Photochromic Heterocyclic Fulgides. Part 6.[1] Base-catalysed Cyclizations of 1-(2,5-Dimethyl-3-furyl and 2,5-Dimethyl-3-thienyl)ethylidene(isopropylidene)-succinic Anhydrides and Related Compounds

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The title fulgides 1a and 3a (X = O or S) rearrange in boiling pyridine to yield deep red cis-8,8a-dihydro-2,4,7,8a-tetramethyl-7H-cyclohepta[b]-furan and -thiophene-5,6-dicarboxylic anhydrides 6a (X = O or S) respectively. The corresponding 2-thienyl fulgide 8 undergoes a similar rearrangement but with a subsequent 1,5-shift of its 3-hydrogen to give the colourless cis-5,6-dihydro-5,8-dimethyl-4H-cyclohepta[b]thiophene-6,7-dicarboxylic anhydride 11. The 3-thienyl-fulgide 1d (X = S) undergoes a similar rearrangement to yield the colourless trans-7,8-dihydro-4,7-dimethyl-6H-cyclohepta[b]thiophene-5,6-dicarboxylic anhydride 7. 3-Methyl-5,5-diphenyl-cyclohepta-1(7),2-diene-1,2-dicarboxylic anhydride 13 is obtained in an analogous reaction from (E)-3,3-diphenylallylidene(isopropylidene)succinic anhydride 12. Structural assignments are based on NMR studies. The mechanistic implications of the reactions are discussed.

Photochemical ring-closures of 3-furyl-, 3-thienyl- and pyrrol-3-ylethylidene(isopropylidene)succinic anhydrides (fulgides) 1a (X = O, S, or NMe) to give highly coloured 7,7a-dihydrobenzofuran, 7,7a-dihydrobenzothiophene and 7,7a-dihydroindole derivatives 2a (X = O, S and NMe) have been reported earlier.[1]

We report now a new and general base-catalysed rearrangement of furyl and thienyl fulgides to yield dihydrocyclohepta[b]-furan and -thiophenedicarboxylic anhydride [DHCF and DHCT] derivatives respectively. This reaction was discovered accidentally[4] during an attempt to isomerise the Z-fulgide 3a (X = O)[2] in boiling pyridine. The pyridine solution turned deep red and the colour was not discharged on acidification. A single deep red crystalline compound, cis-8,8a-dihydro-2,4,7,8a-tetramethyl-7H-cyclohepta[b]furan-5,6-dicarboxylic anhydride 6a (X = O) was obtained in high yield. Its structure follows from its 360 MHz ^{1}H NMR spectrum which showed three singlet signals (δ 2.12, 2.10 and 1.30) assigned to the 2,4 and 8a methyl groups. The 3 H doublet at δ 1.41 (J 7.5 Hz) (which was assigned to the pseudo equatorial 7-methyl group) coupled to a multiplet at δ 3.13. The latter was assigned to the pseudo-axial 7-H because of its large coupling (12 Hz) to the pseudo axial 8-H which gave a resonance at δ 1.99 and its 8 Hz coupling to the pseudo equatorial 8-H at δ 2.37 (See Fig. 1).

It can be seen from molecular models that a pseudo axial–axial arrangement of the 7-methyl and 8a-phenyl substituents in DHCF 6c (X = O) should result in shielding of the 7-methyl by the 8a-phenyl group. The fulgide 1c (X = O) was converted into the red 8,8a-DHCF 6c (X = O) when boiled in pyridine. Its NMR spectrum did not show shielding of the 7-methyl by the 8a-phenyl group, which is in accord with the structural assignment of a pseudo-equatorial methyl in both DHCFs 6a and 6c (X = O). The NMR spectrum of the latter showed shielding of the pseudo-axial 7-H and the pseudo equatorial 8-H by the 8a-phenyl group.

(Z)-2,5-Dimethyl-3-thienylfulgides 3a and 3b (X = S)[3] rearranged to the red cis-8,8a-DHCTS 6a and 6b; (X = S) when boiled in pyridine. Detailed NMR studies indicated that the two DHCTs 6a and 6b (X = S) have structures analogous to the 8,8a-DHCFs 6a (X = O) and a cis-configuration of their 7 and 8a hydrogens. The absorption spectra of the red compounds 6a (X = O) and 6a (X = S) and the 7,7a-DHBF 2a (X = O) are shown in Fig. 2.
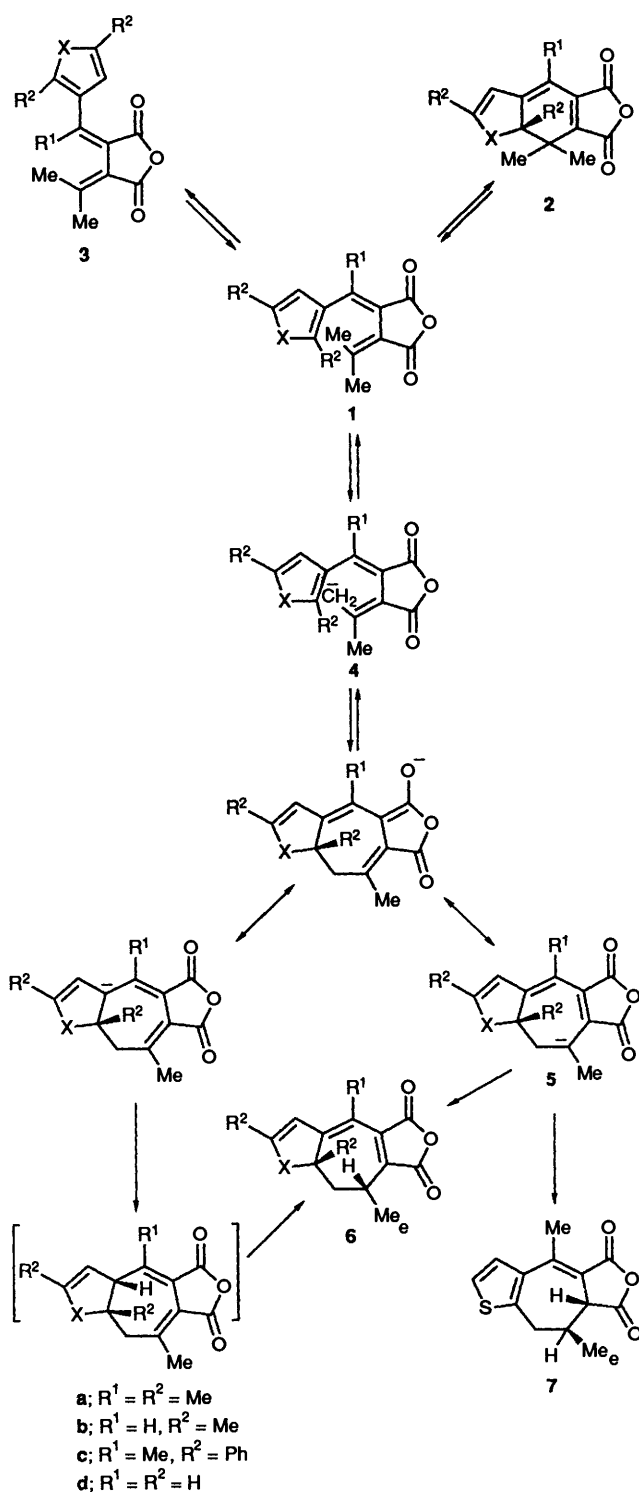
The pale yellow (E)-1,2,5-trimethylpyrrol-3-ylfulgide 1b (X = NMe)[1] gave a deep blue colour in boiling pyridine which was discharged on acidification. NMR analysis of the product indicated that the main reaction was E–Z isomerisation to give a 1:1 mixture of E- and Z-fulgides 1b and 3b (X = NMe). No other products could be identified.

The (E)-3-thienylfulgide 1d (X = S)[3] rearranged to give the colourless trans-7,8-dihydro-4,7-dimethyl-6H-cyclohepta[b]thiophene-5,6-dicarboxylic anhydride 7, on boiling in pyridine. Its structure follows from its NMR spectrum which showed a doublet at δ 2.64 (assigned to the allylic 4-Me) coupled (J 2) to a multiplet at δ 2.81 (pseudo-axial 6-H) which, in turn, was coupled (J 10) to a multiplet at δ 2.95 (assigned to the pseudo-axial 7-H). The large coupling is attributed to an axial–axial arrrangement of 6- and 7-hydrogens. The lowfield doublet at δ 1.37 (J 7) is assigned to the pseudo-equatorial 7-Me which lies in the deshielding zone of a carbonyl of the anhydride ring. The assignment of configuration of the 7-Me as pseudo equatorial is supported by the NOE enhancements seen at the protons assigned as 6β-H, 7α-H and 8β-H on irradiation of the 7-Me.

The (E)-2-thienylfulgide 8[3] showed a similar rearrangement on boiling in pyridine to give the colourless cis-5,6-dihydro-5,8-dimethyl-4H-cyclohepta[b]thiophene-6,7-dicarboxylic anhydride 11. Its NMR spectrum showed a doublet (J 2) at δ 2.80 (assigned to the allylic 8-Me) coupled to the multiplet at δ 3.65 (assigned to the pseudo-axial 6-H). The latter was coupled (J 3) to the multiplet at δ 3.02 (assigned to the pseudo-equatorial 5-H). On the basis of these assignments, it follows that the 5-methyl must be pseudo-axial and remote from the deshielding zone of a carbonyl of the anhydride ring. This is reflected in its highfield chemical signal (δ 0.95) compared to the equatorial 7-methyl (δ 1.37) in isomer 7. The coupling constant (J 4) between the pseudo-equatorial 5-H and the pseudo-axial 4-H is consistent with the assigned stereochemistry. The structure and stereochemistry was confirmed by X-ray crystallographic analyses by M. B. Hursthouse and A. Karaulov[6] (See Fig. 3).

3-Methyl-5,5-diphenylcyclohepta-1(7),2-diene-1,2-dicarboxylic anhydride 13 was obtained in high yield in an analogous reaction when (E)-3,3-diphenylallylidene(isopropylidene)succinic anhydride 12 was boiled in pyridine.

(Z)-Isopropylidene(phenylethylidene)succinic anhydride 14 did not undergo the above rearrangement on boiling in pyridine

Fig. 1 Part of 360 MHz ^{1}H NMR spectrum of *cis*-8,8a-dihydro-2,4,7,8a-tetramethyl-7H-cyclohepta[b]furan-5,6-dicarboxylic anhydride **6a** (X = O).
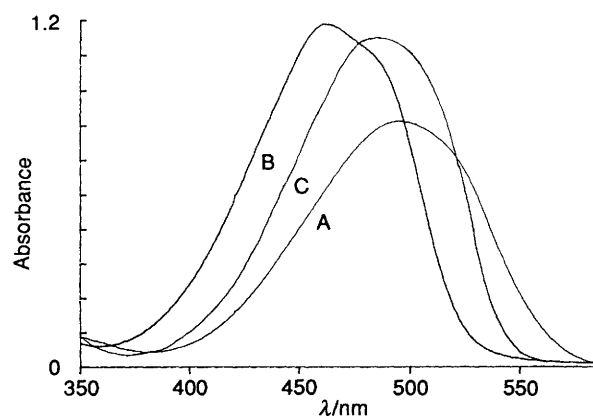
Fig. 2 Absorption spectra of *ca.* 1 × 10^{-4} mol dm^{-3} solutions of compounds **2a** (X = O) (A), **6a** (X = O) (B) and **6a** (X = S) (C) in toluene

is protonation to give *cis* dihydro compounds (*e.g.* **10**) followed by 1,5-H shift in the case of **6a–c** or two 1,5-H shifts in the case of **6d** and **11**).

Compound **7** (X = S), having the *trans*-axial–axial arrangement of 6- and 7a-hydrogens could not be formed by the latter mechanism unless the strained *trans*-4,10-dihydro intermediate was formed initially, which is considered unlikely. The simpler alternative mechanism is that the enolate anion **5** undergoes protonation from the sterically less-hindered side, before or after a 1,5-hydrogen shift has occurred.

Experimental

Procedure for the Base-catalysed Rearrangements of Fulgides.—A 10% w/v solution of the fulgide in anhydrous pyridine

a; R^1 = R^2 = Me
b; R^1 = H, R^2 = Me
c; R^1 = Me, R^2 = Ph
d; R^1 = R^2 = H

but isomerised to give a 6:3:1 mixture of the (*E*)-fulgide **15** and the two 1,5-H-shift products **16** and **17** respectively. A similar product composition was obtained when the (*Z*)-fulgide **14** was heated in CDCl$_3$ in a sealed NMR tube at 140 °C.[5]

The first step in the mechanism for the base-catalysed rearrangements described above is considered to be abstraction of a proton from a methyl of the isopropylidene group, followed by an intramolecular 1,6-addition to give a resonance-stabilised enolate anion which can give rise to different products depending on which carbon is reprotonated.

A probable mechanism for the formation of dihydro derivatives **6a–c** and **11**, is direct protonation of anions **5a–c** or **9** from the sterically less hindered side. An alternative mechanism
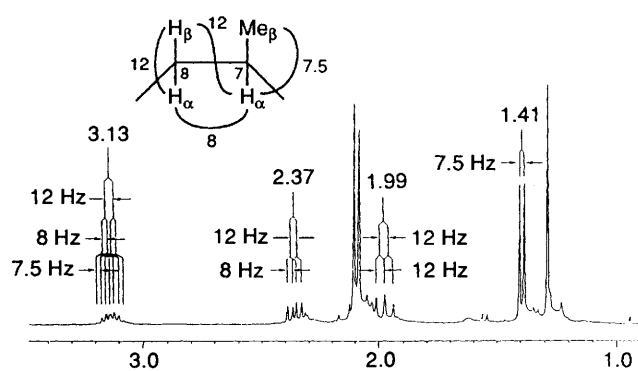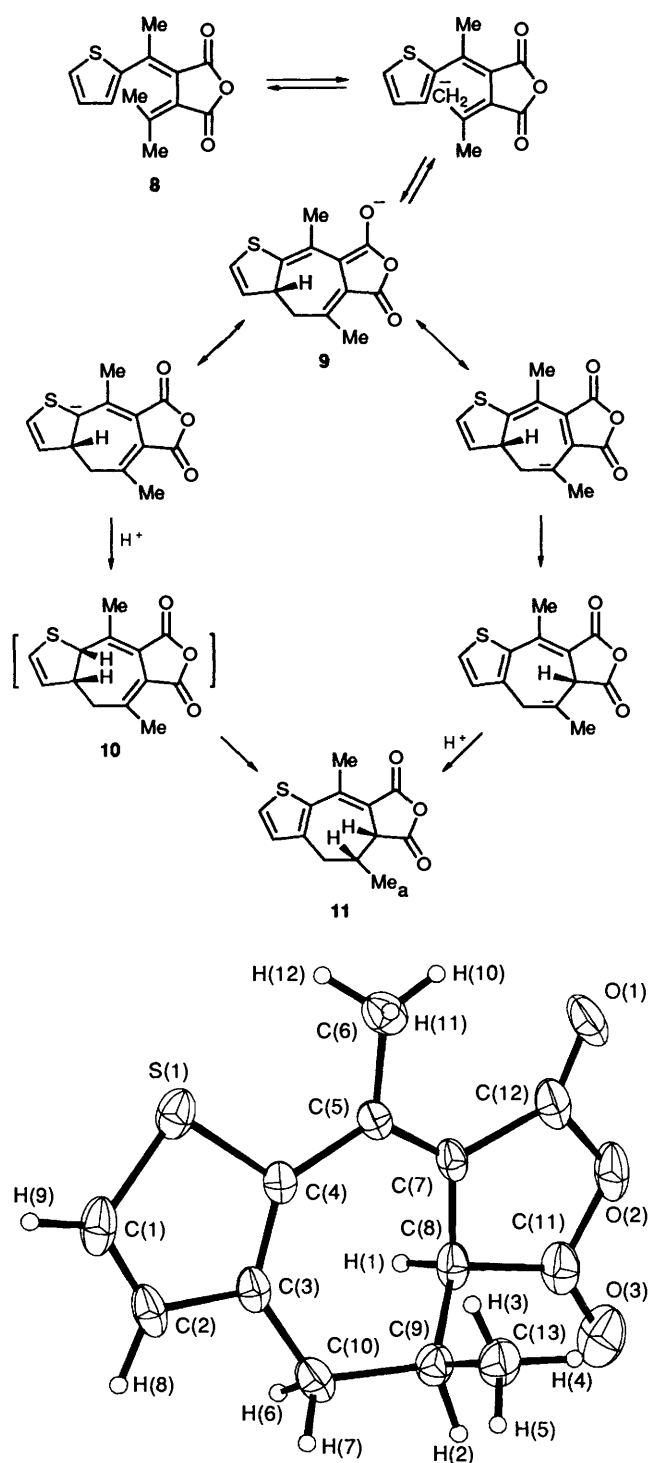
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11

12

13

Fig. 3 X-ray structure of compound 11

was refluxed (3 h), cooled and poured into 3 mol dm^{-3} hydrochloric acid. The aqueous solution was extracted with ether, washed with water, and dried (MgSO$_4$) and removed. The residue was crystallised from chloroform–petroleum.

cis-8,8a-Dihydro-2,4,7,8a-tetramethyl-7H-cyclohepta[b]-furan-5,6-dicarboxylic Anhydride 6a, (X = O).—The cis-8,8a-DHCF 6a (X = O) was obtained in 88% yield from (E)- or (Z)-1-(2,5-dimethyl-3-furyl)ethylidene(isopropylidene)succinic anhydride[2] 1a or 3a (X = O) (1 g), as red plates, m.p. 129–130 °C. (Found: C, 68.95; H, 6.1%; M$^+$, 260. C$_{15}$H$_{16}$O$_4$ requires C, 69.21; H, 6.19%; M, 260); v_{max}/cm^{-1} 1817m, 1741s and
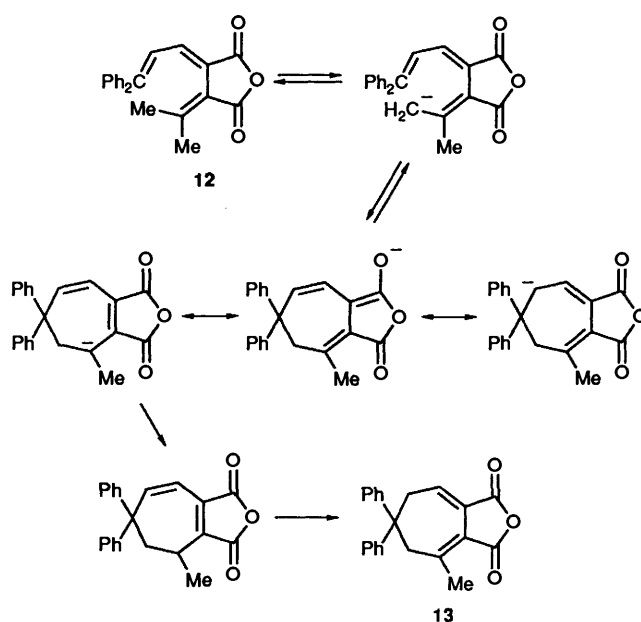
1546s; λ_{max}/nm 461 (ε/dm^3 mol^{-1} cm$^-$ 11 820). NMR spectrum, see Fig. 2.

cis-8,8a-Dihydro-2,4,7,8a-tetramethyl-7H-cyclohepta[b]thio-phene-5,6-dicarboxylic Anhydride 6a (X = S).—The cis-8,8a-DHCT 6a (X = S) was obtained in 67% yield from (Z)-1-(2,5-dimethyl-3-thienyl)ethylidene(isopropylidene)succinic anhy-dride[3] 3a (X = S) (1 g), as red plates, m.p. 142 °C (Found: C, 65.15; H, 5.85%; M$^+$ 276. C$_{15}$H$_{16}$SO$_3$ requires C, 65.24; H, 5.79%; M, 276); v_{max}/cm^{-1} 1838m, 1813m and 1757s; λ_{max}/nm 486 (ε/dm^3 mol^{-1} cm^{-1} 11 670); δ 1.39 (3 H, d, J 7, 7β-Me), 1.54 (3 H, s, 8aβ-Me), 2.20 (6 H, s, 2-Me, 4-Me), 2.33 (1 H, dd, J 14, 12, 8β-H), 2.40 (1 H, dd, J 14, 8, 8α-H), 3.16 (1 H, ddq, J 12, 8, 7,7α-H) and 6.02 (1 H, s, 3-H).

cis-8,8a-Dihydro-2,7,8a-trimethyl-7H-cyclohepta[b]thio-phene-5,6-dicarboxylic Anhydride 6b (X = S).—The cis-8,8a-DHCT 6b (X = S) was obtained in 28% yield from (E)-2,5-dimethyl-3-thienylmethylene(isopropylidene)succinic anhy-dride[3] 1b (X = S) (0.5 g), as red needles, m.p. 138–140 °C (Found: C, 63.85; H, 5.4. C$_{14}$H$_{14}$SO$_3$ requires C, 64.10; H, 5.38%); v_{max}/cm^{-1} 1839m, 1810m and 1753s; λ_{max}/nm 476 (ε/dm^3 mol^{-1} cm^{-1} 14 640); δ 6.20 (1 H, s, olefinic), 5.88 (1 H, s, olefinic), 3.15 (1 H, m, methine 7-H), 2.30 (2 H, m, 2 × methylene 8-H), 2.20 (3 H, s, 2-Me), 1.60 (3 H, s, 8a-Me) and 1.44 (3 H, d, J 7, 7-Me).

cis-5,6-Dihydro-5,8-dimethyl-4H-cyclohepta[b]thiophene-6,7-dicarboxylic Anhydride 11.—The cis-5,6-DHBT 9 was obtained in 98% yield from (E)-1-(2-thienyl)ethylidene(isopropyl-idene)succinic anhydride 8[3] (0.5 g), as pale yellow plates, m.p. 140–141 °C (Found: C, 62.5; H, 4.98%; M$^+$, 248. C$_{13}$H$_{12}$SO$_3$ requires C, 62.90; H, 4.87%; M, 248); v_{max}/cm^{-1} 1818s, 1746s and 1609s; λ_{max}/333 nm (ε/dm^3 mol^{-1} cm^{-1} 16 070); δ 0.95 (3 H, d, J 7, 5α-CH$_3$), 2.80 (3 H, d, J 2, 8-CH$_3$), 2.86 (1 H, ddd, J 17, 4, 1, 4α-H), 3.02 (1 H, qddd, J 7, 6, 4, 3, 5β-H), 3.34 (1 H, dd, J 17, 6, 4β-H), 3.65 (1 H, br, 6β-H), 7.00 (1 H, d, J 5, 3-H) and 7.51 (1 H, d, J 5, 2-H); NOE 5α-Me→5β-H (10%), 5αMe→4β-H (5%), 3-H→4α-H (2.6%) and 3-H→4β-H (1.4%).

trans-7,8-Dihydro-4,7-dimethyl-6H-cyclohepta[b]thiophene-5,6-dicarboxylic Anhydride 7.—The trans-6,7-DHCT 7 was obtained in 93% yield from (E)-1-(3-thienyl)ethylidene-(isopropylidene)succinic anhydride 1d; X = S[3] (0.5 g), as

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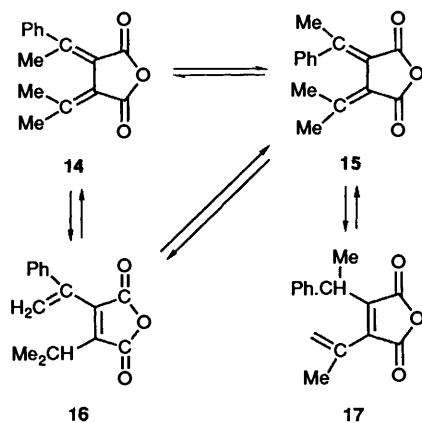
colourless plates, m.p. 149 °C (Found: C, 62.5; H, 4.95%; M^+, 248. $C_{13}H_{12}SO_3$ requires C, 62.90; H, 4.87%; M, 248); v_{max}/cm^{-1} 1817m, 1756s and 1618m; λ_{max}/nm 312 (ε/dm^3 mol^{-1} cm^{-1} 9800); δ 1.37 (3 H, d, J 7, 7β-CH_3), 2.64 (3 H, d, J 2, 4-CH_3), 2.66 (1 H, d, J ca. 13, 8β-H), 2.81 (1 H, dq, J 10, 2, 6β-H), 2.9–3.0 (2 H complex 8α-H and 7α-H), 7.16 (1 H, d, J 6, 3-H) and 7.22 (1 H, d, J 5, 2-H); NOE 3-H→4-Me (5%), 7β-Me→8β-H (2.5%), 7β-Me→6β-H (9%) and 7β-Me→7α-H (8%).

cis-8,8a-*Dihydro*-4,7-*dimethyl*-2,8a-*diphenyl*-7H-*cyclohepta*-[b]*furan*-5,6-*dicarboxylic Anhydride* **6c** (X = O).—From (Z)-1-(2,5-diphenyl-3-furyl)ethylidene(isopropylidene)succinic anhydride **3c** (X = O) (0.25 g), cis-8,8a-DHCF **6c** (X = O) was obtained as red plates, m.p. 167–168 °C (Found: C, 78.1; H, 5.35. $C_{25}H_{20}O_4$ requires C, 78.11, H, 5.24%); δ 7.67 (2 H, m, aromatics), 7.28–7.28 (8 H, m, aromatics), 6.44 (1 H, s, olefinic 3-H), 3.15 (1 H, dd, J 12 and 7.5 methylene 8-H), 2.84 (1 H, ddq, J 12, 7.5 and 7, methine 7-H), 2.42 (3 H, s, 4-Me), 2.35 (1 H, dd, J 12 and 12, methylene 8-H), and 1.37 (3 H, d, J 7, 7-Me).

5,5-*Diphenyl*-3-*methylcyclohepta*-1(7),2-*diene*-1,2-*dicarb*-*oxylic Anhydride* **13**.—The title compound **13** was obtained in 74% yield from (E)-3,3-diphenylallylidene(isopropylidene)succinic anhydride **12** (0.27 g), as colourless needles (from chloroform–light petroleum), m.p. 222 °C (Found: C, 79.75; H,

5.51%; M^+, 330. $C_{22}H_{18}O_3$ requires C, 79.98; H, 5.49%; M, 330); v_{max}/cm^{-1} 1812s, 1757s, 1663m and 1645m; δ 7.2–7.3 (6 H, complex m- and p-ArH); 7.00 (4 H, d, J 7, o-ArH), 3.48 (2 H, s, methylene 7-Hs), (2 H, d, J 2, methylene 5-Hs) and 2.44 (3 H, s, 1-Me).

Attempted Cyclisation of (E)-1,2,5-*Trimethylpyrrol*-3-*yl*-*methylene(isopropylidene)succinic Anhydride* **1b** (X = NMe).—The fulgide (0.35 g)[1] in pyridine (100 cm³) was boiled (4 h). Work-up gave a 1:1 mixture of the (E) and (Z)-fulgides **1b** (X = NMe) and **3b** (X = NMe), no cyclization having occurred.

(Z)-1-(2,5-*Diphenyl*-3-*furyl*)*ethylidene(isopropylidene)*-*succinic Anhydride* **6c** (X = O)*.—A mixture of diethyl isopropylidenesuccinate (5 g) and 3-acetyl-2,5-diphenylfuran (5 g) was added dropwise with stirring to a solution of potassium *tert*-butoxide [prepared by dissolving potassium (3 g) in boiling *tert*-butyl alcohol (100 cm³)] at room temperature. After 3 h, most of the solvent was removed under reduced pressure and water added. On addition of 5 mol dm^{-3} hydrochloric acid, the half ester separated and was hydrolysed with 10% ethanolic KOH. Solvent was removed and the residue acidified with dilute hydrochloric acid. On treatment of the resulting diacid with acetyl chloride the (Z)-*fulgide* **6c** (X = O) separated and was recrystallised from ethanol to give yellow plates (0.3 g), m.p. 156 °C. (Found: C; 78.1, H, 5.3. $C_{25}H_{20}O_4$ requires C, 78.11; H, 5.24%); λ_{max}/nm 310 (ε/dm^3 mol^{-1} cm^{-1} 2820); δ 2.01, 2.21 and 2.50 (9 H three s, three Me s), 6.71 (1 H, s, 4-H) and 7.45–7.90 (10 H, m, ArH).

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