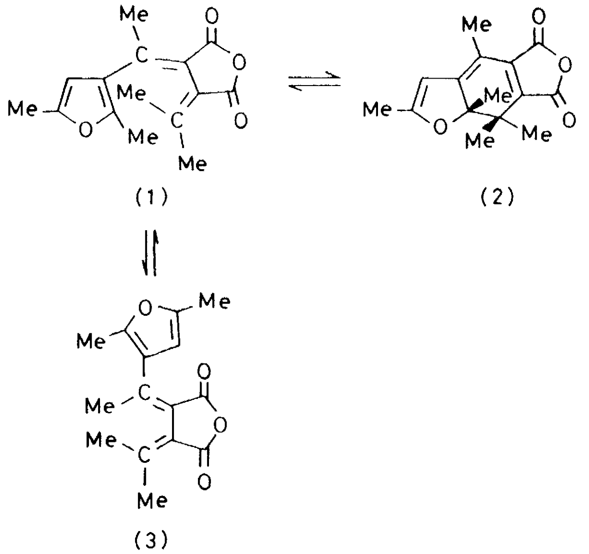
Photochromic Heterocyclic Fulgides. Part 3.[1] The Use of (*E*)-α-(2,5-Dimethyl-3-furylethylidene)(isopropylidene)succinic Anhydride as a Simple Convenient Chemical Actinometer

By **Harry G. Heller** * and **John R. Langan**, Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE

The thermally stable photochemically fatigue resistant title compound and its coloured form provide a photochromic system well suited for chemical actinometry in the near-u.v. and visible spectral regions. A solution of the photochromic compound in many common organic solvents can be used repeatedly and, provided the stirred solution absorbs all the incident radiation, the radiant flux can be determined simply by measuring an absorbance change.

THE pale yellow fulgide, (*E*)-α-(2,5-dimethyl-3-furylethylidene)(isopropylidene)succinic anhydride (1),[1] on irradiation in the region 313—366 nm in a wide range of common organic solvents, undergoes conrotatory ring-closure to give deep red 7,7a-dihydro-2,4,7,7,7a-pentamethylbenzo[*b*]furan-5,6-dicarboxylic anhydride (7,7a-DHBF) (2) in near quantitative yield. The reaction is reversed by white light. The photochromic system is highly resistent to photodegradation (including photo-oxidation) and is thermally stable below 100 °C.



The high quantum yield for photocolouration, the low, quantum yield for reversal, the ease of direct and accurate determination of the concentration of the 7,7a-DHBF (2) spectrometrically, the linearity of response of fulgide (1) to activating radiation, and the reuseability of the solution of the fulgide in a variety of solvents, makes this photochromic system well suited as a chemical actinometer in the near-u.v. and visible regions. This photochromic actinometer is much more convenient to use than actinometers based on other organic photoreactions[2] and has the advantage over the Parker ferrioxalate method[3,4] in that the accurate preparation of standard solutions and of a calibration graph is not required.

Determination of Radiant Flux.—An accurately measured volume (V) of a solution of fulgide (1) in toluene at a concentration sufficient to absorb all the incident radiation, is stirred in a cuvette (1 cm pathlength) and exposed to u.v. light in the region 313—366 nm for a measured time (t) and the increase in absorbance (ΔA) at 494 nm (the maximum of the long wavelength band of the 7,7a-DHBF (2)] is determined.

The radiant flux (I) can be calculated from expression (1) where N is the Avogadro number, 6.023×10^{23}

$$I = \frac{\Delta A.V.N}{\phi.\varepsilon.t} \text{ photons s}^{-1} \qquad (1)$$

mol^{-1}, ϕ is the quantum yield for photocolouration (0.20 for irradiation at 366 nm in toluene), and ε is in the molar extinction coefficient for the 7,7a-DHBF (8 200 at 494 nm for toluene solutions). Quantum yields for colouring at 366 nm in other solvents are given in Table 1.

TABLE 1

Effect of solvent on quantum yields for colouring. Molar extinction coefficients (ε) at the maximum of the long wavelength band ($\lambda_{max.}$) for 7,7a-DHBF (2)

Solvent	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}	$\phi_{1 \rightarrow 2}$ at 366 nm
Butan-2-one	500	8,209	0.20
Ethyl acetate	494	7.874	0.20
Ethanol	502	8,038	0.22
Hexane	473	8,189	0.21
Toluene	494	8,200	0.20

Determination of the Spectrum of 7,7a-DHBF (2).—On irradiation at 334 and at 366 nm, samples of a 9.067×10^{-5} mol dm^{-3} solution of fulgide (1) in toluene in 1 cm pathlength cuvettes showed the same maximum absorbance of 0.735 at 494 nm. When the absorbance change is independent of the wavelength of the activating radiation, the conclusion is that quantitative conversion into the coloured form (2) has occurred,[5] as in this case.[1]

To demonstrate that there were no errors due to sample impurities, in the weighing of samples or preparation of solutions, two batches, (a) and (b), of fulgide (1) were synthesised and purified separately and used to prepare standard solutions. Samples (3 cm^3) were irradiated until maximum photocolouration was attained. The molar extinction coefficient (ε) measured at 494 nm [the maximum of the long wavelength band of the 7,7a-DHBF (2)] was 8 200 $dm^3\ mol^{-1}\ cm^{-1}$ ($\pm 2\%$). Molar extinction coefficients at the maximum of the long wavelength band ($\lambda_{max.}$) of the 7,7a-DHBF (2) for five common solvents are shown in Table 1.

Determination of $\phi_{1\rightarrow 2}$ *at* 366, 334, *and* 313 *nm*.—Because of its wide usage, established reliability, and high sensitivity, the Parker ferrioxalate method [3,4,6,7] was used to determine the quantum yields for photocolouration of fulgide (1) in a variety of solvents.

The slope of the calibration curve for the measurement of absorbance at 510 nm of Fe^{2+} at different concentrations with 1,10-phenanthroline gave a molar extinction coefficient of 1.150 $dm^3\ mol^{-1}\ cm^{-1}$ (lit.,[7] 1.150 $dm^3\ mol^{-1}\ cm^{-1}$). The calculation of radiant flux (I) at 366, 334, and 313 nm was made using quantum yields of 1.26, 1.21, and 1.24, respectively, as determined in the ferrioxalate method by Parker and Hatchard.[4]

Quantum yields ($\phi_{1\rightarrow 2}$) for photocolouration at 366, 334, and 313 nm for a solution of fulgide (1) in toluene, using the Parker ferrioxalate method [3,4] and the electronically integrating actinometer of Schaffner *et al.*[8] are shown in Table 2. The quantum yield appears to be wavelength independent over the range 313—366 nm with an average value of 0.20 for toluene solutions. Quantum yields for five common solvents are given in Table 1.

TABLE 2

Quantum yields for photocolouration of fulgide (1) in toluene determined by Parker's method [3,4] and using the Schaffner actinometer [8]

λ/nm	Parker $\phi_{1\rightarrow 2}$	Schaffner $\phi_{1\rightarrow 2}$	$\phi_{1\rightarrow 2}$ Average
366	0.201	0.204	
	0.205	0.210	0.20
	0.199	0.196	
334	0.229	0.190	
	0.225	0.206	0.20
	0.182	0.191	
313	0.224	0.190	
	0.221	0.186	0.20
	0.192	0.192	

Quantum yields determined for nonstirred solutions were *ca.* 10% lower than for stirred solutions due to the internal filter effect of the 7,7a-DHBF (2), which occurs when the coloured form is allowed to concentrate at the surface of the cuvette exposed to the activating radiation.

Using the Schaffner method,[8] the quantum yield for reversal ($\phi_{2\rightarrow 1}$) at 500 nm was found to be 0.06 for toluene solutions of the 7,7a-DHBF (2).

Linear Response.—On irradiation at 313, 334, and 366 nm, of samples (3 cm^3) of a 5×10^{-3} mol dm^{-3} solution of fulgide (1) in toluene, the absorbance (ΔA) at $\lambda_{max.}$ 494 nm is directly proportional to the time of irradiation until concentrations of the 7,7a-DHBF (2) are greater than 1×10^{-4} mol dm^{-3} [*i.e.* when a 2% conversion ($\Delta A = 1$) has been attained]. The linear response is attributed to the low absorbance of the 7,7a-DHBF (2) in the near-u.v. region (see Figure 1) and a low quantum yield for reversal in this region.

Irradiation at 366 nm of fulgide (1) in toluene produced an absorbance change at 494 nm which is 30 times greater than is produced on irradiation of the *Z*-fulgide (3) under similar conditions, indicating that the quantum yields for $Z \longrightarrow E$ isomerisation in the near-u.v. region are low. Figure 2 shows that the linear response is unaffected by the intensity of radiation.

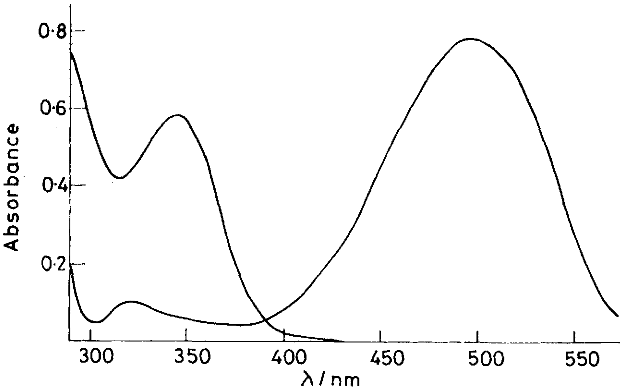


FIGURE 1 Absorption spectra of 1×10^{-4} mol dm^{-3} of fulgide (1) and 7,7a-DHBF (2) in toluene

Effect of Concentration of Fulgide (1) *on* $\phi_{1\rightarrow 2}$.—The quantum yield for photocolouration at 366 nm is independent of the concentration of fulgide (1) in toluene in concentrations up to 10^{-2} mol dm^{-3} and there are no significant errors from multiple reflections in cuvettes. Radiation (366 nm) was passed first into cuvette (a) and then into cuvette (b) placed behind it. When cuvette (a) was filled with solutions of fulgide (1) (3 cm^3) of various concentrations, which allowed transmission of part of the incident radiation through it into cuvette (b) [which contained a 1×10^{-2} mol dm^{-3} solutions of fulgide (1) (3 cm^3) in toluene], the combined absorbance changes ($A_a + A_b$) was the same for each experiment.

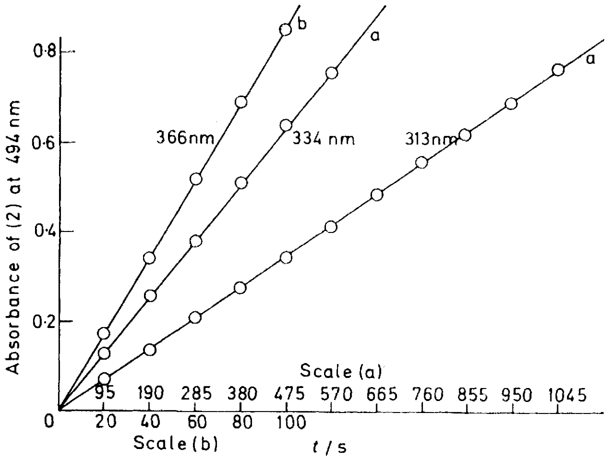


FIGURE 2 Linear response to photocolouration at 313, 334, and 366 nm of a 5×10^{-3} mol dm^{-3} solution of fulgide (1) in toluene. Time scales (a) and (b) are as indicated

When cuvette (a) was filled with toluene and cuvette (b) with a solution of fulgide (1) (3 cm^3), the absorbance of the solution in cuvette (b) was the same as for cuvette (a) when it was filled with the same solution (3 cm^3) and irradiated under similar conditions (see Table 3).

TABLE 3

Effect of reflectance from cell walls

c_1 = concentration of fulgide in toluene in cell 1
c_2 = concentration of fulgide in toluene in cell 2
a_1 = absorbance at 494 nm of solution in cell 1
a_2 = absorbance at 494 nm of solution in cell 2 after irradiation (100 s) at 366 nm

c_1/mol dm^{-3}	c_2/mol dm^{-3}	a_1	a_2	$a_1 + a_2$
4.8×10^{-4}	5×10^{-3}	0.233	0.011	0.244
8.0×10^{-5}	5×10^{-3}	0.113	0.128	0.241
0	5×10^{-3}	0	0.242	0.242

Effect of Temperature on the Quantum Yield for Photocolouration.—Quantum yields for photocolouration are shown to be temperature independent under ambient conditions. On irradiation (380 s) at 366 nm of a 5×10^{-3} mol dm^{-3} solution of fulgide (1) in toluene (3 cm^3) at temperatures ranging from 10 to 40 °C, the absorbance at 494 nm remained constant (0.93).

TABLE 4

Effect of 'cycling' on quantum yield. Irradiation at 366 nm (180 s) of a 5×10^{-3} mol dm^{-3} stirred solution of fulgide (1) in toluene. The solution was bleached using white light

Cycle 1	Absorbance at 494 nm	$\phi_{1 \rightarrow 2}$ at 366 nm
1	0.418	0.196
2	0.437	0.205
3	0.433	0.203
4	0.423	0.198
5	0.428	0.201

Effect of 'Cycling' on the Quantum Yield for Photocolouration.—Quantum yields for photocolouration (and presumably for photoreversal are unaffected by repeated successive irradiation of a solution of fulgide (1) in toluene with u.v. and with visible light. Table 4 shows that on irradiation (180s) at 366 nm of a 5×10^{-3} mol dm^{-3} solution of fulgide (1) in toluene (3 cm^3), the absorbance (ΔA) at 494 nm is constant (only the first five cycles are shown). Other experiments indicate that 30 000 cycles are possible without significant change in the quantum yields at 366 nm. On irradiation at 313 nm, a sample (3 cm^3) of a 6.07×10^{-5} mol dm^{-3} solution of fulgide (1) in toluene [$\lambda_{max.}$ 343 nm (ϵ 6 077)] in a 1 cm pathlength cuvette showed a maximum absorbance of 0.496 at 494 nm. This absorbance value decreased by 0.013 for each successive photocolouration cycle under similar irradiation conditions. The photodegradation (1.6×10^{-6} mol dm^{-3} per cycle for five cycles) does not affect the actinometry method when a 5×10^{-3} mol dm^{-3} solution of fulgide (1) in toluene is used. Photocolouration at 254 nm is accompanied by marked photodegradation and the use of the actinometer below 300 nm is not recommended.

We thank Shropshire County Council for a maintenance grant (to J. R. L.), the European Photochemical Association for a travel grant to carry out studies on the electronically integrating actinometer at the Department of Organic Chemistry of the University of Geneva, Professor K. Schaffner for the use of this facility, and Dr. W. Amrein and Dr. J. Gloor for their assistance.

[0/911 *Received*, 13*th June*, 1980]

REFERENCES

[1] Part 2, P. J. Davey, H. G. Heller, P. J. Strydom, and J. Whittall, *J. Chem. Soc. Perkin Trans. 1*, 1981, 202.

[2] G. F. Vesley and G. S. Hammond, *Mol. Photochem.*, 1973, **5**, 367; G. Gauglitz, *J. Photochem.*, 1976, **5**, 41; J. N. Pitts jun., G. W. Cowell, and D. R. Burley, *Curr. Res.*, 1968, **2**, 435; P. J. Wagner and E. Kemppainen, *J. Am. Chem. Soc.*, 1972, **94**, 7495; G. Zimmerman, L. Chow, and U. Paik, *ibid.*, 1958, **80**, 3528.

[3] C. A. Parker, *Proc. R. Soc.*, London, *Ser. A*, 1953, **220**, 104.

[4] C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.

[5] E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704.

[6] K. C. Kurien, *J. Chem. Soc.* (*B*), 1971, 2081.

[7] M. Wrighton and S. Witz, *Mol. Photochem.*, 1972, **3**, 387.

[8] W. Amrein, J. Gloor, and K. Schaffner, *Chimia*, 1974, **28**, 185.