Photochemistry of chromones: photoreorganisation of 3-alkoxy-2-thienyl-4-oxo-4*H*-1-benzopyrans

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Photoirradiation of a methanolic solution of 3-alkoxy-2-thienyl-4-oxo-4*H*-1-benzopyrans with Pyrex filtered UV light leads to cyclised and cyclodehydrogenated angular products involving both thiophene and alkoxy groups. The reaction is initiated through H-abstraction. The product distribution depends upon the substituents on the thiophene ring.

Enones bearing alkoxy or alkyl groups at C-3, on irradiation with UV light lead to the formation of a 1,4-biradical through abstraction of a H-atom from the alkoxy/alkyl moiety by the excited carbonyl group.[1] The photoproducts formed depend upon the substituents at C-2. The photolysis of 2-phenyl-[2] and 2-furyl-3-alkoxy-4-oxo-4*H*-1-benzopyrans[3] produced angular tetracyclics, 2-styryl derivatives[4] produced linear tricyclics whereas 2-methyl-3-alkoxy derivatives provided both oxetanols and desmethoxy chromones.[5] Here we report the results of our investigations on the phototransformations of some 3-alkoxy-4-oxo-4*H*-1-benzopyrans bearing thiophene at C-2.

In this research we were prompted by two considerations: (a) how a thiophene moiety [stabilisation energy (SE) 32 kcal] affects the product formation/distribution compared with a furan (SE 16–18 kcal) or phenyl moiety (SE 36 kcal) at C-2 and (b) whether phototranspositions could become available in these photoreactions—a route common in the photolysis of 2-aryl/alkyl thiophenes.[6]

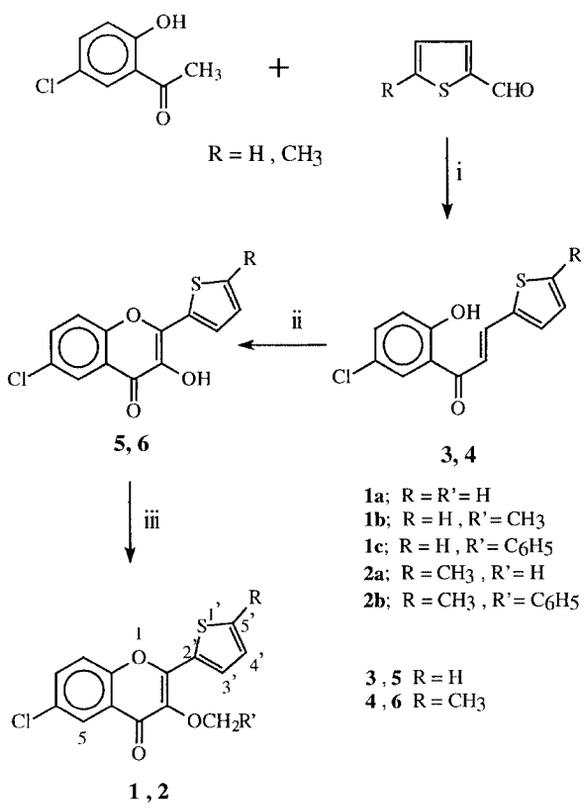
The required thienylbenzopyrans **1** and **2** were synthesised commencing with the condensation of (5-chloro-2-hydroxyphenyl)ethanone with a thiophene-2-carbaldehyde (Scheme 1).

The structures of the benzopyrans **1** and **2** and their precursors were found to be consistent with their spectral parameters (*vide* Experimental section). The ^{1}H NMR spectral assignments were confirmed through decoupling experiments: in **1a** decoupling of signals at δ_H 7.90 (3′-H) converted the dd at δ_H 7.15 (4′-H) into a d (J 5 Hz); similarly the dd at δ_H 7.90 changed to a singlet ($w_{1/2}$ 1.5 Hz) on irradiation of the dd at δ_H 7.15.

The photolysis of **1c** in methanol solution (0.001 M) with Pyrex filtered UV light from a 450 W Hg lamp exhibited the complete disappearance (TLC) of **1c** in 60 min. A chromatographic separation produced **7c** and **8c** (Scheme 2).

That tetracyclic compound **7c** was only a photoreorganised product of **1c** is evident from its mass spectrum, *m*/*z* 368/70 ($M^{+\bullet}$); two other fragments at *m*/*z* 214 and 154 lent further support to the structure **7c** as they could become available through the retro-Diels–Alder (RDA) mode of cleavage. The acceptability of ^{1}H NMR assignments were confirmed as follows: (a) irradiation of the signal at δ_H 6.46 (d, 2-H) converted the dd at δ_H 5.17 (3-H) to a d ($J_{3a,3}$ 3 Hz), (b) decoupling of the d at δ_H 5.05 (11b-H) simplified the multiplet at δ_H 3.45 (3a-H) to a dd ($J_{3a,4}$ 10.5 Hz, $J_{3a,3}$ 3 Hz), (c) signals at δ_H 3.45 were reduced to a dd ($J_{3a,11b}$ 8 Hz, $J_{3a,3}$ 3 Hz) on irradiation of the absorption at δ_H 4.78 (4-H).

The second photoproduct **8c** had in its mass spectrum the molecular ion peak at *m*/*z* 366/68 pointing to the loss of 2 mass units in its formation from **1c**. The other prominent ions were



Scheme 1 *Reactions and conditions*: i, NaOH, EtOH; ii, H_2O_2 (30%), KOH; iii, K_2CO_3, Me_2CO, DMF, R′X (R′ = CH_3, C_2H_5, $C_6H_5CH_2$; X = I, Cl).

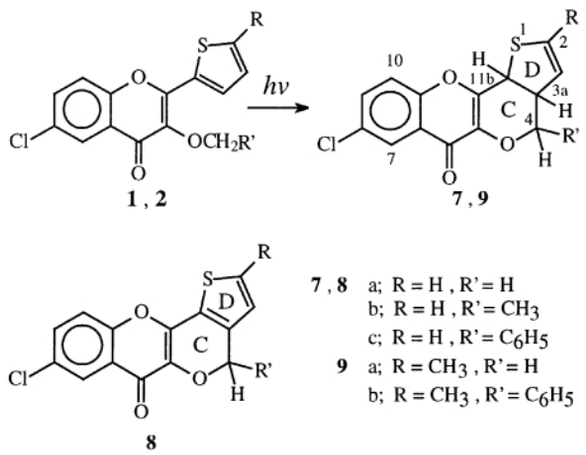
located at *m*/*z* 212 and 154 (RDA). The thienyl protons resonated at δ_H 7.57 (d, J 4.5 Hz, 2-H) and 6.82 (d, J 4.5 Hz, 3-H).

The photolysis of **1a** and **1b** produced **7a**, **8a** and **7b**, **8b** (yield <30%) respectively, although the reaction was much slower as compared to that of **1c**. The only photoproducts obtained from **2a** and **2b** were **9a** and **9b** and not even a trace (<5%) of products corresponding to **8** seemed to be formed (TLC, ^{1}H NMR of crude photolysate). The exclusive formation of **9a** and **9b** was confirmed by recording the UV spectrum of **2b** (2.0×10^{-4} M in MeOH) at different times of irradiations (0, 1, 2, 3, 4 min) when absorption at λ 361 nm started diminishing and the changes in the spectrum involved an isosbestic point at λ 260 nm.[3]

Regarding the C/D ring fusion in **7a**, **7b**, **7c**, **9a** and **9b**, it is concluded from the use of Dreiding models that the five membered ring D and pyran ring C must be *cis* fused and this is

Table 1

Compound	**7a**	**7b**	**7c**	$\Delta\delta_H$	**9a**	**9b**	$\Delta\delta_H$
$\delta_{3\text{-H}}$	5.55	5.55	5.17	0.38	5.10	4.78	0.32



Scheme 2

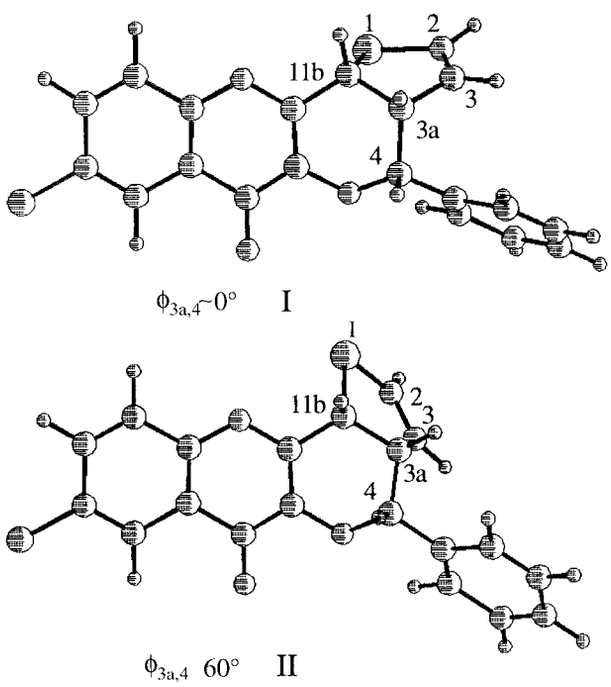
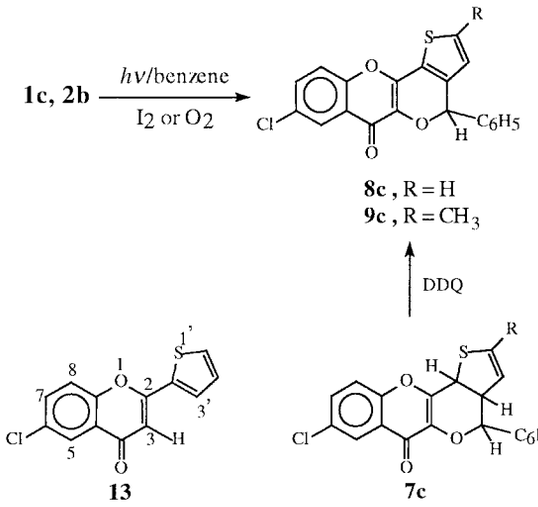


Fig. 1

borne out by the fact[7] that $J_{3a,11b}$ is 8 Hz (φ-3a, 11b 27.32°). Similarly the relative stereochemical disposition of 3a-H and 4-H is *cis*-axial ($\varphi \sim 0°$), thus placing the bulkier group, CH_3 or C_6H_5, in **7b**, **7c** and **9b** in a pseudo-equatorial conformation. Such a contention gets further support from the observation that in **7c** and **9b**, 3-H appeared at higher field[3] than the same proton in **7a**, **7b** and **9a** by ~0.35 ppm (Table 1). The only explanation for such an observation can be that it is only in the pseudo-equatorial position that the phenyl ring at 4-C would shield the proton 3-H (I, Fig. 1). MMP calculations show that in no other conformation such as in II ($\varphi_{3a,4}$ 60°), would 3-H experience shielding.[8]

The compounds **8a**, **8b** and **8c** are formed independently[9] from **1a**, **1b** and **1c** and not *via* **7a**, **7b** and **7c**. This is confirmed from the photoirradiation of **7c** when only polymeric products were obtained and no product corresponding to **8** was realised.

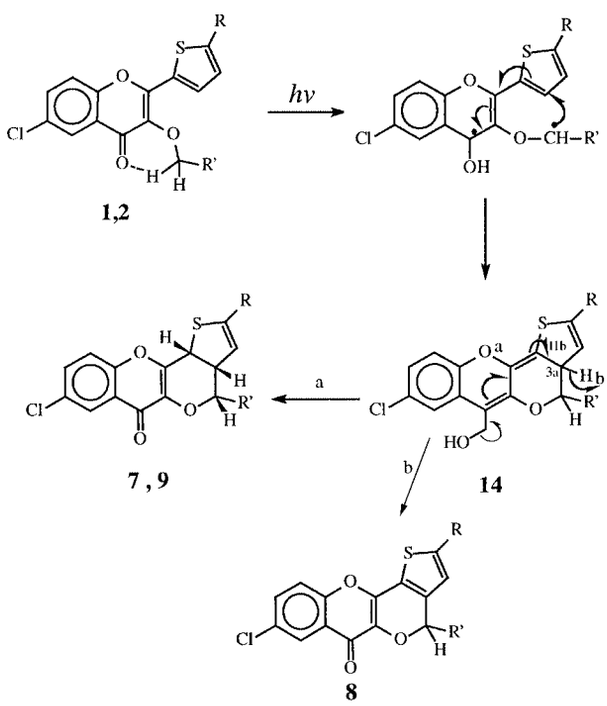
Further confirmation of the structure **7c** was obtained by its DDQ oxidation to **8c** (Scheme 3). Also when the photolysis of



Scheme 3

1c and **2b** was carried out in the presence of I_2 or O_2, only **8c** (R = H) and **9c** (R = CH_3) were produced.

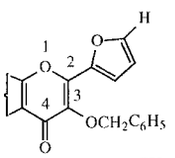
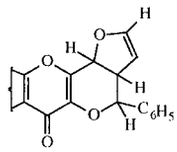
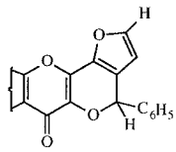
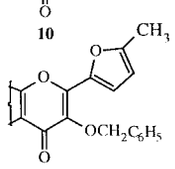
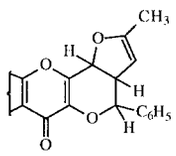
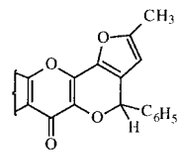
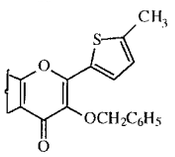
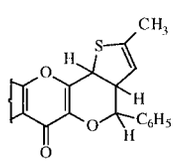
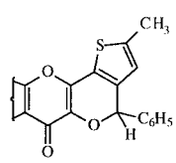
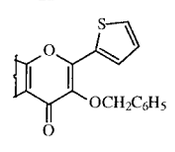
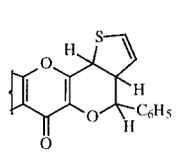
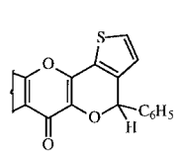
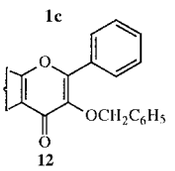
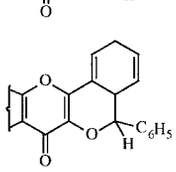
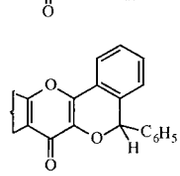
Even the solvent polarity (C_6H_6, MeOH) did not have any significant influence on the product distribution (**7**, **9**:**8**). This suggests that the formation of **7** is intramolecular and probably occurs through a 1,5-sigmatropic migration, in enol **14**, formed initially by the abstraction of H from 3-alkoxy group by the excited C=O group of the pyrone **1**, **2** (Scheme 4).



Scheme 4

Regarding the effect of substitution at C-2 of the pyrone ring in **1** or **2** on product distribution/formation, an examination of Table 2 shows that in the case of furyl or methylfuryl or methylthienyl chromones **10**, **11** and **2b** only the photocyclised products (A) are obtained. In others (**1c** and **12** carrying phenyl or thiophene rings), both photocyclised (A) and photocyclodehydrogenated products (B) are formed. For such dichotomy, the only assignable reason could be the difference in electron density in the ring moiety at C-2. An examination of the results in the Table 2 reveals that as we go down the table, the electron density in the ring at C-2 decreases and the formation of cyclodehydrogenated products (B) become predominant. It is possible that, as shown in Scheme **4**, the transfer of H to the

Table 2

Compounds	A	B	Ratio of A : B[a]
 **10**			1 : 0[3]
 **11**			1 : 0[3]
 **2b**			1 : 0
 **1c**			1 : 0.2
 **12**			1 : 4[2]

[a] Ratios calculated from the isolated yield.

ring junction (at 11-b) is assisted and this becomes faster than cleavage of 3a-H leading to **8**. However in the case of 3-methoxy/ethoxy derivatives, the trend remains the same except that the ratio of A : B reaches 1 : 1 in **1a** and **1b** indicating the effect of the relative stability of the alkoxyl radical at C-3.

Phototranspositions,[6] a reaction prevalent in alkyl/aryl thiophenes through ring opening and isomerisation frequently occur, but in the present study all our attempts to observe such a mode of reaction in the photolysis of **1** and **2** proved unsuccessful. Even in the photolysis of 2-(2′-thienyl)-4-oxo-4*H*-1-benzopyrans **13**, no such reaction could be effected and the compound was recovered unchanged quantitatively.

In summary, the formation and distribution of cyclised and cyclodehydrogenated products from the photoirradiation of 3-alkoxy-2-arylchromones depend upon the electron density in aryl ring at C-2. Hydrogen abstraction from the 3-alkoxy group by the carbonyl of the chromones is preferred to phototranspositions in the 3-alkoxy-2-thienylchromones.

Experimental

Mps were determined on a sulfuric acid bath and are uncorrected. The UV spectra were recorded on a U-2000 Hitachi UV-spectrophotometer. The IR spectra (Nujol) were scanned on a Perkin-Elmer IR-842 spectrophotometer. The ^{1}H NMR spectra ($CDCl_3$) were recorded on a Perkin-Elmer R-32 (90 MHz) spectrometer. The chemical shifts are expressed on the δ scale with $SiMe_4$ as internal standard, with J values given in Hz. Mass spectra were recorded at 70 eV using a VG micromass 7070F instrument. 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″-thienyl)propenone 3

A solution of 1-(5-chloro-2-hydroxyphenyl)ethanone (6.8 g, 0.04 mol) and 2-thiophenecarbaldehyde (4.58 g, 0.04 mol) in methanol at 0 °C was stirred with powdered NaOH (8 g, 0.04 mol) for 5 h and was then poured onto ice–HCl to give **3** (7.58 g, 75%) mp 110–112 °C (lit.,[10] 114 °C); ν_{max}/cm^{-1} 3400(OH), 1635(CO); δ_H(90 MHz; $CDCl_3$) 12.75 (1H, br s, 2′-OH), 7.82 (1H, d, J 2 Hz, 6′-H), 7.55–7.27 (4H, m, 2-, 3-, 4′- and 5″-H), 7.30–7.00 (2H, m, 3″- and 4″-H), 6.95 (1H, d, J 9 Hz, 3′-H).

1-(5′-Chloro-2′-hydroxyphenyl)-3-(5″-methyl-2″-thienyl)-propenone 4. (81%), Mp 138 °C; (Found: C, 60.1; H, 3.8. $C_{14}H_{11}ClO_2S$ requires C, 60.4; H, 4.0%); ν_{max}/cm^{-1} 3400(OH), 1635(CO); δ_H(90 MHz; $CDCl_3$) 12.85 (1H, br s, 2′-OH), 7.80 (1H, d, J 15 Hz, 3-H), 7.72 (1H, d, J 2 Hz, 6′-H), 7.25 (1H, dd, J 2, 9 Hz, 4′-H), 7.18 (1H, d, J 4 Hz, 3″-H), 7.11 (1H, d, J 15 Hz, 2-H), 6.90 (1H, d, J 9 Hz, 3′-H), 6.79 (1H, d, J 4 Hz, 4″-H), 2.50 (3H, s, 5″-Me).

6-Chloro-3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 5

To a stirred solution of compound **3** (3 g, 0.015 mol) in methanol (30 cm^3)–aq. NaOH (10 cm^3, 20%) cooled to 0 °C was added 30% H_2O_2 (5 cm^3) dropwise. The mixture was then poured onto ice–HCl to give **5** (2.58 g, 86%), mp 200–202 °C (lit.,[10] mp 202 °C); ν_{max}/cm^{-1} 3260(OH), 1630(CO); δ_H(90 MHz;

$CDCl_3$) 11.0 (1H, br s, 3-OH), 8.20 (1H, d, *J* 2 Hz, 5-H), 8.00 (1H, dd, *J* 1, 4 Hz, 3′-H), 7.70 (1H, dd, *J* 2, 9 Hz, 7-H), 7.60 (1H, dd, *J* 1, 5 Hz, 5′-H), 7.30 (1H, d, *J* 9 Hz, 8-H), 7.20 (1H, dd, *J* 4, 5 Hz, 4′-H).

6-Chloro-3-hydroxy-2-(5′-methyl-2′-thienyl)-4-oxo-4*H*-1-benzopyran 6. (81%), Mp 215 °C (Found: C, 57.2; H, 3.0. $C_{14}H_9ClO_3S$ requires C, 57.5; H, 3.1%); ν_{max}/cm^{-1} 3260(OH), 1632(CO); δ_H(90 MHz; $CDCl_3$) 11.50 (1H, br s, 3-OH), 8.05 (1H, d, *J* 2 Hz, 5-H), 7.65 (1H, d, *J* 4 Hz, 3′-H), 7.45 (1H, dd, *J* 2, 9 Hz, 7-H), 7.28 (1H, d, *J* 9 Hz, 8-H), 7.10 (1H, d, *J* 4 Hz, 4′-H), 2.50 (3H, s, 5′-Me).

3-Alkoxy-6-chloro-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 1 and 3-alkoxy-6-chloro-2-(5′-methyl-2′-thienyl)-4-oxo-4*H*-1-benzopyran 2

A suspension of compound **5** or **6** (2.8 g, 0.01 mol), alkyl halides (0.01 mol $CH_3I/C_2H_5I/C_6H_5CH_2Cl$), KI (1 g) and freshly ignited K_2CO_3 (5 g) in dry acetone (30 cm^3) was refluxed for 5 h. Filtration, evaporation and percolation of the residue through a column of silica gel gave compound **1a**, **1b** and **1c** and **2a** and **2b**.

3-Benzyloxy-6-chloro-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 1c. (70%), Mp 138 °C (Found: C, 65.4; H, 3.3. $C_{20}H_{13}ClO_3S$ requires C, 65.2; H, 3.5%); λ_{max} (MeOH)/nm 346 and 260.5 (ε/dm^3 mol^{-1} cm^{-1} 49000 and 34000); ν_{max}/cm^{-1} 1630 (CO); δ_H(90 MHz; $CDCl_3$) 8.20 (1H, d, *J* 2 Hz, 5-H), 7.90 (1H, dd, *J* 1, 4 Hz, 3′-H), 7.60–7.20 (8H, m, 7- and 8-H, 5′-H, 3-O$CH_2C_6H_5$), 7.10 (1H, dd, *J* 4, 5 Hz, 4′-H), 5.25 (2H, s, 3-O$CH_2C_6H_5$).

6-Chloro-3-ethoxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 1b. (68%), Mp 135 °C (Found: C, 58.9; H, 3.8. $C_{15}H_{11}ClO_3S$ requires C, 58.8; H, 3.6%); λ_{max} (MeOH)/nm 343.5 and 260.5 (ε/dm^3 mol^{-1} cm^{-1} 34000 and 21000); ν_{max}/cm^{-1} 1630 (CO); δ_H(90 MHz; $CDCl_3$) 8.19 (1H, d, *J* 2 Hz, 5-H), 7.90 (1H, dd, *J* 1, 4 Hz, 3′-H), 7.60–7.40 (2H, m, 5′-H, 7-H), 7.35 (1H, d, *J* 9 Hz, 8-H), 7.20 (1H, dd, *J* 3, 5 Hz, 4′-H), 4.30 (2H, q, *J* 8 Hz, 3-OCH_2CH_3), 1.50 (3H, t, *J* 8 Hz, 3-OCH_2CH_3).

6-Chloro-3-methoxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 1a. (88%), Mp 135–136 °C (Found: C, 57.3; H, 3.3. $C_{14}H_9ClO_3S$ requires C, 57.5; H, 3.1%); λ_{max} (MeOH)/nm 343 and 260.5 (ε/dm^3 mol^{-1} cm^{-1} 33000 and 23000); ν_{max}/cm^{-1} 1628 (CO); δ_H(90 MHz; $CDCl_3$) 8.25 (1H, d, *J* 2 Hz, 5-H), 7.90 (1H, dd, *J* 1, 4 Hz, 3′-H), 7.68–7.58 (2H, m, 5′-H, 7-H), 7.45 (1H, d, *J* 9 Hz, 8-H), 7.15–7.05 (1H, dd, *J* 3.5 Hz, 4′-H), 4.05 (3H, s, 3-OMe).

6-Chloro-3-methoxy-2-(5′-methyl-2′-thienyl)-4-oxo-4*H*-1-benzopyran 2a. (80%), Mp 130 °C (Found: C, 58.9; H, 3.9. $C_{15}H_{11}ClO_3S$ requires C, 58.8; H, 3.6%); λ_{max} (MeOH)/nm 357.5 and 263.5 (ε/dm^3 mol^{-1} cm^{-1} 24600 and 13100); ν_{max}/cm^{-1} 1638 (CO); δ_H(90 MHz; $CDCl_3$) 8.15 (1H, d, *J* 2 Hz, 5-H), 7.65 (1H, d, *J* 4 Hz, 3′-H), 7.45 (1H, dd, *J* 2, 9 Hz, 7-H), 7.35 (1H, d, *J* 9 Hz, 8-H), 6.78 (1H, d, *J* 4 Hz, 4′-H), 3.95 (3H, s, 3-OMe), 2.50 (3H, s, 5′-Me).

3-Benzyloxy-6-chloro-2-(5′-methyl-2′-thienyl)-4-oxo-4*H*-1-benzopyran 2b. (80%), Mp 143–144 °C (Found: C, 65.7; H, 3.7. $C_{21}H_{15}ClO_3S$ requires, C, 66.0; H, 3.9%); λ_{max}(MeOH)/nm 361 and 263.5 (ε/dm^3 mol^{-1} cm^{-1} 28900 and 14700); ν_{max}/cm^{-1} 1638 (CO); δ_H(90 MHz; $CDCl_3$) 8.10 (1H, d, *J* 2 Hz, 5-H), 7.65 (1H, d, *J* 4 Hz, 3′-H), 7.60–7.20 (7H, m, 7- and 8-H, 3-O$CH_2C_6H_5$), 6.78 (1H, d, *J* 4 Hz, 4′-H), 5.20 (2H, s, 3-O$CH_2C_6H_5$), 2.40 (3H, s, 5′-Me).

Irradiation of 3-benzyloxy-6-chloro-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 1c

The benzopyran **1c** (400 mg, 0.001 mol) was dissolved in magnesium-dried methanol (80 cm^3) and the solution was deoxygenated by bubbling in dry nitrogen gas for 10 min. Thereafter the solution was irradiated in an immersion apparatus with a 450 W high-pressure mercury arc (Hanovia) surrounded by a Pyrex water-cooled jacket. After 1 h, removal of the solvent under reduced pressure yielded a dark red gummy 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 the starting compound **1c** (10 mg) followed by a white solid **7c** (100 mg, 25%), mp 190–192 °C (Found: C, 65.5; H, 3.5. $C_{20}H_{13}ClO_3S$ requires C, 65.2; H, 3.5%); ν_{max}/cm^{-1} 1640(CO); *m*/*z* 368/370 (M$^+$); δ_H(90 MHz; $CDCl_3$) 8.20 (1H, d, *J* 2 Hz, 7-H), 7.55 (1H, dd, *J* 2, 9 Hz, 9-H), 7.45–7.20 (6H, m, 10–H, 4-*Ph*), 6.46 (1H, d, *J* 5 Hz, 2-H), 5.17 (1H, dd, *J* 3, 5 Hz, 3-H), 5.05 (1H, d, *J* 8 Hz, 11b-H), 4.78 (1H, d, *J* 10.5 Hz, 4-H), 3.55–3.35 (1H, m, 3a-H).

Further elution of the column with benzene–ethyl acetate (19 : 1) furnished a second white solid compound **8c** (20 mg, 5%), mp 232 °C (Found: C, 65.3; H, 3.2. $C_{20}H_{11}ClO_3S$ requires C, 65.6; H, 3.0%); ν_{max}/cm^{-1} 1640 (CO); *m*/*z* 366/368 (M$^+$); δ_H(90 MHz; $CDCl_3$) 8.23 (1H, d, *J* 2 Hz, 7-H), 7.57 (1H, d, *J* 4.5 Hz, 2-H), 7.53 (1H, dd, *J* 2, 9 Hz, 9-H), 7.48–7.37 (6H, m, 10-H, 4-*Ph*), 6.82 (1H, d, *J* 4.5 Hz, 3-H), 6.53 (1H, s, 4-H).

Irradiation of benzopyran 1c in benzene. A solution of compound **1c** (400 mg, 0.001 mol) in thiophene free dry benzene (80 cm^3) was photolysed under the above conditions. The reaction mixture, on chromatography, gave **7c** in 25% and **8c** in 5% yield respectively.

Irradiation of compound 1c in the presence of O_2. An oxygenated solution of **1c** (300 mg, 0.0008 mol) in dry benzene (80 cm^3), after the usual work up and chromatography provided **8c** (100 mg) in 33% yield characterized by TLC, mp and mmp.

Irradiation of compound 1c in the presence of I_2. Irradiation of **1c** (50 mg) in thiophene free dry benzene (30 cm^3) in the presence of I_2 (10 mg) under the above conditions, produced only **8c** (20 mg) after the usual chromatographic work up.

DDQ treatment of compound 7c. A mixture of **7c** (50 mg, 0.13 mol) and DDQ (30 mg, 0.13 mol) in xylene (20 cm^3) was refluxed for 20 h. Evaporation of solvent and percolation of the residue through a silica gel column eluted **8c** (35 mg), characterized by mmp.

Irradiation of 6-chloro-3-ethoxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 1b

A solution of compound **1b** (400 mg, 0.0013 mol) in methanol (80 ml) was photolysed under similar conditions to those employed for **1c**. The reaction mixture on chromatographic separation with pet. ether–benzene (1 : 1) and benzene–ethyl acetate (19 : 1) provided the starting compound **1b** (100 mg), mp 135 °C (mmp); followed by two tetracyclic compounds **7b** (50 mg, 16%), mp 195–196 °C (Found: C, 59.0; H, 3.8. $C_{15}H_{11}ClO_3S$ requires C, 58.8; H, 3.6%); ν_{max}/cm^{-1} 1640 (CO); *m*/*z* 306/308 (M$^+$); δ_H(90 MHz; $CDCl_3$) 8.10 (1H, d, *J* 2 Hz, 7-H), 7.50 (1H, dd, *J* 2, 9 Hz, 9-H), 7.35 (1H, d, *J* 9 Hz, 10-H), 6.35 (1H, d, *J* 5 Hz, 2-H), 5.55 (1H, dd, *J* 3, 5 Hz, 3-H), 4.92 (1H, d, *J* 8 Hz, 11b-H), 4.05–3.75 (1H, q of d, *J* 6 Hz, 4-H), 3.15–2.95 (1H, m, 3a-H), 1.45 (3H, d, *J* 6 Hz, 4-Me) and **8b** (40 mg, 14%), mp 230 °C (Found: C, 60.0; H, 3.0. $C_{15}H_9ClO_3S$ requires C, 59.2; H, 3.0%); ν_{max}/cm^{-1} 1640 (CO); *m*/*z* 304/306 (M$^+$); δ_H(90 MHz; $CDCl_3$) 8.20 (1H, d, *J* 2 Hz, 7-H), 7.57 (1H, *J* 4.5 Hz, 2-H), 7.53 (1H, dd, *J* 2, 9 Hz, 9-H), 7.37 (1H, d, *J* 9 Hz, 10-H), 6.80 (1H, d, *J* 4.5 Hz, 3-H), 5.55 (1H, q, *J* 7 Hz, 4-H), 1.65 (3H, d, *J* 7 Hz, 4-Me).

The chromone **1b** (30 mg) was photolysed in dry benzene (80 cm^3) in the presence of nitrogen to afford **7b** and **8b** in 10% and 20% yields respectively.

Irradiation of 6-chloro-3-methoxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 1a in methanol

A solution of compound **1a** (300 mg, 0.001 mol) in methanol (80 cm^3) was photolysed under similar conditions to those employed above and was chromatographed to give the starting compound **1a** (70 mg), mp 135–136 °C (mmp and co-TLC) and **7a** (30 mg, 14%), mp 190–192 °C; *m/z* 292/294 (Found: C, 57.2; H, 3.0. $C_{14}H_9ClO_3S$ requires C, 57.5; H, 3.1%); ν_{max}/cm^{-1} 1638 (CO); δ_H(90 MHz; $CDCl_3$) 8.15 (1H, d, *J* 2 Hz, 7-H), 7.60 (1H, dd, *J* 2, 9 Hz, 9-H), 7.35 (1H, d, *J* 9 Hz, 10-H), 6.30 (1H, d, *J* 5 Hz, 2-H), 5.55 (1H, dd, *J* 3, 5 Hz, 3-H), 4.85 (1H, d, *J* 8 Hz, 11b-H), 4.20–4.05 (1H, dd, *J* 4, 10 Hz, 4a-H), 3.85 (1H, d, *J* 10 Hz, 4b-H), 3.75–3.20 (1H, m, 3a-H) and **8a** (20 mg, 10%), mp 228–229 °C (Found: C, 58.0; H, 2.5. $C_{14}H_7ClO_3S$ requires C, 57.9; H, 2.4%); ν_{max}/cm^{-1} 1640 (CO); *m/z* 290/292 (M^+); δ_H(90 MHz; $CDCl_3$) 8.20 (1H, d, *J* 2 Hz, 7-H), 7.60 (1H, d, *J* 2 Hz, 2-H), 7.53 (1H, dd, *J* 2, 9 Hz, 9-H), 7.37 (1H, d, *J* 9 Hz, 10-H), 6.90 (1H, d, *J* 4.5 Hz, 3-H), 5.30 (2H, s, 4-H).

The chromone **1a** was photolysed in dry benzene (75 ml) in nitrogen to afford **7a** and **8a** in 8% and 20% yields respectively.

Irradiation of 6-chloro-3-methoxy-2-(5′-methyl-2′-thienyl)-4-oxo-4*H*-1-benzopyran 2a in dry benzene

The photolysis of a benzene solution of **2a** (400 mg, 0.0013 mol, 80 cm^3, 1 h) and chromatographic separation under similar conditions to those employed earlier provided **2a** in a small amount followed by **9a** (20%), mp 198 °C (Found: C, 60.0; H, 3.7. $C_{15}H_{11}ClO_3S$ requires C, 58.8; H, 3.6%); ν_{max}/cm^{-1} 1640 (CO); δ_H(90 MHz; $CDCl_3$) 8.10 (1H, d, *J* 2 Hz, 7-H), 7.50 (1H, dd, *J* 2, 9 Hz, 9-H), 7.35 (1H, d, *J* 9 Hz, 10-H), 5.10 (1H, d, *J* 3 Hz, 3-H), 4.90 (1H, d, *J* 8 Hz, 11b-H), 4.10–3.90 (3H, m, 3a-, 4a- and 4b-H), 1.90 (3H, s, 2-Me). Irradiation of **2a** in MeOH also provided **9a**.

Irradiation of 3-benzyloxy-6-chloro-2-(5′-methyl-2′-thienyl)-4-oxo-4*H*-1-benzopyran 2b in benzene. This gave **9b** (20%), mp 215 °C (Found: C, 66.0; H, 4.0. $C_{21}H_{15}ClO_3S$ requires C, 66.0; H, 3.9%); ν_{max}/cm^{-1} 1638 (CO); δ_H(90 MHz; $CDCl_3$) 8.20 (1H, d, *J* 2 Hz, 7-H), 7.50 (1H, dd, *J* 2, 9 Hz, 9-H), 7.45–7.20 (6H, m, 10-H, 4-*Ph*), 4.78 (1H, d, *J* 3 Hz, 3-H), 5.05 (1H, d, *J* 8 Hz, 11b-H), 4.75 (1H, d, *J* 11 Hz, 4-H), 3.50–3.30 (1H, m, 3a-H), 1.90 (3H, s, 2-Me).

6-Chloro-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 13

A solution of 1-(5′-chloro-2′-hydroxyphenyl-3-(2″-thienyl)-propenone **3** (1 g, 0.004 mol) in 5 cm^3 DMSO was refluxed in the presence of a crystal of I_2 for 10 min. The dark red solution after 30 min at room temperature was precipitated with H_2O, filtered and crystallised (EtOH–$CHCl_3$) to obtain **13** (900 mg, 90%), mp 170 °C (Found: C, 59.3; H, 2.9. $C_{13}H_7ClO_2S$ requires C, 59.5; H, 2.7%); ν_{max}/cm^{-1} 1635(CO); δ_H(90 MHz; $CDCl_3$) 8.15 (1H, d, *J* 2 Hz, 5-H), 7.80–7.35 (4H, m, 3′-H, 5′-H, 7-H and 8-H), 7.30–7.10 (1H, m, 4′-H), 6.60 (1H, s, 3-H).

Photolysis of 6-chloro-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran 13 in benzene. A benzene solution of **13** (130 mg, 0.005 mol, 80 cm^3) was photolysed (2 h) under similar conditions to those employed for **1c** in benzene. The photolysate on work up gave a solid identified as the starting chromone **13** (TLC, mmp).

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