

Photochromic Heterocyclic Fulgides. Part 2.¹ Electrocyclic Reactions of (*E*)- α -2,5-Dimethyl-3-furylethylidene(alkyl-substituted methylene)succinic Anhydrides

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The pale yellow title compounds undergo reversible photochemical conrotatory electrocyclic reactions to give in quantitative yields deep red 7,7a-dihydrobenzo[*b*]furan-5,6-dicarboxylic anhydrides, which are stable at 100 °C. These photochromic systems, which have high quantum yields for photocoloration, are highly resistant to photodegradation and retain their photochromic properties in a variety of solvents.

OUR studies on (*E*)- α -3-furylethylidene(isopropylidene)succinic anhydride have shown that its photochromic properties result from photocyclisation to the 7,7a-dihydrobenzofuran derivative (7,7a-DHBF), which undergoes the reverse process on exposure to white light. The 7,7a-DHBF, formed also by heating the succinic anhydride derivative above 100 °C, undergoes a suprafacial 1,5-H shift to the 6,7-DHBF at this temperature, as well as an acid-catalysed 1,3-H shift to the 4,7-DHBF.¹

We now report analogous electrocyclic reactions of the pale yellow (*E*)- α -2,5-dimethyl-3-furylethylidene(alkyl-substituted methylene)succinic anhydrides (fulgides) (1) and (4), which photocyclise on exposure to ultraviolet light to give thermally stable deep red 7,7a-DHBFs (2) and (3). The 7,7a-DHBFs (2) and (3) show the reverse process on exposure to white light.

RESULTS AND DISCUSSION

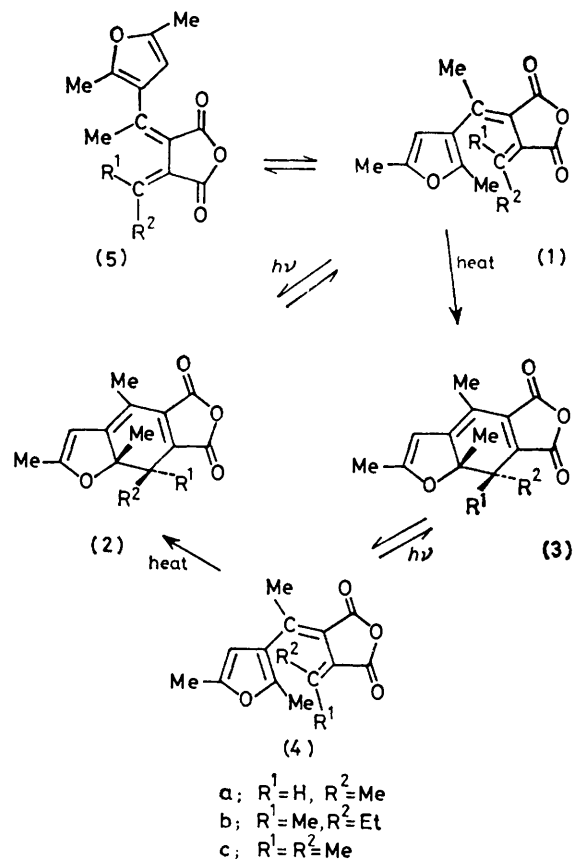
Unless stated otherwise, photoreactions and thermal reactions were carried out for 0.2M solutions of the fulgides in deuteriochloroform in sealed n.m.r. tubes, so that the progress of reactions, the composition of the reaction mixtures, and the structure and stereochemistry of products could be monitored by n.m.r. spectroscopy, as described in the previous paper.¹

The electrocyclic reactions occur in accord with the Woodward-Hoffmann selection rule for pericyclic reactions² and are exemplified by the rearrangements of (*E,Z*)-fulgide (1a), which shows exclusively photochemical conrotatory ring-closure on irradiation at 366 nm and disrotatory ring-closure on heating at 100 °C to give, quantitatively, the red *c*- and *t*-7-methyl-7,7a-DHBFs (2a) and (3a), respectively. The 7,7a-DHBFs (2a) and (3a) undergo conrotatory ring-opening on irradiation (546 nm).

Fulgide (1a) was obtained as one of the products from the Stobbe condensation of fluorenone with diethyl (*E*)- and (*Z*)- α -2,5-dimethyl-3-furylethylidenesuccinates in the presence of sodium ethoxide, followed by cyclisation of the resulting mixed diacids with acetyl chloride. Presumably, acetaldehyde is generated *in situ* by an Oppenauer-type oxidation³ of ethanol by fluorenone in the presence of base, which then condenses with the

succinic esters. This Stobbe reaction gives a number of products showing interesting rearrangements, and is the subject of a later paper.

Fulgide (1b) also undergoes conrotatory photocyclisation to give, in near-quantitative yield, *c*-7-ethyl-



7,7a-DHBF (2b). At no stage in the photoreaction can *t*-7-ethyl-7,7a-DHBF (3b) be detected by n.m.r. spectroscopy, though the spectra show that photoisomerisation of (*E,Z*)-fulgide (1b) to (*Z,Z*)-fulgide (5b) does occur. In due course, the photoequilibrium between the fulgides (1b) and (5b) is shifted in favour of the DHBF (2b). No isomerisation about the 1-methylpropylidene group occurs to give (*E,E*)-fulgide (4b)

under the irradiation conditions.⁴ On irradiation (546 nm), 7,7a-DHBF (2b) is converted quantitatively into (*E,Z*)-fulgide (1b).

When (*Z*)-fulgide (5c) is irradiated (366 nm), it isomerises to (*E*)-fulgide (1c), which in turn photocyclises, presumably in a conrotatory mode, to give 7,7a-DHBF (2c) in near-quantitative yield. The latter undergoes the reverse process quantitatively on exposure to white light.

While fulgides (1a) and (4a) cyclise to the corresponding DHBFs (2a) and (3a), respectively, on heating (k $2.7 \times 10^{-4} \text{ s}^{-1}$ and $3.3 \times 10^{-4} \text{ s}^{-1}$ at 70 °C in toluene, respectively), fulgides (1b) and (1c) do not show these inverse photochromic properties. On heating (25 h) at 180 °C, solutions of fulgides (1b) and (1c) turn red but the colour is not reversible on exposure to white light and is attributed to breakdown products. At an early stage, n.m.r. spectra of the solutions indicate that fulgides (1b) and (1c) thermally isomerise to isomers (5b) and (5c). As heating is continued, the spectra become too complex to interpret. From the position and multiplicity of peaks, it seems likely that the fulgides have undergone thermal 1,5-H shifts to give derivatives of penta- and hexa-1,3-diene-3,4-dicarboxylic anhydride derivatives.⁵

The resonance-stabilised 7,7a-DHBFs are thermally stable. They do not undergo thermal or acid-catalysed shifts of the 7a-methyl group, nor is there elimination of an alkane to give the fully aromatic benzofuran derivative. In addition, in 7,7a-DHBFs (2a), (2b), and (2c), thermal disrotatory ring-opening is prevented by steric interactions between the *cis* 7- and 7a-alkyl groups.

Solutions of fulgides (1a), (4a), (1b), and (1c) (10^{-4} —

10^{-5} M) in toluene undergo quantitative conversions into 7,7a-DHBFs (2a), (3a), (2b), and (2c), respectively, on irradiation at 334 nm, and at 366 nm. The spectra of fulgide (1a), fulgide (4a) [obtained by exposure of the thermally generated 7,7a-DHBF (3a) to green light] and 7,7a-DHBFs (2a) and (3a) ($2.2 \times 10^{-4} \text{ M}$ solutions in toluene), are shown in Figure 1. The quantum yields

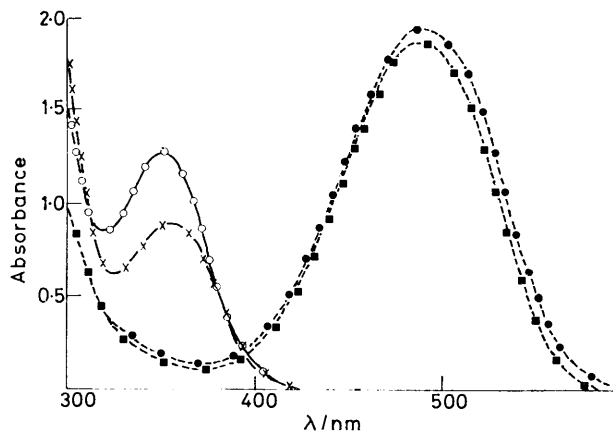


FIGURE 1 Absorption spectra of $2.2 \times 10^{-4} \text{ M}$ solutions of fulgides (1a) (×) and (4a) (○), and 7,7a-DHBFs (2a) (■) and (3a) (●) in toluene

for colouration at 366 nm for fulgides (1a) and (4a) were 0.4 and 0.36 respectively (determined by the Heller and Langan method of actinometry).⁶ The spectra of fulgide (1b) and its 7,7a-DHBF (2b) ($5.5 \times 10^{-5} \text{ M}$ solutions in toluene) are shown in Figure 2, and the spectra of fulgide (1c) and its 7,7a-DHBF (2c) ($9.8 \times 10^{-5} \text{ M}$ in hexane) are shown in Figure 3. In most organic photochromic systems, the photocoloured form absorbs strongly at the

TABLE 1

N.m.r. data for fulgides and 7,7a-DHBFs (τ values)

Fulgides	2-Me	3-H	5-Me	MeC=	R ¹	R ²	J/Hz
(1a)	7.89	4.11	7.70	7.42	3.48 (q)	7.70 (d)	7
(1b)	7.96	4.02	7.72	7.38	8.62	7.18 (d), 8.90 (t)	7.5
(1c)	7.98	4.02	7.72	7.40	8.60	7.63	
7,7a-DHBFs	2-Me	3-H	4-Me	7a-Me	R ¹	R ²	
(2a)	7.92	4.29	7.83	8.91	8.45 (d)	6.78 (q)	8
(3a)	7.96	4.40	7.87	8.62	8.96 (d)	6.88 (q)	7
(2b)	7.95	4.29	7.83	8.90 ^a	8.62 ^a	<i>b</i>	8
(2c)	7.94	4.40	7.83	8.89 ^a	8.67 ^a	8.90 (t) 8.42	

^a Arbitrary assignment. ^b Complex multiplet partially obscured by 2- and 5-Me absorptions.

TABLE 2

U.v. spectral data

Compound	Solvent	Permittivity (20 °C)	$\lambda_{\text{max.}}$ / nm	ϵ		$\lambda_{\text{min.}}$ / nm	ϵ		λ_2 / nm	W_1/W_2 / nm
				$\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$		$\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$		
(1a)	Toluene		356	4 024	373	444	(2a) 488	8 232	590	95
(4a)	Toluene		354	5 754	374	448	(3a) 491	8 684	595	97
(1b)	Toluene		342	6 497	380	576	(2b) 494	7 952	592	94
(1c)	Hexane	1.9	337	6 612	375	817	(2c) 473	8 189	567	83
	Toluene	2.4	343	6 077	378	309	494	8 200	595	92
	Ethyl acetate	6.0	341	5 940	375	495	494	7 874	600	91
	Butan-2-one	18.5	345	5 769	377	486	500	8 209	605	101
	Ethanol	24.3	346	5 915	380	606	502	8 038	605	99

activating wavelengths, so that the photocoloured form acts as an internal filter. The spectra show that the 7,7a-DHBFs have a low absorption in the region 300–400 nm and presumably a low quantum yield for photo-reversal at these wavelengths. This would explain the

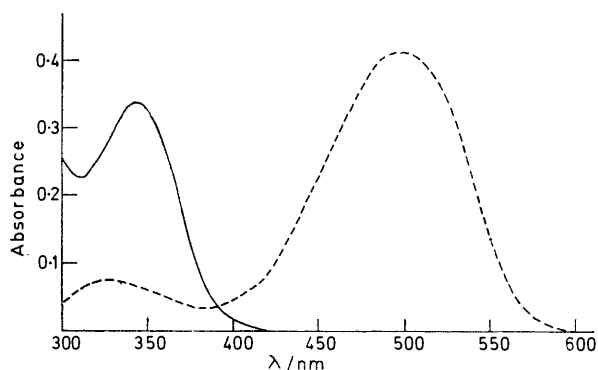


FIGURE 2 Absorption spectra of $5.5 \times 10^{-4} \text{M}$ solutions of fulgide (1b) (—) and 7,7a-DHBF (2b) (---) in toluene

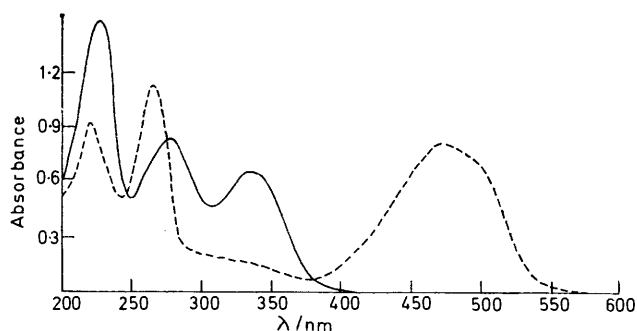


FIGURE 3 Absorption spectra of $9.8 \times 10^{-5} \text{M}$ solutions of fulgide (1c) (—) and 7,7a-DHBF (2c) (---) in hexane

linear response to near-ultraviolet radiation (up to 2% conversion) and the quantitative photocolouration. These properties, taken in conjunction with the high quantum yields for photocolouration of fulgides (1b) and (1c) in toluene (0.13 and 0.20 at 366 nm, respectively), the lower quantum yields for reversal [0.11 for (1a) and 0.06 for (1c) at 500 nm], the high resistance to photodegradation, complete thermal stability, and the retention of these properties in a wide range of organic solvents including hexane, ethanol, butan-2-one and ethyl acetate, make these and related photochromic heterocyclic fulgides ideally suited for use as re-usable chemical actinometers as well as for many commercial applications.^{6,7}

EXPERIMENTAL

3-Acetyl-2,5-dimethylfuran.—A solution of anhydrous tin(IV) chloride (226 g) in benzene (300 ml) was added during 5 h to a stirred solution of 2,5-dimethylfuran (85 g) and acetic anhydride (105 g) in benzene (1 l) maintained at 0 °C. After stirring for a further hour, the reaction mixture was poured onto crushed ice (1.5 kg) and 5M hydrochloric acid (500 ml). The benzene layer was separated, washed with water, dried, the solvent removed, and the residue

distilled, giving 2,5-dimethyl-3-acetylfuran (100 g, 82%), b.p. 58–62 °C/2 mmHg.

(E)- α -2,5-Dimethyl-3-furylethylidene-(Z)-1-methylpropylidenesuccinic Anhydride (1b).—The mixture of esters (23 g), obtained on condensation of butan-2-one with diethyl succinate followed by re-esterification, and 2,5-dimethyl-3-acetylfuran (14 g) was added dropwise to a stirred boiling solution of potassium t-butoxide (12 g) in t-butyl alcohol (250 ml) and boiled (30 min). The reaction mixture was cooled, acidified with 5M hydrochloric acid, and the solvent removed under reduced pressure. The residue was dissolved in ether, extracted with 1M sodium carbonate solution, and the aqueous layer carefully acidified. The liberated oil was extracted with ether, dried over anhydrous magnesium sulphate, filtered, and the ether removed. The residual yellow oil (30 g) was hydrolysed with 5% w/v ethanolic potassium hydroxide and the solid potassium salt (6.5 g) filtered off and acidified. The resulting diacids (4 g) were treated with acetyl chloride (30 ml) and solvent removed, leaving a red oil (3 g) which was chromatographed on silica gel using benzene-petroleum (1:1) as eluant. The photochromic fraction was evaporated and the residue crystallised from petroleum, giving *fulgide* (1b) as pale yellow cubes (100 mg), m.p. 95–97 °C (Found: C, 70.1; H, 6.5. $\text{C}_{16}\text{H}_{18}\text{O}_4$ requires C, 70.05; H, 6.6%).

(E)- and (Z)- α -2,5-Dimethyl-3-furylethylidene(isopropylidene)succinic Anhydride, (1c) and (5c).—A mixture of diethyl isopropylidenesuccinate (22 g, 0.1 mol) and 2,5-dimethyl-3-acetylfuran (14 g, 0.1 mol) was added to a stirred suspension of sodium hydride (10 g, 50% dispersion in oil, 0.2 mol) in toluene (200 ml) at 60 °C. A few drops of ethanol were added to initiate the exothermic reaction. When hydrogen evolution had ceased, the reaction mixture was cooled and poured onto crushed ice (200 g). The organic layer was separated and extracted twice with water (2×50 ml). The combined aqueous extract was acidified, the liberated oil extracted into toluene and the toluene solution washed with water and dried (MgSO_4). On removal of solvent, (E)- and (Z)-half-esters were obtained as a red gum (25 g, 82%), which was hydrolysed by boiling (5 h) with 5% w/v ethanolic potassium hydroxide solution (250 ml). Work-up gave an oil which produced an off-white solid of diacids (7 g, 31%) on digestion with toluene.

The diacids (7 g) were warmed (70 °C) with acetic anhydride (70 ml) until solution was complete. Removal of solvent left a red oil which was dissolved in toluene, washed with 1M sodium carbonate solution, and dried, leaving a red solid (5.5 g, 84%) after removal of toluene. Fractional crystallisation of the solid from chloroform and petroleum afforded a first crop of (Z)-*fulgide* (5c) as pale yellow cubes, m.p. 157–159 °C (Found: C, 69.3; H, 6.1. $\text{C}_{15}\text{H}_{14}\text{O}_4$ requires C, 69.2; H, 6.15%); λ_{max} , 354 nm ($\log \epsilon$ 3.89). Intermediate crops of crystals were mixtures of (E)- and (Z)-fulgides (1c) and (5c). (E)-*Fulgide* (1c) crystallised finally as pale yellow plates, m.p. 126–127 °C (Found: C, 69.5; H, 6.2%).

(E)- α -2,5-Dimethyl-3-furylethylidene-(Z)-ethylidene-succinic Anhydride (1a).—Condensation of 2,5-dimethyl-3-acetylfuran (70 g) with diethyl succinate (140 g), using sodium hydride in toluene gave, after work-up, half-esters as a brown oil (123 g), which were esterified by boiling with ethanol-benzene (3:1) (400 ml) containing concentrated hydrochloric acid (2 ml) in a flask fitted with a Dean and Stark apparatus to remove water as the ternary azeotrope. The resulting diesters were distilled, b.p. 135–138 °C/0.25

mmHg, and obtained as a yellow oil (52 g, 37%). The diester (1 g) and fluorenone (0.9 g) were added to sodium ethoxide [from sodium (0.2 g)] in ethanol (25 ml) and boiled (30 min). The sodium salts were filtered off, acidified, and the resulting diacids treated with acetyl chloride. Removal of the solvent left an oil which on crystallisation from petrol gave *fulgide* (1a), which was recrystallised from propan-2-ol as pale yellow crystals, m.p. 130 °C, giving a deep red melt (Found: C, 68.3; H, 5.4. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.7%).

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