

Photochromic Systems. Part 2.¹ Studies on the Photoreactions and the Photopolychromic Properties of (*E*)-(2,5-Dimethoxyphenyl-substituted)methylene Isopropylidenesuccinic Anhydrides

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Each of the pale yellow title compounds (**1**), in toluene and other appropriate organic solvents, cyclises on irradiation at 366 nm to give purple solutions containing a mixture of a thermally unstable, blue 4-substituted 1,8a-dihydro-5,8-dimethoxy-1,1-dimethylnaphthalene-2,3-dicarboxylic anhydride (**5**) and a thermally stable, red 4-substituted 1,8a-dihydro-6,8a-dimethoxy-1,1-dimethylnaphthalene-2,3-dicarboxylic anhydride (**7**) (1,8a-DHNs). The red and the blue 1,8a-DHNs (**7**) and (**5**) undergo the reverse reactions on exposure to white light. The purple solutions turn red at ambient temperature in the dark or on irradiation at wavelengths at which the red 1,8a-DHNs do not absorb, due to thermal or photochemical reversal of the blue 1,8a-DHNs. When a trace amount of an acid is added to the purple solutions, they turn blue due to the rapid acid-catalysed reversal of the red-1,8a-DHNs. On prolonged irradiation at 366 nm, the red 1,8a-DHNs (**7**) undergo a 1,7-methoxy shift to yield 4,6-dimethoxy-1,4-DHNs (**8**), and the blue 1,8a-DHNs (**5**) undergo an oxidative rearrangement to 4-hydroxy-5,8-dimethoxy-1,4-DHNs (**9**). Photochemical studies on related compounds are described.

In previous papers,^{1,2} we reported that the fulgides (*E*)-1-(3,5-dimethoxy- and -3,4,5-trimethoxy-phenyl)ethylidene(isopropylidene)succinic anhydrides cyclise to blue 1,8a-dihydro-1,8a-DHNs on irradiation at 366 nm and that the 1,8a-DHNs undergo the reverse reaction on exposure to white light. The blue colour is attributed to the influence of the 8-methoxy substituent on the main chromophore. 1,8a-DHNs lacking a strong auxochromic substituent in the 8-position are usually red.

We now report studies on the first photopolychromic fulgides, pale yellow (*E*)-2,5-dimethoxyphenyl-substituted methylene(isopropylidene)succinic anhydrides (**1**; R = Me or Ph). They photocyclise to generate both red and blue 1,8a-DHNs, depending on which *ortho* position of the 2,5-dimethoxyphenyl group is involved in the photocyclisation. The term 'photopolychromic' was introduced by Short in 1969³ to describe compounds (e.g., crystals of dipyrindinium dichloride) which show more than one light-induced reversible major colour change. Our earlier attempts to prepared compounds which showed photopolychromic properties in solution (as distinct from in the crystal) were unsuccessful.^{4,5}

Discussion and Results

(*E*)-1-(2,5-Dimethoxyphenyl)ethylidene(isopropylidene)succinic anhydride (**1**; R = Me) in toluene undergoes two ring-closure processes on irradiation at 366 nm. One involves photocyclisation onto the unsubstituted *ortho* position of the 2,5-dimethoxyphenyl group to produce a blue 8-methoxy-1,8a-DHN (**5**; R = Me), which is thermally unstable and reverts back to the (*E*)-fulgide (**1**; R = Me) at ambient temperatures in the dark. The other involves ring closure onto the 2-position of the 2,5-dimethoxyphenyl group to form a red 1,8a-DHN (**7**; R = Me) (lacking an 8-methoxy substituent), which is thermally stable in the dark at ambient temperatures because its symmetry-allowed disrotatory ring-opening is inhibited by steric

interactions between the angular 8a-methoxy group and the 1-methyl group *cis* to it.¹⁶

Thus, on irradiation at 366 nm, a solution of the (*E*)-fulgide (**1**; R = Me) in toluene shows a pale yellow to deep purple colour change due to the formation of the red and the blue 1,8a-DHNs (**7**; R = Me) and (**5**; R = Me). When the purple solution is left in the dark, the blue 1,8a-DHN (**5**; R = Me) fades away leaving a red solution of the 1,8a-DHN (**7**; R = Me). A similar effect is produced on irradiation of the purple solution at wavelengths longer than 590 nm (e.g., at 633 nm using a helium-neon laser). The blue 1,8a-DHN (**5**; R = Me) photoreverses to the (*E*)-fulgide (**1**; R = Me). Both the red and the blue 1,8a-DHNs (**7**; R = Me) and (**5**; R = Me) ring-open to the (*E*)-fulgide (**1**; R = Me) on exposure to white light.

The thermally stable red 1,8a-DHN (**7**; R = Me) undergoes a rapid acid-catalysed fade reaction whereas the blue 1,8a-DHN (**5**; R = Me) does not. If a crystal of trichloroacetic acid (TCA) or toluene-*p*-sulphonic acid or even a small amount of toluene saturated with hydrogen chloride is added to the purple solution, the red 1,8a-DHN (**7**; R = Me) is lost and the solution turns blue. The spectrum of the (*E*)-fulgide (**1**; R = Me) in toluene prior to irradiation, after irradiation at 366 nm, after the thermal fade of the blue 1,8a-DHN (**5**; R = Me), and after the acid-catalysed fade of the red 1,8a-DHN (**7**; R = Me) is shown in Figure 1. The photopolychromic properties of the (*E*)-fulgide (**1**; R = Me) and the fade characteristics of the blue and the red 1,8a-DHNs (**5**; R = Me) and (**7**; R = Me) are retained in *o*-dichlorobenzene, *p*-chlorotoluene, dichloromethane, and chloroform. Both the blue and the red 1,8a-DHNs (**5**; R = Me) and (**7**; R = Me) show solvatochromic effects, with bathochromic shifts of their long-wavelength absorption bands with increasing solvent polarity. In solvents such as methanol, ethanol, acetone, and acetonitrile, only the red 1,8a-DHN (**7**; R = Me) is formed from the (*E*)-fulgide (**1**; R = Me). The conversion of the (*E*)-fulgide (**1**; R = Me) into the blue and the red 1,8a-DHNs (**5**; R = Me) and (**7**; R = Me) is so much greater on irradiation at 366 nm than on irradiation at 313 or 405 nm that any wavelength dependence of the ratio of red to blue 1,8a-DHNs could not be determined.

On prolonged irradiation (366 nm), the (*E*)-fulgide (**1**; R =

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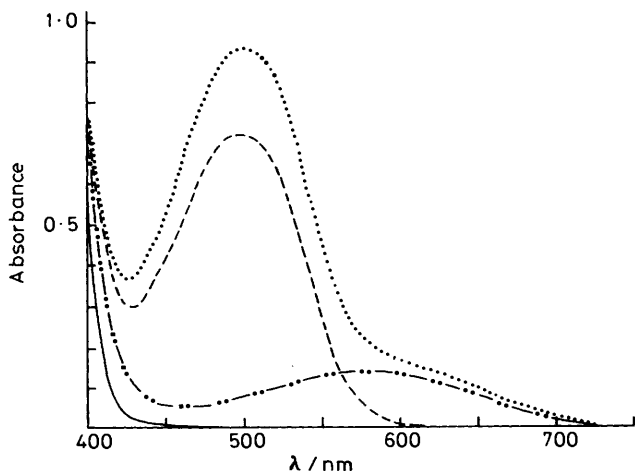
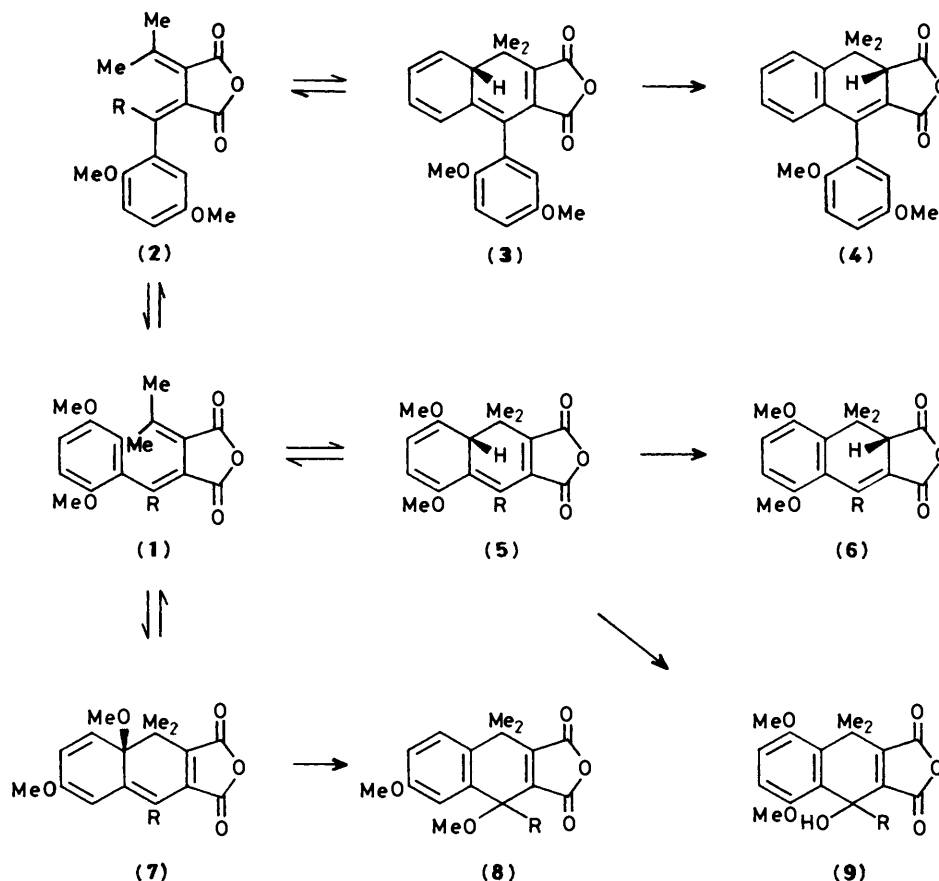


Figure 1. Absorption spectrum of the (*E*)-fulgide (1; R = Me) (2.1×10^{-3} M) in toluene prior to irradiation (—), after irradiation at 366 nm (····), after irradiation at 366 nm and complete thermal fade of the blue 1,8a-DHN (5; R = Me) (---), and after irradiation at 366 nm and complete fade of the red 1,8a-DHN (7; R = Me) following addition of a crystal of TCA to the solution (— · — · —)

Me) in toluene gave the (*Z*)-fulgide (2; R = Me) and two colourless photoproducts, m.p. 170–172 °C and 254–255 °C. The n.m.r. spectrum of the mixture indicated that the 1,2-DHN (6; R = Me) was absent since the spectrum lacked a high-field methyl singlet [*cf.* (6; R = Ph)] (See Table).

The photoproduct with m.p. 170–172 °C is the 4,6-dimethoxy-1,4-DHN (8; R = Me). Its structure is assigned from its elemental analysis, and its characteristic u.v. and n.m.r. spectra.

It is believed to be formed *via* a photochemical 1,7-methoxy shift in the red 1,8a-DHN (7; R = Me). The photoproduct with m.p. 254–255 °C is believed to be the 4-hydroxy-5,8-dimethoxy-1,4-DHN (9; R = Me) from its elemental analysis, mass spectrum, and u.v. and n.m.r. spectra. It is probably formed *via* a photochemical allylic addition–hydrogen-abstraction reaction involving singlet oxygen.⁷

(*E*)-2,5-Dimethoxybenzhydrylidene(isopropylidene)succinic anhydride (1; R = Ph) is photopolychromic and shows a sequence of colour changes and photoreactions similar to those of (*E*)-fulgide (1; R = Me). On irradiation (366 nm), the (*E*)-fulgide (1; R = Ph) in toluene turns from pale yellow to purple with the formation of the blue and the red 1,8a-DHNs (5; R = Ph) and (7; R = Ph). When the purple solution is left in the dark, the blue (1,8a)-DHN (5; R = Ph) fades, leaving the red 1,8a-DHN (7; R = Ph).

On prolonged irradiation (366 nm) of the (*E*)-fulgide (1; R = Ph), the (*Z*)-fulgide (2; R = Ph), the photochemical 1,7-methoxy-shift product (8; R = Ph), and the 4-hydroxy-1,4-DHN (9; R = Ph) are obtained. In addition, the 1,5-H-shift product (6; R = Ph) from the blue 1,8a-DHN (5; R = Ph) and the 1,5-H-shift product (4) from the red 1,8a-DHN (3) [from the (*E*)- and (*Z*)-fulgide (1 and 2; R = Ph) respectively] were formed.

In marked contrast, (*E*)-(2,5-dimethoxyphenyl)methylene-(isopropylidene)succinic anhydride (1; R = H) is not photochromic. On prolonged irradiation of the (*E*)-fulgide (1; R = H) in toluene, a 1 : 1 mixture of the (*E*)- and the (*Z*)-fulgide (1 and 2; R = H) was obtained. This result is consistent with our general observation that fulgides are either not photochromic or only very weakly photochromic if R = H and photocyclisation onto a phenyl group containing an *ortho* or *para* alkoxy group is required.¹ The marked difference in the spectra of the (*E*)- and

Table. ¹H N.m.r. data of fulgides and their rearrangement products, DHNs (δ values)

Compound	R	ArH			Ring of OH	R	Me ^a	Me ^b	OMe	
		J/Hz	J/Hz	J/Hz						
(1)	H	6.87 ^c /d	2	6.78t	2	7.89	2.45	1.60	3.76	3.86
(1)	Me	6.90 ^c /d	2	6.55t	2	2.64	2.21	1.20	3.72	3.81
(1)	Ph	6.87 ^c /d	2	6.51t	2	7.30	2.38	1.35	3.70	3.48
(2)	H	6.82 ^c /d	9	7.61d	3	7.70	2.57	2.37	3.84	3.84
(2)	Me	6.87 ^c /d	2	6.65t	2	2.10	2.47	2.17	3.75	3.78
(2)	Ph	6.37 ^c /d	2	6.59t	2	7.27	2.31	1.31	3.78	3.78
(4)				6.50—7.15			1.90	1.23	3.75	3.80
(6)	Ph			6.50—7.15		3.85 ^e	1.90	1.27	3.55	3.83
(8)	Me	7.38d	9	7.08d	3	7.01q	1.82	1.72	3.88	2.97 ^g
(8)	Ph	7.50d	9	6.72d	3	7.02q	7.32	1.80	3.72	3.15 ^g
(9)	Me			6.93 ^c /s		4.81 ^f	1.88	1.79	3.87	3.20l
(9)	Ph	7.03d	9	6.87d	9	5.10 ^f	7.2—7.4	1.90	3.40	3.97

^a Deshielded by the adjacent carbonyl group in fulgides and 1,2-DHNs. ^b Shielded by the phenyl group in (*E*)-fulgides and is outside the deshielding zone of the adjacent carbonyl in 1,2-DHNs. ^c 2 H. ^d Signal for 2-H is observed by signals at δ 3.7—3.9. ^e 2-H. ^f OH-Signal disappears when the solution is shaken with D₂O. ^g 4-OMe.

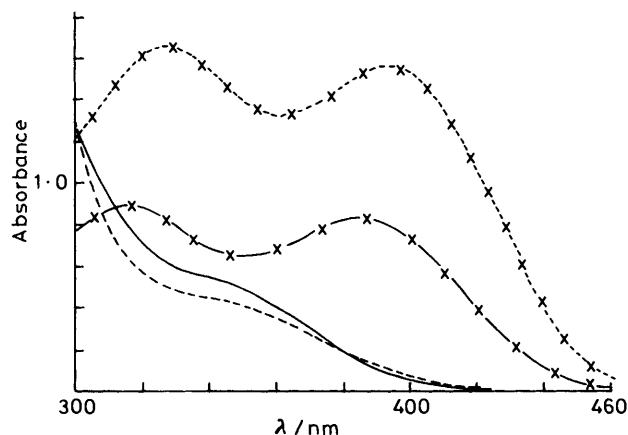


Figure 2. Absorption spectra of the (*E*)-fulgide (1; R = H) (1.13×10^{-4} M) (—x—), (*Z*)-fulgide (2; R = H) (1.29×10^{-4} M) (---x---), (*E*)-fulgide (1; R = Me) (1.48×10^{-4} M) (—), and (*Z*)-fulgide (2; R = Me) (1.54×10^{-4} M) (---).

the (*Z*)-fulgide (1 and 2; R = H) and the (*E*)- and (*Z*)-fulgide (1 and 2; R = Me) can be seen in Figure 2.

Experimental

U.v. and visible spectra were measured in toluene (unless stated otherwise) on a Unicam SP1700B spectrometer with the exception of the spectra shown in Figures 1 and 2, which were obtained using a Hewlett Packard 8451A diode array spectrometer.* The solutions were irradiated at 366 nm, using a 250 W mercury-discharge lamp (type ME/D, Thorn Lighting) with a filter (type OX1, Chance Pilkington). Coloured solutions were allowed to fade in the dark or on exposure to visible monochromatic light of the appropriate wavelength(s).

N.m.r. spectra were obtained with a Perkin-Elmer R32 (90 MHz) spectrometer (tetramethylsilane as internal standard except when monitoring photochemical reactions, for which an external standard was used). Photoreactions were carried out on the fulgide in toluene at 54 °C exposed (10 days) to irradiation (366 nm) from an assembly of four 123 W mercury-discharge lamps (type MBW, Thorn Lighting) with a Wood's glass filter (OX1, Chance Pilkington).

* We thank Dr. Ian A. Tomlinson for measuring these spectra.

Light petroleum refers to the fraction boiling in the range 80—100 °C.

(*E*)- and (*Z*)-1-(2,5-Dimethoxyphenyl)ethylidene(isopropylidene)succinic Anhydrides (1; R = Me) and (2; R = Me).—A mixture of diethyl isopropylidene succinate⁸ (10.7 g, 0.05 mol) and 2,5-dimethoxyacetophenone (9.0 g, 0.05 mol) was added gradually to a stirred, boiling solution of potassium *t*-butoxide [from potassium (2.2 g)] in *t*-butyl alcohol (250 cm³). After 48 h, the solution was cooled, the solvent was removed under reduced pressure, and the residue was boiled with 10% ethanolic KOH (50 cm³). The insoluble potassium salt (5.3 g) was filtered off and acidified with 5M-hydrochloric acid. The resulting diacid was cyclised in refluxing acetyl chloride (20 cm³), and the excess of acetyl chloride was removed. The residue was crystallised from a mixture of CH₂Cl₂ and light petroleum, giving the (*Z*)-fulgide (2; R = Me) as yellow needles, m.p. 127 °C (Found: C, 67.3; H, 6.0. C₁₇H₁₈O₅ requires C, 67.55; H, 6.0%; λ_{\max} (EtOH) 281 nm (log ϵ 4.02).

The filtrate from the potassium salt filtration was acidified with 5M-hydrochloric acid and the precipitated diacid was filtered off, dried, and boiled with acetyl chloride. Removal of the excess of acetyl chloride left a mixture of the (*E*)- and (*Z*)-fulgide (2.84 g) (1; R = Me) and (2; R = Me) which, on fractional crystallisation from CH₂Cl₂-light petroleum, gave the (*E*)-fulgide (1; R = Me) as pale yellow crystals, m.p. 162 °C (Found: C, 67.8; H, 5.85%; λ_{\max} (EtOH) 295 nm (log ϵ 4.01).

Photoreactions. The (*E*)-fulgide (1; R = Me) (810 mg) in toluene (100 cm³) was irradiated. The solvent was removed and the residue was triturated with ether. The 4-hydroxy-5,8-dimethoxy-1,4-DHN (9; R = Me) (80 mg) separated and was filtered off and recrystallised from CH₂Cl₂, to afford pale yellow crystals, m.p. 254—255 °C (Found: *M*⁺, 318; C, 63.8; H, 5.7. C₁₇H₁₈O₆ requires *M*, 318; C, 64.15; H, 5.7%); λ_{\max} (EtOH) 291 nm (log ϵ 3.58); ν_{\max} , 3 500 cm⁻¹. The ethereal filtrate was evaporated and the residue was chromatographed on silica gel, with a (12:1) mixture of CH₂Cl₂ and ethyl acetate as eluant. The first fraction gave the 4,6-dimethoxy-1,4-DHN (8; R = Me) (105 mg), pale yellow crystals from ethanol, m.p. 171—172 °C (Found: C, 67.8; H, 6.2. C₁₇H₁₈O₅ requires C, 67.55; H, 6.0%; λ_{\max} (EtOH) 245, 278, and 286 nm (log ϵ 3.28, 3.30, and 3.25). A mixture of (*E*)- and (*Z*)-fulgide (1; R = Me) and (2; R = Me) (400 mg) was obtained from the second fraction.

(*E*)- and (*Z*)-2,5-Dimethoxybenzhydrylidene(isopropylidene)succinic Anhydrides (1; R = Ph) and (2; R = Ph).—A mixture of

diethyl isopropylidenesuccinate (22.4 g, 0.5 mol) and 2,5-dimethoxybenzophenone (12.1 g, 0.05 mol) [prepared in 90% yield by the reaction of equimolar proportions of benzoyl chloride, 1,4-dimethoxybenzene, and tin(IV) chloride in boiling benzene] was added to potassium t-butoxide [from potassium (2.65 g) in t-butyl alcohol (250 cm³)]. Work-up gave an oil which was boiled with 10% ethanolic potassium hydroxide (50 cm³) as before. Ethanol was removed and the residue was acidified with 5M-hydrochloric acid. The precipitated diacids were filtered off, dried, and treated with a large excess of acetyl chloride. The excess of acetyl chloride was distilled off under reduced pressure and the residue was crystallised from CH₂Cl₂-light petroleum. The mixture of crystals of (*E*)- and (*Z*)-fulgide (**1**; R = Ph) and (**2**; R = Ph) was carefully separated by hand and each isomer was then recrystallised from CH₂Cl₂-light petroleum. The (*E*)-fulgide (**1**; R = Ph) was obtained as pale yellow crystals, m.p. 174 °C (Found: C, 72.8; H, 5.3. C₂₂H₂₀O₅ requires C, 72.5; H, 5.5%; λ_{max.} 345 nm (log ε 4.02). The (*Z*)-fulgide (**2**; R = Ph) separated in pale yellow needles, m.p. 86–88 °C; λ_{max.}(EtOH) 338 nm (log ε 3.92).

Photoreactions. A ca. 1:1 mixture of the (*E*)- and (*Z*)-fulgide (**1**; R = Ph) and (**2**; R = Ph) (830 mg) in toluene (100 cm³) was irradiated. The solvent was removed and the residue was chromatographed on silica gel, with a 1:1 mixture of CH₂Cl₂ and light petroleum as eluant. The first fraction, on work-up, gave an oil (140 mg) which, on trituration with a few drops of ether, gave the 4,6-dimethoxy-1,4-DHN (**8**; R = Ph), needles from CH₂Cl₂-ether, m.p. 140 °C (Found: C, 72.2; H, 5.6. C₂₂H₂₀O₅ requires C, 72.5; H, 5.5%; λ_{max.}(EtOH) 281 and 288 nm (log ε 3.60 and 3.57). The second fraction, on evaporation, gave an oil which, on trituration with a few drops of ether, gave the 4-hydroxy-5,8-dimethoxy-1,4-DHN (**9**; R = Ph) as pale yellow crystals (from CH₂Cl₂-light petroleum), m.p. 220–221 °C (Found: *M*⁺, 380; C, 68.9; H, 5.35. C₂₂H₂₀O₆ requires *M*, 380; C, 69.5; H, 5.3%; λ_{max.}(EtOH) 292 nm log ε 3.66); ν_{max.} 3 500 cm⁻¹.

The filtrates from the above recrystallisations were combined and evaporated to dryness. The residue, a mixture of the 1,2-DHNs (**4**) and (**6**; R = Ph) could not be separated by repeated fractional recrystallisation from CH₂Cl₂-light petroleum. Their n.m.r. spectra could be assigned without difficulty except that the 2-H signal of the 1,2-DHN (**4**) was obscured by other absorptions.

(*E*)-2,5-Dimethoxybenzylidene(isopropylidene)succinic Anhydride (**1**; R = H).—A mixture of diethyl isopropylidenesuccinate

(12.6 g, 0.06 mol) and 2,5-dimethoxybenzaldehyde (9.8 g, 0.06 mol) was added to potassium t-butoxide [from potassium (2 g) in t-butyl alcohol]. Work-up, as before, gave a diacid (10.7 g), which was cyclised with acetyl chloride to afford the (*E*)-fulgide (**1**; R = H), which was obtained as orange crystals (5.1 g) from CH₂Cl₂-light petroleum, m.p. 133–134 °C (Found: C, 66.9; H, 5.5. C₁₆H₁₆O₅ requires C, 66.7; H, 5.6%; λ_{max.} 316 and 386 nm (log ε 3.90 and 3.86).

Photoreaction. A solution of the (*E*)-fulgide (**1**; R = H) (710 mg) in toluene (100 cm³) was irradiated. Removal of the solvent left a ca. 1:1 mixture of (*E*)- and (*Z*)-fulgides (**1**; R = H) and (**2**; R = H) which, on fractional crystallisation first from chloroform-ether and then from CH₂Cl₂-ether, gave the (*Z*)-fulgide (**2**; R = H) as pale yellow needles, m.p. 132.5 °C (Found: C, 66.9; H, 5.65%; λ_{max.} 328 and 392 nm (log ε 4.11 and 4.08).

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