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Photochemical Transformation of some 3-benzyloxy-2-(benzo[*b*]thiophen-2-yl)-4*H*-chromen-4-ones: A Remote Substituent Effect

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Abstract: The effect on photochemical transformations of the substituents present remotely from the reaction site in 3-benzyloxy-2-(benzo[*b*]thiophen-2-yl)-4*H*-chromen-4-ones has been determined. The structure(s) of the substrates and photoproducts were established by spectroscopic techniques (UV, IR, and NMR). The substituents had profound effects on product yield and distribution. Electron withdrawing groups (EWGs) on the benzenoid moiety of the chromenone nucleus increased the yield of the photoproducts whereas electron donating groups (EDGs) decreased the yield. These results may be attributed to "state switching" of the substituents during excitation.

Keywords: photocyclization, substituent effect, 1,4-biradical, angular pentacyclics, chromenones, benzothiophene, photoirradiation.

1 Introduction

Norrish Type II reactions, which involve an intramolecular H-abstraction initiated by a photo-excited carbonyl compound, have found several synthetic applications [1-8]. Various examples in the literature revealed a profound effect of the substituent upon the outcome of Norrish type II reactions [9-13]. Encouraged by the interesting Norrish Type II photochemical properties of the chromones [14], in our previous study, we tested the photochemical behavior of a methanolic solution of 3-alkoxy-6-chloro-2-(benzo[*b*] thiophen-2-yl)-4*H*-chromen-4-ones having different alkoxy groups (benzyloxy, allyloxy, ethoxy and methoxy) on the benzenoid moiety, and the various photoproducts, including the cyclised and cyclodehydrogenated ones [15-17], were determined. In the present communication, we intend to expand the scope of this work. The photolysis of 3-benzyloxy-2-(benzo[*b*]thiophen-2-yl)-4*H*-chromen-4-ones bearing electron-withdrawing and electron-donating groups on the benzenoid moiety has been carried out. The purpose of this study is to determine the effects of remote substituents (i.e. substituents present far away from the reaction centre) [18] on the formation and distribution of the photoproducts.

2 Experimental

2.1 General

^{1}H NMR (300 and 400 MHz) and proton-decoupled ^{13}C NMR (75.4 and 100.6 MHz) spectra were taken on a Bruker spectrometer using TMS as an internal standard. The infrared (IR) spectra were recorded in KBr pellets on a MB3000 FT-IR with HORIZON MB^{TM} FTIR software from ABB Bomen. Melting points were determined in open capillaries and are uncorrected. The photo-irradiation of the solution of substrates was carried out under nitrogen atmosphere from a 125 W (medium pressure) Hg-vapor lamp using a Pyrex filter. The columns for chromatographic separation were packed in petroleum ether with silica gel and were eluted with a mixture of pet ether and ethyl acetate (99:1). The X-ray crystallographic structure was collected on a Bruker Kappa APEX II diffractometer equipped with a CCDC detector and sealed-tube monochromated MoKα radiation using the program APEX2.

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2.2 Synthesis of 3-(benzo[b]thiophen-2-yl)-1 -(2-hydroxy-phenyl)prop-2-en-1-ones 3(a-d)

1(a-d) and benzothiphene-2-carbaldehyde **2** were added to a well-stirred suspension of powdered NaOH (0.8 g, 0.02 mol) in EtOH (100 ml) at 0°C. The reaction mixture was stirred further overnight. Thereafter, it was poured over ice and neutralized with dilute HCl to obtain acrylophenone, which was crystallized from EtOH to give the yellowish-orange needles of **3(a-d).**

2.2.1 3-(Benzo[b]thiophen-2-yl)-1-(5-chloro-2-hydroxy-4-methyl-phenyl)prop-2-en-1-one 3a

Yield 78%, orange solid; mp 161-163°C; IR ν_{max} (cm^{-1}): 3390 (-OH), 1640 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 12.72 (1H, s, OH), 8.12 (1H, d, $J_{2,3}$ = 15.2 Hz, H-3), 7.88 (1H, s, H-6'), 7.70 (2H, m, H-3'' & H-7''), 7.59 (1H, d, $J_{3,2}$ = 15.2 Hz, H-2), 7.47 (3H, m, H-4'', H-5'' & H-6''), 6.93 (1H, s, H-3'), 2.41 (3H, s, CH$_3$); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 192.39, 162.01, 146.02, 145.64, 134.44, 131.14, 129.22, 128.95, 128.80, 127.50, 126.74, 126.30, 124.22, 122.99, 120.61, 120.22, 118.99 and 20.85.

2.2.2 3-(Benzo[b]thiophene-2-yl)-1-(2-hydroxyphenyl) prop-2-en-1-one 3b

Yield 78%, orange solid; mp 154-156°C; IR ν_{max} (cm^{-1}): 3390 (-OH), 1645 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 12.82 (1H, s, OH), 8.02 (1H, dd, J_o = 8.4 Hz, J_m = 1.6 Hz, H-6'), 7.84 (1H, s, H-6''), 7.76 (1H, d, $J_{3,2}$ = 15.2 Hz, H-3), 7.64 (1H, dd, J_o = 7.6 Hz, J_m = 2.0 Hz, H-2''), 7.54 (1H, d, $J_{2,3}$ = 15.6 Hz, H-2), 7.52 (1H, dd, J_o = 8.4 Hz, J_m = 2.4 Hz, H-5''), 7.43 (1H, ddd, J_o = 7.2 Hz, J_m = 1.6 Hz, H-4'), 7.29 (1H, ddd, J_o = 8.4 Hz and 7.2 Hz, J_m = 1.2 Hz, H-5'), 7.09 (1H, ddd, J_o = 8.4 Hz, J_m = 2.0, H-4''), 7.05 (1H, ddd, J_o = 8.4 Hz, J_m = 2.4 Hz, H-3''), 6.99 (1H, dd, J_o = 7.2 Hz, J_m = 1.2 H-3'); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 179.7, 159.8, 144.1, 138.8, 137.1, 135.3, 136.5, 131.4, 129.8, 127.6, 127.1, 124.6, 123.5, 121.1, 119.8, 116.8 and 111.4.

2.2.3 3-(Benzo[b]thiophene-2-yl)-1-(5-methyl-2-hydroxyphenyl)prop-2-en-1-one 3c

Yield 75%, yellowish-Orange solid; mp 166-168°C; IR ν_{max} (cm^{-1}): 3340 (-OH), 1644 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 12.64 (1H, s, OH), 8.15 (1H, d, $J_{3,2}$ = 14.2 Hz, H-3), 7.96 (1H, d, J_m = 1.6 Hz, H-6'), 7.84 (2H, dd, J_o = 8.0 Hz, J_m = 1.6 Hz, H-4' & H-7''), 7.70 (3H, ddd, J_o = 7.2 Hz, J_m = 1.6 Hz, H-4'', H-5'' & H-6''), 7.50 (1H, d, $J_{2,3}$ = 14.2 Hz, H-2), 7.28 (1H, s, H-3''), 6.28 (1H, d, J_o = 8.0 Hz, H-3'), 2.40 (3H, s, CH$_3$); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 192.85, 161.58, 140.45, 140.07, 139.68, 138.11, 137.69, 130.46, 128.28, 128.05, 126.71, 125.07, 124.72, 122.54, 121.38, 119.57, 118.41 and 20.66.

2.2.4 3-(Benzo[b]thiophene-2-yl)-1-(2-hydroxy-5-methoxyphenyl)prop-2-en-1-one 3d

Yield 74%, yellowish-orange solid; mp 159-161°C; IR ν_{max} (cm^{-1}): 3360 (-OH), 1642 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 12.39 (1H, s, -OH), 8.13 (1H, d, $J_{3,2}$= 15.2 Hz, H-3), 7.91 (1H, d, J_m = 1.2 Hz, H-6'), 7.64 (1H, s, 3''), 7.44 (1H, d, $J_{2,3}$ = 15.2 Hz, H-2), 7.35 (2H, d, J_o = 8.4 Hz, J_m = 1.6 Hz, H-4''& H-7''), 7.28 (1H, d, J_o = 7.2 Hz, J_m = 1.2 Hz, H-4'), 7.18 (2H, dd, J_o = 8.8 Hz, J_m = 2.8 Hz, H-5'' & H-6''), 7.02 (1H, d, J_o = 7.2 Hz, H-3'), 3.39 (3H, s, OC**H**$_3$); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 192.60, 158.01, 151.77, 140.48, 139.95, 139.65, 138.47, 130.67, 126.79, 125.10, 124.76, 124.06, 122.56, 121.21, 119.41, 112.87, 107.37 and 56.18.

2.3 Synthesis of 2-(benzo[b]thiophen-2-yl)-3-hydroxy-4H-chromen-4-ones 4(a-d)

To a well stirred suspension of compound **3(a-d)** in MeOH was added aqueous KOH (10.0 ml, 20%). This mixture was cooled to 0°C. H_2O_2 (50%) was added to this dark red solution drop-wise until the colour changed to yellow, and the stirring was continued for 4h. The reaction mixture was neutralized with ice-cold HCl to yield light yellow precipitates, which crystallized to a light yellow solid **4(a-d).**

2.3.1 2-(Benzo[b]thiophen-2-yl)-3-hydroxy-6-methyl-4H-chromen-4-one 4a

Yield 81%, creamish solid; mp 108-110°C; IR ν_{max} (cm^{-1}): 3215 (-OH), 1628 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.20 (1H, s, H-5), 7.87 (1H, s, H-3'), 7.47-7.57 (3H, m, H-4', H-5' and H-6'), 7.28 (1H, m, H-7'), 6.95 (1H, s, H-8), 4.62 (1H, s, OH), 2.43 (3H, s, CH$_3$). ^{13}C NMR [CDCl$_3$, δ (ppm)]: 193.08, 153.65, 142.99, 131.39, 130.89, 130.27, 129.48, 128.89, 128.72, 128.61, 127.75, 127.55, 126.85, 126.14, 124.90, 120.18, 119.94 and 20.95.

2.3.2 2-(Benzo[b]thiophen-2-yl)-3-hydroxy-6-methyl-4H-chromen-4-one 4b

Yield 71%, creamish solid; mp 108-110°C; IR ν_{max} (cm^{-1}): 3215 (-OH), 1620 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]:

8.28 (1H, dd, J_o = 8.0 Hz, J_m = 1.6 Hz, H-5), 7.94 (1H, ddd, J_o = 7.6 Hz, J_m = 2.0 Hz, H-7), 7.73 (1H, s, H-7’), 7.70 (1H, ddd, J_o = 8.0 Hz, J_m = 2.0 Hz, H-6), 7.64 (1H, ddd, J_o = 8.4 Hz, J_m = 2.0 Hz, H-3’), 7.55 (2H, m, H-4’ and 5’’), 7.15 (1H, ddd, J_o = 8.4 Hz, J_m = 2.4 Hz, H-6’), 7.02 (1H, dd, J_o = 7.6 Hz, J_m = 2.0 Hz, H-8); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 173.9, 155.3, 154.7, 145.6, 140.4, 139.7, 138.7, 135.8, 134.5, 128.9, 127.4, 125.1, 124.5, 122.5, 121.5, 119.9, 118.7.

2.3.3 2-(Benzo[b]thiophen-2-yl)-3-hydroxy-6-methyl-4H-chromen-4-one 4c

Yield 69%, creamish-white solid, mp 103-105°C; IR $\boldsymbol{\nu}_{\mathbf{max}}$ (cm^{-1}): 3200 (-OH), 1618 (C=O); ^{1}H NMR [CDCl$_3$, δ(ppm), 400 MHz]: 8.20 (1H, d, J_o = 2.0 Hz, H-5, 7.84 (2H, complicated dd, J_o = 6.8 Hz, J_m = 1.2 Hz, H-5’ and H-6’),7.38-7.36 (2H, m, H-4’ and 5’’), 7.28 (1H, s, H-3’), 7.01 (1H, dd, J_o = 7.6 Hz, J_m = 2.0 Hz, H-7), 6.82 (1H, d, J_o = 8.0 Hz, H-8), 2.33 (3H, s, CH$_3$); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 175.86, 160.65, 160.63, 159.22, 153.41, 153.37, 148.42, 137.45, 130.07, 126.60, 124.63, 124.59, 124.20, 122.45, 119.37, 118.06, 117.72 and 20.43.

2.3.4 2-(Benzo[b]thiophen-2-yl)-3-hydroxy-6-mehoxy-4H-chromen-4-one 4d

Yield 72%, pale yellow solid; mp 114-116°C; IR $\boldsymbol{\nu}_{\mathbf{max}}$ (cm^{-1}): 3212 (-OH), 1620 (C=O); ^{1}H NMR [CDCl$_3$, δ(ppm), 400 MHz]: 8.28 (1H, s, H-3’), 7.92 (1H, d, J_m = 2.8 Hz, H-5), 7.78 (1H, d, J_o = 7.2 Hz, J_m = 2.8 Hz, H-7), 7.66 (1H, d, J_o = 7.6 Hz, H-8), 7.53 (2H, m, H-5’ and H-6’), 7.34 (1H, dd, J_o = 6.4 Hz, J_m = 2.4 Hz, H-4’), 7.28 (1H, dd, J_o = 6.4 Hz, J_m = 2.8 Hz, H-7’), 4.51 (1H, s, -OH), 3.98 (3H, s, OCH3); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 177.42, 150.81, 143.30, 140.11, 139.62, 134.06, 132.88, 127.68, 126.58, 125.62, 124.89, 124.28, 123.67, 123.01, 122.25, 122.12, 119.43 and 55.96.

2.4 Synthesis of 2-(benzo[b]thiophen-2-yl)-3-(benzyloxy)-4H-chromen-4-ones 5(a-d*)*

2.4.1 2-(Benzo[b]thiophen-2-yl)-3-(benzyloxy)-6-chloro-7-methyl-4H-chromen-4-one 5a

Yield 76%, white solid; mp 110-112°C; IR $\boldsymbol{\nu}_{\mathbf{max}}$ (cm^{-1}): 1644 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 7.91 (1H, s, H-3’), 7.87 (1H, s, H-5), 7.76 (2H, complicated ddd, J_o = 7.6 Hz, J_m = 1.6 Hz, H-5’ and 6’), 7.33-7.42 (5H, m, H-2’’, H-3’’, H-4’’, H-5’’ and H-6’’), 7.48 (2H, dd, J_o = 7.6 Hz, J_m = 2.0 Hz, H-7’ and H-4’), 6.97 (1H, s, H-8), 5.18 (2H, s, H-1”), 2.44 (3H, s, CH$_3$); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 197.89, 176.62, 158.45, 154.25, 147.88, 139.66, 138.82, 138.49, 129.11, 128.76, 128.32, 128.25, 127.59, 126.33, 124.38, 124.06, 123.18, 122.27, 119.95, 115.29, 107.63, 71.08 and 20.47.

2.4.2 2-(Benzo[b]thiophen-2-yl)-3-(benzyloxy)-4H-chromen-4-one 5b

Yield 75%, White solid; mp 109-111°C; IR $\boldsymbol{\nu}_{\mathbf{max}}$ (cm^{-1}): 1632 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.29 (1H, dd, J_o = 8.0 Hz, J_m = 1.6 Hz, H-5), 8.21 (1H, s, H-7’), 7.87 (2H, m, H-3’and H-6’), 7.71 (1H, ddd, J_o = 7.2 Hz, J_m = 1.6 Hz, H-7), 7.65 (2H, m, H-4’ and H-5’), 7.59 (1H, ddd, J_o = 8.4 Hz, J_m = 1.6 Hz, H-6), 7.44 (5H, m, H-2’’, H-3’’, H-4’’, H-5’’ and H-6’’), 7.36 (1H, dd, J_o = 7.2 Hz, J_m = 1.6 Hz, H-8), 5.40 (2H, s, H-1”); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 171.9, 155.8, 155.3, 143.8, 140.4, 139.7, 138.4, 134.5, 132.1, 131.2, 128.4, 127.9, 126.2, 125.1, 124.9, 122.5, 121.9, 119.6, 118.4, 117.8, 111.2, 74.9.

2.4.3 2-(Benzo[b]thiophen-2-yl)-3-(benzyloxy)-6-methyl-4H-chromen-4-one 5c

White solid in 72% yield, mp 117-119°C; IR $\boldsymbol{\nu}_{\mathbf{max}}$ (cm^{-1}): 1622 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.19 (1H, s, H-3’), 8.07 (1H, d, J_m = 2.0 Hz, H-5), 7.88 (2H, complicated ddd, J_o = 7.6 Hz, J_m = 2.4 Hz, H-5’ and 6’), 7.66 (2H, dd, J_o = 8.0 Hz, J_m = 1.6 Hz, H-4’ and H-7’), 7.52 (1H, dd, J_o = 8.4 Hz, J_m = 2.0 Hz, H-7), 7.46 (1H, d, J_o = 8.8 Hz, H-8), 7.36-7.44 (5H, m, H-2’’, H-3’’, H-4’’, H-5’’ and H-6’’), 5.41 (2H, s, -OC$\mathbf{H}_2$-), 2.49 (3H, s, -CH$_3$); ^{13}C NMR [CDCl$_3$, δ (ppm)]: 174.24, 153.25, 151.42, 142.02, 138.67, 136.65, 134.93, 134.77, 132.13, 129.17, 128.42, 128.36, 127.50, 126.74, 126.07, 125.04, 124.82, 124.69, 123.95, 122.25, 117.63, 73.91 and 20.83.

2.4.4 2-(Benzo[b]thiophen-2-yl)-3-(benzyloxy)-6-methoxy-4H-chromen-4-one 5d

White solid in 68% yield, mp 119-121°C; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm^{-1}): 1632 (C=O); ^{1}H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.17 (1H, s, H-3’), 7.88 (3H, m, H-5, H-7’ and H-4’), 7.67 (3H, m, H-7, H-5’ and H-6’), 7.34-7.50 (5H, m, H-2’’, H-3’’, H-4’’, H-5’’ and H-6’’), 7.30 (1H, d, J_o = 9.6 Hz, H-8), 5.41 (2H, s, H-1”), 3.93 (3H, s, OCH$_3$). ^{13}C NMR [CDCl$_3$, δ (ppm): 173.95, 156.71, 149.82, 141.99, 138.70, 136.69, 132.08, 129.17, 128.45, 127.66, 126.71, 126.08, 125.04, 124.84, 124.70, 123.88, 122.25, 121.33, 119.32, 105.11, 104.61, 73.90 and 55.93.

2.5 Photo-irradiation of chromenones 5(a-d)

2.5.1 Photolysis of compound (5a)

A dry methanolic solution (100.0 ml) of chromenone **5a** (500 mg) was photo-irradiated with light from a 125 W Hg vapor-lamp in a Photo reactor under an inert nitrogen atmosphere for 30 min. The removal of solvent left a gummy solid, which was chromatographed to yield **6a.**

Compound (6a): Yield 40%, shining white crystalline solid; mp 198-200°C; IR ν_{max} (cm^{-1}): 1628 (C=O); ^{1}H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.08 (1H, s, H-9), 7.33-7.39 (3H, m, H-2, H-2’, H-6’), 7.23-7.28 (3H, m, H-3’, H-4’, H-5’), 7.16 (1H, ddd, J_o = 8.0 Hz, J_o = 7.6 Hz, J_m = 1.2 Hz, H-3), 7.14 (1H, s, H-12), 6.81 (1H, ddd, J_o = 7.6 Hz, J_o = 7.2 Hz, J_m = 1.2 Hz, H-4), 6.16 (1H, d, J_o = 7.6 Hz, H-5), 5.28 (1H, d, $J_{13b,5b}$ = 6.8 Hz, H-13b), 5.08 (1H, d, $J_{6,5b}$ = 10.0 Hz, H-6), 3.91 (1H, dd, $J_{5b,13b}$ = 6.8 Hz, $J_{5b,6}$ = 10.0 Hz, H-5b), 2.47 (3H, s, CH_3); ^{13}C NMR [$CDCl_3$, δ (ppm)]: 198.24, 156.57, 145.21, 142.22, 140.12, 139.36, 135.64, 130.89, 128.81, 128.48, 127.89, 126.75, 126.70, 124.02, 123.46, 122.75, 122.04, 120.64, 115.37, 71.26 (C-13b), 45.13 (C-6), 25.25 (C-5b) and 20.76 (-**C**H_3).

2.5.2 Photolysis of compound (5b)

A dry methanolic solution of **5b** (500 mg) on photolysis for 30 min furnished **6b** and processed as above.

Compound (6b): Yield 54%, white solid; mp 208-210°C; IR ν_{max} (cm^{-1}): 1645 (C=O); ^{1}H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.29 (1H, dd, J_o = 8.0 Hz, J_m = 1.6 Hz, H-9), 7.68 (1H, ddd, J_o = 8.0 Hz and 7.2 Hz, J_m = 1.6 Hz, H-11), 7.54 (1H, ddd, J_o = 8.0 Hz, J_m = 2.0 Hz, H-10), 7.38 (1H, dd, J_o = 8.0 Hz, J_m = 1.6 Hz, H-12), 7.33 (3H, m, H-2, H-2’’ and H-6’’), 7.23 (3H, m, H-3’’, H-4’’ and H-5’’), 7.17 (1H, ddd, J_o = 8.4 Hz and 8.0 Hz, J_m = 1.2 Hz, H-3), 6.79 (1H, ddd, J_o = 8.0 Hz and 7.6 Hz, J_m = 1.2 Hz, H-4), 6.13 (1H, d, J_o = 7.6 Hz, J_m = 1.6 Hz, H-5), 5.28 (1H, d, J = 6.8 Hz, H-13b), 5.06 (1H, d, J = 10.4 Hz, H-6), 3.91 (1H, dd, J = 10.4 Hz and 6.8 Hz, H-5a); ^{13}C NMR [$CDCl_3$, δ (ppm)]: 191.1, 182.3, 172.3, 155.6, 147.9, 138.4, 136.6, 133.5, 131.4, 129.6, 128.9, 128.3, 127.5, 127.0, 126.2, 125.1, 124.5, 124.3, 121.8, 121.4, 118.7, 117.9, 51.9, 47.1.

2.5.3 Photolysis of compound (5c)

A dry methanolic solution of **5c** (500 mg) on photolysis for 30 min furnished **6c** and processed as above.

Compound (6c): Yield 36%, shinning white crystal; mp 207-209°C; IR ν_{max} (cm^{-1}): 1632 (C=O).^{1}H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.09 (1H, d, J_m = 1.2 Hz, H-9), 7.48 (1H, dd, J_o = 8.4 Hz, J_m = 1.2 Hz, H-11), 7.33-7.39 (5H, m, H-2’, H-3’, H-4’, H-5’ and H-6’), 7.26 (2H, ddd, J_o = 8.4 Hz, J_o = 8.0Hz, J_m = 1.2 Hz, H-3 and H-4), 7.18 (1H, dt, J_o = 7.6Hz, J_m = 1.2 Hz, H-2), 6.80 (1H, ddd, J_o = 7.6 Hz, J_m = 1.6 Hz, H-5), 6.16 (1H, d, J_o = 7.6 Hz, H-12), 5.26 (1H, d, $J_{13b,5b}$ = 6.8 Hz, H-13b), 5.06 (1H, d, $J_{6,5b}$ = 10.0 Hz, H-6), 3.90 (1H, dd, $J_{5b,13b}$ = 6.8 Hz, $J_{5b,6}$ = 10.0 Hz, H-5b), 3.18 (3H, s, CH_3); ^{13}C NMR [$CDCl_3$, δ (ppm)]: 171.73, 153.56, 147.82, 139.82, 138.99, 136.70, 136.56, 134.84, 134.48, 132.23, 128.86, 128.41, 128.28, 127.09, 125.41, 124.32, 123.45, 122.25, 117.63, 114.12, 51.96, 47.23 and 29.76.

2.5.4 Photolysis of compound (5d)

A dry methanolic solution of **5d** (500 mg) on photolysis for 30 min furnished **6d** and processed as above.

Compound (6d): Yield 28%, white solid; mp 195-197°C; IR ν_{max} (cm^{-1}): 1638 (C=O); ^{1}H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 7.93 (1H, d, J_m = 1.2 Hz, H-9), 7.84-7.87 (3H, m, H-2, H-2’, H-6’), 7.67 (1H, ddd, J_o = 7.2 Hz, J_o = 6.8 Hz, J_m = 1.2 Hz, H-4), 7.53 (1H, d, J_o = 7.6 Hz, H-5), 7.41-7.47 (3H, m, H-3’, H-4’, H-5’), 7.34 (1H, dd, J_o = 7.6 Hz, J_m = 1.6Hz, H-11), 7.31 (1H, ddd, J_o = 7.6 Hz, J_o = 7.2 Hz, J_m = 2.0 Hz, H-3), 7.14 (1H, d, H-12), 5.43 (1H, d, $J_{13b,5b}$ = 6.8 Hz, H-13b), 5.09 (1H, d, $J_{6,5b}$ = 10.2 Hz, H-6), 3.98 (1H, dd, $J_{5b,13b}$ = 6.8 Hz, $J_{5b,6}$ = 10.2 Hz, H-5b), 3.45 (3H, s, OCH_3); ^{13}C NMR [$CDCl_3$, δ (ppm)]: 166.36, 140.24, 139.44, 138.18, 135.92, 129.71, 128.85, 128.64, 128.35, 127.06, 126.29, 125.58, 124.88, 124.47, 123.59, 122.48, 119.83, 119.09, 112.38, 70.24, 67.15, 31.96 and 29.73.

Ethical approval: The conducted research is not related to the use of either humans or animals.

3 Results and Discussion

In our recent studies [15-17] the 3-alkoxy-6-chloro-2-(benzo[*b*]thiophen-2-yl)-4*H*-chromen-4-ones yielded both dihydrogenated and dehydrogenated products along with a migrated photoproduct following photochemical irradiation. These studies mainly included substrates with different substituents at the C-3 position. In the present study, 3-benzyloxy-2-(benzo[*b*]thiophen-2-yl)-4*H*-chromen-4-ones with different substituents (-Cl & CH_3, -H, -CH_3 and -OCH_3) attached to the benzenoid moiety have been synthesized and photolysed to observe the effects of substituents on photoproduct distribution and formation.

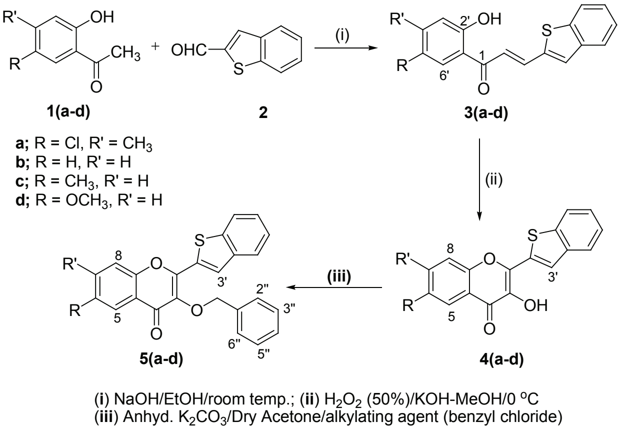
The targets **5(a-d)** were synthesized by (i) condensing the 2-hydroxyacetophenones **1(a-d)** with benzothiophene-2-carbaldehyde in the presence of NaOH/EtOH [19] followed by (ii) the cyclisation of chalcones **3(a-d)** to 3-hydroxychromenones **4(a-d)** under Algar–Flynn–

Oyamada conditions [20-22] and (iii) subsequent alkylation of the latter with benzyl chloride, in the presence of dry acetone, freshly dried K_2CO_3 and tetra *n*-butyl ammonium iodide (Scheme 1). The structure of the compounds **6(a-d)** were found to be consistent with their spectral parameters (IR, $^1H/^{13}C$ NMR *vide* experimental). The yields of all these compounds were in the range of 74-82%.

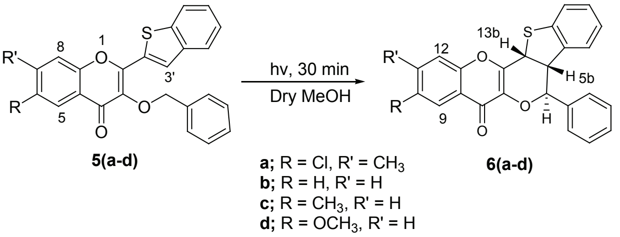
These chromenones **5(a-d)** (absorption maxima (λmax) between 352 and 364 nm in MeOH) were irradiated with Pyrex filtered UV-light. The photolysis of a dry methanolic solution of **5(a-d)** with a 125 W medium pressure Hg-vapor lamp under nitrogen produced photoproducts **6(a-d),** and structures of these photoproducts were established by their spectral data (IR, $^1H/^{13}C$-NMR). Methanol was used as solvent because better yields of photoproducts **6(a-d)** were obtained in polar protic solvents (ethanol and methanol) than in polar aprotic solvents (benzene, C_6H_{12}, DMF and CH_3CN), a result that was in agreement with previous observations [23]. The photoproducts [15] similar to aromatic benzothiophene fused xanthenone, benzyl migrated product and substituted epoxide could not be isolated from the photolysate of these chromenones **5(a-d)**. These photoproducts were produced in minute quantities, as observed by TLC analysis and NMR spectra of the photolysates (data not shown) but they could not be isolated despite our best efforts.

The IR spectrum of crystals of compound **6a** displays a C=O stretch at 1659 cm^{-1}. In the ^1H NMR, benzenoid protons H-9 and H-12 appeared as singlets at: δ 8.08 and δ 7.14. The benzothienyl protons were seen at δ 7.16 (1H, ddd, H-3), δ 6.81 (1H, ddd, H-4) and δ 6.16 (1H, d, H-5). A comparison of the ^1HNMR spectra of **5a** and **6a** exhibited that the resonances at δ 5.18 ($-OCH_2$) and δ 7.91 (H-3') present in the **5a** were missing in the **6a**, thereby pronouncing the involvement of these protons in the photo-conversion. Regarding the rest of the spectrum, the bridgehead protons H-13b and H-5b (Figure 1) were found to be placed at δ 5.28 (d, $J_{13b,5b}$ = 6.8 Hz) and δ 3.91 (dd, $J_{5b,13b}$ = 6.8 Hz, $J_{5b,6}$ =10.0 Hz). The other proton, H-6 was seen at δ 5.08 (d, $J_{6',5b}$ = 10.0 Hz). At the extreme right appeared a singlet δ 2.47 due to $-CH_3$ group. The ^{13}C NMR spectrum of this photoproduct also corroborated the structure proposed, as C-13b and C-5b, the ring junction carbons, resonated at 45.13 and 20.76 ppm respectively. The structures of other photoproducts **6(b-d)** were established similarly (vide experimental).

The MM2 energy minimizations programme [24-26] (Figure 2) was applied to elucidate the stereochemical features of the dihydrogenated photoproduct **6.** The various dihedral angles (*Φ*) and the expected $J^†$ values along with the torsional energies of configurations **6(a-d)** are tabulated in **Table 1.** The observed ^3J values found for **6(a-d)** are in accordance with the $J^†$ values for the energy minimized (MM2) configuration I as in our earlier observations [15] where protons H-5b and H-6 are in *trans* orientation relative to each other (as opposed to configuration II where the protons H-5b and H-6 are in *cis*). Such outcomes have been reported previously from our laboratory [27] as well as for the naturally occurring pterocarpans [28-31].



Scheme 1: Synthesis of Chromenones **5(a-d)**.



Scheme 2: Photolysis of Chromenones **5(a-d).**

A closer look on the effects of different substituents at benzenoid moiety in the present chromones suggests that an increase in electron density by the electron releasing group on the chromenone ring decreases the yield of the dihydro photoproduct (**6a**, R = Cl and R'= CH_3, yield 40%; **6b,** R = H and R'= H, yield 38%; **6c,** R = CH_3 and R'= H, yield 36%; **6d**, R = $-OCH_3$ and R'= H, yield 28%). In our earlier studies, the benzothienyl containing chromones with electron withdrawing groups [15] (R = Cl and R'= H) resulted in a 42% yield of aromatic, 1,5-migrated and dealkoxylated photoproducts. This behavior may be attributed due to the fact that electron donating substituents may cause state switching [32-34] from n→π* to π→π* that may reduce the hydrogen abstraction capacity of the carbonyl group of pyrones [18].

The photo-transformations of target photochemical substrates **5(a-d)** and formation of the angular pentacyclic

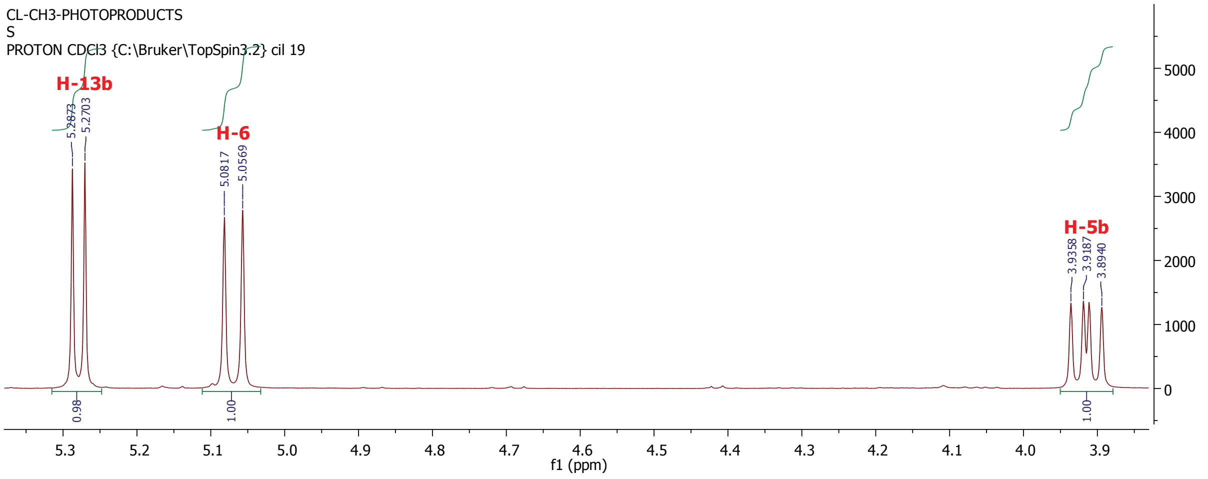


Figure 1: 400MHz ^{1}H spectrum of Photoproduct **6a**.

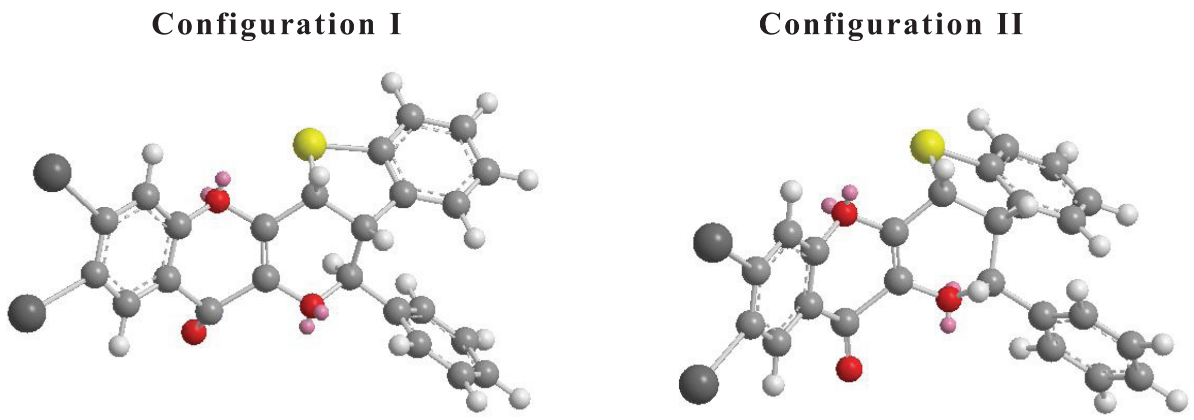


Figure 2: Energy minimized MM2 structures of **6.**

Table 1: Expected coupling constants for the two configurations of **6(a-d).**

Coupling protons H-5b and H-6 in Photoproduct	Configuration I			Configuration II			Observed *J*
	Φ	*J*† (Hz)	E (Kcal/mol)	*Φ*	*J*† (Hz)	E (Kcal/mol)	
6a	144	11.5	19.144	-66.27	4.10	20.312	10.0Hz
6b	145	9.6	18.486	-59.25	2.30	23.761	10.2Hz
6c	143	11.5	18.747	-68.79	4.11	21.166	10.0Hz
6d	144	11.5	20.529	-65.43	4.08	21.711	10.2Hz

J† *Expected value*

dihydrogenated photoproduct described above, i.e. **5a→6a, 5b→6b, 5c→6c, 5d→6d,** can be envisaged to occur simply through an initial H-abstraction from an $-OCH_2$- group by the excited C=O group of the pyrone moiety to produce a 1,4-biradical [15] generated through the Norrish type-II process. The ease of H-abstraction may be the result of a possible six-membered transition state in the

Table 2: Yield/Percentage of photoproducts **6(a-d).**

Photoproduct	Photoproducts yield (%)				
	-Cl [15]	Cl,CH_3	H,H	CH_3	OCH_3
Dihydro photoproduct	42	40	38	36	28

substrates. The photoproducts have been projected to be formed through bond formation between a – ĊH– radical and the C-3'-position of the thiophene ring followed by the concerted sigmatropic 1,5-H shift as reported in our earlier studies [15-17] yielding **6(a-d)**.

4 Conclusion

It may be concluded from the above studies that the electron withdrawing groups (EWG) on the benzenoid moiety of the chromenone favour the formation of dihydrophotoproducts in higher yield than do the electron releasing groups (ERG) due to “state switching”. These substituents also had a profound effect on the distribution of photoproduct(s) as the aromatic 1,5-migrated and dealkoxylated photoproducts were not isolated or realised.

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