgide (6) (50 mg) in deuteriochloroform (0.5 ml), after heating for 400 h at 100 °C or 4 h at 140 °C, gave a quantitative yield of 4,7,7-trimethyl-6,7-dihydrobenzo[b]furan-5,6-dicarboxylic anhydride (9); τ 2.59 (1 H, d, $J_{2,3}$ 2.5 Hz, 2-H), 3.46 (1 H, d, $J_{2,3}$ 2.5 Hz, 3-H), 6.07 (1 H, q, J_{allylic} 3 Hz, 6-H), 7.46 (3 H, d, J_{allylic} 3 Hz, 4-Me), 8.23 (3 H, s, eq-7-Me), and 8.89 (3 H, s, ax-7-Me).

Fulgide (6) (50 mg) in deuteriochloroform containing 2% trichloroacetic acid (0.5 ml), after heating for 20 min at

140 °C, gave 4,7,7-trimethyl-4,7-dihydrobenzo[b]furan-5,6-dicarboxylic anhydride (10) (ca. 60%); τ 2.59 (1 H, d, $J_{2,3}$ 2.5 Hz, 2-H), 3.65 (1 H, d, $J_{2,3}$ 2.5 Hz, 3-H), 6.17 (1 H, q, $J_{4,\text{Me}}$ 7.2 Hz, 4-Me): and 6,7,7-DHBF (8) (ca. 40%).

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