

Photochromic heterocyclic fulgides. Part 8.¹ The condensation of 2,6-dichlorobenzaldehyde with diethyl [1-(2,5-dimethyl-3-furyl)ethylidene]succinate to give 6-chloro-2-(2,5-dimethyl-3-furyl)-1*H*-benzocycloheptene-3,4-dicarboxylic anhydride and photochromic (7*S*,7*aS*)-7-(2,6-dichlorophenyl)-2,4,7*a*-trimethyl-7,7*a*-dihydrobenzofuran-5,6-dicarboxylic anhydride

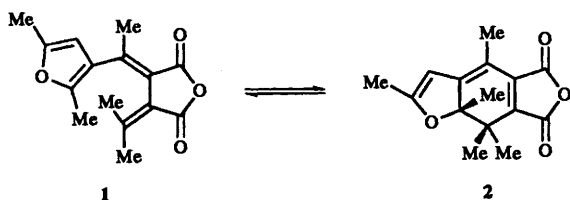
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The dark red photochromic (7*S*,7*aS*)-7-(2,6-dichlorophenyl)-2,4,7*a*-trimethyl-7,7*a*-dihydrobenzofuran-5,6-dicarboxylic anhydride has been synthesised by the Stobbe condensation of 2,6-dichlorobenzaldehyde with diethyl [1-(2,5-dimethyl-3-furyl)ethylidene]succinate in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol. When *tert*-butyl alcohol is replaced by toluene, 6-chloro-2-(2,5-dimethyl-3-furyl)-1*H*-benzocycloheptene-3,4-dicarboxylic anhydride is produced. Use of an aprotic solvent provides a new general method of preparing 2-substituted 6-chloro-1*H*-benzocycloheptene-3,4-dicarboxylic anhydrides *via* a mechanism involving nucleophilic substitution of chlorine in 2,6-dichlorobenzaldehyde, followed by intramolecular condensation.

The Stobbe condensation of 3-acetyl-2,5-dimethylfuran with diethyl isopropylidene succinate in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol or toluene, followed by hydrolysis of the resulting half esters and acidification, and subsequent cyclisation of the resulting diacids with acetyl chloride gave the (*E*)- and (*Z*)-fulgides.

The thermally stable photochromic (*E*)-fulgide **1** cyclised quantitatively to the red 7,7*a*-dihydrobenzofuran derivative (7,7*a*-DHBF) **2** on irradiation at 366 nm. The reverse reaction was induced by white light.² The Stobbe condensation of 2,6-



dichlorobenzaldehyde with a 2:1 *E/Z* mixture of diethyl [1-(2,5-dimethyl-3-furyl)ethylidene]succinates in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol, followed by a similar work-up, gave yellow crystals of the (*Z,Z*)-fulgide **3a** and dark red crystals of (7*S*,7*aS*)-7-(2,6-dichlorophenyl)-2,4,7*a*-trimethyl-7,7*a*-dihydrobenzofuran-5,6-dicarboxylic anhydride (*cis*-7,7*a*-DHBF) **7a**. Its stereochemistry and structure were confirmed by X-ray crystallographic analyses.† Presumably, it is formed by thermal disrotatory ring closure of the (*Z,E*)-fulgide **4a**, the primary product. On exposure to white light, *cis*-7,7*a*-DHBF **7a** underwent conrotatory ring opening to the (*E,E*)-fulgide **5a**, which can be cyclised to *cis*-7,7*a*-DHBF **7a** on irradiation at 366 nm or when heated at 110 °C. The spectrum of *cis*-7,7*a*-DHBF **7a** in toluene, both before and after being bleached with white light and after being heated at 110 °C, is shown in Fig. 1. The thermal reaction must involve isomerisation of the (*E,E*)-fulgide **5a** to the (*Z,E*)-fulgide **4a** followed by disrotatory ring-closure if the reaction is concerted

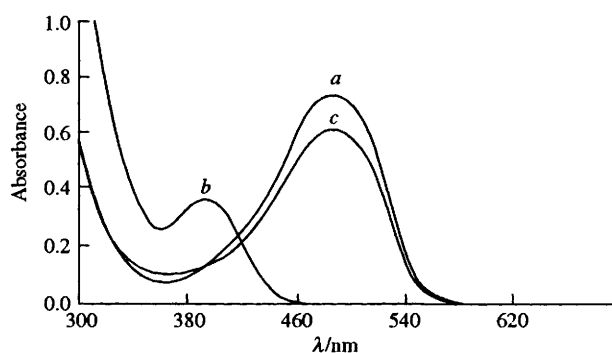


Fig. 1 Absorption spectra of a 7.5×10^{-5} mol dm³ solution of compound **7a** in toluene, (a) before irradiation, (b) after bleaching with white light and (c) after heating at 110 °C

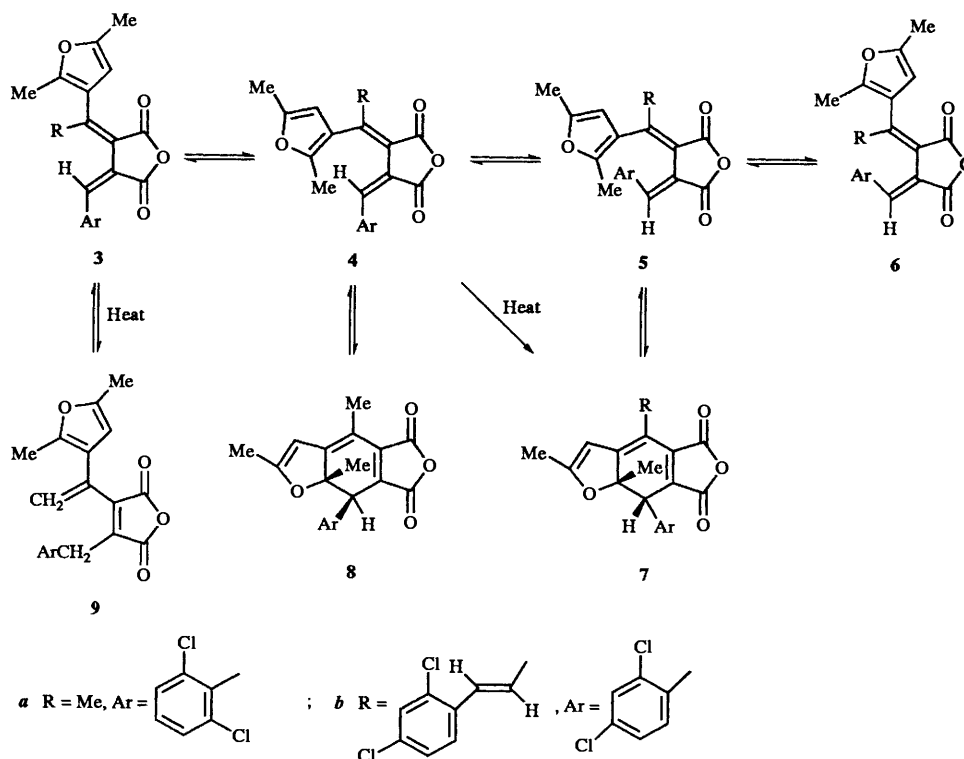
and orbital symmetry is conserved.³ When heated at 180 °C, the (*Z,Z*)-fulgide **3a** underwent a 1,5-H shift to give the maleic anhydride derivative **9a** in near quantitative yield. On prolonged irradiation at 366 nm, the (*Z,Z*)-fulgide **3a** gave a 3:2 mixture of *cis*- and *trans*-7,7*a*-DHBF **7a** and **8a**. These reactions are summarised in Scheme 1.

A Stobbe condensation using potassium *tert*-butoxide in toluene gave an additional and unexpected product, namely 6-chloro-2-(2,5-dimethyl-3-furyl)-1*H*-benzocycloheptene-3,4-dicarboxylic anhydride **10**. A mechanism for its formation is shown in Scheme 2. This reaction can be used to prepare other 2-substituted benzocycloheptene derivatives (*e.g.* **11**, **12**), albeit in poor yield, by condensation of 2,6-dichloro- or 2-chloro-2-fluoro-benzaldehyde with a 1-substituted ethylidenesuccinic ester (Table 1).

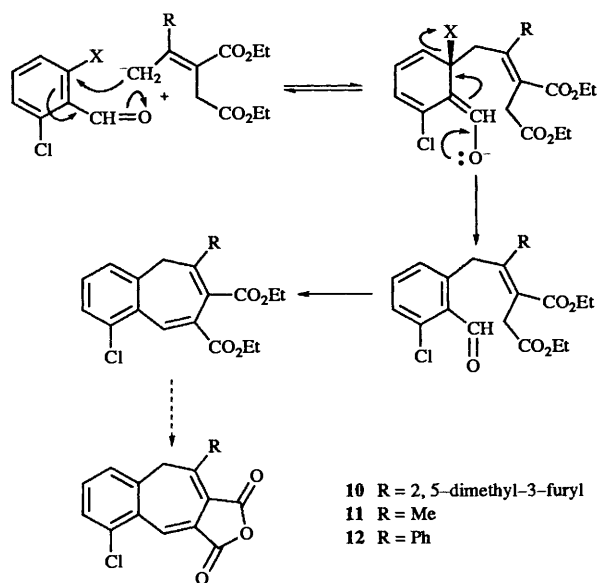
It is suggested that the combination of 2-chloro- and 1-carbonyl-substituents make the 6-chloro- or 6-fluoro-substituent susceptible to nucleophilic substitution under aprotic conditions and that the electronegative substituents in the 2- and 6-positions inhibit attack of the anion on the aldehyde group.

A condensation carried out in toluene under similar con-

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Scheme 1



Scheme 2

Table 1

Compound	Aldehyde X	Bu ^t OK (Mol)	Yield (%)
10	Cl	1	3.3
10	F	2	4.7
11	Cl	2	6.7
12	Cl	2	6.7

ditions, using 2,4-dichlorobenzaldehyde gave no benzocycloheptene derivative but, instead, the photochromic fulgide, (*E*)-2,4-dichlorobenzylidene-(*Z*)-[1-(2,5-dimethylfuryl)-3-(2,4-dichlorophenyl)propylidene]succinic anhydride **6b** was formed. On irradiation (366 nm) this underwent an orange to red colour change in toluene to give *cis*-7,7a-DHBF **7b**. On exposure to white light, *cis*-7,7a-DHBF **7b** gave the (*E*)-

fulgide **5b**, which, when heated at 110 °C, isomerised to the (*Z,E*)-fulgide **4b**; this then cyclised in a disrotatory mode to 7,7a-DHBF **7b** (Scheme 1).

Rearrangements were monitored and the stereochemistry of fulgides was assigned by the measurement of NMR spectroscopic chemical shifts of characteristic signals; the basis for this was the deshielding influence of the carbonyl group on an adjacent group and the shielding of the furyl group on the substituent which it overlaps.⁴

Experimental

UV spectra were measured in toluene on a Cecil CE6600 spectrometer; ¹H NMR spectra were obtained with a Bruker WM 360 spectrometer; *J* values in Hz. Mass spectra were recorded by electron impact on a Varian CH5D mass spectrometer. Light petroleum (LP) refers to the fraction of bp 40–60 °C.

(*E*)- and (*Z*)-Diethyl [1-(2,5-dimethylfuryl)ethylidene]succinate

A mixture of diethyl succinate (112 g, 1 mol), 3-acetyl-2,5-dimethylfuran (138 g, 1 mol) and potassium *tert*-butoxide (112 g, 1 mol) in toluene (400 cm³) was stirred at room temp. for 16 h after which it was poured into water. The aqueous layer was separated, washed with diethyl ether and acidified with 5 mol dm⁻³ hydrochloric acid. The liberated half esters were extracted with diethyl ether and the extracts dried (MgSO₄), filtered and evaporated to leave a brown gum (189 g). Acetyl chloride (20 g) was added to the gum (26 g) in ethanol (200 cm³) and the mixture was heated under reflux for 2 h after which it was evaporated. The residual oil was dissolved in diethyl ether and the solution washed with 10% aqueous sodium hydroxide, dried and evaporated. The residue was passed through a column of silica gel to remove impurities to afford a mixture of the *E*- and *Z*-diesters in a 2:1 ratio as determined by ¹H NMR spectroscopy which showed singlets due to three methyl groups at δ 2.3, 2.2 and 2.1 for the (*E*)-ester and 2.62, 2.52, 2.35 for the (*Z*)-ester.

(7*S*,7*aS*)-7-(2,6-Dichlorophenyl)-2,4,7*a*-trimethyl-7,7*a*-dihydro-benzofuran-5,6-dicarboxylic anhydride (cis-7,7*a*-DHBF) 7*a*

The preceding isomeric mixture (10 g, 34 mmol), 2,6-dichlorobenzaldehyde (6 g, 34 mmol) and potassium *tert*-butoxide (6 g, 54 mmol) in *tert*-butyl alcohol (100 cm³) were stirred at 50 °C for 3 h and then poured into water. *tert*-Butyl alcohol was removed under reduced pressure and the aqueous layer was acidified. The liberated half esters (8 g) were hydrolysed by boiling with 40% (w/v) ethanolic KOH (40 cm³) for 24 h after which the mixture was diluted with water and ethanol removed under reduced pressure. The aqueous layer was acidified with conc. HCl and extracted with diethyl ether. The extract was dried (MgSO₄), filtered, and evaporated, and the residue was treated with acetyl chloride (10 cm³) in dichloromethane (50 cm³). After removal of solvent and excess of acetyl chloride, the residual red oil was dissolved in diethyl ether–light petroleum and the solution was allowed to evaporate slowly to give (*Z,Z*)-2,6-dichlorobenzylidene[1-(2,5-dimethyl-3-furyl)ethylidene]-succinic anhydride **3a** as yellow prisms (0.30 g, 2.3%), mp 174–175 °C (from CH₂Cl₂–LP, 1:1) (Found: C, 60.2; H, 3.7. C₁₉H₁₄Cl₂O₄ requires C, 60.5; H, 3.7%; λ_{\max}/nm 296 and 388 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 8379 and 10 351); δ_{H} 7.28–7.24 (4 H, m, ArH and olefinic), 6.02 (1 H, s, furyl-H), 2.60 (3 H, s, Me *trans* to CO) and 2.30 and 2.24 (6 H, s, 5- and 2-Me respectively). The title compound **7a** formed dark red prisms obtained as a second crop (0.40 g, 3.1%), mp 188–189 °C (from Et₂O) (Found: C, 60.7; H, 3.9%; M⁺, 377. C₁₉H₁₄Cl₂O₄ requires C, 60.5; H, 3.7%; M, 377); $\nu_{\max}/\text{cm}^{-1}$ 1830 and 1751 (CO–O–CO); λ_{\max}/nm 486 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 9710); δ_{H} 7.4 (1 H, d, *J* 7.2, ArH), 7.15 (2 H, q, *J* 7.2, ArH), 5.70 (1 H, s, olefinic), 5.20 (1 H, s, methine) and 2.15, 1.95 and 1.45 (9 H, 3 s, 3 Me).

6-Chloro-2-(2,5-dimethyl-3-furyl)-1*H*-benzocycloheptene-3,4-dicarboxylic anhydride 10

The isomeric succinate mixture (13 g, 44 mmol), 2,6-dichlorobenzaldehyde (8.5 g, 49 mmol) and potassium *tert*-butoxide (5.9 g, 49 mmol) were stirred in toluene (100 cm³) at room temp. for 6 h after which the reaction mixture was poured into water. The aqueous layer was acidified and the liberated half esters were hydrolysed by heating under reflux with 10% (w/v) ethanolic KOH (40 cm³) for 24 h. The mixture was diluted with water after which the ethanol was removed under reduced pressure. The aqueous layer was then acidified with conc. HCl and extracted with diethyl ether. The extract was dried (MgSO₄), filtered and evaporated and the residue was cyclised with acetyl chloride (10 cm³) in dichloromethane (50 cm³). Solvent and excess of acetyl chloride were removed and the residue was chromatographed on silica gel with toluene as eluent.

The first red fraction gave *cis*-7,7*a*-DHBF **7a**, as dark red prisms (0.45 g, 2.4%), mp 188–189 °C (from Et₂O–LP). The second fraction gave the title compound **10** as buff coloured cubes (0.55 g, 3.3%), mp 212–213 °C (from Et₂O–LP) (Found: C, 66.8; H, 3.8%; M⁺, 340. C₁₉H₁₃ClO₄ requires C, 67.0; H, 3.85%; M, 340); $\nu_{\max}/\text{cm}^{-1}$ 1768 and 1243 (CO–O–CO); δ 8.5 (1 H, s, olefinic), 7.45 (2 H, q, ArH), 7.1 (1 H, d, *J* 7.2, ArH), 6.3 (1 H, s, ArH), 3.55 (2 H, s, methylene), 2.22, 2.16 and 2.12 (9 H, 3 s, 3 Me). The isomeric succinate mixture (6 g, 20 mmol), 2-chloro-6-fluorobenzaldehyde (3.7 g, 24 mmol) and potassium *tert*-butoxide (5.5 g, 44 mmol) were stirred in toluene (40 cm³) for 20 h. Work-up gave the benzocycloheptene **10**, mp 211–213 °C, as the sole product (0.32 g, 4.7%).

6-Chloro-2-methyl-1*H*-benzocycloheptene-3,4-dicarboxylic anhydride 11

The isomeric succinate mixture (5 g, 23 mmol), 2,6-dichlorobenzaldehyde (4.5 g, 26 mmol) and potassium *tert*-butoxide

(5.9 g, 49 mmol) were stirred in toluene (60 cm³) at room temp. for 6 h and then poured into water. Work-up gave colourless needles of (*Z*)-2,6-dichlorobenzylidene(isopropylidene)succinic anhydride (1.3 g, 19%), mp 204–205 °C (from Et₂O–LP) (C₁₄H₁₀Cl₂O₃ requires C, 56.6; H, 3.4%; M⁺, 261. Found: C, 56.8; H, 3.3%; M, 261); δ_{H} 7.5–7.1 (4 H, m, ArH and olefinic); 2.62 (3 H, s, Me) and 2.42 (3 H, s, Me) (and buff coloured plates of the title compound **11**), mp 169–170 °C (0.40 g, 6.7%) (Found: C, 64.3; H, 3.3. C₁₄H₉ClO₃ requires C, 64.5; H, 3.5%; $\nu_{\max}/\text{cm}^{-1}$ 1832, 1771 and 1246.8 (CO–O–CO); δ_{H} 8.43 (1 H, s, olefinic), 7.48 (2 H, m, ArH), 7.18 (1 H, d, *J* 7.2, ArH), 3.39 (2 H, s, CH₂) and 2.66 (3 H, s, Me).

6-Chloro-2-phenyl-1*H*-benzocycloheptene-3,4-dicarboxylic anhydride 12

Diethyl (*E*)-(1-phenylethylidene)succinate (10 g, 36 mmol), 2,6-dichlorobenzaldehyde (6.9 g, 40 mmol) and potassium *tert*-butoxide (11.1 g, 90 mmol) were stirred in toluene (100 cm³) at room temp. for 20 h. Work-up gave (*Z*)-2,6-dichlorobenzylidene-(*E*)-1-phenylethylidenesuccinic anhydride as yellow needles (0.8 g, 6.2%), mp 194–195 °C (from CH₂Cl₂) (Found: C, 63.6; H, 3.5%. C₁₉H₁₂Cl₂O₃ requires C, 63.50; H, 3.4%; $\nu_{\max}/\text{cm}^{-1}$ 1815.5, 1760.4 and 1218.3 (CO–O–CO); δ_{H} 7.50–7.29 (9 H, m, ArH and olefinic), 2.71 (3 H, s, Me) and the benzocycloheptene derivative **12** as buff crystals (0.78 g, 6.7%), mp 187–188 °C (from Et₂O–LP) (Found: C, 70.5; H, 3.5. C₁₉H₁₁ClO₃ requires C, 70.7; H, 3.4%; $\nu_{\max}/\text{cm}^{-1}$ 1832, 1774 and 1239 (CO–O–CO); δ_{H} 8.57 (1 H, s, olefinic), 7.64–7.41 (7 H, m, ArH), 7.05 (1 H, d, *J* 7.2, ArH) and 3.75 (2 H, s, methylene).

(*E*)-2,4-Dichlorobenzylidene-(*Z*)-[1-(*E*)-(2,5-dimethyl-3-furyl)-3-(2,4-dichlorophenyl)propylidene]succinic anhydride 6*b*

The isomeric succinate mixture (15 g, 51 mmol), 2,4-dichlorobenzaldehyde (10.3 g, 59 mmol) and potassium *tert*-butoxide (14.5 g, 108 mmol) were stirred in toluene (100 cm³) at room temp. for 6 h. Work-up gave the (*E,Z*)-fulgide **6b** as red prisms (1.3 g, 16.6%), mp 149–150 °C (from Et₂O–LP) (Found: C, 58.3; H, 3.2%; M⁺, 534. C₂₆H₁₆Cl₄O₄ requires C, 58.5; H, 3.0%; M, 534); $\nu_{\max}/\text{cm}^{-1}$ 1809, 1762 and 1143 (CO–O–CO); λ_{\max}/nm 398 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 11 500); δ_{H} 7.82 (1 H, s, olefinic), 7.36 (1 H, s, ArH), 7.14–6.91 (5 H, m, ArH and olefinic), 6.82 (1 H, d, *J* 14.4, olefinic), 5.85 (1 H, s, ArH) and 2.3, 2.29 (6 H, 2 s, 2 Me).

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