

## Overcrowded Molecules. Part 14.<sup>1</sup> Photochromic Systems Involving (Z)-1-Methylpropylidene(diphenylmethylene)succinic and (E)-3,5-Dimethoxybenzylidene(alkyl-substituted methylene)succinic Anhydrides

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Photochromic (Z)-1-methylpropylidene(diphenylmethylene)succinic anhydride undergoes photochemical conrotatory ring closure and thermal disrotatory ring closure reactions to form red 1,8a-dihydronaphthalene intermediates (1,8a-DHNs) which undergo a facile thermal 1,5-H shift to yield colourless 1,2-DHNs. Yellow (E)-3,5-dimethoxybenzylidene(alkyl-substituted methylene)succinic anhydrides undergo reversible photochemical ring closure to form deep blue solvatochromic 6,8-dimethoxy-1,8a-DHNs which do not undergo 1,5-H shifts at ambient temperatures but photochemical 1,7-H shifts to yield 1,4-DHNs. The spectra of blue 1,8a-DHNs can be determined using the Fisher method.

In 1905, Stobbe gave the name 'fulgides' to derivatives of bismethylenesuccinic anhydride and showed that if one of the substituents was phenyl, the compound was photochromic.<sup>2</sup> Our studies on fulgides have shown that the photochromic properties result from photocyclisation of these yellow to orange compounds to give red 1,8a-dihydronaphthalene intermediates (1,8a-DHNs) which undergo the reverse process on exposure to white light.<sup>1,3</sup> These stereospecific processes occur in accord with the Woodward-Hoffmann selection rule for pericyclic reactions<sup>4</sup> and are exemplified by the reactions of (Z)-1-methylpropylidene(diphenylmethylene)succinic anhydride (1), which undergoes photochemical conrotatory ring closure followed by a thermal 1,5-H shift on irradiation at 366 nm in toluene at 60 °C and disrotatory ring closure followed by a 1,5-H shift on heating in *o*-dichlorobenzene at 180 °C to give *c*- and *t*-1-ethyl-1,2-dihydro-1-methyl-4-phenylnaphthalene-2,3-dicarboxylic anhydride (3) and (6) respectively, in quantitative yield. No thermal reaction occurs below 140 °C. When fulgide (1) or its rearrangement products (3) and (6) are heated above 200 °C, 1-methyl-4-phenylnaphthalene-2,3-dicarboxylic anhydride (7) is obtained in high yield, presumably with evolution of ethane.

When fulgide (1) in toluene at 18 °C is irradiated, the solution rapidly changes from pale yellow to red and on further irradiation at 366 nm, becomes colourless. The

<sup>1</sup> Part 13, R. J. Hart, H. G. Heller, R. M. Megitt, and M. Szewczyk, *J.C.S. Perkin I*, 1975, 2227.

<sup>2</sup> H. Stobbe, *Ber.*, 1905, **38**, 3673; *Annalen*, 1906, **349**, 333.

<sup>3</sup> H. G. Heller and M. Szewczyk, *J.C.S. Perkin I*, 1974, 1487; H. G. Heller and R. J. Hart, *ibid.*, 1972, 1321.

1,2-DHNs (3) and (6) are obtained in 85 and 15% yield respectively. We believe that the 1,8a-DHN (2) undergoes two competing thermal reactions, namely a 1,5-H shift to give the 1,2-DHN (3) and disrotatory ring opening to the isomeric fulgide (4) which cyclises to the 1,8a-DHN (5) which, in turn, undergoes the same two competing thermal reactions to give the 1,2-DHN (6) and the fulgide (1) respectively. Isomerisation of the (Z)-fulgide (1) to the *E*-isomer (4) does not occur either directly or *via* the maleic anhydride intermediate (8) since prolonged irradiation of the fulgide (1) in toluene with u.v. and white light causes no change. Under dual irradiation conditions, the solution does not turn red because any 1,8a-DHN (2) generated by u.v. light is converted back into fulgide (1) by white light (Scheme 1).

Colour-structure relationships in organic molecules have been reviewed by Griffiths<sup>5</sup> and the influence of auxochromic groups on the colour of dyes discussed by Bury<sup>6</sup> as early as 1935. It is well known that the introduction of methoxy-substituents into an organic compound causes a marked bathochromic shift of the long wavelength absorption band of the compound when the substituents are in direct conjugation with the main chromophore of the molecule. The introduction of 3- and 5-methoxy-groups into a phenyl substituent of a fulgide causes only minor changes in its spectrum. A weak

<sup>4</sup> R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.

<sup>5</sup> J. Griffiths, 'Colour and Constitution of Organic Molecules,' Academic Press, London, 1976.

<sup>6</sup> C. R. Bury, *J. Amer. Chem. Soc.*, 1935, **57**, 2115.

hypsochromic shift is observed. But on photocyclisation of fulgide (9), a 1,8a-DHN (10) is produced in which the 6- and 8-methoxy-substituents are in conjugation with the main chromophore and cause a marked bathochromic shift as well as broadening of the long wavelength absorption band [ $\lambda_{\max}$ , 560 for (10;  $R^1 = R^2 = \text{Me}$ ) compared with  $\lambda_{\max}$ , 490 nm for (2)] (see Figure 1).

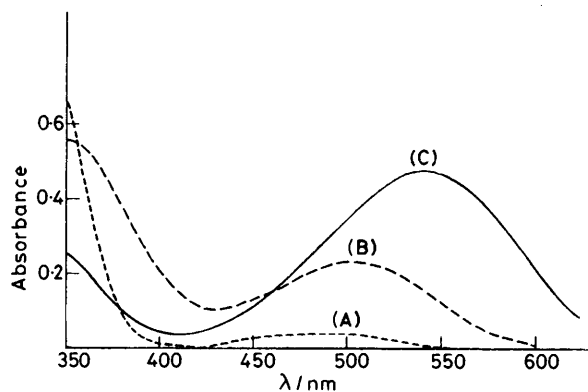


FIGURE 1 Absorption spectra of  $10^{-4}\text{M}$  solutions of fulgides (14;  $R = \text{H}$ ) (A), (14;  $R = \text{Ph}$ ) (B), and (9;  $R^1 = R^2 = \text{Me}$ ) (C) in toluene at  $20^\circ$  after irradiation at 366 nm to the photo-stationary state

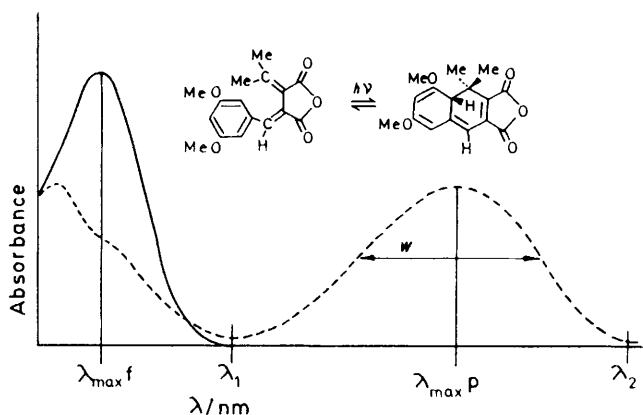


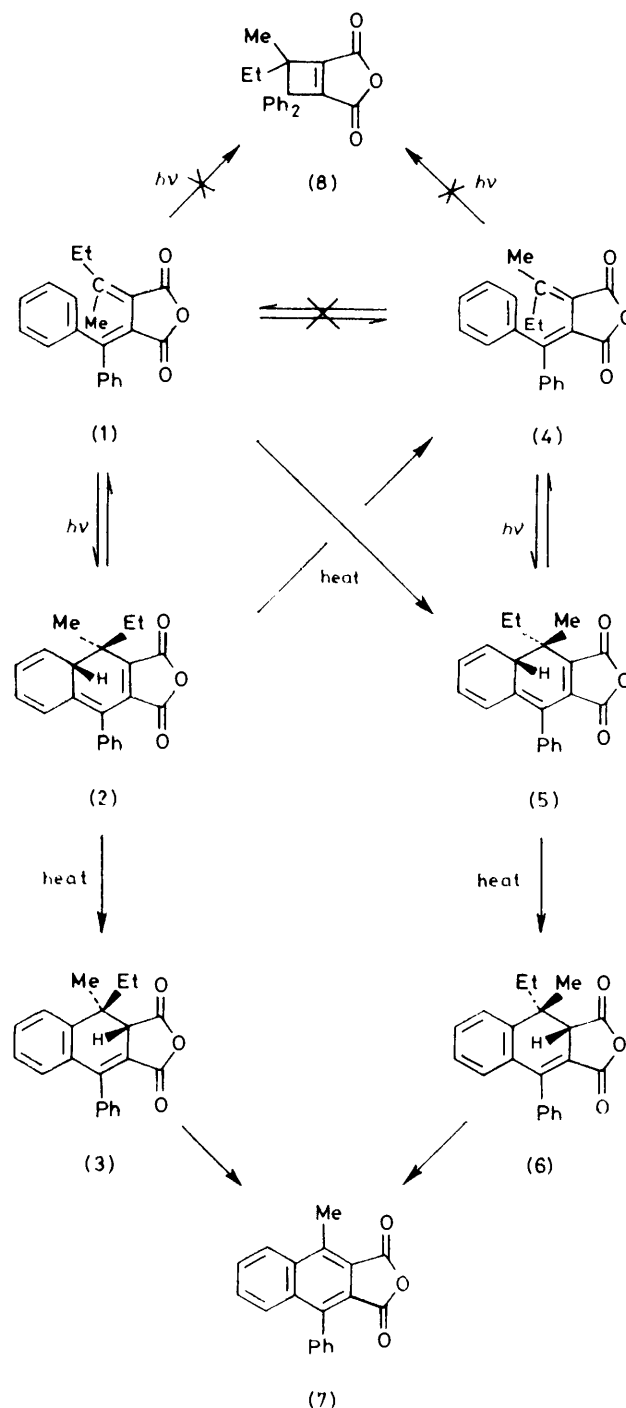
FIGURE 2 Absorption spectra of (*E*)-3,5-dimethoxybenzylidene-(1-methylethylidene)succinic anhydride (9;  $R^1 = R^2 = \text{Me}$ ) before and after irradiation at 366 nm showing the change in solvatochromic properties with solvent

Solvent	Permittivity (20 °C)	Fulgide		Photochrome			<i>W</i>
		$\lambda_{\max} f / \text{nm}$	$\log \epsilon$	$\lambda_1 / \text{nm}$	$\lambda_{\max} P / \text{nm}$	$\lambda_2 / \text{nm}$	
Methylcyclohexane	2.0	329	4.18	410	520	595	103
Carbon tetrachloride	2.2	332	4.07	412	525	608	100
Toluene	2.4	336	3.92	420	540	632	111
<i>o</i> -Dichlorobenzene	9.9	336	4.11	426	560	650	122

*W* = Full width at half maximum.

Fulgides (9) in the crystalline state or dissolved in organic solvents or plastic matrix undergo a pale yellow to purple or deep blue colour change on irradiation, the colour being reversed by white light. Solvatochromism, the solvent dependence of the position and intensity of absorption bands, is most pronounced in the case of organic molecules that can be described as resonance

hybrids that differ markedly in polarity.<sup>5,7</sup> Thus the blue 1,8a-DHNs (10) with resonance contribution (11)



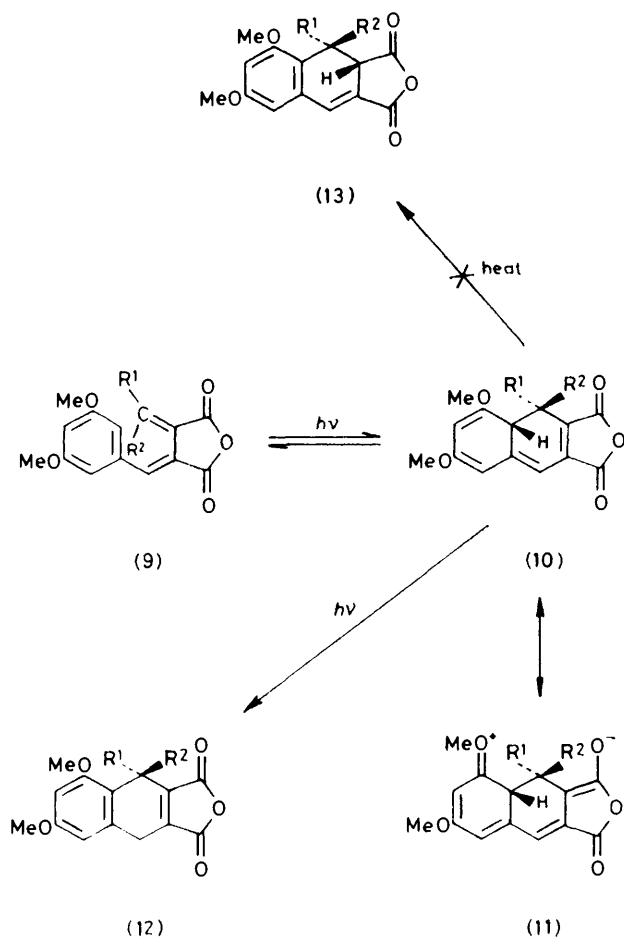
SCHEME 1

show marked solvent shifts (Figure 2) while the red 1,8a-DHNs (2), (5), and (15) lacking methoxy-substituents do not.

The blue 1,8a-DHNs (10) are resonance stabilised by

<sup>7</sup> W. Liptay, *Angew. Chem. Internat. Edn.*, 1969, **8**, 177.

the mesomeric effect of the 6- and 8-methoxy-substituents increasing the activation energy barrier for the 1,5-H shift reaction and, in addition, molecular models indicate that the 1,5-H shift is inhibited by molecular crowding between the 8-methoxy, the equatorial alkyl, and the

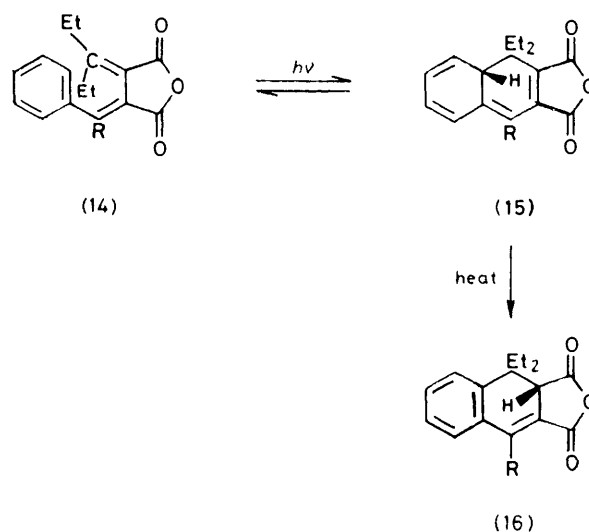


SCHEME 2

carbonyl groups and that thermal disrotatory ring opening is hindered by steric interactions between the equatorial alkyl and the 8-methoxy-groups. On prolonged irradiation at 366 nm, the blue 1,8a-DHNs (10) undergo a photochemical 1,7-H shift to give the near colourless 1,4-DHNs (12) quantitatively. This photo-rearrangement is not observed for the red 1,8a-DHNs (2), (5), and (15) because of the fast competing thermal 1,5-H shift reaction. Rates studies show that the red 1,8a-DHN (15; R = Ph) ( $k$   $240 \times 10^{-6} \text{ s}^{-1}$  at  $19^\circ \text{C}$ ) fades 58 times faster than the blue 1,8a-DHN (10;  $R^1 = R^2 = \text{Et}$ ) ( $k$   $4.13 \times 10^{-6} \text{ s}^{-1}$  at  $19^\circ \text{C}$ ) in toluene. The rate constant of the red 1,8a-DHN (15; R = H) could not be determined accurately because of its fast fade and the low concentration produced on irradiation of fulgide (14; R = H) to the photostationary state (see Figure 1). From the fade rates of the blue 1,8a-DHNs (10) in toluene measured from the change in absorbance at 545 nm with time, the activation energies for dis-

rotatory ring opening were calculated and found to be  $60 \pm 2$  (when  $R^1 = R^2 = \text{Me}$ ),  $78.5 \pm 3$  (when  $R^1 = R^2 = \text{Et}$ ), and  $79 \pm 9 \text{ kJ mol}^{-1}$  (when  $R^1 = \text{Et}$ ,  $R^2 = \text{Me}$ ). The rate constants from which these data were calculated are shown in Table 1.

It is usually difficult to determine accurately the extent of conversion of a photochromic compound into its coloured form and hence calculate the spectrum of the coloured form because of thermal instability and irreversible reactions which are usually associated with most photochromic systems.<sup>8</sup> The Fischer method<sup>9</sup> is applicable when (a) the system  $A \rightleftharpoons B$  is sufficiently thermally and photochemically stable to make possible the establishment of two true photostationary states on



SCHEME 3

TABLE I

Rate constants for disrotatory ring opening of blue 1,8a-DHNs(10) measured in toluene

$T/^\circ \text{C}$	$R^1 = R^2 = \text{Me}$		$R^1 = R^2 = \text{Et}$		$R^1 = \text{Et}$ $R^2 = \text{Me}$	
	$10^{-5}k/\text{s}^{-1}$	$t_{1/2}/\text{h}$	$10^{-5}k/\text{s}^{-1}$	$t_{1/2}/\text{h}$	$10^{-5}k/\text{s}^{-1}$	$t_{1/2}/\text{h}$
19			0.413	46.6	0.79	24.1
28	2.37	8.1	0.909	21.1	1.19	16.2
31	3.01	6.4	1.44	13.1	2.60	7.4
37	4.54	4.2	2.66	7.2		
38			3.08	6.3	4.47	4.3
49	14.7	1.7	7.79	2.5	1.48	1.3

irradiation at two different wavelengths, (b) the spectrum of A is known, and (c) the ratio of the quantum yields,  $Q_A (A \rightarrow B)/Q_B (B \rightarrow A)$ , does not differ for the two irradiating wavelengths. This method is well suited for determining the conversion of fulgides (9) into the corresponding blue 1,8a-DHNs (10). For example, on irradiation (at 334 and 366 nm) of a  $1.11 \times 10^{-4} \text{ M}$  solution of fulgide (9;  $R^1 = R^2 = \text{Et}$ ), A, in toluene at  $19^\circ \text{C}$ , the photostationary states were reached

<sup>8</sup> 'Photochromism,' ed. G. H. Brown, Wiley-Interscience, New York, 1971.

<sup>9</sup> E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704.

in under 2 min. White light reversal gave the spectrum of the fulgide unaltered indicating that an insignificant amount of photorearrangement takes place during the irradiation period, which is as expected since the rates of photochemical 1,7-H shift at 366 nm under irradiating conditions ( $1.55 \times 10^{-4} \text{ s}^{-1}$ ) and thermal ring opening ( $4.13 \times 10^{-6} \text{ s}^{-1}$ ) were slow compared to the rate of colouring. The conversion of fulgide (9;  $R^1 = R^2 = \text{Et}$ ), A, into the 1,8a-DHN (10;  $R^1 = R^2 = \text{Et}$ ), B, was found to be 62% using the Fisher equation (1) where

$$\alpha_2 = (\Delta_1/D_{A_1} - \Delta_2/D_{A_2})/[1 + \Delta_1/D_{A_1} - n(1 + \Delta_2/D_{A_2})] \quad (1)$$

$D_{A_1}$  is the absorbance of A at 366 nm prior to irradiation (0.66) and  $D_{A_2}$  is the absorbance of A at 334 nm prior to irradiation (1.25).  $D_1$  is the absorbance at 366 nm after irradiation at 366 nm (0.30),  $D_2$  is the absorbance at 334 nm after irradiation at 334 nm (0.74),  $D_{B_1}$  is the absorbance of B at 550 nm after irradiation at 366 nm (0.73),

calculated absorption spectrum for a  $1.11 \times 10^{-4} \text{ M}$  solution,  $\lambda_{\text{max}}$  550 nm ( $\epsilon$  10 900), is shown in Figure 3.

The stereochemistry of the described fulgides, 1,2-DHNs and 1,4-DHNs was determined by n.m.r. spectroscopy by analogy with previous work on related compounds.<sup>1,3,10</sup> In fulgides, an alkyl group *cis* to a carbonyl gives a signal at lower field than in the *trans* arrangement owing to the deshielding effect of the carbonyl in the former and the shielding effect of a phenyl or 3,5-dimethoxyphenyl in the latter. In 1,2-DHNs, the equatorial alkyl group is deshielded by a carbonyl and gives a signal at lower field than the axial alkyl group. In the symmetrical 1,4-DHNs, the two alkyl groups have the same chemical shift which appears at higher field than those of the equatorial alkyl groups of 1,2-DHNs because of the smaller deshielding effect of the carbonyl. The 1,4-DHN (12;  $R^1 = \text{Et}$ ,  $R^2 = \text{Me}$ ), obtained on irradiation of (*Z*)- and (*E*)-1-methylpropylidene-3,5-dimethoxybenzylidenesuccinic anhydrides (9;

TABLE 2  
Chemical shifts ( $\tau$ )

	R <sup>1</sup>	R <sup>2</sup>	R <sup>1</sup>		R <sup>2</sup>		
			CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub>	H-C-H	CH <sub>3</sub>
(a) Arylbismethylenesuccinic anhydrides (fulgides)							
(1)			7.23 (q)	8.97 (t)			8.72 (s)
(14; R = Ph)			7.18 (q)	8.94 (t)	8.26 (q)		9.37 (t)
(9)	CH <sub>3</sub>	CH <sub>3</sub>		7.55 (s)			8.34 (s)
	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	7.20 (q)	8.90 (t)			8.35 (s)
	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>		7.60 (s)	8.05 (q)		9.12 (t)
	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	7.16 (q)	8.89 (t)	8.06 (q)		9.20 (t)
(b) 1,2-DHNs							
(3)	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>		8.17 (s)	8.35 (m)		9.28 (t)
(6)	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	7.55 (m)	8.94 (t)			8.76 (s)
(16; R = Ph)	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	7.61 (m)	8.97 (t)	8.37 (m)		9.30 (t)
(c) 1,4-DHNs							
(12)	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub>	R <sup>1</sup>		H-C-H	
	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	6.20 (s)	8.25 (s)			
	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	6.23 (s)	8.24 (s)	7.41 (st)	7.92 (st)	9.55 (t)
	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	6.18 (s)		7.43 (st)	7.92 (st)	9.54 (t)

s = Singlet, t = triplet, J 7–8 Hz; q = quartet, J 7–8 Hz; m = multiplet; st = sextet.

$D_{B_2}$  is the absorbance of B at 550 nm after irradiation at 334 nm (0.59), and  $\Delta_1 = D_1 - D_{A_1}$ ,  $\Delta_2 = D_2 - D_{A_2}$ , and

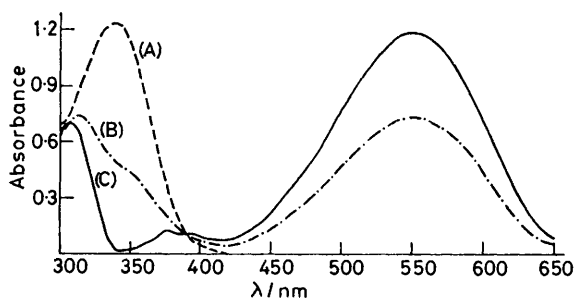


FIGURE 3 U.v. and visible spectrum of a  $1.11 \times 10^{-4} \text{ M}$  solution of (*E*)-3,5-dimethoxybenzylidene-(1-ethylpropylidene)succinic anhydride (9;  $R^1 = R^2 = \text{Et}$ ) in toluene before (A) and after irradiation at 366 nm to the photostationary state (B), and the spectrum (C) of the corresponding 1,8a-DHN (10;  $R^1 = R^2 = \text{Et}$ ), calculated using the Fisher method

$n = D_{B_2}/D_{B_1}$ . Thus  $\alpha_2 =$  extent of conversion at the photostationary state after irradiation at 366 nm. The

$R^1 = \text{Et}$ ,  $R^2 = \text{Me}$  and  $R^1 = \text{Me}$ ,  $R^2 = \text{Et}$ ) in toluene, showed the methylene absorptions of the ethyl group as a pair of sextets having a 14 Hz geminal and a 7 Hz vicinal coupling in the 220 MHz spectrum, confirmed by double resonance irradiation of the methyl triplet of the ethyl group when the two sextets collapsed to a pair of doublets. The different chemical shifts occur because the methylene hydrogens cannot have their positions interchanged by any symmetry operation, *i.e.* they are diastereotopic.

#### EXPERIMENTAL

U.v. spectra were measured in toluene (unless stated otherwise) on a Unicam SP 1700B spectrometer; n.m.r. spectra were obtained for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) or Varian HA 220 (220 MHz) spectrometer (tetramethylsilane as internal standard except when monitoring photochemical reactions, for which an external standard was used). Photoreactions were carried out for 0.1–0.5% w/v solutions of fulgides in 10 mm

<sup>10</sup> H. G. Heller and M. Szweczyk, *J.C.S. Perkin I*, 1974, 1483.

cells, stirred, and exposed to 366 nm radiation from a 250 W mercury discharge lamp (type ME/D, Thorn Lighting) with a filter (type OX1, Chance-Pilkington) focused on one side of the cell unless stated otherwise. Petroleum refers to the fraction b.p. 80—100° unless stated otherwise. The work-up of condensation reactions was described in detail earlier.<sup>10</sup>

Photoreactions were complete when the solutions which initially changed from pale yellow to red or blue, became colourless. Solvent was removed and product composition determined by n.m.r. spectroscopy.

(*Z*)-1-Methylpropylidene(diphenylmethylene)succinic Anhydride (1).—A mixture of diethyl succinate (174 g) and butan-2-one (58 g) was added dropwise to a stirred suspension of sodium hydride (48 g of a 60% dispersion in oil) in toluene (400 ml). After 12 h, the mixture was poured onto crushed ice and the aqueous layer separated and acidified with 5M-hydrochloric acid. The liberated half-ester<sup>11</sup> was esterified with hydrogen chloride in ethanol. The diesters (35 g), b.p. 108—110° at 0.5 mmHg, and benzophenone (32 g) was added to potassium *t*-butoxide [from potassium (14 g)] in *t*-butyl alcohol (320 ml) and boiled (1 h). Hydrolysis of the half-ester gave a mixture of diacids which were treated with acetyl chloride (200 ml). Fractional crystallisation of the oil from petroleum gave anhydride (1) (5 g) photochromic yellow needles, m.p. 147—148° (Found: C, 79.4; H, 5.8. C<sub>21</sub>H<sub>18</sub>O<sub>3</sub> requires C, 79.2; H, 5.7%), λ<sub>max.</sub> (benzene) 354 nm (log ε 3.96).

Rearrangement Reactions.—(a) The anhydride (1) (400 mg) was heated (14 h) in *o*-dichlorobenzene (30 ml). Work-up gave *t*-1-ethyl-1, *r*-2-dihydro-1-methyl-4-phenyl-naphthalene-2,3-dicarboxylic anhydride (6), needles [from petroleum (b.p. 100—120°)], m.p. 164—165° (Found: C, 79.3; H, 5.7. C<sub>21</sub>H<sub>18</sub>O<sub>3</sub> requires C, 79.2; H, 5.7%), λ<sub>max.</sub> (EtOH) 235 and 311 nm (log ε 4.10 and 4.03).

(b) The anhydride (1) (400 mg) in toluene (50 ml) at 60° was irradiated (20 h) at 366 nm until the red solution became colourless. The solvent was removed and *c*-1-ethyl-1, *r*-2-dihydro-1-methyl-4-phenyl-naphthalene-2,3-dicarboxylic anhydride (3) crystallised from petroleum, giving rods, m.p. 183—184° (Found: C, 79.4; H, 5.5%), λ<sub>max.</sub> (EtOH) 233 and 310 nm (log ε 4.18 and 4.05).

(c) Anhydride (1) (2 g) in benzene (500 ml) was irradiated (20 h) in a 11 Hanovia Photoreactor using a medium pressure lamp in a Pyrex glass thimble, *i.e.* with u.v. and white light. Pure anhydride (1) (1.8 g) was recovered and t.l.c. and n.m.r. studies on the residue showed only starting material.

(d) Anhydride (1) (100 mg) in benzene (15 ml) at 54 °C was irradiated (20 h) simultaneously with two 125 W medium pressure lamps (type MBW Thorn Lighting) having Wood's glass filters and two 100 W tungsten filament lamps in a reflecting aluminium housing. A quantitative recovery of starting compound was obtained showing no trace of rearrangement products in its n.m.r. spectrum.

(e) When photoreaction (b) was repeated (96 h) at 18 °C, an 85:15 mixture of the anhydrides (3) and (6) was obtained.

(f) Anhydride (1) (400 mg) was heated (18 h) at 205°. The product was chromatographed on silica gel using benzene as eluant. A blue fluorescent band gave 1-methyl-4-phenyl-naphthalene-2,3-dicarboxylic anhydride (7) (320 mg), plates (from acetic acid), m.p. 260° (Found: C, 79.0; H, 4.2. C<sub>19</sub>H<sub>23</sub>O<sub>3</sub> requires C, 79.1; H, 4.2%), λ<sub>max.</sub> (CHCl<sub>3</sub>) 268, 319, 350, and 366 nm (log ε 4.70, 3.88, 3.77, and 3.88), τ 1.5—2.9 (9 H, complex m, ArH) and 6.78 (3 H, s Me).

(g) A 1:1 mixture of anhydrides (3) and (6) (150 mg) were heated (4 h) at 205°. A quantitative yield of anhydride (7) was obtained.

Diphenylmethylene-(1-ethylpropylidene)succinic Anhydride (14; R = Ph).—Diethyl diphenylmethylenesuccinate (20 g), pentan-3-one (5 g), and potassium *t*-butoxide (6.5 g) in *t*-butyl alcohol heated for 1 h, gave an oil (20 g) which on trituration with petroleum gave a solid which was crystallised from chloroform-petroleum (b.p. 40—60°). Ethyl diphenylmethylenesuccinate (2.5 g) separated first. A second crop of crystals gave ethyl diphenylmethylene-(1-ethylpropylidene)succinate, rods, m.p. 133—134°. Hydrolysis of the latter (10 g) gave a diacid of which 3 g was taken and boiled with acetyl chloride (50 ml) for 30 min. Work-up gave the anhydride (14; R = Ph), pale yellow needles from chloroform-petroleum (b.p. 40—60°), m.p. 178—179°, (Found C, 79.15; H, 6.1. C<sub>22</sub>H<sub>20</sub>O<sub>3</sub> requires C, 79.5; H, 6.1%), λ<sub>max.</sub> 355 nm (log ε 3.95).

Photoreaction.—The anhydride (14; R = Ph) (50 mg) in CDCl<sub>3</sub> (0.5 ml) was irradiated (45 h) at 20°. Removal of solvent gave 1,2-dihydro-1,1-diethyl-4-phenyl-naphthalene-2,3-dicarboxylic anhydride (16; R = Ph), rods from petroleum, m.p. 169—171° (Found C, 79.6; H, 6.2. C<sub>22</sub>H<sub>20</sub>O<sub>3</sub> requires C, 79.5; H, 6.1%), λ<sub>max.</sub> 306 nm (log ε 3.91).

(*E*)-Benzylidene-(1-ethylpropylidene)succinic Anhydride (14; R = H).—Dimethyl (*E*)-benzylidenesuccinate (12 g), pentan-3-one, and potassium *t*-butoxide [from potassium (6 g)] in *t*-butyl alcohol (200 ml) heated for 20 min, gave an oil which was hydrolysed to the diacid. Treatment of the diacid (1 g) with acetyl chloride (10 ml) gave anhydride (14; R = H) as pale yellow prisms from ethanol, m.p. 144—146° (Found: C, 74.8; H, 6.25. C<sub>16</sub>H<sub>16</sub>O<sub>3</sub> requires C, 75.0; H, 6.3%), λ<sub>max.</sub> 330 nm (log ε 4.04).

(*E*)-3,5-Dimethoxybenzylidene-(1-methylethylidene)-succinic Anhydride (9; R<sup>1</sup> = R<sup>2</sup> = Me).—Diethyl isopropylidenesuccinate<sup>12</sup> (11.2 g), 3,5-dimethoxybenzaldehyde (8.3 g), and potassium *t*-butoxide (6 g) in *t*-butyl alcohol (70 ml) heated for 30 min, gave an oil which was hydrolysed to the diacid (6.2 g). The latter was boiled (1 h) with acetyl chloride (80 ml), and the resulting anhydride (9; R<sup>1</sup> = R<sup>2</sup> = Me) crystallised from toluene, giving yellow needles (3.3 g), m.p. 161—162° (Found: C, 66.7; H, 5.7. C<sub>16</sub>H<sub>16</sub>O<sub>5</sub> requires C, 66.7; H, 5.7%), λ<sub>max.</sub> 336 nm (log ε 3.92).

(*E*)-3,5-Dimethoxybenzylidene-(*Z*)-1-methylpropylidene-succinic Anhydride (9; R<sup>1</sup> = Et, R<sup>2</sup> = Me).—The mixture of diesters (from the condensation of butan-2-one with diethyl succinate) (10 g), 3,5-dimethoxybenzaldehyde (8.3 g), and potassium *t*-butoxide (5 g) in *t*-butyl alcohol (60 ml) heated for 30 min, gave an oil which was hydrolysed. The resulting diacid (7 g) was boiled (1 h) with acetyl chloride (80 ml) and solvent removed, leaving a 2:3 mixture of (*Z*) and (*E*)-1-methylpropylidene-(*E*)-3,5-dimethoxybenzylidenesuccinic anhydrides (9; R<sup>1</sup> = Et, R<sup>2</sup> = Me and R<sup>1</sup> = Me, R<sup>2</sup> = Et) respectively from which the (*Z,E*)-anhydride (9; R<sup>1</sup> = Et, R<sup>2</sup> = Me) was obtained pure by repeated recrystallisations from toluene, pale yellow needles, m.p. 165—166° (Found: C, 67.5; H, 6.0. C<sub>17</sub>H<sub>18</sub>O<sub>5</sub> requires C, 67.5; H, 6.0%), λ<sub>max.</sub> 347 nm (log ε 4.08). The (*E,E*)-isomer (9; R<sup>1</sup> = Me, R<sup>2</sup> = Et) could not be obtained free from the (*Z,E*)-anhydride.

(*E*)-3,5-Dimethoxybenzylidene-(1-ethylpropylidene)-succinic Anhydride (9; R<sup>1</sup> = R<sup>2</sup> = Et).—A mixture of

<sup>11</sup> H. Stobbe, *Annalen*, 1894, **282**, 301.

<sup>12</sup> C. G. Overberger and C. W. Roberts, *J. Amer. Chem. Soc.*, 1949, **71**, 3618.

dimethyl succinate (24 g), 3,5-dimethoxybenzaldehyde (27 g), and potassium t-butoxide (18 g) in t-butyl alcohol (250 ml) heated for 30 min, gave methyl (*E*)-3,5-dimethoxybenzylidenesuccinate (38 g, 85%). The diester (15 g), b.p. 188–194° at 2.5 mmHg, and pentan-3-one (5 g) were added to potassium t-butoxide [from potassium (2 g)] in t-butyl alcohol and heated (20 min). Hydrolysis of the half-ester gave a brown intractable oil which was triturated with ether. The ether extract was evaporated and the residual brown oil (0.5 g) boiled with acetyl chloride (10 ml) for 10 min. Work up gave the *anhydride* (9; R<sup>1</sup> = R<sup>2</sup> = Et), yellow plates from ethanol (0.1 g), m.p. 144–146° (Found: C, 68.6; H, 6.4. C<sub>18</sub>H<sub>20</sub>O<sub>5</sub> requires C, 68.3; H, 6.2%), λ<sub>max.</sub> (hexane) 262, 268, and 331 nm (log ε 4.02, 4.01, and 4.07); λ<sub>max.</sub> (toluene) 338 nm (log ε 4.12).

*Photoreactions.*—The anhydride (9; R<sup>1</sup> = R<sup>2</sup> = Me) (150 mg) in toluene (8 ml) at 54° was irradiated (14 h). The solution turned from pale yellow to dark blue and gradually became colourless. The n.m.r. spectrum of the product showed only the characteristic absorptions of 1,4-*dihydro*-1,1-*dimethyl*-6,8-*dimethoxynaphthalene*-2,3-*dicarboxylic anhydride* (12; R<sup>1</sup> = R<sup>2</sup> = Me), pale yellow prisms from chloroform-petroleum, m.p. 155–157° (Found: C, 66.6; H, 5.5. C<sub>16</sub>H<sub>16</sub>O<sub>5</sub> requires C, 66.7; H, 5.6%), λ<sub>max.</sub> (hexane) 230, 248sh, and 279 nm (log ε 3.75, 3.53, and 3.36). The anhydride (90 mg) in CDCl<sub>3</sub> (0.5 ml) at 12°, on irradiation

(24 h), gave the same product. A mixture of anhydrides (9; R<sup>1</sup> = Et, R<sup>2</sup> = Me and R<sup>1</sup> = Me, R<sup>2</sup> = Et) (50 mg) in CDCl<sub>3</sub> (0.5 ml) at 20° was irradiated (5 h) until the dark blue solution became colourless. The n.m.r. spectrum of the product showed only characteristic absorptions of 1,4-*dihydro*-1-*ethyl*-1-*methyl*-6,8-*dimethoxynaphthalene*-2,3-*dicarboxylic anhydride* (12; R<sup>1</sup> = Et, R<sup>2</sup> = Me), pale yellow flakes from chloroform-petroleum, m.p. 142–144° (Found: C, 67.1; H, 6.3. C<sub>17</sub>H<sub>18</sub>O<sub>5</sub> requires C, 67.5; H, 6.1%), λ<sub>max.</sub> (hexane) 228, 249, and 278 nm (log ε 3.84, 3.56, and 3.57). Irradiation (12 h) of these anhydrides (50 mg) in benzene (10 ml) at 54° gave the same product. The anhydride (9; R<sup>1</sup> = R<sup>2</sup> = Et) (56 mg) in toluene (2 ml) at 12° was irradiated (2 weeks) until the dark blue solution became colourless. The n.m.r. spectrum of the product showed only the characteristic absorptions of 1,4-*dihydro*-1,1-*diethyl*-6,8-*dimethoxynaphthalene*-2,3-*dicarboxylic anhydride* (12; R<sup>1</sup> = R<sup>2</sup> = Et) pale yellow rods from toluene-petroleum, m.p. 135° (Found: C, 68.4; H, 6.4. C<sub>18</sub>H<sub>20</sub>O<sub>5</sub> requires C, 68.3; H, 6.4%), λ<sub>max.</sub> (hexane) 250 and 282 nm (log ε 3.61 and 3.42).

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