On the Mechanism for the Phototransformation of 3-Alkoxy-2-(2'-furyl)-4-oxo-4*H*-1-benzopyrans

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Photoirradiation of 3-alkoxy-6-chloro-2-(2'-furyl)-4-oxo-4*H*-1-benzopyrans **3** led to the formation of methyl 8-chloro-10-oxo-2-phenyl-2,3,4,10-tetrahydropyrano[3,2-*b*][1]benzopyran-3-ylacetate **4**. The reaction proceeds through the formation of 8-chloro-4-phenyl-3a,4,6,11b-tetrahydrofuro-[2',3':4,5]pyrano[3,2-*b*]benzopyran-6-one **5a**, which subsequently undergoes a ring contraction–ring expansion mechanism to give the cyclopropanecarbaldehyde **8** followed by its rearrangement to ketene **10** *via* the carbene **9** to furnish ester **4**. The various intermediates have been isolated and identified, and their stereochemistry was established from their ^{1}H NMR spectra.

Conjugated enones with suitable substituents at the α-position, when subjected to photolysis, are known to undergo γ-H abstractions.[1] The products obtained depend invariably upon the nature of the substituents present in the substrates: *viz.* 2-alkyl-3-arylcyclohex-2-enones[2] and 3-alkoxy-2-phenyl-4-oxo-4*H*-1-benzopyrans[3] afforded photocyclised angular products whereas 3-benzyloxy-2-styrylchromones,[4] upon exposure to UV light, yielded tricyclic linear products. In contrast 3-methoxy-2-methylchromone has been found to lead to the formation of a novel dimeric oxetanol.[5] It thus became of interest to investigate the photochemistry of 3-alkoxy-chromones bearing a furyl group instead of a Me, Ph or CH=CHPh at C(2), since furans themselves are known to undergo phototransformations.[6] Such a system allows another dimension, here, to be studied as it becomes a bichromophoric system, an enone coupled to a furan.

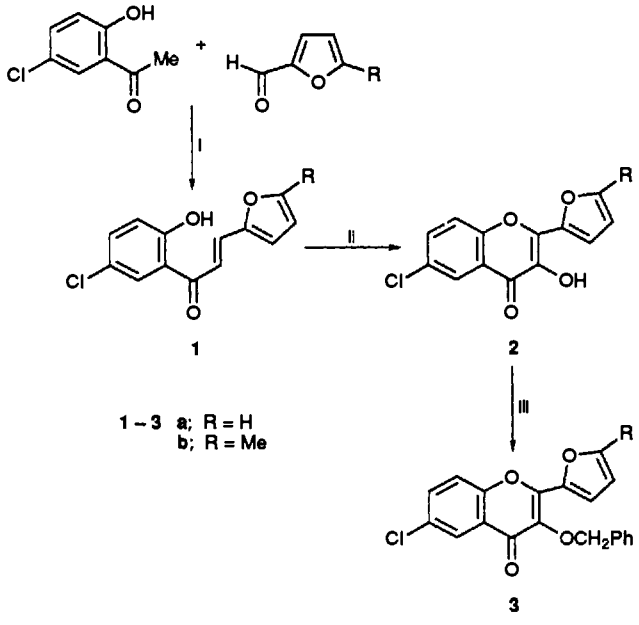
Results and Discussion

The target molecules, *i.e.*, 2-(2'-furyl)-**3a**[7] and 2-(5'-methyl-2'-furyl)-3-benzyloxy-4-oxo-4*H*-1-benzopyran **3b** were synthesised as follows (Scheme 1).

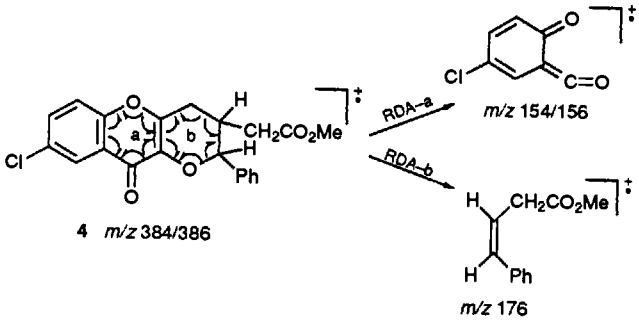
Photoirradiation of **3a** in methanol produced ester **4**, whose structure became evident from its ^{1}H NMR and mass spectra. The ^{1}H NMR spectrum (100 MHz) of compound **4** showed a doublet at δ_H 5.01 (1 H, *J* 8 Hz, 2-H), a complex multiplet at δ_H 3.20–2.60 (3 H, 4-H_2 and 3-H), a doublet at δ_H 2.43–2.31 (2 H, *J* 6 Hz, CH_2CO_2Me), and a singlet at δ_H 3.64 ($CH_2CO_2\mathit{Me}$). The relative chemical shifts assigned to the alicyclic protons were confirmed by irradiation of the cluster in the range δ_H 3.20–2.60, which converted the doublets due to 2-H and 3-CH_2CO_2Me into singlets. The structure of compound **4** has been further corroborated by its mass spectrum, which showed two retro-Diels–Alder (RDA) fragmentation modes, thereby indicating the presence of both chromone and pyran moieties in compound **4** (Scheme 2).

Regarding the stereochemistry of the pyran ring C it is assumed to be in the inverting half-chair form with two groups Ph and 3-CH_2CO_2Me in ψ-equatorial positions[8] (*J* 8 Hz) (Fig 1).

The transformation **3a** ⟶ **4** can be rationalised as follows: compound **3a** on photolysis undergoes a γ-H abstraction by the excited carbonyl group of the chromone moiety to give **5a** as analogously reported in earlier cases.[2–4] Compound **5a**, under the reaction conditions, may then undergo a ring contraction–ring expansion process[9] to produce biradical intermediate **6a** which, through the intervention of the mesomeric biradical **7a**, can give the cyclopropanecarbaldehyde **8a**. Alternatively, biradical **7a** may rearrange through carbene **9** to give the ketene[10] **10** which then adds to methanol to form the ester **4** (Scheme 3).



Scheme 1 *Reactions and conditions:* i, NaOH, EtOH; ii, H_2O_2, NaOH; iii, K_2CO_3, $PhCH_2Cl$, Me_2CO



Scheme 2

To confirm this speculative mechanism, compound **3a** was irradiated in benzene instead of methanol, under the above reaction conditions, which provided tetracycle **5a** whose

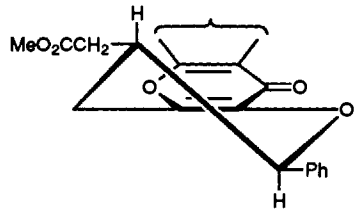
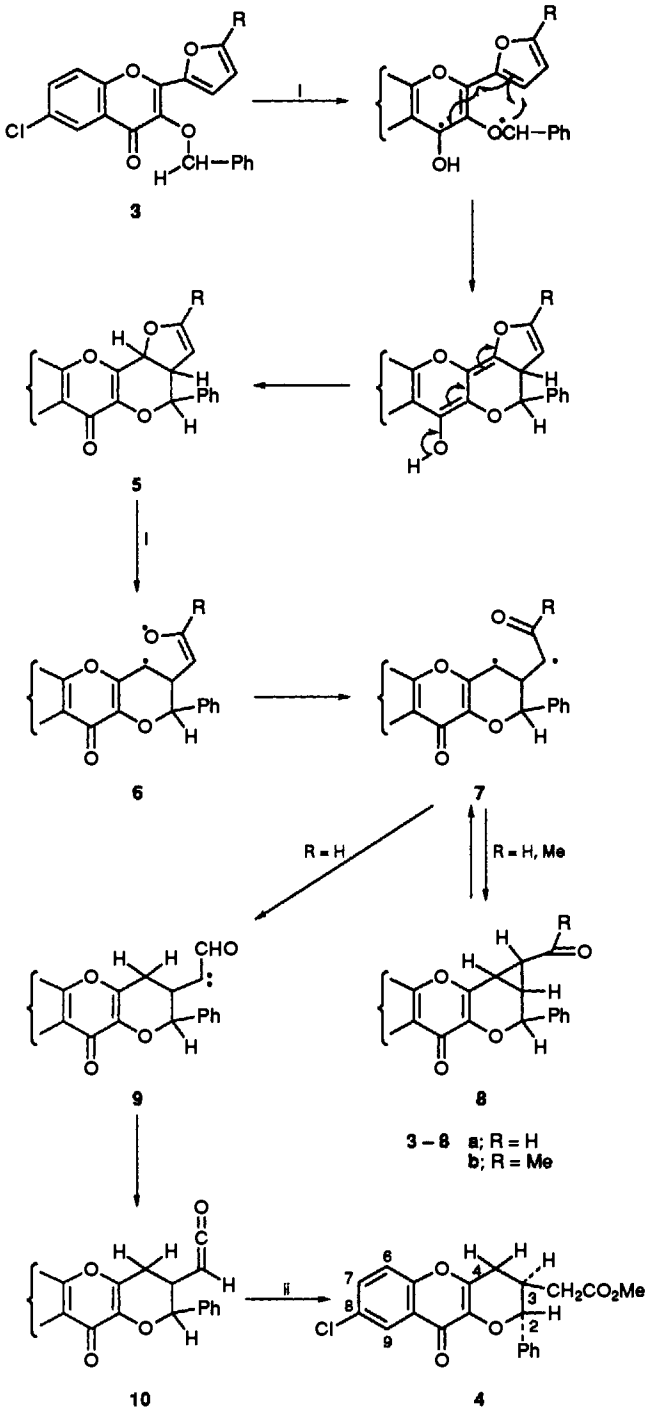


Fig. 1



Scheme 3 *Conditions:* i, *hν*; ii, MeOH

structure was again confirmed by its ^{1}H NMR and mass spectra. That **3a** ⟶ **5a** is only a photorearrangement was confirmed by the peak at M^+ 352/354. The ^{1}H NMR spectrum of **5a** revealed that protons belonging to the furan moiety in substrate **3a** had moved to higher field, and the signals due to 3-

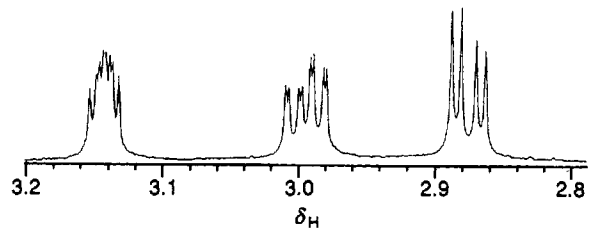
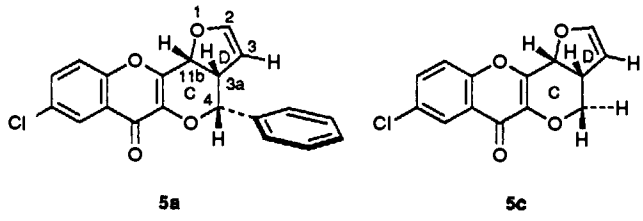


Fig. 2 500 MHz ^{1}H NMR spectrum of the cyclopropanecarbaldehydic protons of compound **8a**

OCH_2Ph (δ_H 5.27 present in compound **3a**) were missing. The spectrum showed resonances at δ_H 6.55 (1 H, d, J 2.8 Hz, 2-H), 5.20 (1 H, d, J 8.2 Hz, 11b-H), 4.83 (1 H, m, 3-H), 4.32 (1 H, d, J 10.8 Hz, 4-H) and a complex multiplet at δ_H 3.35–3.02 (1 H, m, 3a-H). Double irradiation of the signals between δ 3.35 and 3.02 converted the doublets at δ_H 5.20 and 4.32 into singlets and the multiplet at δ_H 4.83 into a doublet (J 2 Hz). Regarding the stereochemistry of ring junction C/D in compound **5a**, it could be a result of the preferred direction of protonation of the preceding enol; a consequence of the formation of the lower energy *cis*-isomer compared with the *trans* one.

That the three methine protons (11b-H, 3a-H and 4-H) are in a *cis*-orientation has been confirmed by coupling constants $J_{11b,3a}$ 8.2 Hz [11] and $J_{3a,4}$ 10.8 Hz. That the ring C is in a half-chair conformation with the phenyl ring held in an equatorial position is borne out by the fact that 3-H becomes shielded as compared with a similar proton in the parent compound **5c**,[12] where no phenyl group is available at C(4).



5a **5c**

The tetracyclic compound **5a** on further irradiation in benzene was completely converted into the cyclopropanecarbaldehyde **8a**, which showed ν_{max}/cm^{-1} at 1695 (CHO) and 1640 (CO), and m/z 352/354 (M^+, 8%), indicating again only a molecular rearrangement of the furan **5a** to the cyclopropanecarbaldehyde **8a**. A 500 MHz ^{1}H NMR spectrum (Fig. 2) of compound **8a** showed resonances at δ_H 9.410 (1 H, d, J 2.9 Hz, CHO), 3.151–3.130 (1 H, ddd, 1-H), 3.007–2.977 (1 H, ddd, 1a-H) and 2.885–2.861 (1 H, dd, 9b-H). Decoupling of the doublet at δ 9.410 converted the ddd at δ 3.14 (1-H) into a quartet (J 3.5 and 4.8 Hz) and, conversely, irradiation of the signal at δ 3.14 converted the ddd due to 1a-H to a quartet (J 1.2 and 8.9 Hz), and the dd due to 9b-H to a doublet (J 8.9 Hz). The coupling constants between the various protons proved helpful in elucidating their stereochemical relationships. That 9b-H and 1a-H are *cis* to each other and that 1-H is *trans* to both 9b-H and 1a-H is brought out by the fact that $J_{9b,1}$, $J_{1,1a}$ and $J_{9b,1a}$ are 3.5, 4.8 and 8.8 Hz, respectively.[13] Padwa and Koehn [14] have observed that in cyclopropanecarbaldehydes fused to cyclohexanes, 1-H appears at δ_H ~2.6, about 0.55 ppm upfield of the signal observed in the present case (δ_H 3.15). It may be suggested here, of course with a little reservation, that the pyran ring is in a boat form and in such a conformation the separation between 1-H and one of the sp^3-orbitals of oxygen (of the pyran) would be minimal. This would offer extra deshielding to 1-H, thus implying that the CHO group is *exo*. From Molecular Mechanics Program (MMP) calculations (Fig. 3), such a suggestion can be seen to be tenable. We mention here that the

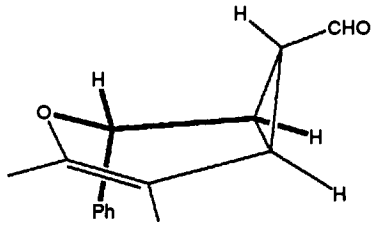
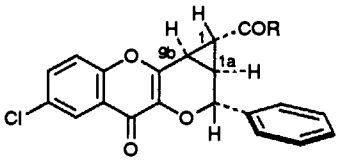


Fig. 3 MMP calculations on the conformation of rings C and D in compound **8a**

tendency of the pyran ring to exist in the boat form, rather than in a preferred chair form, is probably due to the presence of the fused cyclopropane ring which makes the energy difference between the chair form and boat form considerably less than it normally is. Of principal significance here was the signal at δ_H 5.57 which could be assigned to 2-H. Its splitting (1.2 Hz) shows that the planes containing 1a-H and 2-H possess a torsion angle φ tending to 90°. The carbon skeleton of compound **8a** was further confirmed from its fully decoupled ^{13}C NMR spectrum (see Experimental section).

Alternatively to the above proposed biradical mechanism (Scheme 3), these ring-contraction mechanisms may be looked upon as 1,3-sigmatropic shifts, at least formally.[16] Taking a cue from the above experiments, when compound **3a** was photolysed in methanol and the reaction was carefully monitored (TLC), it was found that the ester **4** was formed through the intermediacy of tetracycles **5a** and **8a**. In order to gain additional information about these transformations, we irradiated compound **3b** separately in methanol and benzene and obtained intermediates **5b** and **8b** in each case. The structure of each of these compounds was confirmed from NMR (^1H, ^{13}C) and mass spectral data.



8a; R = H
b; R = Me

It has been observed that, in the photolysis of compound **3a**, the formation of the aldehyde **8a** commences after almost the complete depletion of the furan intermediate **5a**, whereas the formation of the cyclopropyl ketone **8b** begins long before intermediate **5b** completely disappears. The reason for such behaviour is hard to comprehend, but a possible explanation is that the presence of the Me group might render the cleavage of the C–O bond thermodynamically easier than in the intermediate **5a**. That compound **5a** is the sole primary photoproduct of substrate **3a** (in methanol or benzene) was confirmed by irradiation of the latter for different times. The band at λ_{max} 323 (due to C=O in **3a**) rapidly decreased in intensity and the absorption belonging to compound **5a** rapidly appeared; in addition, the changes in the spectrum involved an isosbestic point at 255 nm (Fig. 4).

Experimental

M.p.s were measured on a sulfuric acid bath and are uncorrected. The IR spectra (Nujol) were scanned on a Perkin-Elmer IR-842 spectrophotometer and the NMR (^1H, ^{13}C) spectra ($CDCl_3$) were recorded on a Perkin-Elmer R-32 (90 MHz) spectrometer or a JEOL 100, Bruker WH 200, or GE 500 MHz spectrometer. The chemical shifts are expressed on the

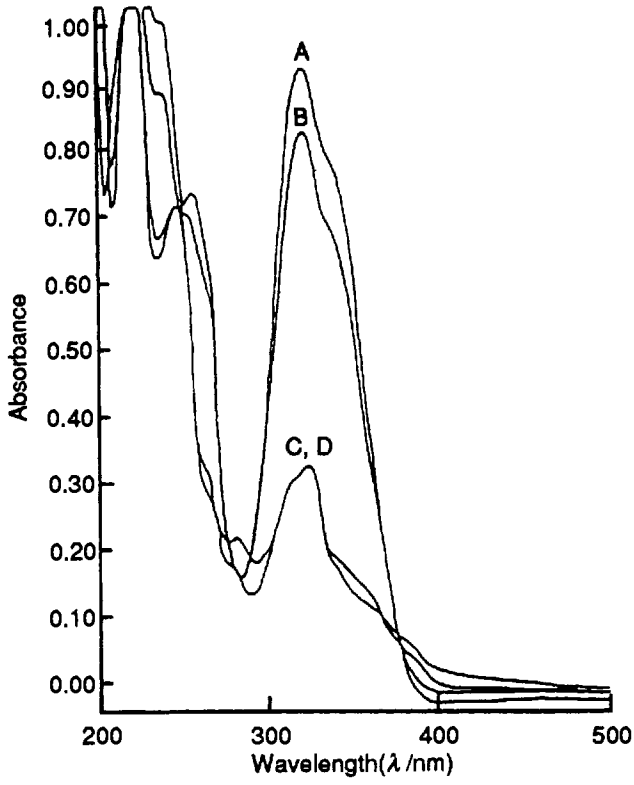


Fig. 4 UV spectrum of compound **3a** for different irradiation times: A (0 min), B (1 min), C (2 min), D (3 min)

δ scale with $SiMe_4$ as internal standard, with J values given in Hz. Mass spectra were recorded on a JMA 2000 on-line spectrometer with a direct insertion probe at 70 eV. TLC plates were coated with silica gel-G (suspended in water) and iodine vapour was used as the visualising agent. Silica gel (60–120 mesh) was used for column chromatography. The columns were packed and left overnight, before being used for fractionations. Light petroleum refers to the fraction with distillation range 60–80 °C.

1-(5′-*Chloro*-2′-*hydroxyphenyl*)-3-(2″-*furyl*)*propenone* **1a**.—A solution of 1-(5-chloro-2-hydroxyphenyl)ethanone (6.8 g, 0.04 mol) and 2-furaldehyde (3.8 g, 0.04 mol) in ethanol at 0 °C was stirred with powdered NaOH (8.0 g, 0.2 mol). The reaction mixture, deep red, was stirred for 3 h and then acidified with dil. HCl to give *compound* **1a** as a yellow solid (8.0 g, 80%), m.p. 90–91 °C (lit.,[7] 85 °C); ν_{max}/cm^{-1} 3200 (OH) and 1660 (CO); δ_H(90 MHz; $CDCl_3$) 12.75 (1 H, br s, 2′-OH), 7.82 (1 H, d, 6′-H), 7.75–7.15 (4 H, m, 4′-, 2-, 3- and 5″-H), 6.95 (1 H, d, 3′-H), 6.82 (1 H, d, 3″-H) and 6.55 (1 H, dd, 4″-H) (Found: C, 62.7; H, 3.5. $C_{13}H_9ClO_3$ requires C, 62.78; H, 3.62%).

1-(5′-*Chloro*-2′-*hydroxyphenyl*)-3-(5″-*methyl*-2″-*furyl*)*propenone* **1b**.—(86%), m.p. 156–157 °C; ν_{max}/cm^{-1} 3200 (OH) and 1650 (CO); δ_H(90 MHz; $CDCl_3$) 12.85 (1 H, br s, 2′-OH), 7.85 (1 H, d, J 2, 6′-H), 7.60–7.20 (3 H, m, 2-, 3- and 4′-H), 6.94 (1 H, d, 3′-H), 6.70 (1 H, d, 3″-H), 6.15 (1 H, d, 4″-H) and 2.42 (3 H, s, 5″-Me) (Found: C, 63.85; H, 4.2. $C_{14}H_{11}ClO_3$ requires C, 64.00; H, 4.19%).

6-*Chloro*-2-(2′-*furyl*)-3-*hydroxy*-4-*oxo*-4H-1-*benzopyran* **2a**.—To a stirred solution of compound **1a** (3.4 g, 13.6 mmol) in methanol (20 cm^3)–aq. NaOH (10 cm^3; 20%) cooled to 0 °C was added 30% H_2O_2 (5 cm^3) dropwise (5 h). The reaction mixture, on decomposition with dil. HCl, gave *compound* **2a** as a yellow solid (1.3 g, 60%), m.p. 198 °C (lit.,[7] 168 °C); ν_{max}/cm^{-1} 3260

(OH) and 1635 (CO); δ_H(90 MHz; $CDCl_3$) 12.80 (1 H, br s, 3-OH), 8.18 (1 H, br s, 5-H), 7.75 (2 H, m, 7- and 8-H), 7.58 (1 H, m, 5'-H), 7.37 (1 H, m, 3'-H) and 6.25 (1 H, m, 4'-H) (Found: C, 58.4; H, 2.6. $C_{13}H_7ClO_4$ requires C, 58.43; H, 2.67%).

6-Chloro-3-hydroxy-2-(5'-methyl-2'-furyl)-4-oxo-4H-1-benzopyran **2b**.—(71%), m.p. 204–206 °C; ν_{max}/cm^{-1} 3240 (OH) and 1636 (CO); δ_H(90 MHz; $CDCl_3$) 12.80 (1 H, br s, 3-OH), 8.15 (1 H, d, *J* 2.4, 5-H), 7.70 (2 H, m, 7- and 8-H), 7.37 (1 H, br s, 3'-H), 6.20 (1 H, d, 4'-H) and 2.47 (3 H, s, 5'-Me) (Found: C, 60.6; H, 3.1. $C_{14}H_9ClO_4$ requires C, 60.76; H, 3.25%).

3-Benzyloxy-6-chloro-2-(2'-furyl)-4-oxo-4H-1-benzopyran **3a**.—A suspension of compound **2a** (4.0 g, 15 mmol), benzyl chloride (1.72 cm^3, 15 mmol), KI (4.0 g) and K_2CO_3 (15 g) in acetone (200 cm^3) was refluxed for 6 h. Filtration, evaporation and passage of the residue through a column of silica gel gave compound **3a** (4.5 g, 83%), m.p. 122 °C; ν_{max}/cm^{-1} 1620 (CO); δ_H(200 MHz; $CDCl_3$) 8.16 (1 H, d, *J* 2, 5-H), 7.65–7.15 (9 H, m, 7-, 8-, 3'- and 5'-H and 3-OCH_2Ph), 6.58 (1 H, dd, 4'-H) and 5.27 (2 H, s, 3-OCH_2Ph) (Found: C, 68.2; H, 3.7. $C_{20}H_{13}ClO_4$ requires C, 68.08; H, 3.68%).

3-Benzyloxy-6-chloro-2-(5'-methyl-2'-furyl)-4-oxo-4H-1-benzopyran **3b**.—(83%), m.p. 127–129 °C; ν_{max}/cm^{-1} 1635 (CO); δ_H(90 MHz; $CDCl_3$) 8.18 (1 H, d, *J* 2, 5-H), 7.60–7.25 (7 H, m, 7- and 8-H, 3-OCH_2Ph), 7.17 (1 H, d, *J* 2, 3'-H), 6.16 (1 H, d, *J* 2, 4'-H), 5.28 (2 H, s, 3-OCH_2Ph) and 2.42 (3 H, s, 5'-Me) (Found: C, 68.8; H, 3.8. $C_{21}H_{15}ClO_4$ requires C, 68.85; H, 4.09%).

Irradiation of 3-Benzyloxy-6-chloro-2-(2'-furyl)-4-oxo-4H-1-benzopyran in Methanol **3a**.—The benzopyran **3a** (600 mg) was dissolved in magnesium-dried methanol and the solution was refluxed for 5 min. The solution was outgassed with nitrogen for 1 h and was then irradiated in an immersion apparatus with a 450 W high-pressure mercury arc (Hanovia) surrounded by a Pyrex water-cooled jacket. After 1.5 h, removal of the solvent under reduced pressure yielded a crude product, which was chromatographed over silica gel. The column was eluted with light petroleum (300 cm^3), light petroleum–benzene (100 cm^3; 1 : 1) to elute starting compound **3a**; continued elution, with benzene–ethyl acetate (19 : 1), extracted *tricycle* **4** (60 mg, 20%), m.p. 211–212 °C; *m/z* 384/386 (M^+, 25%) and 117 (100); ν_{max}/cm^{-1} 1735 (CO) and 1640 (CO); δ_H(100 MHz; $CDCl_3$) 8.22 (1 H, d, *J* 2, 9-H), 7.57 (1 H, dd, *J* 2 and 8, 7-H), 7.48–7.25 (6 H, m, 6-H and 2-Ph), 5.01 (1 H, d, *J* 8, 2-H), 3.64 (3 H, s, OMe), 3.20–2.60 (3 H, m, 4-H_2 and 3-H) and 2.43–2.31 (2 H, d, *J* 6, 3-CH_2CO_2Me) (Found: C, 65.4; H, 4.4. $C_{21}H_{17}ClO_5$ requires C, 65.53; H, 4.42%).

Irradiation of Compound **3a** *in Benzene*.—A solution of compound **3a** (1.0 g) in thiophene-free, dry benzene (100 cm^3) was photolysed under the above conditions for 25 min. The reaction mixture, on chromatography, provided starting compound **3a** (40 mg recovery) and the *tetracycle* **5a** (900 mg, 90%), m.p. 173–174 °C; ν_{max}/cm^{-1} 1649 (CO); *m/z* 352/354 (M^+, 100%); δ_H(90 MHz; $CDCl_3$) 8.16 (1 H, d, *J* 2.5, 7-H), 7.57–7.20 (7 H, m, 9- and 10-H, and 4-Ph), 6.55 (1 H, d, *J* 2.8, 2-H), 5.20 (1 H, d, *J* 8.2, 11b-H), 4.83 (1 H, m, 3-H), 4.32 (1 H, d, *J* 10.8, 4-H and 3.35–3.02 (1 H, m, 3a-H) (Found: C, 68.1; H, 3.75. $C_{20}H_{13}ClO_4$ requires C, 68.08; H, 3.68%).

Irradiation of Compound **5a** *in Benzene*.—A solution of compound **5a** (500 mg) in benzene (80 cm^3) was photolysed (450 W Hanovia lamp) and the reaction mixture was then chromatographed to give the *cyclopropanecarbaldehyde* **8a**, (80 mg, 16%), m.p. 150–151 °C; *m/z* 352/354 (M^+, 8%) and 323/325 (M^+ – CHO, 100); ν_{max}/cm^{-1} 1695 (CO) and 1640 (CO); δ_H(500 MHz; $CDCl_3$) 9.410 (1 H, d, *J* 2.9, CHO), 8.16 (1 H, d, *J* 2.5, 5-H), 7.57 (1 H, dd, *J* 8.0 and 2.5, 7-H), 7.41–7.21 (6 H, m, 8-H and 2-Ph), 5.57 (1 H, d, *J* 1.2, 2-H), 3.151–3.130 (1 H, ddd, *J* 2.9, 3.5 and 4.8, 1-H), 3.007–2.977 (1 H, ddd, *J* 1.2, 4.8 and 8.8, 1a-H) and 2.885–2.861 (1 H, dd, *J* 3.5 and 8.8, 9b-H); δ_C(125 MHz; $CDCl_3$) 196.30 (CHO), 169.62 (C-4), 153.30 (C-8a), 152.10 (C-9a), 137.33 (C-3a), 133.50 (C-6), 133.30 (C-7), 130.84, 126.74, 125.48 and 125.44 (C-Ph), 128.83 (C-5), 125.13 (C-4a), 119.40 (C-8), 71.56 (C-2), 33.95 (C-1a), 31.85 (C-1) and 21.88 (C-9b) (Found: C, 68.1; H, 3.8. $C_{20}H_{13}ClO_4$ requires C, 68.08; H, 3.68%).

Irradiation of Compound **8a** *in Methanol*.—A solution of compound **8a** (50 mg) in methanol (50 cm^3) was photolysed to give the ester **4**, identified through its IR and NMR spectra.

Irradiation of Compound **3b** *in Benzene*.—A solution of compound **3b** (500 mg) in benzene (70 cm^3) was irradiated for 60 min, and the reaction mixture on chromatography gave the *tetracycle* **5b** (175 mg, 35%), m.p. 166–168 °C; ν_{max}/cm^{-1} 1660 (CO); δ_H(90 MHz; $CDCl_3$) 8.20 (1 H, d, *J* 2, 7-H), 7.60–7.25 (7 H, m, 9- and 10-H, and 4-Ph), 5.25 (1 H, d, *J* 9, 11b-H), 4.48 (1 H, d, *J* 2.5, 3-H), 4.37 (1 H, d, *J* 11, 4-H), 3.32–3.02 (1 H, m, 3a-H) and 1.90 (3 H, s, 2-Me) [Found: M^+, 366.0648 (100%). $C_{21}H_{15}ClO_4$ requires *M*, 366.0658].

Further elution of the column with benzene–ethyl acetate furnished a second solid, *compound* **8b** (250 mg, 50%), m.p. 180–182 °C; ν_{max}/cm^{-1} 1700 (CO) and 1645 (CO); δ_H(200 MHz; $CDCl_3$) 8.157 (1 H, d, *J* 2.4, 5-H), 7.561–7.264 (7 H, m, 7- and 8-H, 2-Ph), 5.58 (1 H, d, *J* 0.8, 2-H), 3.094–3.053 (1 H, dd, *J* 3.5 and 4.8, 1-H), 2.943–2.874 (1 H, ddd, *J* 0.8, 4.8 and 8.9, 1a-H), 2.766–2.724 (1 H, dd, *J* 3.5 and 8.9, 9b-H) and 2.421 (3 H, s, 1-COMe); δ_C(50 MHz; $CDCl_3$) 206.13 (*C*OMe), 169.60 (C-4), 153.31 (C-8a), 152.95 (C-9a), 137.59 (C-3a), 133.37 (C-6), 133.15 (C-7), 130.77, 126.80, 125.67 and 125.46 (C-Ph), 128.76 (C-5), 125.27 (C-4a), 119.40 (C-8), 71.57 (C-2), 33.42 (C-1a), 32.69 (Me), 31.32 (C-1) and 22.62 (C-9b) [Found: M^+, 366.0653 (6%), 323.0462 (M^+ – COMe, 100). $C_{21}H_{15}ClO_4$ requires *M*, 36.0658).

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