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Photocyclisation of *o*-xylylbischromones: proximity effect

Satish C. Gupta*, Mohamad Yusuf, Mandeep Thakur and Ramesh C. Kamboj

Department of Chemistry, Kurukshetra University, Kurukshetra – 136 119, Haryana, India

The photocyclisation of thiophene and furan substituted *o*-xylylbischromones is described. The reaction occurs through a 1,4-biradical species. The proximity of the two chromophores due to intramolecular complex formation affects the chemical efficiency of the reaction.

Keywords: *o*-xylylbischromones, photocyclisation

Photoreactions of bichromophoric organic molecules wherein two chromophores are separated by a carbon skeleton have been the subject of study both for chemists and spectroscopists.[1] The conformational flexibility of the intervening carbon chain (spacer) has been invoked to explain the photochemical efficiency of the reactions occurring therein. In our studies on the bischromones, the length of the intervening carbon chain has been found to have a profound effect on the product formation/distribution; a bischromone with a spacer comprising of four atoms failed to undergo any reaction whereas molecules with a spacer comprising of more than four atoms underwent reactions.[2] This diversity has been explained on the enhanced probability of the formation of intramolecular complexes in molecules with a shorter spacer that may lead to deactivation of the excited chromophores. Further, when the straight chain spacer was replaced by a *p*-xylyl moiety[3] the two chromophores behaved independently as the intramolecular complex formation in such molecules is almost impossible due to the rigidity of the spacer.

We now report the results of our investigations involving the photochemical transformations of bischromones **1**, **2** built around *o*-xylene as the spacer. The impetus behind this study has been to explore the effect of restricted conformational mobility and greater proximity of the two chromophores on the photoreactions of these chromones.

The bischromones **3** and **4** were synthesised by reacting 2-aryl-6-chloro-3-hydroxy-4-oxo-4*H*-1-benzopyran **1** (X = S)[4] and **2** (X = O)[5] with α,α′-dibromo-*o*-xylene in the presence of K_2CO_3/*n*-$Bu_4N^+I^-$ in dry acetone. The monoalkylated products formed in the reaction mixture were removed by chromatography.

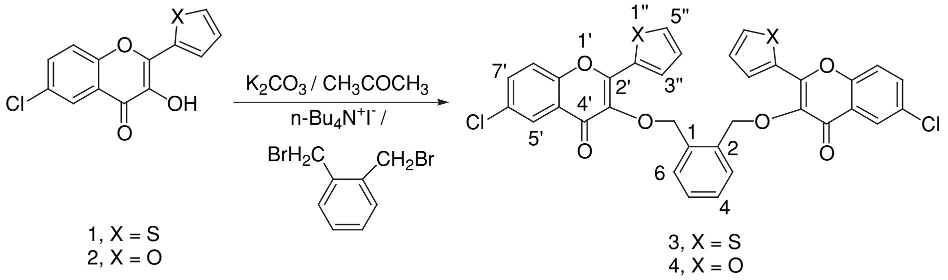
The photo-irradiation of **3** (X = S) dissolved in dry benzene with Pyrex filtered light produced three products **5a** (X = S), **6a** (X = S) and **7** (X = S) [see CAUTION in Experimental section].

The structures of these products were ascertained from their spectroscopic properties (see the experimental section).

That the photoproducts **5a** and **7** were obtained through the involvement of only one of the two chromophores was revealed by two IR absorptions due to enone moieties at 1645 and 1637 cm^{-1} in the former and 1648 and 1640 cm^{-1} in the latter; in the IR spectrum of **6a** only one absorption was observed at 1652 cm^{-1-}, thus indicating the involvement of both the chromophores. These observations found further support from the ^{1}H NMR spectra (see the experimental section) of the photoproducts. The stereochemical dispositions of the hydrogens at C-3a, C-4 and C-11b in **5a** and **6a** were derived from J and Φ parameters; that all the hydrogens lie on the same side is evident from $J_{3a,4}$ = 11 Hz (Φ ~ 0°) and $J_{11b,3a}$ = 8.5 Hz (Φ ~ 27°).[4-6] From the photolysis of **4** (X = O) in benzene two photoproducts **5b** and **6b** could be isolated whose structures exhibited the similar spectral parameters as that of **5a** and **6a**.

The rationale behind these photo-reorganisations[3-6] is that the photoexcited C=O of the pyrone moiety abstracts a H-atom from –O–CH_2Ph, resulting in the formation of 1,4-biradical that leads to cyclisations. In the photo-irradiation of **3** (X = S), in addition to the photoproducts **5a**, **6a** and **7**, there could be another product similar to **6a** where both the thienyl rings are aromatic. Also in the photolysis of **4** (X = O) the reaction products **5b** and **6b** could have undergone further photolytic reorganisation to cyclopropyl aldehydes[5] through a ring contraction and a ring expansion mechanism. The ^{1}H NMR of the crude photolysates of **3** and **4** did indicate the formation of such products but due to their very low yields their isolation was unsuccessful.

In the present study, the chemical efficiency of the photoreaction is poor as the recovery of the bischromones (**3** and **4**) has been around 80% and this is in spite of the fact that the photoreactions here are initiated through the involvement of benzylic hydrogens. This may be explained on the basis of the ease of intramolecular complex formation between the two units of the substrate that may come in close proximity (MM2 energy minimised structure,[7] Fig. 1) to each other in one of the many conformations leading to the deactivation of the excited molecule. This proximity view finds support from an earlier observation from our laboratory where the bischromone with ethylene[2] as the spacer failed to undergo any photoreaction whereas in the *p*-xylene-based bischromones[3] the recovery of



Scheme 1

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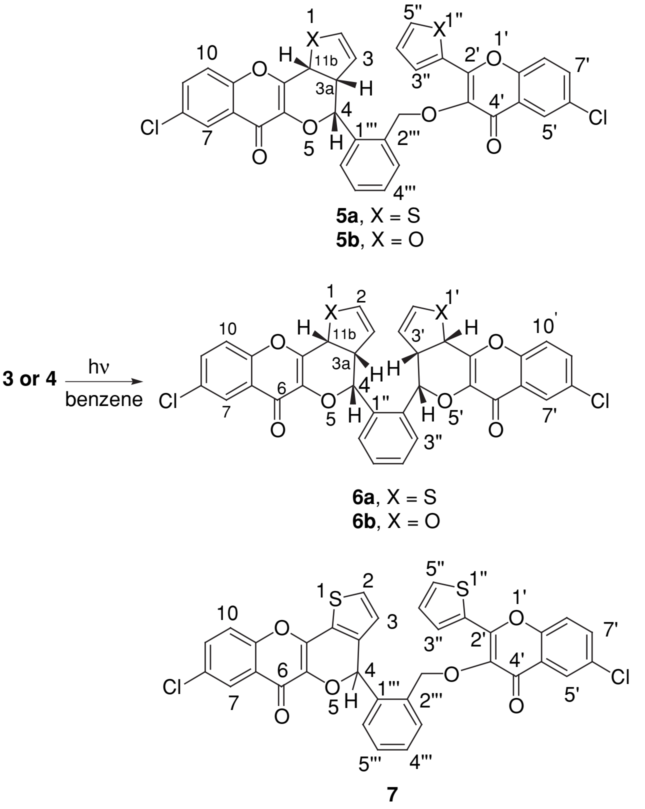
* Correspondent. E-mail: scguptaku@rediffmail.com



5a, X = S
5b, X = O

6a, X = S
6b, X = O

7

Scheme 2

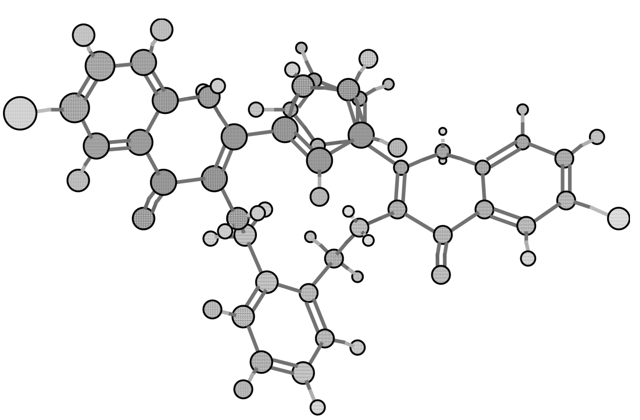


Fig. 1 Energy minimised structure of **4**.

the substrate was around 60%. In the latter the chromophores were too far apart to be involved in complex formation.

In conclusion, the proximity of the two chromophores affects the product formation and no intramolecular [2+2] photocycloadditions between two furan moieties have been observed.

Experimental

^{1}H NMR spectra were recorded on a 300 MHz Bruker spectrometer using TMS as internal standard. IR spectra were recorded on a Buck Scientific 500 spectrophotometer using KBr pellets and UV spectra on U-2000 Hitachi-spectrophotometer. Melting points reported are uncorrected.

CAUTION: Benzene, which is used extensively in this work is toxic and appropriate precautions should be taken.

1,2-Bis[6'-chloro-2'-(2"-thienyl)-4'-oxo-4'H-1'-benzopyran-3'-oxy] dimethylbenzene 3: A suspension of 6-chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4*H*-1-benzopyran[4] 1 (X = S) (2.8 g, 0.01 mol), α,α'-dibromo-*o*-xylene (1.3 g, 0.005 mol), tetrabutylammonium iodide (2.0 g) and freshly dried K_2CO_3 (1.2 g) was refluxed in dry acetone (25 ml) for 1h. The colour of the reaction mixture changed from deep red to colourless. The reaction mixture after filtration and distillation of solvent was poured on iced dil. HCl to obtain a mixture of monochromone and bischromone. This mixture was then chromatographed on a column of silica-gel (10–200 mesh) using benzene as eluent and crystallised from a $CHCl_3$-MeOH mixture to obtain pure bischromones **3**, as a white solid.

3: Yield (55%), m.p. 224–226 °C; ν_{max} cm^{-1} 1642 (C=O); λ_{max} THF 302 nm, 247 nm, 214 nm ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (2H, d, J_m=2.4Hz, H-5'), 7.84 (2H, dd, $J_{3'',4''}$=3.8Hz, $J_{3'',5''}$=1.2Hz, H-3"), 7.73 (2H, dd, J=3.5Hz, 5.7Hz, H-3,6), 7.56 (2H, dd, $J_{m,o}$=2.4Hz, 9.0Hz, H-7'), 7.47 (2H, dd, $J_{5'',3''}$=1.2Hz, $J_{5'',4''}$=5.1Hz, H-5"), 7.44 (4H, m, H-8',4,5), 7.07 (2H, dd, $J_{4'',5''}$=5.1Hz, $J_{4'',3''}$=3.8Hz, H-4"), 5.55 (4H, s, -OCH_2). Anal. Calcd. for $C_{34}H_{20}Cl_2O_6S_2$ C 61.9, H 3.1; Found: C 61.9, H 3.2.

1,2-Bis[6'-chloro-2'-(2"-furyl)-4'-oxo-4'H-1'-benzopyran-3'-oxy] dimethylbenzene **4**: The bischromone **4** was synthesised by the alkylation of 6-chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4*H*-1-benzopyran 2 (X = O) (2.6 g, 0.01 mol) with α,α'-dibromo-*o*-xylene (1.3 g, 0.005 mol), according to the same procedure as used for **3** (X = S).

4: Yield (60%), m.p. 205–207 °C; ν_{max} cm^{-1} 1644 (C=O); λ_{max} THF 324 nm, 257 nm, 214 nm ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (2H, d, J_m=2.6Hz, H-5'), 7.64 (2H, dd, *J*=3.4Hz, 5.6Hz, H-4,5), 7.58 (2H, br s, H-5"), 7.55 (2H, dd, *J*=2.6Hz, 9.0Hz, H-7'), 7.47 (2H, d, J_o=9.0Hz, H-8'), 7.39 (2H, dd, *J*=5.6Hz, 3.4Hz, H-3,6), 7.15 (2H, d, $J_{3'',4''}$=3.6Hz, H-3"), 6.45 (2H, dd, *J*=1.6Hz, 3.6Hz, H-4"), 5.50 (4H, s, -OCH_2). Anal. Calcd. for $C_{34}H_{20}Cl_2O_8$ C 65.1, H 3.2 Found C 65.0, H 3.3.

Photolysis of 1,2-Bis[6'-chloro-2'-(2"-thienyl)-4'-oxo-4'H-1'-benzopyran-3'-oxy] dimethylbenzene **3** *(X = S)*: A benzene solution of (100 ml) of **3** (100 mg, 0.00015 mol) was irradiated with light from a 125 W mercury lamp in a Pyrex vessel under N_2 atmosphere for 40 min. The progress of the reaction was monitored by TLC (benzene-EtOAc, 9:1). After removal of the solvent by distillation the photolysate was chromatographed over a column of silica gel (100–200 mesh) packed in benzene. Elution of the column with benzene–EtOAc (3:1) provided the starting compound 3 (30%, co-TLC and m.p.) and three new compounds **5a**, **6a** and **7**.

5a: Yield (3%), m.p. 189–191 °C; ν_{max} cm^{-1} 1645 (C=O), 1637 (C=O); λ_{max} THF 324 nm, 256 nm, 214 nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (1H, m, H-7,5'), 7.91 (1H, dd, $J_{3'',4''}$=3.6Hz, $J_{3'',5''}$=1.1Hz, H-3"), 7.70 (7H, m, H-9,7',5",3''',4''',5''',6'''), 7.46 (2H, d, J_o=9.0Hz, H-10,8'), 7.16 (1H, dd, $J_{4'',5''}$=5.0Hz, $J_{4'',3''}$=3.6Hz, H-4"), 6.44 (1H, d, $J_{2,3}$=6.1Hz, H-2), 5.39 (3H, m, H-4, H-4, -OCH_2), 5.24 (1H, d, $J_{11b,\ 3a}$=8.1Hz, H-11b), 5.17 (1H, dd, $J_{3,2}$=6.1Hz, $J_{3,3a}$=3.6Hz, H-3), 3.78 (1H, m, H-3a); HRMS: *m/z* 658.008 (M$^+$, found. $C_{34}H_{20}O_6S_2Cl_2$ requires 658.0078 (3.0), 655.9749 (4.0), 381.9907 (22.4), 277.9822 (100.0), 248.9769 (11.6), 225.0378 (10.2), 154.9907 (22.9), 123.9983 (12.7), 110.9909 (15.0). Anal. Calcd. for $C_{34}H_{20}Cl_2O_6S_2$ C 61.9, H 3.1; Found: C 61.9, H 3.2.

6a: Yield (2%), m.p. 231–234 °C; ν_{max} cm^{-1} 1652 (C=O); λ_{max} THF 324 nm, 256 nm, 214 nm ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (2H, d, J_m=2.5Hz, H-7,7'), 7.60 (2H, dd, $J_{m,o}$=2.5Hz, 8.9Hz, H-9,9'), 7.38 (2H, d, J_o=8.9Hz, H-10,10'), 7.44 (4H, m, H-3",4",5",6"), 6.48 (2H, d, $J_{2,3}$=6.1Hz, H-2,2'), 5.24 (2H, dd, $J_{3,2}$=6.1Hz, $J_{3,3a}$=3.0Hz, H-3,3'), 5.20 (2H, d, $J_{4,3a}$=10.5Hz, H-4,4'), 5.06 (2H, d, $J_{11b,3a}$=8.1Hz, H-11b,11b'), 3.75 (2H, d{dd}, $J_{3a,3}$=3.0Hz, $J_{3a,11b}$=8.1Hz, $J_{3a,4}$=10.5Hz, H-3a,3a'); HRMS: *m/z* 658.0052 (M$^+$, found. $C_{34}H_{20}O_6S_2Cl_2$ requires 658.0052 (36.6), 656.0041 (5.6), 365.0067 (5.6), 291.9962 (9.0), 277.9822 (10.2), 153.9832 (100.0), 123.9955 (11.3). Anal. Calcd. for $C_{34}H_{20}Cl_2O_6S_2$ C 61.9, H 3.1; Found: C 61.9, H 3.2.

7: Yield (3%), m.p. 212–215 °C; ν_{max} cm^{-1} 1648 (C=O), 1640 (C=O); λ_{max} THF 327 nm, 257 nm, 214 nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (1H, d, J_m=2.4Hz, H-7), 8.16 (1H, d, J_m=2.4Hz, H-5'), 7.96 (1H, dd, $J_{3'',4''}$=3.6Hz, $J_{3'',5''}$=1.1Hz, H-3"), 7.70 (1H, dd, $J_{5'',3''}$=1.1Hz, $J_{5'',4''}$=5.1Hz, H-5"), 7.67 (1H, d, $J_{2,3}$=5.6Hz, H-2), 7.61 (2H, dd, $J_{m,o}$=2.4Hz, 8.9Hz, H-9,7'), 7.52 (2H, d, J_o=8.9Hz, H-10,8'), 7.38 (4H, m, H-3''',4''',5''',6'''), 7.19 (1H, dd, $J_{4'',3''}$=3.6Hz, $J_{4'',5''}$=5.1Hz, H-4"), 6.73 (1H, d, $J_{3,2}$=5.6Hz, H-3), 5.74 (1H, s, H-4), 5.42(2H,s,-OCH_2); HRMS: *m/z* 656.0074 (M$^+$, found. $C_{34}H_{18}O_6S_2Cl_2$ requires 656.0074 (3.0), 379.9649 (18.1), 277.9822 (100.0), 225.0368 (7.0), 153.9826 (8.4), 124.9983 (12.7). Anal. Calcd. for $C_{34}H_{18}Cl_2O_6S_2$ C 62.1, H 2.8; Found: C 62.0, H 2.9.

Photolysis of 1,2-Bis[6'-chloro-2'-(2"-furyl)-4'-oxo-4'H-1'-benzopyran-3'-oxy] dimethylbenzene **4**: A benzene solution (100 ml) of **4** (X = O) (100 mg, 0.00015 mol) was photolysed with the light from a

125 W mercury lamp in a pyrex reactor under the similar conditions as employed earlier. The photolysate was chromatographed over a column of silica gel (100–200 mesh) to provide **4** (80%, co-TLC and mmp.), **5b** and **6b**.

5b:Yield (3%), m.p. 220–223 °C; ν_{max} cm^{-1} 1656 (C=O), 1650 (C=O); λ_{max} THF 324 nm, 257 nm, 214 nm ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (1H, d, J_m=2.4Hz, H-7), 8.05 (1H, d, J_m=2.4Hz, H-5'), 7.64 (1H, br s, H-5''), 7.60 (2H, dd, $J_{m,o}$=2.4Hz, 8.9Hz, H-9,7''), 7.47 (2H, d J_o=8.9Hz, H-10,8'), 7.41 (4H m, H-3''',4''',5''',6'''), 7.24 (1H, d, $J_{3'',4''}$=3.6Hz, H-3''), 6.58 (1H, d, $J_{2,3}$=2.7Hz, H-2), 6.54 (1H, dd, $J_{4'',3''}$=3.6Hz, $J_{4'',5''}$=1.5Hz, H-4''), 5.45 (1H, d, $J_{11b,3a}$=8.3Hz, H-11b), 5.33 (2H, s, -OCH_2), 4.97 (1H, d, $J_{4,3a}$=11.0Hz, H-4), 4.88 (1H, dd, $J_{3,3a}$=1.0Hz, $J_{3,2}$ 2.7Hz, H-3), 3.59 (1H, m, H-3a); HRMS: *m/z* 626.0538 (M^+, found. $C_{34}H_{20}O_8Cl_2$ requires 626.0535), 336.0551 (1.6), 335.04616 (1.8), 154.9909 (5.3), 153.9823 (3.3), 125.9869 (2.2). Anal. Calcd. for $C_{34}H_{20}Cl_2O_8$ C 65.1, H 3.2; Found C, 65.0; H, 3.3.

6b:Yield (2.5%), m.p. 247-250 °C; ν_{max} cm^{-1} 1660 (C=O); λ_{max} THF 324 nm, 257 nm, 214 nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (2H, d, J_o=2.4Hz, H-7,7'), 7.60 (2H, dd, $J_{m,o}$=2.4Hz, 8.9Hz, H-9,9'), 7.46 (6H, m, H-10,10',3'',4'',5'',6''), 6.42 (2H, br s, H-2,2'), 5.25 (2H, d, $J_{11b,3a}$=8.1Hz, H-11b,11b'), 5.07 (2H, dd, $J_{3,2}$=2.7Hz, $J_{3,3a}$=1.0Hz, H-3,3'), 4.65 (2H, d, $J_{4,3a}$=11.0Hz, H-4,4'), 3.55 (2H, m, H-3a,3a'); HRMS: *m/z* 626.0538 (M^+, found. $C_{34}H_{20}O_8Cl_2$ requires 626.0535), 380.0459 (2.7), 351.0398 (3.6), 336.0528 (28.2), 335.0471 (40.8), 262.0027 (95.5), 154.9913 (5.2), 153.9928 (5.0). Anal. Calcd. for $C_{34}H_{20}Cl_2O_8$ C 65.1, H 3.2; Found C, 65.1; H, 3.3.

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