

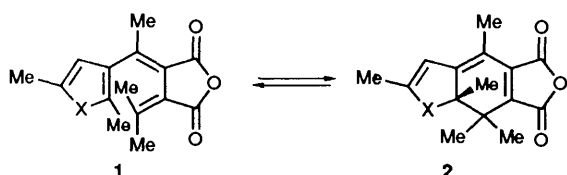
Photochromic Heterocyclic Fulgides. Part 5.¹ Rearrangement Reactions of (*E*)- α -1,2,5-Trimethyl-3-pyrrolethylidene(isopropylidene)succinic Anhydride and Related Compounds

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The pale yellow (*E*)-isopropylidene- $[\alpha$ -(1,2,5-trimethyl-3-pyrrolethylidene)succinic anhydride **3b** undergoes a reversible photochemical reaction to give the deep blue 7,7a-dihydro-1,2,4,7,7a-hexamethylindole-5,6-dicarboxylic anhydride **4b** which is thermally stable at ambient temperatures. The pale yellow anhydride **3b**, on heating at 140°C in the presence of an acid catalyst, rearranges quantitatively to the colourless 4,5-dihydro-1,2,3,4,4,7-hexamethylisoidole-5,6-dicarboxylic anhydride **6b**. The corresponding isopropylidene(2,5-dimethyl-1-phenyl-3-pyrrolethylidene)succinic anhydride **3c** undergoes an analogous sequence of reactions but the related isopropylidene(2,5-dimethyl-1-phenyl-3-pyrrolylmethylene)succinic anhydride **3g** undergoes neither photochemical nor thermal ring closure to indole nor isoidole derivatives but only *E*-*Z* isomerisation under similar reaction conditions.

In previous papers,^{1,2} we have reported that the pale yellow fulgides, *E*- α -2,5-dimethyl-3-furyl- and 3-thienyl-ethylidene-(isopropylidene)succinic anhydrides **1** (X = O and X = S) undergo conrotatory ring-closure to the deep red 7,7a-dihydro-2,4,7,7a-pentamethylbenzofuran and the purple benzothio-phen-5,6-dicarboxylic anhydrides **2** (X = O and X = S) res-



pectively in near quantitative yield on irradiation at λ 366 nm in a wide range of common organic solvents. The reactions are reversed on exposure to white light. These photochromic systems are highly resistant to photodegradation and are thermally stable up to 160°C but these coloured compounds **2** (X = O and X = S) show little or no absorption above λ 600 nm. The absorption characteristics, the near quantitative conversion into coloured forms, the thermal stability of the coloured forms and their resistance to degradation make the photochromic fulgides **1** (X = O and X = S) potentially suitable for use in recording media for optical information storage. With the development of laser diodes which emit radiation at wavelengths as short as λ 670 nm, it is of interest to modify the structure of photochromic fulgides so that their coloured forms absorbed in the λ 600–700 nm region.

These studies illustrate how the colour of the ring-closed forms can be altered to deep blue simply by replacing the 3-furyl or 3-thienyl group by a 3-pyrrolyl group*. (See Fig. 1.) The photochromic properties of substituted 2-methyl-3-pyrrolylfulgides **3a–e** are described for solutions in toluene. Similar photochromic properties are exhibited in a wide range of organic solvents, in rigid plastic matrix, and in the crystal.

Thermal and photochemical reactions were carried out for ca. 0.2 mol dm⁻³ solutions in deuteriochloroform in sealed tubes so that the progress of reactions, the composition of

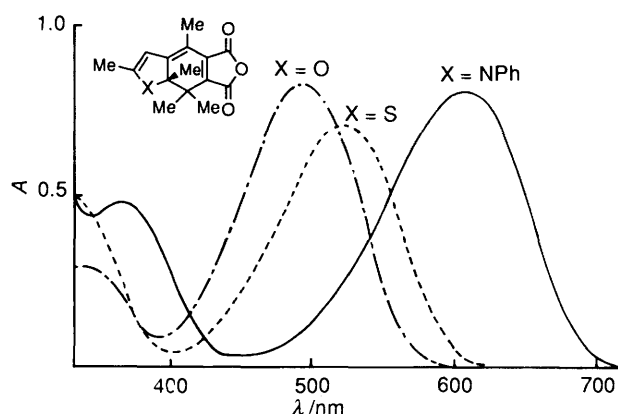


Fig. 1 Absorption spectra of the coloured forms (X = O, S and NPh) obtained on irradiation (λ 366 nm) of ca. 1×10^{-4} mol dm⁻³ solutions of the corresponding fulgides in toluene to the photostationary states

mixtures, and the structure and stereochemistry of products could be conveniently determined by NMR spectroscopic studies. The *E*-3-pyrrolylfulgides **3a–f** were characterised by their high field singlet absorptions at 1.2–1.6 ppm respectively, assigned to the methyl (Me^a) of the isopropylidene group which is shielded by the overlapping 3-pyrrolyl group. NMR spectroscopic data is summarised in Table 1.

Black intractable oils were formed in the Stobbe condensations of substituted 3-acetylpyrroles with diethyl isopropylidenesuccinate, from which the (*E*)-2,5-dimethyl-3-pyrrolylfulgides **3a–e** or their precursors were difficult to isolate and purify. The (*E*)-fulgides **3a–e** were obtained, albeit in poor yield, by column chromatography on silica gel, as yellow crystals. The near colourless solutions of these (*E*)-fulgides **3a–e** in toluene or other common organic solvents changed to deep blue on irradiation at λ 366 nm. The deep blue colour, which does not fade in the dark, is attributed to the thermally stable 7,7a-dihydroindole derivatives (7,7a-DHI) **4a–e**. The reaction can be reversed and the colour bleached by exposure to visible light. In dilute solutions (1×10^{-4} mol dm⁻³ in toluene) the conversion of the (*E*)-3-pyrrolylfulgides **3a–e** into their respective 7,7a-DHIs **4a–e** is near quantitative.

In more concentrated solutions (0.2 mol dm⁻³ in deuterio-

* Throughout 3-pyrrolyl is used to refer to the pyrrol-3-yl group.

Table 1 Analyses and NMR spectroscopic data

Compound	Mol. formula	Found			Requires		
		C	H	N	C	H	N
3a	C ₁₅ H ₁₇ NO ₃	69.5	6.6		69.5	6.6	
3b	C ₁₆ H ₁₉ NO ₃	70.5	7.0	5.2	70.3	7.0	5.1
3c	C ₂₁ H ₂₁ NO ₃	74.9	6.3	4.2	75.2	6.3	4.2
3d	C ₂₂ H ₂₃ NO ₃	75.6	6.7	4.1	75.6	6.6	4.0
3e	C ₂₆ H ₂₃ NO ₃	78.2	5.8	3.7	78.6	5.8	3.5
3f	C ₁₅ H ₁₇ NO ₃	69.5	6.6	5.4	69.5	6.6	5.4
5g	C ₂₀ H ₁₉ NO ₃	74.4	5.9	4.5	74.7	6.0	4.3
6c	C ₂₁ H ₂₁ NO ₃	75.4	6.4	4.5	75.2	6.3	4.2

Compound	δ_{H}						
	NMe	R ³	Me	Me	Me	Me	H
1; X = O		2.60	1.40	2.02	2.23	2.28	5.98
1; X = S		2.66	1.31	2.18	2.34	2.45	6.60
3a	3.52	6.13d ^a	1.21	1.92	2.31	2.67	6.58d ^a
3b	3.37	2.62	1.20	1.88	2.20	2.30	5.88
3c		2.70	1.39	1.70	2.00	2.37	6.02
3d		2.68	1.37	1.59	1.99	2.35	6.00
3e			1.47	1.87	2.42	2.78	6.43
3f	3.17	7.29	1.55	1.90	2.01	2.10	5.50
3g		— ^b	2.36	2.06	1.90	1.86	5.92
4a	3.10	5.42d ^a	1.19	1.36	1.68	2.02	6.93d ^a
4b	3.03	2.11	1.15	1.38	1.70	2.01	5.38
4c		2.07	1.01	1.18	1.55	1.80	5.51
4d		2.10	1.20	1.35	1.58	1.95	5.56
5a	3.60	6.22d ^a	1.96	2.18	2.18	2.43	6.58d ^a
5b	3.45	2.42	1.88	1.93	2.16	2.16	6.00
5c		2.42	1.97	1.97	2.02	2.21	6.12
5f	3.47	7.33	2.25	2.31	2.33	2.50	7.21
5g		— ^b	2.52	2.05	2.17	2.33	5.47
6b	3.41	2.68d ^a	1.04	1.83	2.31	2.45	3.50q ^a
6c		2.65d ^a	1.07	1.83	2.19	2.00	3.59q ^a
6d		2.70d	1.10	1.97	2.05	2.22	3.65m ^b

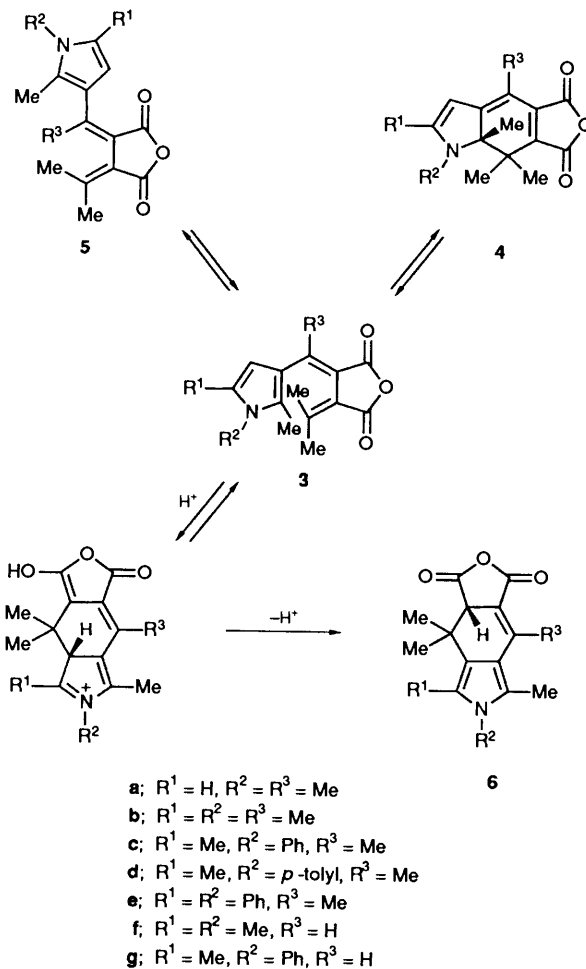
^a J 3 Hz. ^b Obscured by aromatics.

Table 2 Photostationary states on irradiation (λ 366 nm) of fulgides (0.2 mol dm⁻³ solution in CDCl₃)

Compound	<i>E</i>	<i>Z</i>	2
1; X = O	0	0	100
1; X = S	0	0	100
	<i>E</i> form 3	<i>Z</i> form 5	4
3a	25	25	50
3b	50	20	30
3c	20	20	60
3d	30	20	50
3e	30	10	60
3f	40	60	0

chloroform), a photostationary state between the *E*- and *Z*-2,5-dimethyl-3-pyrrolylfulgides **3a–e** and **5a–e** and the corresponding 7,7a-DHI **4a–e** is obtained on irradiation at λ 366 nm, in which the concentration of the latter varies between 30 and 60% as determined by NMR spectroscopy, (Table 2). The thermal stability of the 7,7a-DHIs is attributed to the steric interactions between the *cis* 7- and 7a-methyl groups, which prevent ring-opening by the symmetry-allowed disrotatory mode. The photochemical symmetry-allowed conrotatory ring-opening is not subject to steric constraints.

In most photochromic organic compounds, the photocoloured form absorbs strongly at the activating wavelengths, acting as an internal filter and inhibiting photocoloration. The UV and VIS spectra of the (*E*)-1,2-dimethyl-3-pyrrolylfulgide **3a** in toluene before and after irradiation at λ 366 nm is shown in

**Table 3** Ultra violet and visible spectra

Compound	Solvent	Permittivity at 20 °C	
		$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$
1; X = O	toluene	343	6 080
1; X = S	toluene	333	6 360
3a	toluene	364	6 980
3b	toluene	377	7 420
3c	hexane	2.4	365
3c	toluene	1.9	373
3c	acetonitrile	37.4	378
3d	toluene		374
3e	toluene		373
3f	toluene		389
5g	toluene		392
6c	toluene		366
2; X = O	toluene	494	8 200 ^a
2; X = S	toluene	520	4 500 ^a
4a	toluene	620	6 980 ^a
4b	toluene	632	7 300 ^a
4c	hexane	584	7 750 ^a
4c	toluene	2.4	615
4c	acetonitrile	1.9	642
4d	toluene	37.4	615
4e	toluene		605

^a Calculated assuming quantitative conversion into coloured forms on irradiation (λ 366 nm) of the respective fulgides shown above, and no photodegradation.

Fig. 2. 7,7a-DHIs have a relatively weak absorption in the λ 300–400 nm region so that the internal filter effect is not large.

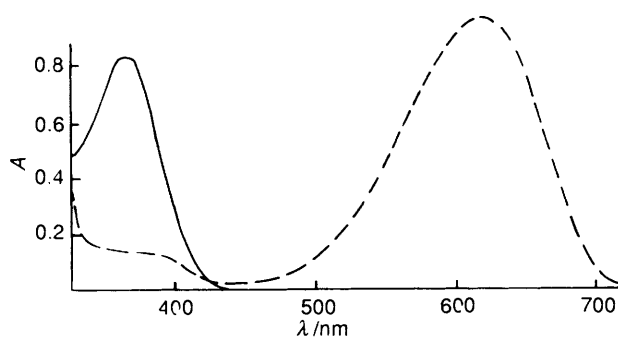


Fig. 2 Absorption spectra of a ca. 1×10^{-4} mol dm $^{-3}$ solution of the fulgide **3a** in toluene before (—) and after (---) irradiation at λ 366 nm to give the photostationary state

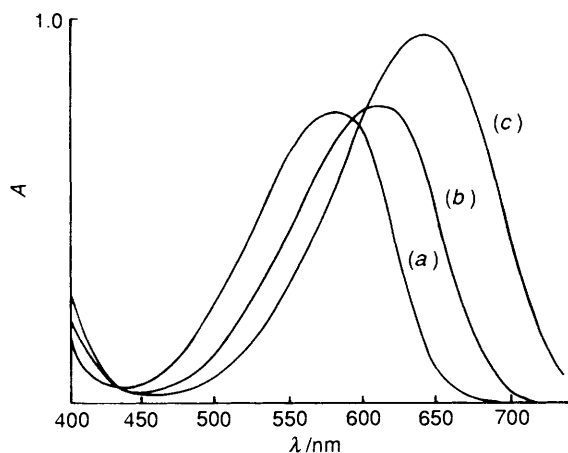


Fig. 3 Absorption spectra of ca. 1×10^{-4} mol dm $^{-3}$ solutions of fulgide **3c** in hexane (a), in toluene (b), and in acetonitrile (c) after irradiation at λ 366 nm to give the photostationary states

The influence of organic solvents on the absorption spectra of the (*E*)-2,5-dimethyl-3-pyrrolylfulgides **3c** and its 7,7a-DHI **4c** was investigated. As illustrated in Fig. 3 and Table 3, the 7,7a-DHI **4c** is markedly solvatochromic and shows such large bathochromic shifts in solvents of high permittivity as to become IR active. The quantum yields for colouring at λ 366 nm of *E*-3-pyrrolylfulgide **3c** in toluene and for bleaching at λ 546 nm of the 7,7a-DHI **4c** in toluene at 21 °C, determined using the Heller and Langan method of actinometry,³ were 0.20 and 0.044 respectively for freshly prepared solutions. The spectrum of the fulgide **3c**, (1×10^{-4} mol dm $^{-3}$ in toluene) after maximum conversion into the 7,7a-DHI **4c** on irradiation at λ 366 nm, followed by complete reversal by exposure to green light (λ 546 nm) showed a ca. 2% decrease in the absorbance maximum of the fulgide **3c** which is attributed to photodegradation. A further ca. 2% decrease in the absorbance at λ 372 nm was observed for each subsequent colour-bleach cycle. The photochromic system based on 1,2,5-trimethyl-3-pyrrolylfulgide **3b** shows a similar susceptibility to photodegradation. 1,2-Dimethyl-3-pyrrolylfulgides **3a** lacking a substituent in the 5-position, degraded more rapidly.

(*E*)-1,2,5-Trimethyl-3-pyrrolylfulgides **3f** and (*Z*)-2,5-dimethyl-1-phenylpyrrolylfulgide **5g** undergo almost exclusively *E*-*Z* isomerisation and only a trace of blue coloration, attributed to electrocyclic ring-closure, can be detected spectroscopically. In this respect, they resemble the *E*-3-furyl or thienylmethylene fulgides which are not photochromic and undergo only *E*-*Z* isomerisation on irradiation at λ 366 nm.²

(*E*)-2,5-Dimethyl-3-furyl- or thienylfulgides **1** (X = O or S) in deuteriochloroform undergo *E*-*Z* isomerisation on heating at 180 °C. (*E*)-2,5-Dimethyl-3-pyrrolylfulgides **3a-d** also undergo *E*-*Z* isomerisation on heating at 140 °C but, in addition,

fulgides **3b-d** undergo acid-catalysed thermal rearrangements to yield the isoindole derivatives **6b-d**. The acid-catalysed thermal rearrangement reactions of fulgide **3a** were not investigated. In contrast, the lower homologues **3f** and **5g** undergo only *E*-*Z* isomerisation under similar conditions and no trace of the corresponding isoindoles could be detected by NMR spectroscopy. At 180 °C, degradation occurred to give black intractable oils.

Experimental

UV spectra were measured in toluene on a Unicam SP8-200 spectrometer; NMR spectra were obtained with a Perkin-Elmer R32 (90 MHz) spectrometer (tetramethylsilane as internal standard except when monitoring thermal and photochemical reactions, for which an external standard was used), all *J* values are given in Hz. Photoreactions were carried out for 0.2 mol dm $^{-3}$ solutions in deuteriochloroform in a sealed NMR tube and exposed to irradiation (λ 366 nm) from a 250 W mercury discharge lamp (type ME/D, Thorn Lighting) with a filter (type OX1, Chance Pilkington) focussed on to the solution which was shaken occasionally. Light petroleum refers to the fraction of b.p. 60–80 °C. Reagents and solvents were purified before use.

(*E*)- α -1,2-Dimethyl-3-pyrrolylidenemethylsuccinic Anhydride **3a**.—A mixture of diethyl isopropylidenesuccinate⁴ (15.6 g) and 3-acetyl-1,2-dimethylpyrrole (10 g) was added dropwise to a stirred gently boiling solution of potassium *tert*-butoxide (9 g) in *tert*-butyl alcohol (200 cm 3). The mixture was boiled (24 h) and most of the solvent removed under reduced pressure. The residue was poured into water and extracted with toluene. 3-Acetyl-1,2-dimethylpyrrole (4.1 g) was recovered. The aqueous layer was acidified with 5 mol dm $^{-3}$ HCl. The liberated oil was hydrolysed by boiling with ethanolic KOH (10% w/v). On acidification with dilute hydrochloric acid, the liberated oil was stirred (5 h) with acetic anhydride (50 cm 3) at 50 °C. The solvent was removed and the residual black oil was chromatographed on silica gel using chloroform-cyclohexane (1:15) as eluent. The photochromic fraction was evaporated and the residual oil crystallised from chloroform-light petroleum *E*-fulgide **3a** as yellow crystals (320 mg), m.p. 148–149 °C.*

(*E*)- α -1,2,5-Trimethyl-3-pyrrolylidenemethylsuccinic Anhydride **3b**.—A mixture of diethyl isopropylidenesuccinate (22 g) and 3-acetyl-1,2,5-trimethylpyrrole⁵ (16 g) was added dropwise to a stirred gently boiling solution of potassium *tert*-butoxide in *tert*-butyl alcohol [freshly prepared by dissolving potassium (4.4 g) in boiling *tert*-butyl alcohol (400 cm 3)]. The mixture was boiled (24 h) and most of the solvent removed under reduced pressure. The residue was poured into water, extracted with toluene and the aqueous layer was acidified with 5 mol dm $^{-3}$ HCl. The liberated oil (12.7 g) was hydrolysed by boiling with ethanolic KOH (10% w/v) and the potassium salt, which separated on cooling, was filtered off, dissolved in water and acidified with dilute hydrochloric acid. The resulting diacids were treated with acetyl chloride and the solvent was removed, leaving a black oil which was chromatographed on silica gel using chloroform-light petroleum (3:2) as eluent. The photochromic fraction was evaporated and the residue crystallised from chloroform-light petroleum, giving (*E*)-fulgide **3b** as yellow plates (250 mg), m.p. 151 °C.

(*E*)- α -2,5-Dimethyl-1-phenyl-3-pyrrolylidenemethylsuccinic anhydride **3c**. The above procedure was repeated

* This procedure is similar to that used to prepare the analogous 2,5-dimethyl-3-furylfulgide.²

with replacement of 3-acetyl-1,2,5-trimethylpyrrole by 3-acetyl-2,5-dimethyl-1-phenylpyrrole (20.1 g). The photochromic fraction was evaporated and the residue crystallised from chloroform–light petroleum giving (*E*)-fulgide **3c** as yellow plates (1.8 g) m.p. 172 °C.

(*E*)- α -2,5-Dimethyl-1-*p*-tolyl-3-pyrrolylethylidene(isopropylidene)succinic anhydride **3d**. The procedure was repeated using 3-acetyl-2,5-dimethyl-1-*p*-tolylpyrrole (23 g). Work-up gave the (*E*)-fulgide **3d** as yellow needles (2 g) (from chloroform–light petroleum), m.p. 129 °C.

(*E*)- α -2-Methyl-1,5-diphenyl-3-pyrrolylethylidene(isopropylidene)succinic anhydride **3e**. The procedure was repeated using 3-acetyl-2-methyl-1,5-diphenylpyrrole (24 g). Work-up gave the *E*-fulgide **3e** as yellow crystals (30 mg), m.p. 198 °C (from chloroform–light petroleum).

(*E*)-1,2,5-Trimethyl-3-pyrrolylmethylene(isopropylidene)succinic anhydride **3f**. The procedure was repeated using 1,2,5-trimethylpyrrole-3-carbaldehyde. The non-photochromic fulgide **3f** was purified by chromatography and recrystallised from methanol, giving yellow needles (3.6 g), m.p. 151 °C.

(*Z*)-2,5-Dimethyl-1-phenyl-3-pyrrolylmethylene(isopropylidene)succinic anhydride **5g**. The procedure was repeated using 2,5-dimethyl-1-phenyl-pyrrolecarbaldehyde.⁶ Work-up gave the *Z*-fulgide (**5g**) as yellow needles, m.p. 233 °C (from chloroform–light petroleum).

3-Acetyl-1,2,5-trimethylpyrrole.—POCl₃ (25 g) in 1,2-dichloroethane (35 cm³) was added dropwise to *N,N*-dimethylacetamide (14.4 g) at 15–20 °C followed by a solution of 1,2,5-trimethylpyrrole (17 g). The mixture was refluxed (15 min) cooled and poured into water (150 cm³). A solution of NaOH (30 g) in water (120 cm³) was added and the mixture refluxed (15 min). After cooling, the mixture was extracted with chloroform (3 × 50 cm³), and the combined extracts dried (MgSO₄) and filtered. Solvent was removed from the filtrate and the residual oil distilled at 0.5 mmHg. The ketone⁵ was obtained in 55% yield. The procedure is essentially that

described by Kleinspehn and Broid⁵ for the preparation of 3-acetyl-2,5-dimethylpyrrole.

3-Acetyl-2,5-dimethyl-1-phenyl- and 1-*p*-tolyl-pyrroles were obtained in 50 and 80% yield respectively by this procedure using 2,5-dimethyl-1-phenyl- and 1-*p*-tolyl-pyrrole respectively.

Thermal Rearrangements.—4,5-Dihydro-1,2,3,4,4,7-hexamethylisindole-5,6-dicarboxylic anhydride **6b**. On heating (*E*)-fulgide **3b** (R = Me) (50 mg) in CDCl₃ (0.5 cm³) at 140 °C for 1 h, a 1:1 mixture of *E*- and *Z*-fulgides was formed. On continued heating for 24 h, after addition of a catalytic amount of trichloroacetic acid, the mixture was converted quantitatively into the isindole derivative **6b** as determined by NMR spectroscopy.

4,5-Dihydro-1,3,4,4,7-pentamethyl-2-phenylisindole-5,6-dicarboxylic anhydride **6c**. On heating (*E*)-fulgide **3c** (R = Ph) (25 mg) in CDCl₃ (2 cm³) containing a catalytic amount of trichloroacetic acid at 140 °C for 24 h, the isindole derivative **6c** was obtained in quantitative yield as colourless plates from chloroform–light petroleum, m.p. 234 °C.

(*E*)-fulgide **3d** undergoes an analogous reaction quantitatively.

References

- Part 4. A. P. Glaze, S. A. Harris and H. G. Heller, *J. Chem. Soc., Perkin Trans 1*, 1985, 957.
- Part 2. P. J. Darcy, H. G. Heller, P. J. Strydom and J. Whittall, *J. Chem. Soc., Perkin Trans. 1*, 1981, 202.
- Part 3. H. G. Heller and J. R. Langan, *J. Chem. Soc., Perkin Trans. 2*, 1981, 341.
- C. G. Overberger and C. W. Roberts, *J. Am. Chem. Soc.*, 1949, **71**, 3618.
- G. G. Kleinspehn and A. E. Broid, *J. Org. Chem.*, 1961, **26**, 1652.
- L. G. S. Brooker and R. H. Sprague, *J. Am. Chem. Soc.*, 1945, **67**, 1869.

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