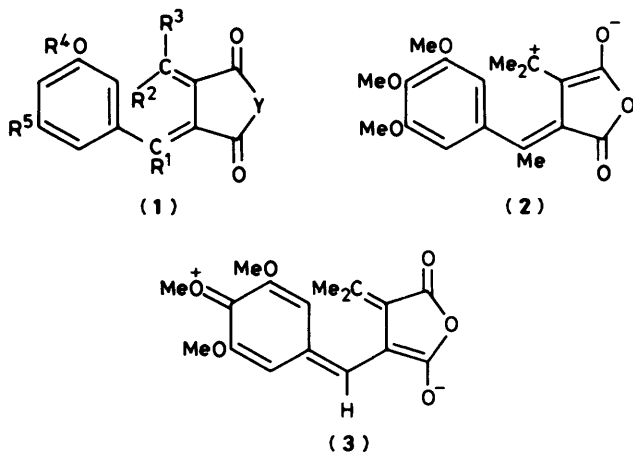


Photochromic Systems. Part 1. Photochemical Studies on (*E*)-2-Isopropylidene-3-[1-(3,4,5-trimethoxyphenyl)ethylidene]succinic Anhydride and Related Compounds.

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The title compound photocyclises to a deep blue solvatochromic 1,8a-dihydronaphthalene (1,8a-DHN), which undergoes a thermal 1,5-H shift to yield a colourless 1,2-DHN, in addition to thermal ring-opening. The rates of these competitive reactions have been determined by measuring the thermal fade rate of the corresponding 5,8a-dideuterio-1,8a-DHN, which does not show a thermal 1,5-D shift at ambient temperatures but only a photochemical 1,7-D shift. Its thermal fade is due solely to ring-opening. The corresponding imides show similar photochromic properties. An explanation is offered for the loss or the substantial reduction of photochromic properties in *ortho* or *para* substituted alkoxyphenylmethylene(substituted methylene)succinic anhydrides and imides.

Photochromism in fulgides¹ and fulgimides² is due to an electrocyclic reaction.³ Fulgides and fulgimides of the general formula (1), in which R² and R³ are the same or different alkyl groups or one of them is hydrogen, R⁴ is alkyl, R⁵ is a hydrogen or an alkyl or alkoxy group, and Y is oxygen, an imino group, or an imino group with an alkyl, phenyl, or substituted phenyl group, exhibit marked photochromic properties provided that:

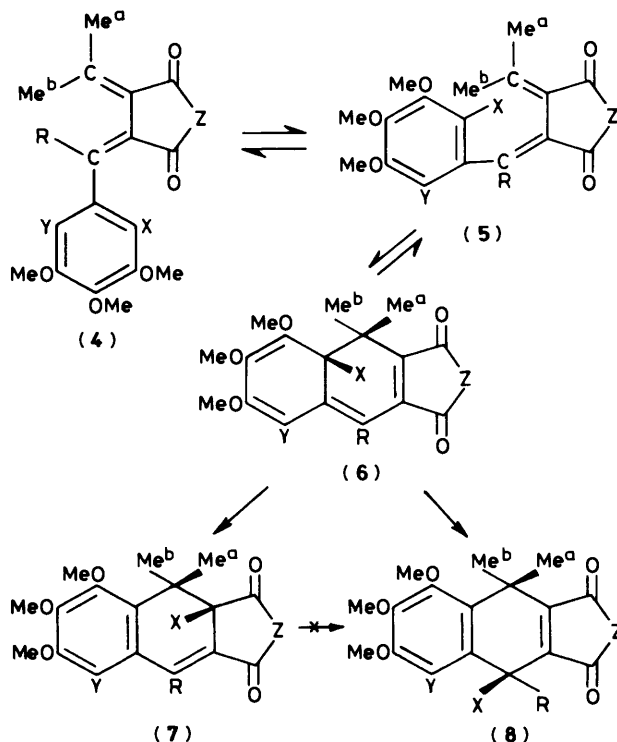


(a) there is no alkoxy group in the *ortho* or *para* position when R¹ is hydrogen, or (b) where there is an alkoxy group in the *ortho* or *para* position, R¹ is an alkyl or phenyl group but not hydrogen. From our own studies and from a literature survey,⁴ we have noted that fulgides are not photochromic or are only weakly photochromic, if R¹ is hydrogen and photocyclisation on to a phenyl group containing an *ortho* or *para* alkoxy substituent is required, irrespective of the nature of R² and R³ (See Table 1).

It is suggested that when R¹ in fulgides is an alkyl or an aryl group, there is a steric interaction between R¹ and the adjacent carbonyl group of the anhydride moiety which inhibits attainment of coplanarity of this α,β -unsaturated carbonyl chromophore, and results in excitation of the other α,β -

unsaturated carbonyl chromophore as the predominant photo-process [e.g. the dipolar structure (2) can be written to represent the excited state of fulgide (5; Z = O, R = Me, X = Y = H)], and hence in photocyclisation to a coloured 1,8a-DHN as the main photoreaction. When R¹ is hydrogen, coplanarity of this α,β -unsaturated carbonyl chromophore is more readily attained and if there is an *ortho* or *para* alkoxy substituent on the phenyl group, irradiation gives rise to an excited state which can be represented as a dipolar structure [e.g. (3), representing the excited state of fulgide (5; Z = O, R = X = Y = H)], leading to *E*-Z isomerisation as the only or main photoreaction.

The (*E*)-fulgide (5; Z = O, R = Me, X = Y = H) in toluene, on irradiation at 366 nm, photocyclises to the deep blue 1,8a-dihydronaphthalene intermediate (1,8a-DHN) (6; Z = O, R = Me, X = Y = H), which undergoes the reverse process on



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Table 1. The influence of substituent groups on photochromism in fulgides.

Ar ^a	R ¹	R ²	R ³	b	Ref.
<i>o</i> -MP	H	Me	Me	(-)	4
<i>p</i> -MP	H	Me	Me	(-)	4
<i>p</i> -MP	H	<i>p</i> -MP	H	(-)	4
P	H	Pip	H	(-)	4
3,4-DMP	H	3,4-DMP	H	(-)	4
3,4,5-TMP	H	Pip	H	(-)	4
3,4,5-TMP	H	3,4,5-TMP	H	(-)	4
2,5-DMP	H	Me	Me	(-)	
2,5-DMP	Me	Me	Me	(+)	
2,5-DMP	Me	Ph	H	(+)	
3,5-DMP	H	Me	Me	(+)	3
3,5-DMP	Me	Me	Me	(+)	
3,5-DMP	Me	4-MP	H	(+)	
2,3,4-DMP	H	Me	Me	(-)	
2,3,4-TMP	Me	Me	Me	(+)	
2,4,5-TMP	Me	Me	Me	(+)	

^a MP = methoxyphenyl; DMP = dimethoxyphenyl; TMP = trimethoxyphenyl; Pip = piperonyl. ^b (-) non-photochromic; (+) photochromic

exposure to white light. On prolonged irradiation (366 nm) of the fulgide (**5**; Z = O, R = Me, X = Y = H) in cold or boiling toluene, the solution becomes colourless and the 1,2-DHN (**7**; Z = O, R = Me, X = Y = H) is obtained in quantitative yield. The 1,2-DHN (**7**; Z = O, R = Me, X = Y = H) shows neither a photochemical nor an acid-catalysed rearrangement. While the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H) in toluene fades by first-order kinetics, its fade rate (k_1) is due to two thermal processes, namely disrotatory ring opening and a 1,5-H shift. It was expected that the replacement of the 8a-hydrogen by deuterium in the 1,8a-DHN (**6**; Z = O, R = Me, X = D, Y = H or D) would cause the 1,5-shift reaction to become so slow compared to the ring-opening process that the thermal fade of the 1,8a-DHN (**6**; Z = O, R = Me, X = D, Y = H or D) in toluene would be due exclusively to disrotatory ring-opening. This proved to be the case. By measuring the rate constant (k_2) for the fade of the 1,8a-DHNs (**6**; Z = O, R = Me, X = D, Y = X or D), the rate constant (k_3) for the 1,5-H shift in the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H) $k_3 = k_1 - k_2$ together with the activation energy for the process could be calculated. The expectation was based on the reports that deuterium primary kinetic isotope effects exhibit typical k_H/k_D values of 5–8 at 25 °C,⁵ with values as high as 24 having been recorded.⁶

The (*E*)-2,6-dideuteriofulgide (**5**; Z = O, R = Me, X = Y = D) was synthesized as described in the Experimental section. The deuteriated product had an isotopic purity of 80%, based on n.m.r. studies (*i.e.* by measuring the integral of the aromatic signal against the integral of the methyl signals). Mass spectral data indicated a near statistical distribution of (*E*)-dideuteriofulgide (**5**; Z = O, R = Me, X = Y = D) (62.6%), (*E*)-monodeuteriofulgide (**5**; Z = O, R = Me, X = H, Y = D) (33%) and (*E*)-fulgide (**5**; Z = O, R = Me, X = Y = H) (4.4%).

After prolonged irradiation (366 nm) in deuteriochloroform, the (*E*)-dideuteriofulgide (**5**; Z = O, R = Me, X = Y = D) gave the (*Z*)-fulgide (**4**; Z = O, R = Me, X = Y = D) and the 4,5-dideuterio-1,4-DHN (**8**; Z = O, R = Me, X = Y = D) [resulting from a photochemical 1,7-D-shift in the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = D)] as the sole products detectable by n.m.r. spectroscopy. Under similar conditions, the (*E*)-fulgide (**5**; Z = O, R = Me, X = Y = H) gave the 1,2-DHN (**7**; Z = O, R = Me, X = Y = H) [*via* a thermal 1,5-H shift in the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H)] and the

Table 2. Rate constants (k_3) for the 1,5-H shift in the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H)^a

Temp (°C)	k_1 ^b /s ⁻¹	k_2 ^b /s ⁻¹	k_3 ^b /s ⁻¹
16	39.56	2.84	36.72
21.5	51.20	3.94	47.26
26.3	62.85	4.42	58.43
30.3	71.96	5.09	66.87
35	93.80	9.27	84.54
39	111.40	12.48	98.92

^a Calculated from its fade rate (k_1) and that of its 8a-deuterio derivatives (**6**; Z = O, R = Me, X = D, Y = H or D), (k_2) for solutions in toluene.

^b Values $\times 10^{-6}$.

1,4-DHN (**8**; Z = O, R = Me, X = Y = H) [*via* a photochemical 1,7-H shift in the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H)]. The (*E*)-2-deuteriofulgide (**5**; Z = O, R = Me, X = H, Y = D) would be expected to show the same photorearrangements as the (*E*)-fulgide (**5**; Z = O, R = Me, X = Y = H) *via* the 1,8a-DHN (**6**; Z = O, R = Me, X = H, Y = D) and as the (*E*)-dideuteriofulgide (**5**; Z = O, R = Me, X = Y = D) *via* the 1,8a-DHN (**6**; Z = O, R = Me, X = D, Y = H). Unfortunately the presence or absence of mono-deuterio compounds in the presence of dideuterio and non-deuteriated compounds could not be established by n.m.r. studies.

The fade rates of the 8a-deuterio-1,8a-DHNs (**6**; Z = O, R = Me, X = D, Y = H or D) and of the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H) in toluene were measured by monitoring the change in absorbance at 546 nm with time. Since the isotopic purity of the 8a-deuterio-1,8a-DHNs (**6**; Z = O, R = Me, X = D, Y = H or D) was only 80%, 20% of the blue 1,8a-DHNs was allowed to disappear before rate measurements were made. In this way, all the blue colour due to the much faster fading 1,8a-DHN impurities (**6**; Z = O, R = Me, X = H, Y = H or D) was removed and the fade rate of the 5,8a-dideuterio-1,8a-DHNs (**6**; Z = O, R = Me, X = D, Y = H or D) could be determined. The marked differences in the fade rates of the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H) and its 8a-deuterio derivatives (**6**; Z = O, R = Me, X = D, Y = H or D), k_1 and k_2 respectively, are shown in Table 1. From the rate constants (k_3), the activation energy for the 1,5-H shift process has been calculated to be 33 kJ mol⁻¹.

While the yellow (*E*)-fulgide (**5**; Z = O, R = Me, X = Y = H), as crystallites impregnated into filter paper or dissolved in common organic solvents or in a plastic matrix, shows a rapid reversible colour change (usually to deep blue) when irradiated at 366 nm (see Figure 1 and Table 3), the orange (*E*)-fulgide (**5**; Z = O, R = X = Y = H) is only very weakly photochromic in the crystalline state or in toluene (see Figure 2). When the (*E*)-fulgide (**5**; Z = O, R = X = Y = H) in toluene was irradiated continuously at 366 nm for 3 weeks, the (*Z*)-fulgide (**4**; Z = O, R = X = Y = H) and the 1,4-DHN (**8**; Z = O, R = X = Y = H) were the only photoproducts, indicating that the observed rapid thermal fade of the purple 1,8a-DHN (**6**; Z = O, R = X = Y = H) was due to ring-opening and not to the 1,5-H shift reaction which occurs in the 1,8a-DHN (**6**; Z = O, R = Me, X = Y = H). The 1,4-DHN (**8**; Z = O, R = X = Y = H) is formed *via* a photochemical 1,7-H shift in the 1,8a-DHN (**6**; Z = O, R = X = Y = H).

In deuteriochloroform, the slight change in the orange colour which occurs on exposure to u.v. light and which cannot be reversed by white light, is due to photoisomerisation to the (*Z*)-fulgide (**4**; Z = O, R = X = Y = H). When the (*E*)-fulgide (**5**; Z = O, R = X = Y = H) in deuteriochloroform at 13 °C is irradiated at 366 nm for 12 days, the 1,4-DHN (**8**; Z = O,

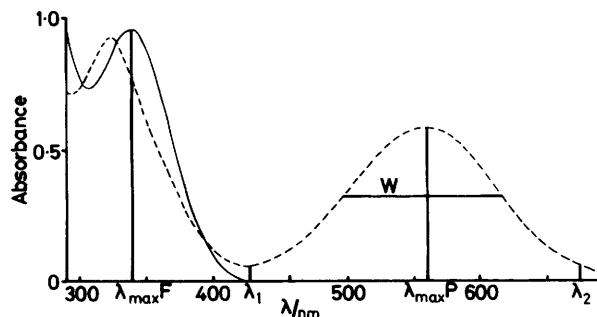


Figure 1. Absorption spectra of a 1.46×10^{-4} M solution of (*E*)-2-isopropylidene-3-[1-(3,4,5-trimethoxyphenyl)ethylidene]succinic anhydride (**5**; $Z = O$, $R = \text{Me}$, $X = Y = \text{H}$) in toluene prior to irradiation (—) and showing maximum colouration after irradiation at 366 nm for 3 min (---). Table 3 illustrates solvatochromic properties.

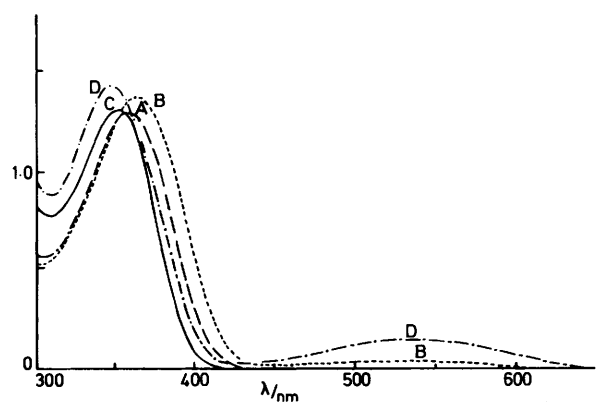


Figure 2. Absorption spectra of 10^{-4} M solutions of the fulgide (**5**; $Z = O$, $R = X = Y = \text{H}$) and the fulgimide (**5**; $Z = \text{NPh}$, $R = X = Y = \text{H}$) in toluene prior to irradiation [(A) and (C) respectively] and showing maximum colouration after irradiation at 366 nm for 24 min [(B) and (D) respectively].

$R = X = Y = \text{H}$) is obtained in 45% yield, admixed with the (*E*)- and (*Z*)-fulgides (**5** and **4**; $Z = O$, $R = X = Y = \text{H}$) in 20 and 35% yields, respectively (determined by n.m.r. spectroscopy). While no purple colouration due to the 1,8a-DHN (**6**; $Z = O$, $R = X = Y = \text{H}$) can be detected either visually or spectroscopically, the 1,4-DHN (**8**; $Z = O$, $R = X = Y = \text{H}$) can only be formed through this intermediate.

Fulgides are more highly coloured than their corresponding fulgimides.⁷ The (*E*)-fulgimides (**5**; $Z = \text{NH}$, NMe , NPh , *N-p*-tolyl, and *N-p*- MeOC_6H_4 , $R = \text{Me}$, $X = \text{H}$) show hypsochromic shifts of their long wavelength absorption bands compared to the corresponding (*E*)-fulgide (**5**; $Z = O$, $R = \text{Me}$, $X = Y = \text{H}$) but all their corresponding 1,8a-DHNs (**6**; $R = \text{Me}$, $X = Y = \text{H}$) are blue with absorption bands extending from ca. 430 to 700 nm. The (*E*)-fulgimide (**5**; $Z = \text{NH}$, $R = \text{Me}$, $X = Y = \text{H}$) in toluene is converted quantitatively into the 1,2-DHN (**7**; $Z = \text{NH}$, $R = \text{Me}$, $X = Y = \text{H}$) on irradiation at 366 nm until the deep blue solution becomes colourless.

In contrast, the (*E*)-fulgimide (**5**; $Z = \text{NPh}$, $R = X = Y = \text{H}$), like the (*E*)-fulgide (**5**; $Z = O$, $R = X = Y = \text{H}$) is only weakly photochromic (see Figure 2) with a slow colouring response. On continuous irradiation at 366 nm for 3 weeks, it gave a small amount of the 1,4-DHN (**8**; $Z = \text{NPh}$, $R = X = Y = \text{H}$) via the 1,8a-DHN (**6**; $Z = \text{NPh}$, $R = X = Y = \text{H}$), admixed with the (*Z*)-fulgide (**4**; $Z = \text{NPh}$, $R = X = Y = \text{H}$)

Table 3.

Solvent	Permittivity (20 °C)	Fulgide		1,8a-DHN			W
		$\lambda_{\text{max}}/\text{nm}$	$\log \epsilon$	λ_1/nm	$\lambda_{\text{max}}/\text{nm}$	λ_2/nm	
CCl_4	2.2	340	3.90	427	550	650	111
PhMe	2.4	341	3.81	427	560	676	120
PhCl	5.7	342	3.86	434	570	692	125
CH_2Cl_2	9.1	340	4.01	432	582	710	133

W = Full width at half maximum.

and unchanged reactant. The 1,2-DHN (**7**; $Z = \text{NPh}$, $R = X = Y = \text{H}$) could not be detected in the crude photoproduct by n.m.r. spectroscopy. N.m.r. data for fulgides, fulgimides, and their rearrangement products, (DHNs) are given in Table 4.

Experimental

Reactions were carried out under anhydrous conditions using freshly distilled or recrystallised reagents. Toluene was dried over sodium wire, *t*-butyl alcohol was distilled from calcium hydride, and deuteriochloroform (99.8% isotopic purity) was boiled with and distilled from Na_2CO_3 . Extracts were dried over anhydrous MgSO_4 and filtered. Petroleum refers to the light petroleum fraction of b.p. 80–100 °C.

U.v. and visible spectra were measured in toluene (unless stated otherwise) on a Unicam SP8-200 spectrometer, which was also used for the kinetics studies using a thermostatted cell housing; 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). The mass spectra were measured on an AEI MS30 Double Beam Mass Spectrometer. Photochemical reactions in toluene were carried out in small round-bottomed flasks, 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). Photoreactions in deuteriochloroform were carried out in n.m.r. tubes with the above light source focussed onto the solution which was shaken occasionally.

(*Z*)- and (*E*)-2-Isopropylidene-3-[1-(3,4,5-trimethoxyphenyl)ethylidene]succinic Anhydrides (**4**) and (**5**) ($Z = O$, $R = \text{Me}$, $X = Y = \text{H}$).—A mixture of 3,4,5-trimethoxyacetophenone (52.5 g, 0.4 mol) and diethyl isopropylidenesuccinate⁹ (55 g, 0.27 mol) in *t*-butyl alcohol (100 cm^3) was added dropwise to a boiling solution of potassium *t*-butoxide (28 g, 0.25 mol) in *t*-butyl alcohol (200 cm^3). When the addition was complete, the mixture was boiled (5 h). The solvent was removed under reduced pressure by means of a rotatory evaporator and the residue was dissolved in water (300 cm^3) and extracted with toluene. The aqueous solution was acidified with 5M hydrochloric acid and the liberated oil was extracted with toluene. The toluene extracted was dried and the solvent removed, leaving half esters (78 g), which were hydrolysed by boiling (5 h) with 10% (w/v) ethanolic potassium hydroxide. Ethanol was removed and the residue was dissolved in water, and acidified with 5M-hydrochloric acid. The liberated mixture of *E/Z* diacids (44 g) was boiled (1 h) with acetyl chloride (400 cm^3) and the excess of reagent was removed under reduced pressure. The residual (*E*)- and (*Z*)-fulgides (30 g) were fractionally crystallised from dichloromethane–petroleum. (*Z*)-2-Isopropylidene-3-[1-(3,4,5-trimethoxyphenyl)ethylidene]succinic anhydride (**4**; $Z = O$, $R = \text{Me}$, $X = Y = \text{H}$) separated out first as pale yellow crystals, m.p. 149 °C, after recrystallisation (Found:

Table 4. N.m.r. data of fulgides, fulgimides, and their rearrangement products, DHNs (δ values)

Compd.	Z	R	X,Y	ArH	Methine	J/Hz	R	J/Hz	Me ^{a,d}	Me ^{b,d}	OMe		
4	O	H	H	6.32			7.18		2.57 ^b	2.39 ^b	3.91	3.91	3.91
4	O	Me	H	6.56			2.07		2.47 ^b	2.22 ^b	3.85	3.85	3.90
5	O	H	H	6.65			7.66		2.45	1.74	3.93	3.83	3.92
5	O	Me	H	6.57			2.27		2.73	1.28	3.82	3.82	3.90
5	NPh	H	H	6.75			7.67		2.49	1.71	3.88	3.88	3.95
5	NM	Me	H	6.57			2.22		2.72	1.19	3.82	3.82	3.88
5	NMe	Me	H	6.54			2.24		2.74	1.18	3.83	3.83	3.89
5	NPh	Me	H	6.63			2.28		2.78	1.26	3.85	3.85	3.91
5	<i>N-p</i> -tolyl	Me	H	6.63			2.27		2.77	1.25	3.85	3.85	3.90
5	<i>N-p</i> -MeOC ₆ H ₄	Me	H	6.56			2.28		2.75	1.28	3.82	3.82	3.90
7	O	Me	H	6.90	3.62q	3	2.64d	3	2.03	1.15	3.95	3.95	3.95
7	NH	Me	H	6.89	3.34q	3	2.63d	3	2.04	1.13	3.92	3.92	3.92
8	O	H	H	6.50	3.76		3.76		1.76	1.76	3.87	3.87	4.01
8	O	Me	H	6.61	<i>a</i>		1.57d	8	1.78 ^b	1.80 ^b	3.92	3.94	4.08

^a Obscured by methoxy absorptions. ^b Arbitrary assignments. ^c d = Doublet, q = quartet. ^d Me^a is deshielded by the adjacent carbonyl group in fulgides and 1,2-DHNS; Me^b is shielded by the phenyl group in (*E*)-fulgides and is outside the deshielding zone of the adjacent carbonyl in 1,2-DHNS⁸.

C, 65.1; H, 6.1. C₁₈H₂₀O₆ requires C, 65.05; H, 6.1%); λ_{\max} , 338 nm (log ϵ 4.01). The intermediate crop of crystals was (*E*)-2-isopropylidene-3-[1-(3,4,5-trimethoxyphenyl)ethylidene]succinic anhydride (**5**; Z = O, R = Me, X = Y = H), obtained as yellow cubes, m.p. 139 °C, after crystallisation (Found: C, 65.0; H, 6.0); λ_{\max} , 341 nm (log ϵ 3.81).

Photorearrangement Reactions.—(a) The (*E*)-fulgide (**5**; Z = O, R = Me, X = Y = H) (350 mg) in toluene (50 cm³) at 13 or 110 °C was irradiated at 366 nm until the deep blue solution became colourless. 1,2-DHN (**7**; Z = O, R = Me, X = Y = H) was obtained in quantitative yield as pale yellow crystals (from toluene), m.p. 208–209 °C (Found: C, 65.0; H, 6.1%); λ_{\max} , 322 nm (log ϵ 4.12).

(b) The (*E*)-fulgide (**5**; Z = O, R = Me, X = Y = H) (85 mg) in CDCl₃ at 13 °C was irradiated at 366 nm until the blue solution became colourless. The n.m.r. spectrum showed a 13:87 mixture of 1,2-DHN (**7**; Z = O, R = Me, X = Y = H) and 1,4-DHN (**8**; Y = O, R = Me, X = H). On addition of petroleum (0.5 cm³), the 1,4-DHN (**8**; Y = O, R = Me, X = H) separated and gave colourless prisms, m.p. 128–130 °C (from chloroform–petroleum) (Found: C, 64.85; H, 6.2%); λ_{\max} (hexane) 248, 268, and 310 nm (log ϵ 3.58, 3.42, and 3.06).

2,6-Dibromo-3,4,5-trimethoxybenzoic Acid.—Potassium carbonate (13.8 g, 0.1 mol) was dissolved in acetic acid (250 cm³), followed by 3,4,5-trimethoxybenzoic acid (21.2 g, 0.1 mol). A solution of bromine (35.2 g, 2.2 mol) in acetic acid (50 cm³) was added dropwise over 45 min. The mixture was stirred and boiled (3 h), cooled, poured into water, and extracted with ether. The ether extract was dried and the solvent removed. Recrystallisation of the residue from ether–petroleum gave the dibromo acid as colourless needles, m.p. 145–146 °C (lit.,¹⁰ m.p. 145–146 °C).

2,6-Dideuterio-3,4,5-trimethoxybenzoic Acid.—Zinc powder (28 g) was added to a mixture of acetic anhydride (13 cm³) and D₂O (99.7% isotopic purity) (50 cm³) followed by the dibromo acid (10 g). The mixture was stirred vigorously and boiled for 6 days, cooled, and filtered. The residue and the filtrate were extracted with chloroform. The combined extracts were washed with water, dried, and concentrated and a small amount of petroleum was added. 2,6-Dideuterio-3,4,5-trimethoxybenzoic acid¹¹ separated as colourless crystals (72%), m.p. 172–173 °C.

2,6-Dideuterio-3,4,5-trimethoxyacetophenone.—An ethereal solution of methyl-lithium (1.4M; 80 cm³) was added slowly to the 2,6-dideuterio-acid (6.75 g, 0.315 mol) in anhydrous dioxane under nitrogen. The reaction mixture was boiled (4 h), cooled, and poured with stirring onto a mixture of ice, water, and hydrochloric acid. The mixture was extracted with ether and the ether extract washed with aqueous sodium carbonate. The ether layer was dried and solvent removed to leave a solid which crystallised from dichloromethane–petroleum to give 2,6-dideuterio-3,4,5-trimethoxyacetophenone as colourless crystals, (46% yield) with an isotopic purity of ca. 80% as determined by n.m.r. spectroscopy.

(*Z*)- and (*E*)-2-Isopropylidene-3-[1-(2,6-dideuterio-3,4,5-trimethoxyphenyl)ethylidene]succinic anhydrides (**4**) and (**5**) (Z = O, R = Me, X = Y = D).—2,6-Dideuterio-3,4,5-trimethoxyacetophenone (2.5 g) was condensed with diethyl isopropylidenesuccinate (3 g) in *t*-butyl alcohol (40 cm³), using potassium *t*-butoxide (1.4 g) as catalyst. The half esters (4.5 g) were hydrolysed with 10% ethanolic potassium hydroxide (15 cm³) and the resulting diacids (3.6 g) were treated with acetyl chloride (20 cm³). The mixture of (*E*)- and (*Z*)-fulgides (1.76 g), separated as described above, was fractionally crystallised from dichloromethane–petroleum. The first crop of crystals (315 mg) was pure (*Z*)-2-isopropylidene-3-[1-(2,6-dideuterio-3,4,5-trimethoxyphenyl)ethylidene]succinic anhydride (**4**; Z = O, R = Me, X = Y = D), m.p. 149 °C, and the final crop of crystals (470 mg) was the pure (*E*)-isomer (**5**; R = Me, Z = O, X = Y = D) m.p. 139 °C. Both isomers had an isotopic purity of 80%.

Photorearrangement Reactions.—The deuteriated (*E*)-fulgide (**5**; Z = O, R = Me) (80% isotopic purity) (400 mg) in toluene (50 cm³) at 40 °C was irradiated (366 nm) until the deep blue solution became colourless. The solvent was removed and the residue was dissolved in a small quantity of ether. On slow evaporation of solvent with time, 1,2-DHN (**7**; Z = O, R = Me, X = H, Y = H or D) (35 mg) separated. (*Z*)-Fulgides (**4**; Z = O, R = Me, X = H, Y = H and/or D) (55 mg) separated as the second crop of crystals. The ether solution was evaporated to dryness and the residue (300 mg) redissolved in CDCl₃. The n.m.r. spectrum showed that the residue consisted mainly of the 1,4-DHNs (**8**; Z = O, R = Me, X = H or D,

Y = H or D). No peaks characteristic of the 1,2-DHN (7; Z = O, R = Me, X = D, Y = H or D) could be detected.

(E)-2-Isopropylidene-3-(3,4,5-trimethoxyphenylmethylene)succinic Anhydride (5; Z = O, R = X = Y = H).—A mixture of 3,4,5-trimethoxybenzaldehyde (9.2 g) and diethyl isopropylidene succinate (10 g) in t-butyl alcohol (20 cm³) was added in small quantities to a boiling solution of potassium t-butoxide (5.2 g) in t-butyl alcohol (50 cm³). The half-ester was hydrolysed with 10% ethanolic KOH and the resulting diacid (4.3 g), obtained after acidification, was converted into the (E)-fulgide (5; Z = O, R = X = Y = H) by treatment with acetyl chloride. The (E)-fulgide was obtained as non-photochromic orange plates, m.p. 147–148 °C (from toluene–petroleum) (Found: C, 63.9; H, 5.8. C₁₇H₁₈O₆ requires C, 64.1; H, 5.7%); λ_{max}. 348 nm (log ε 4.10).

Photorearrangement.—The (E)-fulgide (5; Z = O, R = X = Y = H) (100 mg) in CDCl₃ at 13 °C was irradiated at 366 nm. No visual colour change was observed. After 12 days continuous irradiation, the solution contained a ca. 3:2:5 mixture of (E)- and (Z)-fulgides (5) and (4) (Z = O, R = X = Y = H) and the 1,4-DHN (8; Z = O, R = X = Y = H), as determined by n.m.r. spectroscopy. Petroleum (1 cm³) was added and the solution was cooled. With time, the (E)- and (Z)-fulgides separated and were filtered off. The filtrate was evaporated and the residual oil was crystallised from petroleum to give the 1,4-dihydro-6,7,8-trimethoxy-1,1-dimethylnaphthalene-2,3-dicarboxylic anhydride (8; Z = O, R = X = Y = H) as colourless crystals, m.p. 118–119 °C (Found: C, 64.2; H, 5.8%).

(E)-Fulgimides (5; Z = NPh, N-p-tolyl, or N-p-MeOC₆H₄, R = Me, X = Y = H) and (5; Z = NPh, R = X = Y = H).—The (E)-fulgide (1 g, 3 mmol) was boiled (12 h) with aniline, p-toluidine, or p-anisidine (3 mmol) in toluene (20 cm³). The solvent was removed and the residue was heated (1 h) with acetic anhydride (10 cm³) at 60 °C. Excess of reagent was distilled off under reduced pressure and the residual fulgimide was crystallised from ethanol.

(E)-Fulgimide (5; Z = NPh, R = Me, X = Y = H), colourless crystals, m.p. 143 °C (Found: C, 70.8; H, 6.1. C₂₄H₂₅NO₅ requires C, 70.7; H, 6.2%); λ_{max}. 285 and 326 nm (log ε 4.11 and 3.97).

(E)-Fulgimide (5; Z = N-p-tolyl, R = Me, X = Y = H), colourless crystals, m.p. 162–163 °C (Found: C, 71.2; H, 6.5. C₂₅H₂₇NO₅ requires C, 71.2; H, 6.5%).

(E)-Fulgimide (5; Z = N-p-MeOC₆H₄, R = Me, X = Y = H), colourless needles, m.p. 134 °C (Found: C, 65.2; H, 6.1. C₂₅H₂₇NO₆ requires C, 65.8; H, 6.1%); λ_{max}. 340 nm (log ε 3.89).

(E)-Fulgimide (5; Z = NPh, R = X = Y = H), pale yellow needles, m.p. 158 °C (from isopropyl dione) (Found: C, 70.2; H, 5.9. C₂₃H₂₃NO₅ requires C, 70.2; H, 5.9%); λ_{max}. 352 nm (log ε 4.15).

(E)-Fulgimides (5; Z = NH or NMe; R = Me, X = Y = H).—The (E)-fulgide (5; Z = O, R = Me, X = Y = O) (1.6 g, 5 mmol) in acetone was treated with a 2.5 molar excess of concentrated ammonia or 25% aqueous methylamine solution and heated on a water-bath until the solution became colourless. Acetone was removed under reduced pressure and

the remaining solution was acidified with 5M-hydrochloric acid. The liberated succinamic acid was extracted with ether and the ether extract was dried. An ethereal solution of diazomethane was added. Ether was distilled off. The residual methyl ester was cyclised by heating with 2% methanolic sodium methoxide. Fulgimide (5; Z = NH, R = Me, X = Y = H) was obtained as pale yellow crystals (47%) (from ethanol), m.p. 189 °C (Found: C, 65.5; H, 6.3. C₁₈H₂₁NO₅ requires C, 65.3; H, 6.3%); λ_{max}. 328 nm (log ε 3.93).

Fulgimide (5; Z = NMe, R = Me, X = Y = H) was obtained as pale yellow crystals (from chloroform–petroleum), m.p. 146 °C (Found: C, 66.1; H, 6.6. C₁₉H₂₃NO₅ requires C, 66.1; H, 6.7%); λ_{max}. 323 nm (log ε 3.92).

Photorearrangement.—The (E)-fulgimide (5; Z = NH, R = Me, X = Y = H) (30 mg) in toluene (50 cm³) at 20 °C was irradiated (366 nm) until the deep blue solution became colourless. The solvent was removed, the residue was dissolved in CDCl₃, and the n.m.r. spectrum measured. The spectrum indicated a quantitative conversion into the 1,2-DHN (7; Z = NH, R = Me, X = Y = H). The solvent was removed and the 1,2-DHN (7; Z = NH, R = Me, X = Y = H) was crystallised from ethanol to give colourless needles, m.p. 244–245 °C (Found: C, 65.2, H, 6.3. C₁₈H₂₁NO₅ requires C, 65.2, H, 6.2%); λ_{max}. 314 nm (log ε 4.14).

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References

- 1 H. Stobbe, *Chem. Ber.*, 1905, **38**, 3673; *Annalen*, 1906, **349**, 333.
- 2 R. J. Hart, H. G. Heller, and K. Salisbury, *Chem. Commun.*, 1968, 1627.
- 3 P. J. Darcy, R. J. Hart, and H. G. Heller, *J. Chem. Soc., Perkin Trans. 1*, 1978, 571.
- 4 H. Stobbe, *Annalen*, 1984, **282**, 280; *Chem. Ber.*, 1906, **39**, 761; L. S. El-Assal and A. H. Shebab, *J. Chem. Soc.*, 1963, 2983; D. C. Ayres, B. G. Carpenter, and R. C. Denny, *J. Chem. Soc.*, 1965, 3578; D. P. Chakraborty, T. Sleigh, R. Stevenson, G. A. Swoboda, and B. Weinstein, *J. Org. Chem.*, 1966, **31**, 3342; G. Brunow and H. Tylli, *Acta Chem. Scand.*, 1968, **22**, 590; M. D. Cohen, H. W. Kaufmann, D. Sinnreich, and G. M. J. Schmidt, *J. Chem. Soc. B*, 1970, 1035; R. Paetzold and H-D Ilge, *J. Signal AM* 3, 1975, 2, 93.
- 5 K. B. Wiberg, *Chem. Rev.*, 1955, **55**, 733.
- 6 E. S. Lewis and L. H. Funderbuck, *J. Am. Chem. Soc.*, 1967, **89**, 2322.
- 7 R. J. Hart and H. G. Heller, *J. Chem. Soc., Perkin Trans 1*, 1972, 1321.
- 8 H. G. Heller and M. Szweczyk, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1487.
- 9 C. G. Overberger and C. W. Roberts, *J. Am. Chem. Soc.*, 1949, **71**, 3618.
- 10 F. Dallacker, *Annalen.*, 1963, **665**, 78.
- 11 J. Grimshaw, C. S. Sell, and R. J. Haslett, *Org. Mass Spectrom.*, 1974, **8**, 381.

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