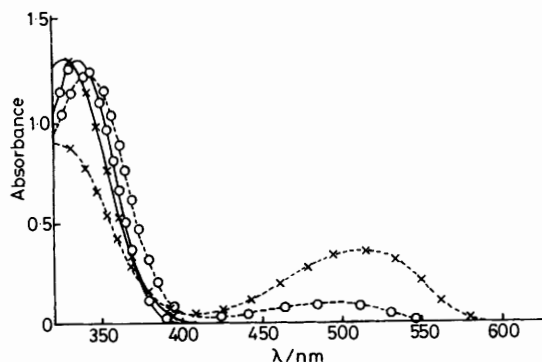


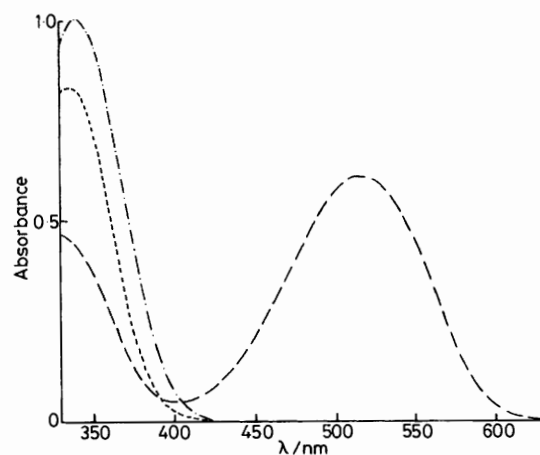
The numbering scheme shown is that of the benzothiophene moiety



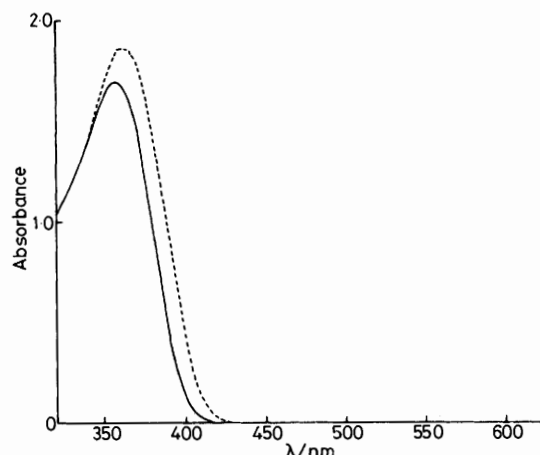
**Figure 1.** Absorption spectra of  $1.45 \times 10^{-4}\text{M}$  and  $1.16 \times 10^{-4}\text{M}$  solutions, respectively, of fulgides (1a) (— x —) and (1d) (— o —) in toluene before and after irradiation at 366 nm to give the photostationary states (--- x ---) and (--- o ---) respectively

It was therefore all the more surprising that the (*E*)-fulgide (1c) was not photochromic. On prolonged irradiation (366 nm) (2 weeks), it isomerised to give a *ca.* 3:2 equilibrium mixture of (*E*)- and (*Z*)-fulgides (1c) and (2c) (Figure 3). When the (*E*)-fulgide (1c) was heated in deuteriochloroform at  $180^\circ\text{C}$  for 3 days, a *ca.* 2:1 mixture of (*E*)- and (*Z*)-fulgide (1c) and (2c) was obtained.

The (*E*)-fulgide (1d) was photochromic (Figure 1) but, in comparison with (*E*)-fulgides (1a) and (1b), its photochromic properties were weak and its photoconversion into the red 7,7a-DHBT (3d) was too low to be detected by n.m.r. spectroscopy.



**Figure 2.** Absorption spectra of  $1.33 \times 10^{-4}\text{M}$  solution of the fulgide (1b) (---), the fulgide (2b) (— · — · —), and the 7,7a-DHBT (3b) (—) in toluene

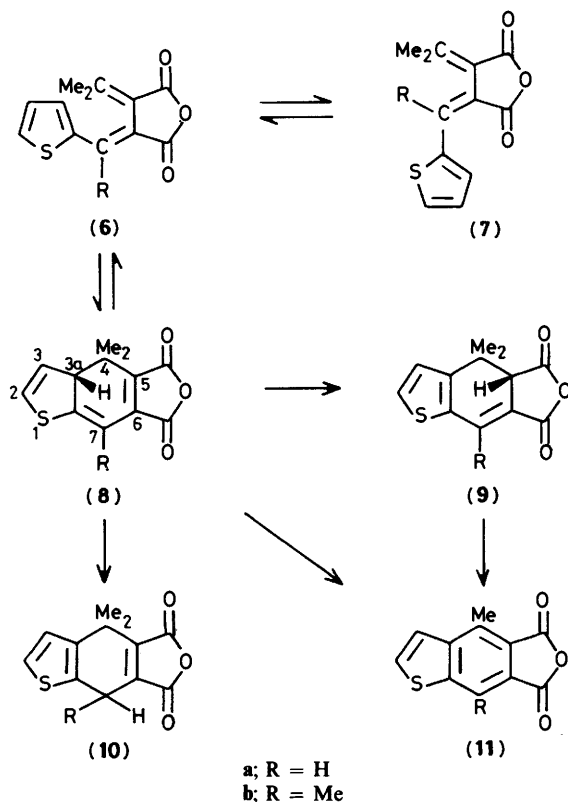


**Figure 3.** Absorption spectrum of a  $1.40 \times 10^{-4}\text{M}$  solution of the fulgide (1c) (—) in toluene before and after irradiation at 366 nm to give the photostationary state (---)

On prolonged irradiation (366 nm) of the (*E*)-fulgide (1d) in deuteriochloroform, a *ca.* 7:3 equilibrium mixture of (*E*)- and (*Z*)-fulgide (1d) and (2d) was obtained. The 7,7a-DHBT (3d) did not undergo hydrogen-shift reactions to give the 6,7- and 4,7-DHBT (4d) and (5d) respectively under these conditions. However, when the (*E*)-fulgide (1d) was heated ( $140^\circ\text{C}$ ) for 10 h, it cyclised to the red 7,7a-DHBT (3d) which, on exposure to white light, regenerated the (*E*)-fulgide (1d). When a similar thermal reaction was attempted in the presence of a catalytic amount of trichloroacetic acid, the (*E*)-fulgide (1d) was converted quantitatively into the 4,7-DHBT (5d), presumably *via* the 7,7a-DHBT (3d). When the (*E*)-fulgide (1d) was heated in *o*-dichlorobenzene in a sealed n.m.r. tube at  $180^\circ\text{C}$  for 1 h, the 6,7-DHBT (4d) was obtained in quantitative yield. Neither 6,7-DHBT, (4a) or (4d), underwent acid-catalysed rearrangements to the respective 4,7-DHBT (5a) and (5d) on being heated at  $140^\circ\text{C}$  in the presence of a small amount of trichloroacetic acid.

The (*E*)-2-thienylfulgide (6a) [*cf.* the (*E*)-3-thienylfulgide (1c)] was not photochromic. The slight colour change observed on prolonged irradiation at 366 nm was due to the formation of the more highly coloured (*Z*)-isomer (7a), and was not reversed on exposure to white light. When the (*E*)-fulgide (6a) was heated in *o*-dichlorobenzene in a sealed n.m.r. tube at  $180^\circ\text{C}$  for 2 h, a mixture of the (*Z*)-fulgide (7a) and the 4,5-DHBT (9a) was

obtained, as indicated by n.m.r. spectroscopy. On prolonged heating (120 h), the 4,5-DHBT (**9a**) was converted quantitatively into 4-methylbenzo[*b*]thiophene-5,6-dicarboxylic anhydride (**11a**). It is suggested that the (*E*)-fulgide (**6a**) thermally isomerises to the (*Z*)-fulgide (**7a**) and also cyclises to the 3a,4-DHBT (**8a**) which undergoes a 1,5-hydrogen shift to give the 4,5-DHBT (**9a**). On being heated in deuteriochloroform containing a catalytic amount of trichloroacetic acid (140 °C), the (*E*)-fulgide (**6a**) [*cf.* the (*E*)-fulgide (**1d**)] is converted quantitatively into the 4,7-DHBT (**10a**), presumably *via* the 3a,4-DHBT (**8a**).



The (*E*)-2-thienylfulgide (**6b**) is photochromic. On irradiation (366 nm) or on being boiled in toluene, this (*E*)-fulgide (**6b**) cyclised to give the orange 3a,4-DHBT (**8b**) ( $\lambda_{\text{max}}$ , 470 nm), which underwent reversal on exposure to white light and an irreversible 1,5-hydrogen shift at ambient and higher temperatures. In *o*-dichlorobenzene at 180 °C the (*E*)-fulgide (**6b**) was converted quantitatively into the 4,5-DHBT (**9b**). The (*E*)-fulgide (**6b**) [*cf.* the (*E*)-fulgide (**1a**)] did not undergo an acid-catalysed isomerisation into the corresponding 4,7-DHBT (**10b**) on being heated (140 °C) in deuteriochloroform containing a catalytic amount of trichloroacetic acid, but instead gave the 4,5-DHBT (**9b**) which, under the reaction conditions, was converted quantitatively into 4,7-dimethylbenzo[*b*]thiophene-5,6-dicarboxylic anhydride (**11b**).

## Discussion

From these studies of the photochromic properties of the fulgides (**1a**), (**1b**), (**1c**), (**1d**), (**6a**), and (**6b**), and of the furyl analogues reported previously,<sup>2,3</sup> it is suggested that when R<sup>1</sup> in fulgides (**1**) and R in fulgides (**6**) is other than hydrogen (*e.g.* R<sup>1</sup> or R = Me), there is a steric interaction between R<sup>1</sup> or R and the adjacent carbonyl group of the anhydride moiety which inhibits attainment of coplanarity of this  $\alpha,\beta$ -unsaturated carbonyl chromophore and results in excitation of the other  $\alpha,\beta$ -unsaturated carbonyl chromophore as the predominant photoprocess and hence in photocyclisation to a DHBT as the

main photoreaction. When R<sup>1</sup> or R is hydrogen, coplanarity of this  $\alpha,\beta$ -unsaturated carbonyl chromophore is more readily attained, leading to  $\pi-\pi^*$  excitation as the predominant photoprocess and to *E-Z* isomerisation as the main photoreaction.

The fulgide (**1b**) photocyclises quantitatively to give the 7,7a-DHBT (**3b**) (see Figure 2) while the fulgide (**1c**) shows only photochemical *E-Z* isomerisation under similar conditions (see Figure 3). Fulgides (**1a**) and (**1d**) undergo photocyclisation to give 7,7a-DHBTs and *E-Z* isomerisation (see Figure 1) but, under similar irradiation conditions, *E-Z* isomerisation predominates for the fulgide (**1d**) and photocyclisation for the fulgide (**1a**). The fulgide (**6a**) [like fulgide (**1c**)] does not photocyclise on irradiation at 366 nm, whereas the fulgide (**6b**) [like the fulgide (**1a**)] photocyclises to the 3a,4-DHBT (**8b**) (see Figure 4).

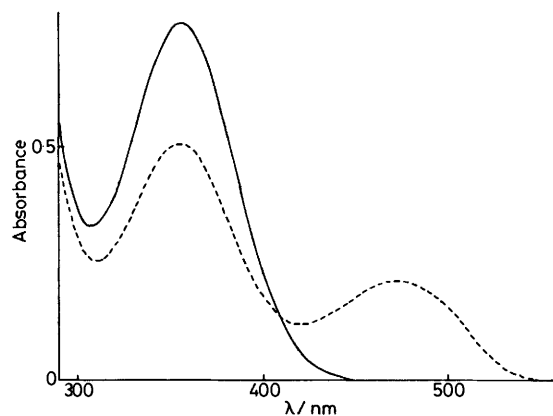


Figure 4. Absorption spectrum of a  $8.34 \times 10^{-4}$  M solution of the fulgide (**6b**) (—) in toluene before and after irradiation at 366 nm to give the photostationary state (----)

Fulgides (**1d**) and (**6a**) undergo thermal ring-closure and acid-catalysed 1,3-H shifts to yield, quantitatively, the 4,7-DHBTs (**5d**) and (**10a**) respectively. In contrast, the fulgides (**1a**) and (**6b**) cyclise and undergo 1,5-H shifts under the same reaction conditions.

The different rearrangement reactions appear to be dependent on the ease of protonation in the 4-position of the 7,7a-DHBT (**3**) and in the 7-position of the 3a,4-DHBT (**8**). In the absence of a substituent on the 4- and 7-position, protonation and the associated 1,3-H shifts occur rapidly. When there is a methyl substituent on the 4- and 7-position, protonation is so slow that only the 1,5-H shift reaction is observed.

## Experimental

U.v. spectra were measured in toluene on a Unicam SP8-200 spectrophotometer; 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).

Thermal and photoreactions were carried out on *ca.* 30 mg reactant in deuteriochloroform (0.5 cm<sup>3</sup>) in a sealed n.m.r. tube exposed to irradiation (366 nm) from a 250 W mercury-discharge lamp (type ME/D, Thorn Lighting) with a filter (type OX1, Chance Pilkington) focussed onto 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 (xylene, 140 °C; *o*-dichlorobenzene,

180 °C). Deuteriochloroform (99.8%) was boiled with, and distilled from, anhydrous Na<sub>2</sub>CO<sub>3</sub> before use. 10% w/v Ethanolic KOH was used and light petroleum refers to the fraction of b.p. 60–80 °C. Reagents and solvents were purified before use and extracts were dried over anhydrous MgSO<sub>4</sub> and filtered.

**2,5-Dimethylthiophene-3-carbaldehyde.**—Dichloromethyl butyl ether (15.7 g, 0.1 mol) was added slowly to a stirred solution of 2,5-dimethylthiophene (11.2 g, 0.1 mol) and tin(IV) chloride (18 cm<sup>3</sup>, 0.16 mol) in dichloromethane (100 cm<sup>3</sup>) at 5 °C. The reaction mixture was maintained at below 10 °C until the vigorous evolution of hydrogen chloride had subsided. The reaction mixture was poured into a mixture of water and crushed ice. The organic layer was washed successively with water and dil. aqueous Na<sub>2</sub>CO<sub>3</sub> and dried. The solvent was removed under reduced pressure and the residue was distilled to give 2,5-dimethylthiophene-3-carbaldehyde (9.2 g, 65%), b.p. 62–64 °C/0.7 mmHg; δ<sub>H</sub> 9.92 (1 H, s, CHO), 6.97 (1 H, s, 4-H), 2.70 (3 H, s, 5-Me), and 2.45 (3 H, s, 2-Me).

**3-Acetyl-2,5-dimethylthiophene.**—A solution of anhydrous tin(IV) chloride (32.5 g) in benzene (30 cm<sup>3</sup>) was added dropwise to a stirred solution of 2,5-dimethylthiophene (14.1 g) and acetic anhydride (14.5 g) in benzene (200 cm<sup>3</sup>) and the mixture was maintained at 15–20 °C. After being stirred for 1 h, the reaction mixture was poured onto a mixture of crushed ice (200 g) and 6M hydrochloric acid (50 cm<sup>3</sup>). The benzene layer was separated, washed with water, dried, and the solvent was removed under reduced pressure, and the residue was distilled to give 3-acetyl-2,5-dimethylthiophene (12 g, 60%), b.p. 62 °C/0.25 mmHg.

**2-Isopropylidene-3-[α-(3-thienyl)ethylidene]succinic Anhydride (1a).**—A mixture of 3-acetylthiophene (12.6 g, 0.1 mol) and diethyl isopropylidenesuccinate (20.5 g, 0.1 mol) in toluene (50 cm<sup>3</sup>) was added dropwise to a stirred suspension of sodium hydride (10.4 g; 50% dispersion in oil, 0.2 mol) in toluene (150 cm<sup>3</sup>). A few drops of ethanol were added to initiate the reaction. When the addition was complete, the reaction mixture was stirred (3 h) at ambient temperature and then poured into a mixture of crushed ice and water and the aqueous layer was separated and acidified with 5M HCl. The liberated half-ester was hydrolysed with ethanolic KOH. The dipotassium salt of the diacid was filtered off and acidified and the resulting (dried) diacid was treated with acetyl chloride (30 cm<sup>3</sup>). Excess of reagent was removed under reduced pressure and the residue was crystallised from light petroleum to give the (E)-fulgide (1a), yellow crystals (2.4 g, 10%), m.p. 93 °C (Found: C, 63.2; H, 4.9. C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>S requires C, 62.9; H, 4.9%); λ<sub>max</sub>. 328 nm (log ε 3.96).

**(Z)-2-[α-(2,5-Dimethyl-3-thienyl)ethylidene]-3-isopropylidenesuccinic Anhydride (2b).**—A mixture of diethyl isopropylidenesuccinate (10.2 g) and 3-acetyl-2,5-dimethylthiophene (7.7 g) was added during 30 min to a stirred suspension of sodium hydride (4.8 g; 50% dispersion in oil) in benzene (100 cm<sup>3</sup>). When hydrogen evolution had ceased, the reaction mixture was poured onto crushed ice and the aqueous layer was separated and acidified with 2M hydrochloric acid to liberate the (Z)-half-ester as a black oil (9 g) which was hydrolysed (13 h) in refluxing ethanolic KOH (75 cm<sup>3</sup>). Work-up gave the (Z)-diacid (6 g, 41%) as crystals from diethyl ether–light petroleum, m.p. 204–205 °C.

The (Z)-diacid (3 g) was treated (1 h) with acetyl chloride (50 cm<sup>3</sup>) and the excess of reagent was removed under reduced pressure. The residue crystallised from chloroform–light petroleum to give the (Z)-fulgide (2b) (2.54 g, 90%) as pale yellow plates, m.p. 155–156 °C (Found: C, 65.4; H, 5.9. C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>S requires C, 65.2; H, 5.8%); λ<sub>max</sub>. 345 nm (log ε 3.87).

**(E)-2-(2,5-Dimethyl-3-thienylmethylene)-3-isopropylidene-succinic Anhydride (1c).**—A mixture of diethyl isopropylidenesuccinate (4.6 g) and 2,5-dimethylthiophene-3-carbaldehyde (3 g) in toluene (25 cm<sup>3</sup>) was added to a stirred suspension of sodium hydride (2 g; 50% dispersion in oil) in toluene (25 cm<sup>3</sup>). Hydrolysis of the resultant half-ester and cyclisation of the diacid obtained [as described for the fulgide (1a)] gave the (E)-fulgide (1c) as yellow plates from methanol, m.p. 116 °C (Found: C, 64.5; H, 5.4. C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>S requires C, 64.1; H, 5.4%); λ<sub>max</sub>. 357 nm (log ε 4.08).

**(E)-2-Isopropylidene-3-(3-thienylmethylene)succinic Anhydride (1d).**—A mixture of thiophene-3-carbaldehyde (5.6 g) and diethyl isopropylidenesuccinate (10.7 g) was added dropwise to a stirred, boiling solution of potassium t-butoxide [prepared by dissolving potassium (3 g) in t-butyl alcohol] in t-butyl alcohol (200 cm<sup>3</sup>). After 40 min, the reaction mixture was allowed to cool and was dissolved in water and extracted with ether. The aqueous layer was acidified with 5M HCl and the liberated half-ester was extracted with ether. The ether was removed under reduced pressure and the residue was hydrolysed with ethanolic KOH to give the crude diacid (13 g).

The diacid (2 g), on being refluxed in toluene (100 cm<sup>3</sup>) containing toluene-*p*-sulphonic acid (0.5 g) with removal of water, was converted into the (E)-fulgide (1d), which crystallised from light petroleum as yellow prisms (1 g, 54%), m.p. 119–121 °C (Found: C, 61.7; H, 4.6. C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>S requires C, 61.5; H, 4.3%); λ<sub>max</sub>. 339 nm (log ε 4.07).

**(E)-2-Isopropylidene-3-(2-thienylmethylene)succinic Anhydride (6a).**—A mixture of diethyl isopropylidenesuccinate (21.4 g) and thiophene-2-carbaldehyde (11.2 g) was added slowly to a stirred suspension of sodium hydride (14 g; 50% dispersion in oil) in benzene (300 cm<sup>3</sup>) and the reaction mixture was carefully maintained at 15–25 °C for 1.5 h to prevent an extremely vigorous reaction. Work-up gave ethyl (E)-2-isopropylidene-3-(2-thienylmethylene)succinate (27 g, 93%) as an oil which was hydrolysed in refluxing ethanolic KOH (100 cm<sup>3</sup>). A sample of the resulting diacid (1.8 g) was treated with acetyl chloride (20 cm<sup>3</sup>) and the excess of reagent was removed under reduced pressure. The residue gave the (E)-fulgide (6a) (1.2 g, 72%) as yellow cubes from chloroform–light petroleum, m.p. 83–84 °C (Found: C, 61.55; H, 4.3; S, 13.7. C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>S requires C, 61.5; H, 4.3; S, 14.0%); λ<sub>max</sub>. 276 and 363 nm (log ε 3.87 and 4.22).

**(E)-2-Isopropylidene-3-[α-(2-thienyl)ethylidene]succinic Anhydride (6b).**—A mixture of diethyl isopropylidenesuccinate (21.4 g) and 2-acetylthiophene (12.6 g) was added, during 30 min, to a stirred suspension of sodium hydride (10 g; 50% dispersion in oil) in toluene (30 cm<sup>3</sup>) and the reaction mixture was stirred overnight at room temperature. Work-up gave the (Z)-half-ester (65%) as a red oil which was hydrolysed with ethanolic KOH (75 cm<sup>3</sup>). The diacid, obtained on acidification, was cyclised with acetyl chloride. Excess of reagent was removed under reduced pressure and the residue was crystallised from methanol to give the (E)-fulgide (6b) as yellow prisms, m.p. 86 °C (Found: C, 62.9; H, 4.8. C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>S requires C, 62.9; H, 4.9%); λ<sub>max</sub>. 355 nm (log ε 3.96).

**Rearrangement Reactions of Thienyl Fulgides.**—The (E)-fulgide (1a) (100 mg), dissolved in deuteriochloroform (0.5 cm<sup>3</sup>), was heated (180 °C) for 20 min. The sample was allowed to cool, and the product, the 6,7-DHBT (4a), crystallised from chloroform–light petroleum as plates, m.p. 168 °C (Found: C, 62.4; H, 5.0. C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>S requires C, 62.9; H, 4.9%).

The (E)-fulgide (1b) was prepared by irradiation (366 nm) of the (Z)-fulgide (2b) (100 mg) in toluene (30 cm<sup>3</sup>) until a nearly quantitative conversion of the (Z)-fulgide (2b) into the 7,7a-

DHBT (**3b**) was obtained. The deep red solution was exposed to white light until the solution was nearly colourless, indicating that the 7,7a-DHBT (**3b**) has been photoisomerised to the (*E*)-fulgide (**1b**). Removal of solvent followed by recrystallisation of the residue from ethanol gave the (*E*)-fulgide (**1b**) as pale yellow needles, m.p. 110 °C (Found: C, 65.1; H, 5.9. C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>S requires C, 65.2; H, 5.8%);  $\lambda_{\max}$ . 335 nm (log  $\epsilon$  3.80).

When  $1.33 \times 10^{-4}$  M solutions of (*E*)- and (*Z*)-fulgides (**1b**) and (**2b**) ( $\epsilon$  6 306 and  $\epsilon$  7 452 respectively) in toluene were irradiated (366 nm), the fulgides were converted quantitatively into the 7,7a-DHBT (**3b**) which gave the (*E*)-fulgide (**1b**) on exposure to white light. The solution of the fulgide (**1b**) showed a decrease in absorbance (3%) compared with the original solution of compound (**1b**); this is attributed to photodegradation of the fulgide (**1b**), since a further 3% decrease in absorbance was noted for each repeat cycle for the solutions of compound (**1b**) and the 7,7a-DHBT (**3b**). On this basis, the corrected molar extinction coefficient for the 7,7a-DHBT (**3b**) is  $4\,680 \pm 50$  at 520 nm.

The (*Z*)-fulgide (**2b**) in deuteriochloroform, on being heated (180 °C) for 24 h, gave a *ca.* 1:9 mixture of (*E*)- and (*Z*)-fulgide (**1b**) and (**2b**). The same equilibrium mixture was obtained when the (*E*)-fulgide (**1b**) was heated at 180 °C for 72 h under similar conditions.

The (*E*)-fulgide (**1c**) in deuteriochloroform was heated (180 °C) until thermal equilibrium was established (3 days). The equilibrium mixture was a *ca.* 2:1 mixture of (*E*)- and (*Z*)-fulgide (**1c**) and (**2c**). Irradiation (366 nm) of the (*E*)-fulgide (**1c**) in deuteriochloroform for 1 week gave, at the photostationary state, a 2:3 mixture of (*E*)- and (*Z*)-fulgide (**1c**) and (**2c**). In neither experiment could the 7,7a-DHBT (**3c**) be detected by its colour or by n.m.r. spectroscopy.

The (*E*)-fulgide (**1d**) in deuteriochloroform, on being heated (180 °C) for 1 h, gave the 6,7-DHBT (**4d**), in quantitative yield, as pale yellow crystals (from chloroform–light petroleum), m.p. 207–208 °C (Found: C, 61.3; H, 4.2. C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>S requires C,

61.5; H, 4.3%);  $\lambda_{\max}$ . (EtOH) 242 and 332 nm (log  $\epsilon$  4.08 and 3.61). The fulgide (**1d**) in deuteriochloroform containing 5% w/v trichloroacetic acid gave, on being heated (140 °C) for 10 h, a quantitative yield of the 4,7-DHBT (**5d**) as plates (from chloroform–light petroleum), m.p. 209–211 °C (Found: C, 61.3; H, 4.2. C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>S requires C, 61.5; H, 4.3%);  $\lambda_{\max}$ . (EtOH) 231 nm (log  $\epsilon$  3.79).

A solution of the (*E*)-fulgide (**6a**) in deuteriochloroform was irradiated (366 nm) for 2 weeks. A photostationary state of a 1:1 mixture of (*E*)- and (*Z*)-fulgide (**6a**) and (**7a**) was obtained and no other products could be detected.

A solution of the (*E*)-fulgide (**6a**) (200 mg) in tetrachloromethane (40 cm<sup>3</sup>) at 54 °C was irradiated (366 nm) for 24 h. As the solution cooled, the (*Z*)-fulgide (**7a**) crystallised as yellow prisms (60 mg), m.p. 165–166 °C (Found: C, 61.0; H, 4.6. C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>S requires C, 61.5; H, 4.3%);  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 278 and 369 nm (log  $\epsilon$  3.76 and 4.25).

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