Indian Journal of Chemistry
Vol. 48B, May 2009, pp. 685-691

Photo-reorganization of some 3-alkoxy-2-(alkoxyphenyl)chromones

Ramesh C Kamboj*, Urmila Berar, Surinder Berar, Mandeep Thakur & Satish C Gupta

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

E-mail: rckamboj@rediffmail.com

Received 31 December 2007; accepted (revised) 30 December 2008

A photo-reorganization of 3-alkoxy-2-(alkoxyphenyl)chromones to the isomeric angular tetracyclic compounds through the 1,4-biradical generated by the excited carbonyl group through the γ-hydrogen abstraction has been described. Substituent effect of the 3-alkoxy group and the effect of position of alkoxy group in the 2-phenyl ring are explained.

Keywords: Chromone, photoirradiation, H-abstraction, tetracyclics, photocyclisation

Intramolecular hydrogen-abstractions initiated by the photo excited C=O group are common in nature and have found several synthetic applications[1-14]. 3-Alkoxy-2-aryl (furan, thiophene or phenyl)chromones on photoirradiation undergo cyclisation to the angular tetracyclic products with clipping of 3-alkoxy carbon and 2-aryl moiety. The product formation depends upon the nature of 2-aryl (furan[15], thiophene[16], phenyl[17], styryl[18], alkyl[19,20]) groups and occurs through the formation of the 1,4-biradical through type-II H-abstraction process from the 3-alkoxy moiety by the photo-excited C=O group[21-23]. In this communication, is reported the results of investigations on the phototransformations of the 3-alkoxy-4-oxo-4*H*-1-benzopyrans bearing alkoxyphenyl group at C-2 having the alkoxy groups at either 2′- or 3′- or 4′-positions.

Results

The required 3-alkoxy-2-(alkoxyphenyl)chromones **4-7** were synthesized starting from 5-chloro-2-hydoxyacetophenone according to **Scheme I**. 5-Chloro-2-hydroxyacetophenone on condensation with aldehyde **1a-c** in the presence of NaOH/EtOH gave the chalcones[24,25] **2a-c** which under Algar-Flynn-Oyamada (AFO) reaction conditions[26] ($H_2O_2/^-OH$) were converted into 3-hydroxy-2-hydroxyphenyl chromones **3a-c** that were subsequently alkylated with suitable alkyl halide (2 moles) to obtain ethers **4a-7a, 4b-7b** and **4c-7c**. The structures of these benzopyrans were found to be consistent with their spectral parameters (^{1}H NMR).

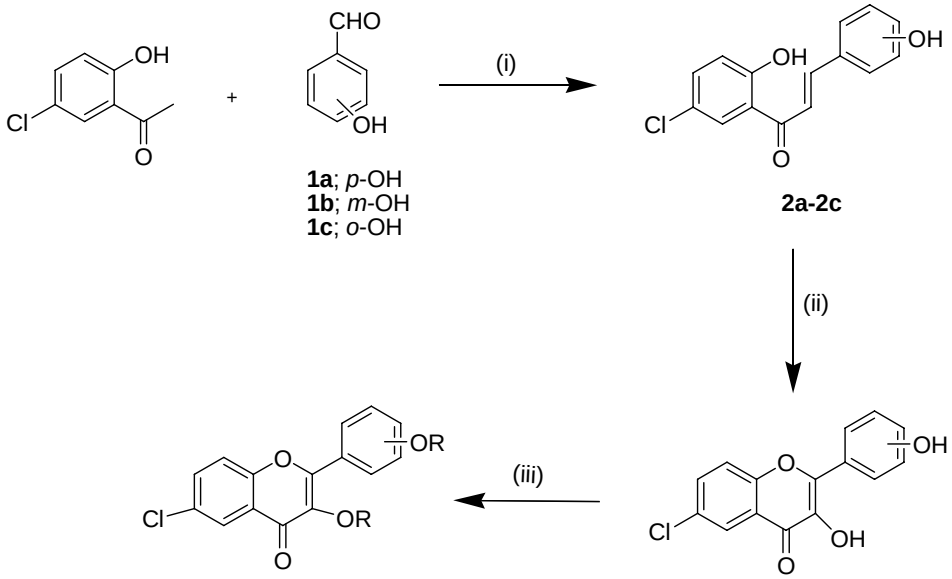
The 6-chloro-3-alkoxy-2-(alkoxyphenyl)chromones **4a-7a** on photoirradiation with pyrex filtered UV light furnished the products **8a-11a** in 20-50% yield (**Scheme II**).

The photolysis of compounds **4b-7b** produced two isomeric angular tetracyclic products **8b-11b** and **8′b-11′b** (**Scheme III**) which have alkoxy group at the 2- and 4-position respectively. The ratio of these photoproducts formed depended upon the nature of alkoxy group in phenyl ring. In most of the cases except that of **8b,** the photo-products with the alkoxy group at 2-position had better chemical yields than the products with alkoxy group at 4-position.

The photolysis of **4c** produced compound **8c** in 27% yield (**Scheme IV**) while the chromones **5c-7c** did not undergo phototransformation even on prolonged photoirradiation.

Discussion

The structures of the photoproducts were ascertained from their spectral data (*vide* experimental section). The chromones **4a-7a** on photolysis yielded only one type of product; **8a-11a** as in all these compounds 2′- and 6′-positions are equivalent. But, in case of the chromones **4b-7b** these positions not being equivalent, two isomeric photoproducts; **8b-11b** and **8′b-11′b** were realized whose structures were established through proton decoupling experiments. It has been observed from photolysis of **5b-7b** that the yields of photoproducts **9b-11b** obtained through coupling of 6′-position with 3-alkoxy carbon are higher than those (**9′b-11′b)** obtained through 2′-



R = -CH_3 **4a** (88%) **4b** (85%) **4c** (80%)

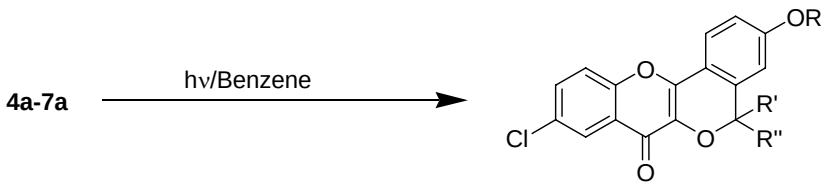
= -$CH_2C_6H_5$ **5a** (85%) **5b** (80%) **5c** (70%)

= -CH_2-CH=CH_2 **6a** (85%) **6b** (78%) **6c** (75%)

= -$CH(CH_3)_2$ **7a** (50%) **7b** (60%) **7c** (45%)

i) HO(*o*- or *m*- *or p*-)C_6H_4CHO/C_2H_5OH/NaOH/RT; ii) KOH/H_2O_2(30%);
iii) K_2CO_3/ Dry Acetone/$Bu_4N^+I^-$/RX

Scheme I — Synthesis of 6-chloro-3-alkoxy-2-(alkoxyphenyl)-4-oxo-4*H*-1-benzopyrans

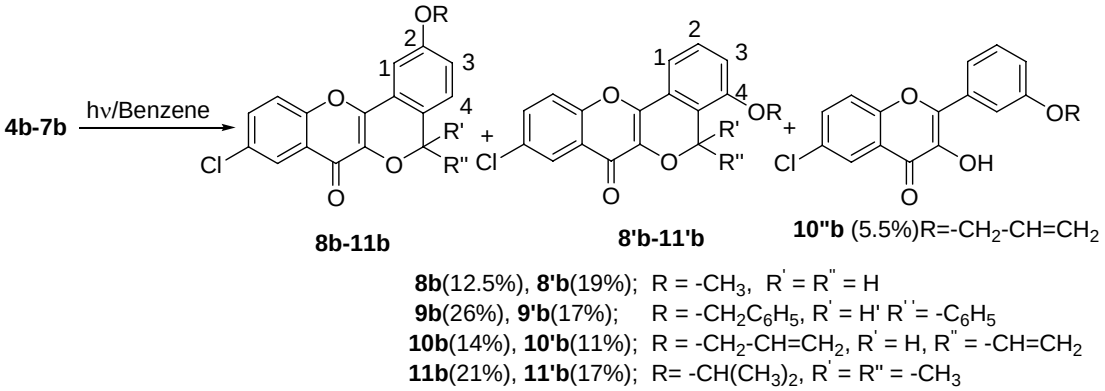


8a(22%); R = -CH_3, R' = R'' = H
9a(26%); R = -$CH_2C_6H_5$, R' = H' R'' = -C_6H_5
10a(34%); R = -CH_2-CH=CH_2, R' = H, R'' = -CH=CH_2
11a(46%); R= -$CH(CH_3)_2$, R' = R'' = -CH_3

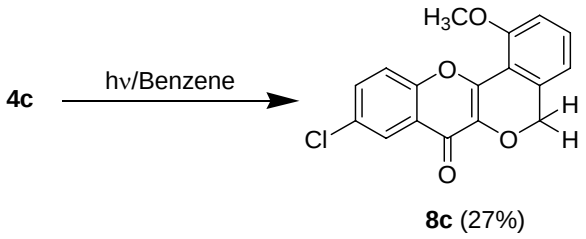
Scheme II — Photolysis of 6-chloro-3-alkoxy-2-(4′-alkoxyphenyl)-4-oxo-4*H*-1-benzopyrans

position coupling. This may be attributed to the steric repulsion between 3-alkoxy group and alkoxy group in the 2-phenyl ring. The MM2 minimized energy programme[27] run on chromones **5b-7b** showed that the close contacts between 3-alkoxy carbon and the 6′-C of the 2-phenyl ring are shorter than those between 3-alkoxy carbon and the 2′-C which indicate the facile coupling between the former two. In case of chromone **4b** the methoxy group is less bulky and this trend is reverse. In addition to the photocyclistaion, selective dealkylation in **5b** from the 3-position was also observed.

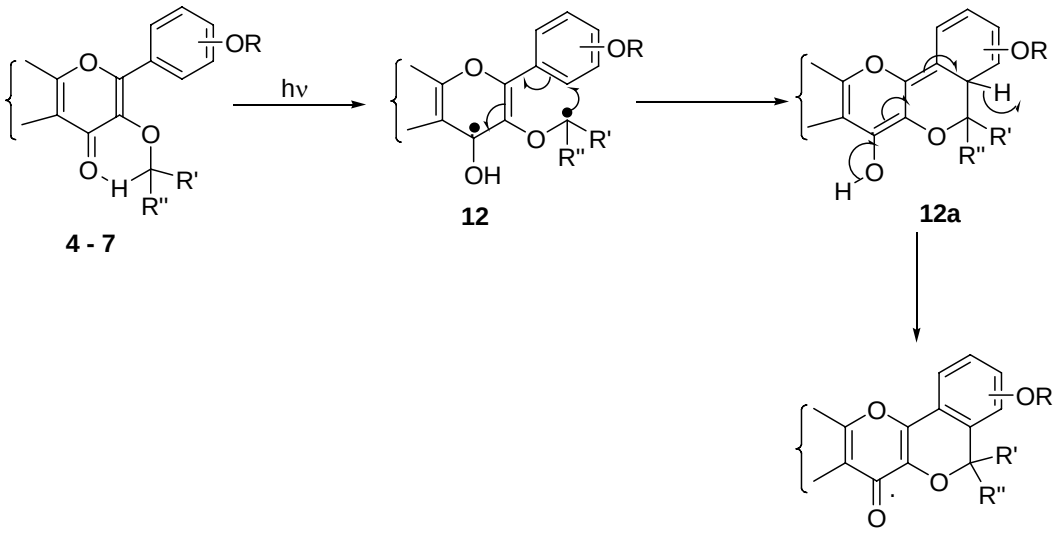
Among the chromones **4c-7c,** only **4c** got photo-transformed to **8c**. The other chromones **5c-7c** do not



Scheme III — Photolysis of 6-chloro-3-alkoxy-2-(3′-alkoxyphenyl)-4-oxo-4*H*-1-benzopyrans



Scheme IV — Photolysis of 6-chloro-3-methoxy-2-(2′-methoxyphenyl)-4-oxo-4*H*-1-benzopyrans



Scheme V — Mechanism of product formation from 6-chloro-3-alkoxy-2-(alkoxyphenyl)-4-oxo-4*H*-1-benzopyrans by photolysis

undergo photolysis even after prolonged photolysis and in these cases the starting chromones were recovered as such.

These photo-conversions of the 3-alkoxy chromones **4-7** to angular photocyclodehydrogenated products **8-11** may be visualized to occur through an initial H-abstraction from 3-alkoxy group by the excited carbonyl triplet of the pyrone moiety to produce the 1,4-biradical **12** which undergoes a bond formation by clipping of alkoxy radical with 2′- or 6′-position of the 2-phenyl ring, followed by fast expulsion of the two hydrogens from enol[10] **12a** to furnish the final product (**Scheme V**).

Experimental Section

IR spectra were recorded on a Buck Scientific 500 spectrophotometer using KBr pellets. ^{1}H NMR spectra were recorded on a 300 MHz Bruker spectrometer using TMS as internal standard. Melting points were determined in open capillaries and are uncorrected. The yields reported are calculated by excluding the recovered starting compound. The progress of the photoreaction was monitored by TLC as well as ^{1}H NMR spectra of photolysate at different intervals of time. The photoirradiation of the deaerated solutions of the substrates was carried out in a Pyrex reactor with a 125 W Hg vapor lamp under nitrogen (99.9%) atmosphere. Any trace of oxygen and moisture from the procured nitrogen was removed by passing through alkaline pyragallol solution and concentrated sulphuric acid respectively.

General method for the synthesis of 6-chloro-3-methoxy-2-(4′-methoxyphenyl)-4-oxo-4*H*-1-benzopyran 4a

The 3-hydroxychromone, **3a** (2.80 g, 0.01 mole), methyl iodide (2.80 g, 0.02 mole), dry K_2CO_3 (2.0 g) and tetrabutylammonium iodide (100 mg) were refluxed in acetone (50 mL) for 4 hr. The reaction mixture was filtered, evaporated and the residue was purified by re-crystallization from methanol to obtain **4a**.

The other ethers **5a-7a, 4b-7b** and **4c-7c** were obtained by using this procedure starting from compounds **3a, 3b** and **3c** respectively by reacting with suitable alkyl halides.

Compound **4a** (R = -CH_3). Yield 88%, white solid; m.p.126-28ºC; IR (KBr): 1642 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 8.20 (1H, d, J_m = 2.4 Hz, H-5), 8.03 (2H, d, J_o = 8.4 Hz, H-2′,6′), 7.60 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.48 (1H, d, J_o = 9.0 Hz, H-8), 7.03 (2H, d, J_o = 8.4 Hz, H-3′, 5′), 3.90 (3H, s, 4′-OCH_3), 3.88 (3H, s, 3-OCH_3); MS (EI): *m/z* 316 (M^+, 100%). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.46; H, 4.14. Found: C, 64.30; H, 4.11%.

Compound **5a** (R = -CH_2Ph). Yield 85%, white solid; m.p. 156-58ºC; IR (KBr): 1636.6 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 8.17 (1H, d, J_m = 2.7 Hz, H-5), 7.94 (2H, d, J_o = 7.2 Hz, H-2′, 6′), 7.53 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz H-7), 7.40 (1H, d, J_o = 9.0 Hz, H-8), 7.10-7.39 (10H, m, H-2″-6″, 2‴-6‴), 6.97 (2H, d, J_o = 7.2 Hz H-3′,5′), 5.09 (2H, s, 4′-OCH_2), 5.05 (2H, s, 3 -OCH_2); MS (EI): *m/z* 468 (M^+, 100%). Anal. Calcd for $C_{29}H_{21}ClO_4$: C, 74.28; H, 4.51. Found: C, 74.05; H, 4.53%.

Compound **6a** (R = -CH_2-CH=CH_2). Yield 85%, white solid; m.p. 99-101ºC; IR (KBr): 1633.5 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 8.15 (1H, d, J_m = 2.4 Hz, H-5), 8.03 (2H, d, J_o = 9.9 Hz, H-2′, 6′), 7.53 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.40 (1H, d, J_o = 9.0 Hz, H-8), 6.95 (2H, d, J_o = 9.9 Hz, H-3′, 5′), 6.06 (1H, m, H-2″), 5.75 (1H, m, H-2‴), 5.35 (2H, m, H-1″), 5.15 (2H, m, H-1‴), 4.58 (4H, m, H-3″, 3‴); MS (EI): *m/z* 368 (M^+, 100%). Anal. Calcd for $C_{21}H_{17}ClO_4$: C, 68.39; H, 4.65. Found: C, 68.45; H, 4.62%.

Compound **7a** (R = -$CH(CH_3)_2$).Yield 50%, light yellow solid; m.p. 121-23ºC; IR (KBr): 1633.6 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 8.22 (1H, d, J_m = 2.7 Hz, H-5), 8.14 (2H, d, J_o = 9.0 Hz, H-2′, 6′), 7.62 (1H, dd, $J_{m,o}$ = 2.7 Hz, 8.7 Hz, H-7), 7.49 (1H, d, J_o = 8.7 Hz, H-8), 6.99 (2H, d, J_o = 9.0 Hz, H-3′, 5′), 4.69 (2H, m, 4′-OCH, 3-OCH), 1.40 (6H, d, J_{vic} = 6.3 Hz, H-α), 1.25 (6H,d, J_{vic} = 6.3 Hz, H- ß); MS (EI): *m/z* 372 (M^+, 100%). Anal. Calcd for $C_{21}H_{21}ClO_4$: C, 67.65; H, 5.68. Found: C, 67.70; H, 5.65%.

Compound **4b** (R = -CH_3). Yield 85%, light yellow solid; m.p. 98-101ºC; IR (KBr): 1639.8 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 8.16 (1H,d, J_m =2.7 Hz, H-5), 7.61 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-7), 7.43 (1H, d, J_o = 9.0 Hz, H-8), 7.37 (1H, t, J_o = 9.0 Hz, H-5′), 7.01 (1H, td, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-4′), 7.59 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-6′) 7.53 (1H, t, J_m = 2.4 Hz, H-2′), 3.82 (6H, s, 3-OCH_3, 3′-OCH_3); MS (EI): *m/z* 316 (M^+, 100%). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.46; H, 4.14. Found: C, 64.32; H, 4.09%.

Compound **5b** (R = -CH_2Ph). Yield 80%, white solid, m.p. 105-07ºC; IR (KBr): 1640.6 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 8.17(1H, d, J_m = 2.7 Hz, H-5), 7.42 (1H, d, J_o = 9.0 Hz, H-8), 7.50-7.59 (3H, m, H-7, 2′, 6′), 7.1-7.39 (10H, m, H-5′, H-2″-6″, 2‴-6‴), 6.94 (1H, td, $J_{m,o}$ = 2.4 Hz, 8.7 Hz, H-4′), 5.06 (2H, s, 3′-OCH_2), 4.91 (2H, s, 3-OCH_2); MS (EI): *m/z* 468 (M^+, 100%). Anal. Calcd for $C_{29}H_{21}ClO_4$: C, 74.28; H, 4.51. Found: C, 74.09; H, 4.48%.

Compound **6b** (R = -CH_2-CH=CH_2). Yield 78%, white solid; m.p. 66-69ºC; IR (KBr): 1636.3 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 8.15 (1H,d, J_m = 2.7 Hz, H-5), 7.55 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-7), 7.43 (1H, d, J_o = 9.0 Hz, H-8), 7.35 (1H, t, J_o = 8.4 Hz, H-5′), 7.01 (1H, td, $J_{m,o}$ = 2.1 Hz, 8.4 Hz, H-4′), 7.63-7.61 (2H, m, H-2′-6′), 4.56 (4H, m, H-1″, 1‴), 6.02 (1H, m, H-2″), 5.87 (1H, m, H-2‴), 5.11-5.38 (4H, m, H-3″, 3‴); MS (EI): *m/z* 368 (M^+, 100%). Anal. Calcd for $C_{21}H_{17}ClO_4$: C, 68.39; H, 4.65. Found: C, 68.48; H, 4.67%.

Compound **7b** (R = -$CH(CH_3)_2$). Yield 60%, white solid; m.p. 54-56°C; IR (KBr): 1636.3 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.14 (1H, d, J_m = 2.4 Hz, H-5), 7.57 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.42 (1H, d, J_o = 9.0 Hz, H-8), 7.32 (1H, t, J_o = 8.4 Hz, H-5′), 7.59-7.62 (2H, m, H-2′, 6′), 6.96 (1H, td, $J_{m.o}$ = 2.4 Hz, 8.4 Hz, H-4′), 4.58 (2H, m, 3′-OCH, 3-OCH), 1.32 (6H, d, J_{vic} = 6.0 Hz, H-α), 1.12 (6H, d, J_{vic} = 6.3 Hz, H-ß); MS (EI): *m/z* 372 (M^+, 100%). Anal. Calcd for $C_{21}H_{21}ClO_4$: C, 67.65; H, 5.68. Found: C, 67.39; H 5.65%.

Compound **4c** (R = -CH_3). Yield 80%, white solid, m.p. 145-47°C; IR (KBr): 1651.9 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.18 (1H, d, J_m = 2.7 Hz, H-5), 7.51 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-7), 7.35 (1H, d, J_o = 9.0 Hz, H-8), 7.37 (1H, dd, $J_{m,o}$ = 1.5 Hz, 7.5 Hz, H-6′), 7.03 (1H, dt, $J_{m,o}$ = 1.5 Hz, 7.5 Hz, H-5′), 7.43 (1H, dt, $J_{m,o}$= 1.5 Hz, 7.5 Hz, H-4′). 6.98 (1H, dd, $J_{m,o}$ = 1.5 Hz, 7.5 Hz, H-3′), 3.79 (3H, s, 2′-OCH_3), 3.74 (3H, s, 3-OCH_3); MS (EI): *m/z* 316 (M^+, 100%). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.46; H, 4.14. Found: C, 64.29; H, 4.16%.

Compound **5c** (R = -CH_2Ph). Yield 70%, pale yellow solid, m.p. 98-100°C; IR (KBr): 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.29 (1H, d, J_m = 2.4 Hz, H-5), 7.60 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.43 (1H, d, J_o = 9.0 Hz, H-8), 7.48 (1H, dd, $J_{m,o}$ =1.8 Hz, 9.0 Hz, H-6′), 6.99-7.43 (13H, m, H-5′, 4′, 3′, 2″-6″, 2‴-6‴), 5.07 (2H, s, 2′-OCH_2), 5.03 (2H, s, 3-OCH_2); MS (EI): *m/z* 468 (M^+, 100%). Anal. Calcd for $C_{29}H_{21}ClO_4$: C, 74.28; H, 4.51. Found: C, 72.13; H, 4.49%.

Compound **6c** (R = -CH_2-CH=CH_2). Yield 75%, pale yellow solid, m.p. 58-61°C; IR (KBr): 1643.2 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.18 (1H, d, J_m = 2.4 Hz, H-5), 7.51 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-7), 7.48 (1H, dd, $J_{m,o}$ = 1.8 Hz, 8.4 Hz, H-6′), 7.34 (1H, d, J_o = 9.0 Hz, H-8), 7.39 (1H, dt, $J_{m,o}$ = 1.8 Hz, 8.4 Hz, H-4′). 7.00 (1H, dt, $J_{m,o}$ = 0.9 Hz, 8.7 Hz, H-5′), 6.95 (1H, dd, $J_{m,o}$ = 0.9 Hz, 8.7 Hz, H-3′), 5.88 (1H, m, H-2″), 5.69 (1H, m, H-2‴), 5.00-5.16 (4H, m, H-3‴, 3″), 4.52 (4H, m, H-1″,1‴); MS (EI): *m/z* 368 (M^+, 100%). Anal. Calcd for $C_{21}H_{17}ClO_4$: C, 68.39; H, 4.65. Found: C, 68.30; H, 4.63%.

Compound **7c** (R = -$CH(CH_3)_2$). Yield 45%, colourless solid, m.p. 111-13°C; IR (KBr): 1640 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.27 (1H, d, J_m = 2.7 Hz, H-5), 7.59 (1H, dd, $J_{m,o}$ = 2.7 Hz, 8.7 Hz, H-7), 7.41 (1H, d, J_o = 8.7 Hz, H-8), 7.50 (1H, dd, $J_{m,o}$ =1.5 Hz, 7.5 Hz, H-6′), 7.47 (1H, dt, $J_{m,o}$ = 1.5 Hz, 7.5 Hz, H-4′), 7.04 (1H, dt, $J_{m,o}$ = 1.5 Hz, 7.5 Hz, H-5′), 7.02 (1H, dd, $J_{m,o}$ =1.5 Hz, 7.5 Hz, H-3′), 4.65 (1H, septet, J_{vic} = 6.0 Hz, 2′-OCH), 4.44 (1H, septet, J_{vic} = 6.0 Hz, 3-OCH), 1.30 (6H, d, J_{vic} = 6.0 Hz, H-α), 1.06 (6H, d, J_{vic} = 6.0 Hz, H-ß); MS (EI): *m/z* 372 (M^+, 100%). Anal. Calcd for $C_{21}H_{21}ClO_4$: C, 67.50; H, 5.68. Found: C, 67.59; H, 5.70%.

Photolysis of 6-chloro-3-methoxy-2-(4′-methoxyphenyl))-4-oxo-4*H*-1-benzopyran, 4a

General procedure: A deaerated solution of chromone **4a** (200 mg) in dry benzene (150 mL) was irradiated in a pyrex reactor under nitrogen atm. for 90 min with a 125 W Hg vapor lamp. The removal of solvent under reduced pressure yielded a red gummy mass that was chromatographed over a column of silica gel to yield **8a**.

Other compounds **5a-7a, 4b-7b** and **4c-7c** were also photolysed by following the same procedure to yield respective products.

Compound **8a** Yield 22%,colorless solid; m.p. 240-42°C; IR (KBr): 1640 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.27 (1H, d, J_m = 2.4 Hz, H-8), 7.78 (1H, d, J_o = 8.7 Hz, H-1), 7.57 (1H, dd, $J_{m,o}$ = 2.4 Hz, 8.7 Hz, H-10), 7.48 (1H, d, J_o = 8.7 Hz, H-11), 7.00 (1H, dd, $J_{m,o}$ = 2.1 Hz, 8.7 Hz, H-2), 6.61 (1H, d, J_m = 2.1 Hz, H-4), 5.95 (2H, s, H-5), 3.91 (3H, s, 3-OCH_3); MS (EI): *m/z* 314 (M^+, 100%). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.74; H, 3.55%.

Compound **9a** Yield 26%, yellow solid; m.p. 230-33°C; IR (KBr): 1618.5 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.18 (1H, d, J_m = 2.4 Hz, H-8), 7.79 (1H, d, J_o = 8.7 Hz, H-1), 7.50 (1H, dd, $J_{m,o}$ = 2.4 Hz, 8.7 Hz, H-10), 7.40 (1H, d, J_o = 8.7 Hz, H-11), 7.19-7.33 (10 H ,m, H-2′-6′, 2″-6″), 7.04 (1H, dd, $J_{m,o}$ = 2.1 Hz, 8.7 Hz, H-2), 6.61 (1H, d, J_m = 2.1 Hz, H-4), 6.21 (1H, s, H-5), 5.03 (2H, s, 3-OCH_2); MS (EI): *m/z* 466 (M^+, 100%). Anal. Calcd for $C_{29}H_{19}ClO_4$: C, 74.60; H, 4.10. Found: C, 74.52; H, 4.13%.

Compound **10a** Yield 34%, off-white solid; m.p. 149-51°C; IR (KBr): 1628.0 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.21 (1H, d, J_m = 2.7 Hz, H-8), 7.74 (1H, d, J_o = 8.7 Hz, H-1), 7.52 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-10), 7.40 (1H, d, J_o = 9.0 Hz, H-11), 6.95 (1 H, dd, $J_{m,o}$ = 2.1 Hz, 8.7 Hz, H-2), 6.69 (1H, d, J_m = 2.1 Hz, H-4), 5.68 (1H, d, J_{vic} = 5.4 Hz, H-5), 5.99 (2H, m, H-2′, 1″), 5.15-5.40 (4H, m, H-3′, 2″), 4.67 (2H, d, J_{vic} =6.0 Hz, H-1′); MS (EI): *m/z* 366 (M^+, 100%). Anal. Calcd for $C_{21}H_{15}ClO_4$: C, 68.76; H, 4.12. Found: C, 68.88; H, 4.11%.

Compound **11a** Yield 46%, yellow solid; m.p. 197-99°C; IR (KBr): 1644.1 cm^{-1} (C=O); ^1H NMR

($CDCl_3$): δ 8.21 (1H, d, J_m = 2.7 Hz, H-8), 7.74 (1H, d, J_o = 8.7 Hz, H-1), 7.51 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-10), 7.43 (1H, d, J_o = 9.0 Hz, H-11), 6.89 (1 H, dd, $J_{m,o}$ = 2.4 Hz, 8.7 Hz, H-2), 6.69 (1H, d, J_m = 2.4 Hz, H-4), 4.59 (1H, m, J_{vic} = 6.0 Hz , 3-OCH), 1.65 (6H, s, 5-CH_3), 1.31 (6H, d, J_{vic} = 6.0 Hz, H-α); MS (EI): *m/z* 370 (M^+, 100%). Anal. Calcd for $C_{21}H_{19}ClO_4$: C, 68.02; H, 5.16. Found: C, 68.20; H, 5.12%.

Compound **8b** Yield 12.5%,brown solid; m.p. 135-38°C; IR (KBr): 1645.9 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.22 (1H, d, J_m = 2.4 Hz, H-8), 7.55 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-10), 7.47 (1H, d, J_o = 9.0 Hz, H-11), 7.27 (1H, d, J_m = 2.4 Hz, H-1), 7.06 (1H, d, J_o = 8.4 Hz, H-4), 6.94 (1H, dd, $J_{m,o}$ = 2.4 Hz, 8.4 Hz, H-3), 5.17 (2H, s, H-5), 3.84 (3H, s, 2-OCH_3); MS (EI): *m/z* 314 (M^+, 100%). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.70; H, 3.53%.

Compound **8′b** Yield 19%, brown solid; m.p. 232-35°C; IR (KBr): 1663.3 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.22 (1H, d, J_m = 2.4 Hz, H-8), 7.54 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-10), 7.45 (1H, d, J_o = 9.0 Hz, H-11), 7.38 (1H, t, J_o = 7.2 Hz, H-2), 7.33 (1H, dd, $J_{m,o}$ = 2.1 Hz, 7.2 Hz, H-1), 6.95 (1H, dd, $J_{m,o}$ = 2.1 Hz, 7.2 Hz, H-3), 5.30 (2H, s, H-5), 3.82 (3H, s, 4-OCH_3); MS (EI): *m/z* 314 (M^+, 100%). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.76; H, 3.50%.

Compound **9b** Yield 26%, white solid; m.p. 158-61°C; IR (KBr): 1655.4 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.18 (1H, d, J_m = 2.4 Hz, H-8), 7.52 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-10), 7.35 (1H, d, J_o = 9.0 Hz, H-11), 7.25 (1H, dd, $J_{m,o}$ = 2.4 Hz, 8.4 Hz, H-3), 6.93 (1H, d, J_o = 8.4 Hz, H-4), 7.20-7.44 (11H, m, H-1, 2′-6′, 2″-6″), 6.23 (1H, s, H-5), 5.11 (2H, s, 2-OCH_2); MS (EI): *m/z* 466 (M^+, 100%). Anal. Calcd for $C_{29}H_{19}ClO_4$: C, 74.60; H, 4.10. Found: C, 74.67; H, 4.09%.

Compound **9′b** Yield 17%, brown solid; m.p. 173-75°C; IR (KBr): 1647.0 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.15 (1H, d, J_m = 2.4 Hz, H-8), 7.49 (1H, dd, $J_{m,o}$ = 2.4 Hz, 8.7 Hz, H=10), 7.47 (1H, dd, $J_{m,o}$ = 1.2 Hz , 8.1 Hz, H-1), 7.40 (1H, t, J_o = 8.1 Hz, H-2), 7.39 (1H, d, J_o = 8.7 Hz, H-11), 7.14-7.30 (10H, m, H-2′-6′, 2″-6″), 7.08 (1H, dd, $J_{m,o}$ = 1.2 Hz, 8.1 Hz, H-3), 6.78 (1H, s, H-5), 5.09 (2H, s, 4-OCH_2); MS (EI): *m/z* 466 (M^+, 100%). Anal. Calcd for $C_{29}H_{19}ClO_4$: C, 74.60; H, 4.10. Found: C, 74.58; H, 4.13%.

Compound **10b** Yield 14%, white solid; m.p. 101-03°C; IR (KBr): 1657.2 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.22 (1H, d, J_m = 2.7 Hz, H-8), 7.55 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-10), 7.45 (1H, d, J_o = 9.0 Hz, H-11), 7.33 (1H, d, J_m = 2.1 Hz, H-1), 7.06 (1H, d, J_o = 8.4 Hz, H-4), 6.98 (1 H, dd, $J_{m,o}$ = 2.1 Hz, 8.4 Hz, H-3), 5.95-6.12 (2H, m, H-2′, 1″), 5.72 (1H, d, J_{vic} = 6.0 Hz, H-5), 5.08-5.43 (4H, m, H-3′, 2″), 4.58 (2H, d, J_{vic} = 4.5 Hz, H-1′); MS (EI): *m/z* 366 (M^+, 100%). Anal. Calcd for $C_{21}H_{15}ClO_4$: C, 68.76; H, 4.12. Found: C, 68.52; H, 4.14%.

Compound **10′b** Yield 11%, creamy solid; m.p. 126-29°C; IR (KBr): 1641.2 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.25 (1H, d, J_m = 2.7 Hz, H-8), 7.53 (1H, dd, $J_{m.o}$ = 2.7 Hz, 9.0 Hz, H-10), 7.43 (1H, d, J_o = 9.0 Hz, H-11), 7.42 (1H, dd, $J_{m,o}$ = 1.2 Hz, 7.8 Hz, H-1), 7.36 (1H, t, J_o = 8.1 Hz, H-2), 6.96 (1 H, dd, $J_{m,o}$ = 2.1 Hz, 8.1 Hz, H-3), 6.18 (1H, d, J_{vic} = 6.0 Hz, H-5), 5.86-6.02 (2H, m, H-2′, 1″), 5.04-5.30 (4H, m, H-3′, 2″), 4.62 (2H, d, J_{vic}=5.1 Hz, H-1′); MS (EI): *m/z* 366 (M^+, 100%). Anal. Calcd for $C_{21}H_{15}ClO_4$: C, 68.76; H, 4.12. Found: C, 68.60; H, 4.10%.

Compound **10″b** Yield 5.5%, yellow solid; m.p. 181-83°C; IR (KBr): 1612.7 cm^{-1} (C=O), 3256.0 cm^{-1} (OH); ^1H NMR ($CDCl_3$): δ 8.15 (1H, d, J_m = 2.7 Hz, H-5), 7.58 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-7), 7.53-7.58 (2H, m, H-2′, 6′), 7.49 (1H, d, J_o = 9.0 Hz, H-8), 7.38 (1H, t, J_o = 7.8 Hz, H-5′), 6.98 (1H, td, J_o = 7.8 Hz ,H-4′), 6.90 (1 H, br s, 3-OH), 6.05 (1H, m, H-2″), 5.40 (1H, td, $J_{allyl,trans}$ = 1.2 Hz, 17.1 Hz, H-3″a), 5.27 (1H, m, $J_{allyl,trans}$ = 1.2 Hz, 9.6 Hz, H-3″b), 4.57 (2H, m, H-1″); MS (EI): *m/z* 328 (M^+, 100%). Anal. Calcd for $C_{18}H_{13}ClO_4$: C, 65.76; H, 3.99. Found: C, 65.83; H, 4.01%.

Compound **11b** Yield 21%, creamy solid ; m.p. 176-79°C; IR (KBr): 1637.0 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.21 (1H, d, J_m = 2.7 Hz, H-8), 7.54 (1H, dd, $J_{m,o}$ = 2.7 Hz ,9.0 Hz, H-10), 7.45 (1H, d, J_o = 9.0 Hz, H-11), 7.27 (1H, d, J_m = 2.4 Hz, H-1), 7.08 (1H, d, J_o = 8.4 Hz, H-4), 6.92 (1H, dd, $J_{m,o}$ = 2.4 Hz, 8.4 Hz, H-3), 4.59 (1H, septet, J_{vic} = 6.0 Hz, 2-OCH), 1.65 (6H, s, 5-CH_3), 1.33 (3H, d, J_{vic} = 6.0 Hz, H-α); MS (EI): *m/z* 370 (M^+, 100%). Anal. Calcd for $C_{21}H_{19}ClO_4$: C, 68.02; H, 5.16. Found: C, 68.05; H, 5.15%.

Compound **11′b** Yield 17%, white solid; m.p. 183-85°C; IR (KBr): 1649.9 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.20 (1H, d, J_m = 2.4 Hz, H-8), 7.51 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-10), 7.43(1H, d, J_o = 9.0 Hz, H-11), 7.29 (1H, t, J_o = 7.8 Hz, H-2), 7.39 (1H, dd, $J_{m,o}$ = 0.9 Hz, 7.8 Hz, H-1), 6.94 (1H, dd, $J_{m,o}$ = 0.9 Hz, 7.8 Hz, H-3), 4.61 (1H, septet, J_{vic} = 6.0 Hz, 4-OCH), 1.76 (6H, s, 5-CH_3), 1.33 (6H, d, J_{vic} = 6.0 Hz,

H-α); MS (EI): *m/z* 370 (M^+, 100%). Anal. Calcd for $C_{21}H_{19}ClO_4$: C, 68.02; H, 5.16. Found: C, 67.83; H, 5.15%.

Compound **8c** Yield 27%, white solid; m.p. 175-78°C; IR (KBr): 1643.6 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 8.21 (1H, d, J_m = 2.4 Hz, H-8), 7.53 (1H, dd, $J_{m,o}$= 2.4 Hz, 9.0 Hz, H-10), 7.44 (1H, d, J_o = 9.0 Hz, H-11), 7.38 (1H, t, J_o = 8.1 Hz, H-4), 6.93 (1H, dd, $J_{m,o}$ = 1.5 Hz, 8.1 Hz, H-3), 6.75 (1H, dd, $J_{m,o}$ = 1.5 Hz, 7.8 Hz, H-2), 5.07 (2H, s, H-5), 3.91 (3H, s, 1-OCH_3); MS (EI): *m/z* 314 (M^+, 100%). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.95; H, 3.55%.

Conclusion

Hydrogen abstraction from the 3-alkoxy group by the C=O is the preferred reaction pathway for the formation of photoproducts and it is concluded that the formation and distribution of the tetracyclic products from 6-chloro-3-alkoxy-2-(3′-alkoxyphenyl)-4-oxo-4*H*-1-benzopyrans depend upon the position and size of the alkoxy group in the 2-phenyl moiety.

Acknowledgement

The authors thank the University Grants Commission (UGC) and the Council of Scientific and Industrial Research (CSIR), New Delhi for the financial support of this work.

References

1 Wagner P J, *Acc Chem Res*, 22, **1989**, 83.
2 Carless H A J & Kibende S M, *J Chem Soc, Chem Commun* **1987,** 1673.
3 Wilson R M, Padwa A, Marcel E & Dekker, *Organic Photochemistry*, New York, 5, **1981**, 273.
4 Wagner P J, *Acc Chem Res*, 66, **1976**, 1.
5 Kraus G A, Zhang W & Wu Y, *J Chem Soc, Chem Commun*, **1996**, 2439.
6 Kraus G A & Wu Y, *J Am Chem Soc*, 114, **1992**, 8705.
7 Park K K, Han I K & Park J W, *J Org Chem*, 66, **2001**, 6800.
8 Gupta S C, Saini A, Sharma S, Kapoor M & Dhawan S N, *Tetrahedron Lett*, 37**, 1996**, 8913.
9 Sumathi T & Balsubramanian K K, *Tetrahedron Lett*, 30, **1990**, 3775.
10 Sumathi T & Balsubramanian K K, *Tetrahedron Lett*, 33, **1992**, 2213.
11 Henry-Logan K R & Chen C G, *Tetrahedron Lett*, 14, **1973**, 1103.
12 Jorgenson M J & Patumtevapibal S, *Tetrahedron Lett*, 11, **1970**, 489.
13 Yang N C & Rivas C, *J Am Chem Soc*, 83, **1961**, 2213.
14 Gupta S C, Thakur M, Sharma S, Berar U, Berar S & Kamboj R C, *Beilstein J Org Chem*, 3, **2007**, 14.
15 Gupta S C, Saini A, Kumar D, Yadav N S, Chand K, Mor S & Dhawan S N, *J Chem Soc, Perkin Trans I*, **1995**, 177.
16 Gupta S C, Sharma S, Saini A & Dhawan S N, *J Chem Soc, Perkin Trans I*, **1999**, 2391.
17 Gupta S C, Yadav N S & Dhawan S N, *J Indian Chem Soc*, 67, **1990**, 770.
18 Gupta S C, Yusuf M, Sharma S, Saini A, Arora S & Kamboj R C, *Tetrahedron*, 60, **2004**, 8445.
19 Mandal P, Nath A & Venkateswaran, *Tetrahedron*, 52, **1996**, 7855.
20 Gupta S C & Mukherjee S K, *Tetrahedron Lett*, **1973**, 5073.
21 Feigenbaum A, Fort Y, Pete J P & Scholler D, *J Org Chem*, 51, **1986**, 4424.
22 Cossy J & Pete P T, *Heterocycles*, 22, **1984**, 97.
23 Smith A B & Agosta W C, *J Am Chem Soc*, 95, **1973**, 1961.
24 Simpson T H & Whalley B, *J Chem Soc*, **1955**, 166.
25 Joshi K C & Jauhar A K, *J Indian Chem Soc*, 39, **1962,** 463.
26 Dean F M & Podimuang V, *J Chem Soc*, **1965**, 3978.
27 Minimize Energy to Minimum RMS Gradient of 0.100 by MM2 incorporated in Chem Office 8.0 Chem 3D ultra 8.0.