Photolysis of some 3-alkoxy-2-thienylchromones

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Abstract
Photo induced cyclisation of some 3-alkoxy-2-thienylchromones has been described. The photoreactions occur through intramolecular H-abstraction by the carbonyl group to provide 1,4-biradical that yield dihydrocyclised and dehydrocyclised compounds. The total photolytic conversion and stereochemistry of the dihydrocyclised products are controlled by the nature of substituents present at the carbon undergoing photo H-abstraction.

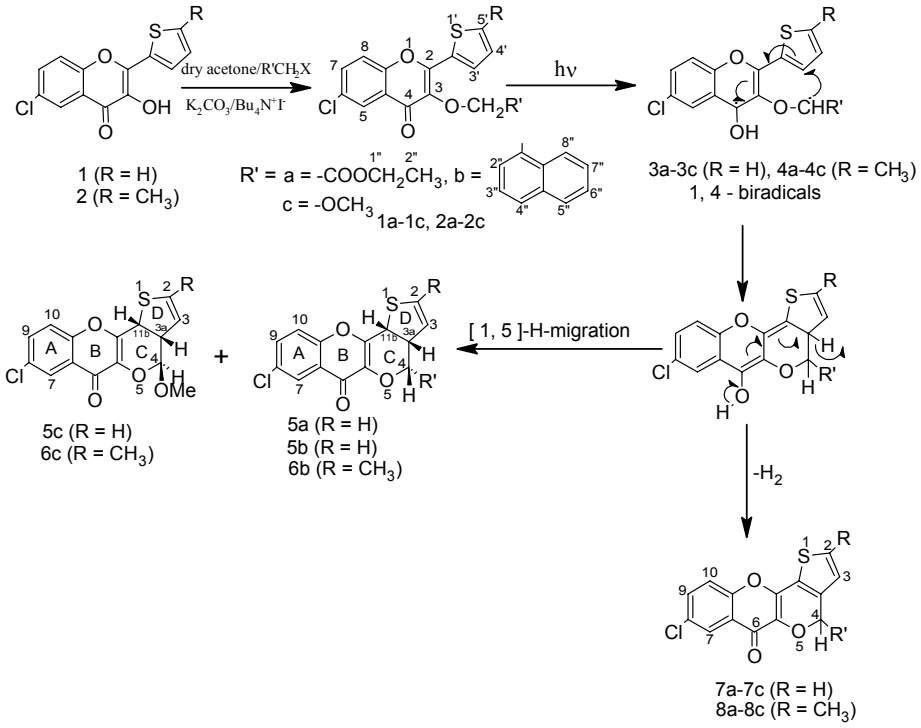
Keywords: Photocyclisation, H-abstraction, 1,4-biradical, chromones, stereoselectivity

Introduction

The photochemical H-abstraction in the carbonyl compounds has attracted the attention of organic chemists in the past and these photo processes have emerged as a promising synthetic tool for obtaining numerous carbocyclic and heterocyclic products.[1] 3-Alkoxy-2-arylchromones are the substrates that undergo easy intramolecular H-abstraction by the photo excited carbonyl chromophore to provide cyclised products.[2] In the recent past, we have reported the photo transformations of some 3-alkoxy/benzyloxy chromones[3] and bischromones[4] where photoreactions occur through intramolecular H-abstraction that furnish angular tetracyclic compounds. Now, we wish to report the results of our investigations upon the photolysis of chromones **1a-1c** and **2a-2c.** The major aim of this study was to investigate the effect of various substituents like ester, naphthalene and methoxy present in 3-alkoxy moiety for the formation of photoproducts and their stereochemical features.

Results and Discussion

The chromones **1a-1c** and **2a-2c** needed for this study, were obtained from the O-alkylation of the 3-hydroxycompounds[3] **1** and **2** with an appropriate alkylating agent (like bromoethylacetate, 1-chloromethylnaphthalene and chloromethylmethylether). The structures of these chromones were characterized by thorough analysis of their spectral data (UV-Vis, IR, ^{1}H NMR and mass).



Scheme 1. Synthesis and mechanism of photolysis of chromones.

IR spectra of the chromones **1a-1c** and **2a-2c** exhibited an intense absorption in the region of 1635-1645 cm^{-1} that confirmed an enone moiety in their structures while an additional absorption has emerged in spectra of **1a** and **2a** at 1752 and 1756 cm^{-1} respectively that suggested the presence of ester (-COOEt) functionality in these compounds.

Table 1. The δ values of C_3-OC**H**$_2$- protons in chromones

Compounds	**1a**	**2a**	**1b**	**2b**	**1c**	**2c**
δ (C_3-OC**H**$_2$)	5.06(s)	5.02(s)	5.73(s)	5.72(s)	5.51(s)	5.50(s)

The downfield resonance of C_3-OC**H**$_2$- protons in **1c** and **2c** than **1a** and **2a** could be ascribed to the presence of two oxygen atoms on both sides of methylene group and the same hydrogens in **1b** and **2b** at δ5.73 (s) and δ 5.72 (s) it could be attributed to their benzylic nature.

The photoirradiation of chromones **1a-1c** and **2a-2c** was carried out in dry benzene using pyrex filtered light from a 125 W mercury arc lamp. The silica gel (100-200 mesh) column chromatographic separation of the photolysates yielded dihydrocyclised **5a-5c**, **6b**,**6c** and dehydrocyclised **7a-7c** and **8a-8c** compounds. In our repeated and best efforts, we were unable to isolate dihydroproduct, similar to **5a**, from the photolysis of **2a**. The TLC of its photolysate exhibited the formation of such product, but it might be formed in extremely low yields that its isolation in pure state has always remained unsuccessful. The structures of photoproducts were deduced from their spectral characteristics (UV, IR & ^{1}H NMR, see Experimental Section). The mass spectra of the photoproducts also proved very helpful in the corroboration of their structures. All the compounds provided rDA (retro Diels Alder) fragment (*m/z* 154/156) in their mass spectra which is the characteristic fragment of the chromone moiety.[5]

The photo-conversions described above may be explained through an initial H-abstraction from the C_3-OCH_2- group by the photoexcited C=O of the pyrone moiety that leads to 1,4-biradicals **3a-3c** and **4a-4c** (Scheme 1). These intermediates further undergo cyclisation followed by [1,5] H-migration to yield **5a-5c** and **6b**,**6c** while their oxidation lead to **7a-7c** and **8a-8c**.

The stereochemical features of dihydro products **5a-5c** and **6b**,**6c** were analyzed by correlation between dihedral angle (ϕ) and coupling constant (J).[6] The vicinal coupling constant (J_{vic}) between H-3a and H-11b was found to be 8.1 Hz in **5b** and **6b** that reflects the *cis* fusion of ring C and D, which is in concurrence with the reported data.[7] The hydrogen atoms at C-4 and C-3a are also *cis* to each other ($J_{3a,4}$=10.0 Hz, ϕ~0^o) in **5b** and **6b**, placing –COOEt and naphthalene moieties in pseudo-equatorial conformation on pyran ring C. Such a view is in conformity with the literature that a heavier group always prefers equatorial an disposition[6] in cyclohexane. All the three hydrogens (H-11b, 3a & 4) are above the plane of molecule with dihydrothiophene ring being '*exo*' to the pyran ring C that is in the pseudo-chair conformation. The energy-minimized structure[8] of compound **5b** is shown in Figure 1.

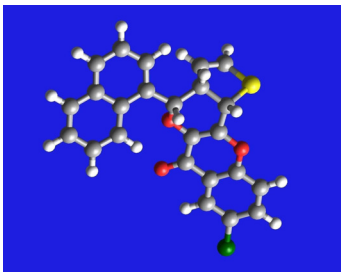
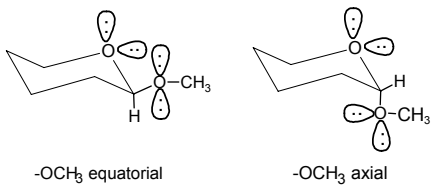


Figure 1. Energy minimized structute of **5b**.

Regarding the stereochemical implications in **5c** and **6c**, evidently the C/D ring fusion is *cis* as derived from ($J_{3a,11b}$=10.0 Hz, ϕ~0^o). The methoxy group (-OCH_3) at C-4 is placed in pseudo-axial position on pyran ring C, a conclusion derived from $J_{4,3a}$=3.0Hz, which explains the *trans* disposition of H-3a and H-4. Here, the preference of the methoxy group (-OCH_3) for axial

disposition can be rationalized on the basis of the anomeric effect[9] as evident in **I** and **II** (Figure 2).



(More interaction- less stable) (Less interaction-more stable)

I **II**

Figure 2. Anomeric effect.

It is worth mentioning here that photolysis of chromones **1b**, **2b** provide better chemical efficiency than of **1c**, **2c** and **1a**, **2a**.

Table 2 shows that the total photolytic conversion furnished by **1b**, **2b** has been about two times greater than of **1c**, **2c** and up to an extent of four times than of **1a**, **2a**. These results could be ascribed to the relative stabilities of intermediate 1,4- biradicals **3a-3c** and **4a-4c** involved in the phtoreactions. The naphthalene moiety provides more delocalisation thus generating highly stabilized biradicals **3b** and **4b**. Although, the -COOEt moiety also provides delocalization to biradicals **3a** and **4a,** but here it appears that its electron-withdrawing inductive effect may offset this behaviour.[10] The methoxy (-OCH_3) group gives the stability of intermediate order to **3c** and **4c**, which is well documented in literature.[10]

Table 2. Yield and distribution of photoproducts

Compound photolysed	Dihydro product yield (%)	Oxidized product yield (%)	Total photolytic conversion
1a	5	10	15
2a	-	12	12
1b	22	44	66
2b	20	40	60
1c	12	23	35
2c	10	20	30

Conclusions

It may be concluded that the total photolytic conversion and the stereochemistry of dihydrocyclised products are dependent upon the nature of the substituent at the 3-alkoxy group of the chromone moieties. The methoxy (-OCH_3) substituted dihydrocyclised compounds contains the heavier group at the pseudo-axial position on the pyran ring C while such groups prefer the pseudo-equatorial position in the naphthalene and ester substituted derivatives.

Experimental Section

General Procedures. Melting points reported are uncorrected. The anhydrous K_2CO_3 used in the synthesis of 3-alkoxychromones was freshly heated over a flame to remove any trace of moisture. IR spectra were recorded on a Perkin Elmer spectrophotometer using KBr pellets and UV spectra on Elico SL-164 spectrophotometer. ^{1}H NMR spectra were recorded on a 400 MHz Bruker spectrophotometer using TMS as internal standard. The mass spectra were recorded on a Schimatzu QP-5000. All photochemical reactions were conducted under a 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. TLC Plates were coated with silica gel G suspended in MeOH-$CHCl_3$. Silica gel (60-120 mesh) and (100-200 mesh) were used for column chromatography.

Synthesis of chromones 1a-1c and 2a-2c

Ethyl[(6-chloro-4-oxo-2-thienyl-4*H*-chromen-3-yl)oxy]acetate 1a. A suspension of 6-chloro-3-hydroxy-2-(2-thienyl)-4*H*-chromen-4-one[3] **1** (2.8 g, 0.01 mol), bromoethylacetate (1.7 g, 0.01 mol), freshly heated anhydrous K_2CO_3 (1.0 g) and tetrabutylammonium iodide (1.0 g) in dry acetone (25 ml) was refluxed for 1h with stirring. A subsequent filtration of the reaction mixture followed by distillation of the solvent yielded a light yellow solid that was percolated through a column of silica-gel (60-120 mesh) using petroleum ether-benzene (1:1) as eluent and further crystallized from EtOH to afford **1a.** Yield (78%), colorless needles, m.p. 100-102 ^{o}C; IR: υ_{max} cm^{-1} 1635, 1752 (C=O); UV(THF): λ_{max} THF 340 nm, 320 nm, 250 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (1H, *d*, J_m=2.6Hz, H-5), 8.10 (1H, *dd*, $J_{3',5'}$=1.1Hz, $J_{3',4'}$=3.8Hz, H-3'), 7.66 (1H, *dd*, $J_{5',4'}$=5.2Hz, $J_{5',3'}$=1.1Hz, H-5'), 7.63 (1H, *dd*, $J_{m,o}$=2.6Hz, 8.9Hz, H-7), 7.51 (1H, *d*, J_o=8.9Hz, H-8), 7.23 (1H, *dd*, $J_{4',5'}$=5.2Hz, $J_{4',3'}$=3.8Hz, H-4'), 5.06 (2H, *s*, -O**CH_2**), 4.25 (2H, *q*, J_{vic}=8.0Hz, H-1"), 1.27 (3H, *t*, J_{vic}=8.0Hz, H-2"). MS: *m/z* 364 (M^+, 100%), Anal. Calcd. For $C_{17}H_{13}O_5ClS$ C 55.97, H 3.59; Found: C 55.94, H 3.56.

Ethyl[(6-chloro-4-oxo-2-(5-methylthienyl)-4*H*-chromen-3-yl)oxy]acetate (2a). Prepared using the procedure similar to above, by taking 6-chloro-3-hydroxy-2-(5-methyl-2-thienyl)-4*H*-chromen-4-one[3] **2** (2.9 g, 0.01 mol) and bromoethylacetate (1.7 g, 0.01 mol). **2a.** Yield (74%), colorless needles, m.p. 104-106 ^{o}C; IR: υ_{max} cm^{-1} 1638, 1756 (C=O); UV(THF): λ_{max} THF 343

nm, 324 nm, 255 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (1H, *d*, J_m=2.7Hz, H-5), 7.90 (1H, *d*, $J_{3',4'}$=3.7Hz, H-3'), 7.58 (1H, *dd*, $J_{m,o}$=2.7Hz, 8.9Hz, H-7), 7.46 (1H, *d*, J_o=8.9Hz, H-8), 6.88 (1H, *dd*, J_{allyl}=1.1Hz, $J_{4',3'}$=3.7Hz, H-4'), 5.02 (2H, *s*, -O**CH$_2$**), 4.24 (2H, *q*, J_{vic}=8.0Hz, H-1") , 2.58 (3H, *s*, $C_{5'}$-**CH$_3$**), 1.26 (3H, *t*, J_{vic}=8.0Hz, H-2"). MS: *m/z* 378 (M^+, 100%), Anal. Calcd. For $C_{18}H_{15}O_5ClS$ C 57.07, H 3.99; Found: C 57.09, H 3.96.

6-Chloro-3-(1-naphthylmethoxy)-2-(2-thienyl)-4*H*-chromen-4-one (1b). Prepared using the procedure similar to above, by taking 6-chloro-3-hydroxy-2-(2-thienyl)-4*H*-chromen-4-one[3] **1** (2.8 g, 0.01 mol) and chloromethylnaphthalene (2.76 g, 0.01 mol). **1b.** Yield (80%), colorless needles, m.p. 139-140 ^{o}C; IR: υ_{max} cm^{-1} 1642 (C=O); UV(THF): λ_{max} THF 342 nm, 322 nm, 257 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (1H, *d*, J=8.4, H-8"), 8.30 (1H, *d*, J_m=2.5Hz, H-5), 8.10 (1H, *dd*, $J_{3',5'}$=1.1Hz, $J_{3',4'}$=3.8Hz, H-3'), 7.67 (2H, *m*, H-7",2"), 7.61 (1H, *dd*, $J_{5',4'}$=5.0Hz, $J_{5',3'}$=1.1Hz, H-5'), 7.60 (1H, *dd*, $J_{m,o}$=2.5Hz, 8.9Hz, H-7), 7.50 (4H, *m*, H-3",4",5",6"), 7.45 (1H, *d*, J_o=9.0Hz, H-8), 7.14 (1H, *dd*, $J_{4',5'}$=4.9Hz, $J_{4',3'}$=3.9Hz, H-4'), 5.73 (2H, *s*, -O**CH$_2$**). MS: *m/z* 418 (M^+, 100%), Anal. Calcd. For $C_{24}H_{15}O_3ClS$ C 68.81, H 3.61; Found: C 68.78, H 3.65.

6-Chloro-3-(1-naphthylmethoxy)-2-(5-methylthienyl)-4*H*-chromen-4-one (2b). Pepared using the procedure similar to above, by taking 6-chloro-3-hydroxy-2-(5-methyl-2-thienyl)-4*H*-chromen-4-one[3] **2** (2.9 g, 0.01 mol) and chloromethylnaphthalene (2.76 g, 0.01 mol). **2b.** Yield (71%), colorless needles, m.p. 144-145 ^{o}C; IR: υ_{max} cm^{-1} 1645 (C=O); UV(THF): λ_{max} THF 345 nm, 322 nm, 260 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (1H, *d*, J=8.5, H-8"), 8.27 (1H, *d*, J_m=2.5Hz, H-5), 7.85 (1H, *d*, $J_{3',4'}$=3.8Hz, H-3'), 7.65 (2H, *m*, H-7",2"), 7.60 (1H, *dd*, $J_{m,o}$=2.4Hz, 8.9Hz, H-7), 7.50 (4H, *m*, H-3",4",5",6"), 7.40 (1H, *d*, J_o=9.0Hz, H-8), 7.10 (1H, *dd*, J_{allyl}=1.0Hz, $J_{4',3'}$=3.8Hz, H-4'), 5.72 (2H, *s*, -O**CH$_2$**), 2.51 (3H, *s*, $C_{5'}$-**CH$_3$**). MS: *m/z* 432 (M^+, 100%), Anal. Calcd. For $C_{25}H_{17}O_3ClS$ C 69.36, H 3.96; Found: C 69.39, H 3.99.

6-Chloro-3-(methoxymethoxy)-2-(2-thienyl)-4*H*-chromen-4-one (1c). Prepared using the procedure similar to above, by taking 6-chloro-3-hydroxy-2-(2-thienyl)-4*H*-chromen-4-one[3] **1** (2.8 g, 0.01 mol) and chloromethylmethylether (0.8 g, 0.01 mol). **1c.** Yield (75%), colorless needles, m.p. 120-122 ^{o}C; IR: υ_{max} cm^{-1} 1640 (C=O); UV(THF): λ_{max} THF 344 nm, 324 nm, 257 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (1H, *d*, J_m=2.5Hz, H-5), 8.02 (1H, *dd*, $J_{3',5'}$=1.1Hz, $J_{3',4'}$=3.8Hz, H-3'), 7.63 (1H, *dd*, $J_{5',4'}$=5.1Hz, $J_{5',3'}$=1.1Hz, H-5'), 7.61 (1H, *dd*, $J_{m,o}$=2.5Hz, 8.9Hz, H-7), 7.48 (1H, *d*, J_o=8.9Hz, H-8), 7.22 (1H, *dd*, $J_{4',5'}$=5.1Hz, $J_{4',3'}$=3.8Hz, H-4'), 5.51 (2H, *s*, -O**CH$_2$**), 3.51 (3H, *s*, -O**CH$_3$**). MS: *m/z* 322 (M^+, 100%), Anal. Calcd. For $C_{15}H_{11}O_4ClS$ C 55.82, H 3.44; Found: C 55.86, H 3.41.

6-Chloro-3-(methoxymethoxy)-2-(5-methylthienyl)-4*H*-chromen-4-one (2c). Prepared using the procedure similar to above, by taking 6-chloro-3-hydroxy-2-(5-methyl-2-thienyl)-4*H*-chromen-4-one[3] **2** (2.9 g, 0.01 mol) and chloromethylmethylether (0.8 g, 0.01 mol). **2c.** Yield (71%), colorless needles, m.p. 125-126 ^{o}C; IR: υ_{max} cm^{-1} 1644 (C=O); UV(THF): λ_{max} THF 345 nm, 322 nm, 260 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (1H, *d*, J_m=2.5Hz, H-5), 7.80 (1H, *d*, $J_{3',4'}$=3.7Hz, H-3'), 7.61 (1H, *dd*, $J_{m,o}$=2.4Hz, 9.0Hz, H-7), 7.45 (1H, *d*, J_o=9.1Hz, H-8), 6.80 (1H, *dd*, J_{allyl}=1.0Hz, $J_{4',3'}$=3.9Hz, H-4'), 5.50 (2H, *s*, -O**CH$_2$**), 3.50 (3H, *s*, -O**CH$_3$**), 2.50 (3H, *s*,

$C_{5'}$-**CH_3**). MS: *m/z* 336 (M^+, 100%), Anal. Calcd. For $C_{16}H_{13}O_4ClS$ C 57.06, H 3.89; Found: C 57.02, H 3.92.

Photoirradiation of chromones 1a-1c and 2a-2c

Photoirradiation of ethyl[(6-chloro-4-oxo-2-thienyl-4H-chromen-3-yl)oxy]acetate (1a). A deoxygenated solution of **1a** (200 mg, 0.00055 mol) in dry benzene (100 ml) was photolysed with light from a 125 W mercury arc lamp in pyrex reactor under pure N_2 atmosphere for 50 min. The progress of reaction was monitored by tlc. The photolysate on chromatographic work up over a column of silica-gel (100-200 mesh), packed in petroleum ether-benzene (2:1) and eluted with benzene-EtOAc (3:1), furnished starting compound **1a** (35%, co-tlc & mmp.) and two new compound **5a** and **7a**.

Ethyl[8-chloro-3a,11b-dihydro-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*]anthracen-6-one]-4-carboxylate (5a). Yield (5%), pale yellow powder, m.p. 170-171 ^oC; IR: υ_{max} cm^{-1} 1651, 1750 (C=O); UV(THF): λ_{max} THF 328 nm, 284 nm, 235 nm; ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (1H, *d*, J_m=2.6Hz, H-7), 7.62 (1H, *dd*, $J_{m,o}$=2.6Hz, 9.0Hz, H-9), 7.43 (1H, *d*, J_o=8.9Hz, H-10), 6.28 (1H, *dd*, $J_{2,3a}$=1.2Hz, $J_{2,3}$=6.0Hz, H-2), 5.54 (1H, *dd*, $J_{3,3a}$=2.4Hz, $J_{3,2}$=6.0Hz, H-3), 5.35 (1H, *d*, $J_{4,3a}$=10.1.1Hz, H-4), 4.80 (1H, *d*, $J_{11b,3a}$=8.1Hz, H-11b), 4.00 (2H, *q*, J_{vic}=8.0Hz, H-1"), 3.72 (1H, *d{dd}*, $J_{3a,3}$=2.2Hz, $J_{3a,11b}$=8.1, $J_{3a,4}$=10.1Hz, H-3a), 1.26 (3H, *t*, J_{vic}=8.0Hz, H-2"); MS: *m/z* 364 (M^+, 60%); Anal. Calcd. For $C_{17}H_{13}O_5ClS$ C 55.97, H 3.59; Found: C 55.95, H 3.57.

Ethyl[8-chloro-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*]anthracen-6-one]-4-carboxylate (7a). Yield (10%), pale yellow powder, m.p. 175-177 ^oC; IR: υ_{max} cm^{-1} 1638, 1752 (C=O); UV(THF): λ_{max} THF 328 nm, 285 nm, 238 nm; ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (1H, *d*, J_m=2.6Hz, H-7), 7.65 (1H, *d*, $J_{2,3}$=5.0Hz, H-2), 7.60 (1H, *dd*, $J_{m,o}$=2.6Hz, 9.0Hz, H-9), 7.45 (1H, *d*, J_o=9.0Hz, H-10), 7.20 (1H, *d*, $J_{3,2}$=5.0Hz, H-3), 6.50 (1H, *s*, H-4), 4.10 (2H, *q*, J_{vic}=8.1Hz, H-1"), 1.26 (3H, *t*, J_{vic}=8.0Hz, H-2"); MS: *m/z* 362 (M^+, 70%); Anal. Calcd. For $C_{17}H_{11}O_5ClS$ C 56.28, H 3.06; Found: C 56.32, H 3.10.

Photoirradiation of ethyl[(6-chloro-4-oxo-2-(5-methylthienyl)-4*H*-chromen-3-yl)oxy]acetate (2a). A deoxygenated solution of **2a** (200 mg, 0.00068 mol) in dry benzene (100 ml) on photolysis for 1h furnished **8a**.

Ethyl[8-Chloro-2-methyl-4H-5,11-dioxa-1-thia-cyclopenta[a]anthracen-6-one]-4-carboxylate (8a). Yield (12%), pale yellow powder, m.p. 180-181 ^oC; IR: υ_{max} cm^{-1} 1640, 1750 (C=O); UV(THF): λ_{max} THF 324 nm, 281 nm, 241 nm; ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (1H, d, J_m=2.6Hz, H-7), 7.60 (1H, dd, $J_{m,o}$=2.6Hz, 9.0Hz, H-9), 7.45 (1H, d, J_o=9.0Hz, H-10), 6.95 (1H, d, J_{allyl}=1.1Hz, H-3), 6.65 (1H, J=4.9Hz, H-4), 4.20 (2H, q, J_{vic}=8.1Hz, H-1") 2.60 (3H, s, $C_{2'}$-CH_3), 1.27 (3H, t, J_{vic}=8.0Hz, H-2"); MS: *m/z* 376 (M^+, 66%); Anal. Calcd. For $C_{18}H_{13}O_5ClS$ C 57.37, H 3.48; Found: C 55.33, H 3.51.

Photoirradiation of 6-chloro-3-(1-naphthylmethoxy)-2-(2-thienyl)-4H-chromen-4-one (1b). A deoxygenated solution of **1b** (200 mg, 0.00048 mol) in dry benzene (100 ml) on photolysis for 1h furnished **5b** and **7b**.

8-Chloro-4-naphthalenyl-3a,11b-dihydro-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*]anthracen-6-one (5b). Yield (22%), pale yellow powder, m.p. 203-205 ^{o}C; IR: υ_{max} cm^{-1} 1650 (C=O); UV(THF): λ_{max} THF 322 nm, 281 nm, 236 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (1H, *d*, J=8.5, H-8"), 8.20 (1H, *d*, J_m=2.6Hz, H-7), 7.81 (2H, *m*, H-7",2"), 7.60 (1H, *dd*, $J_{m,o}$=2.6Hz, 9.0Hz, H-9), 7.52 (4H, *m*, H-3",4",5",6"), 7.45 (1H, *d*, J_o=8.9Hz, H-10), 6.26 (1H, dd, $J_{2,3a}$=1.2Hz, $J_{2,3}$=6.0Hz, H-2), 5.56 (1H, *dd*, $J_{3,3a}$=2.4Hz, $J_{3,2}$=6.0Hz, H-3), 5.30 (1H, *d*, $J_{4,3a}$=10.1.1Hz, H-4), 4.90 (1H, *d*, J_{11b3a}=8.1Hz, H-11b), 3.75 (1H, *d{dd}*, $J_{3a,3}$=2.2Hz, $J_{3a,11b}$=8.1, $J_{3a,4}$=10.1Hz, H-3a). MS: *m/z* 418 (M^+, 56%); Anal. Calcd. For $C_{24}H_{15}O_3ClS$ C 68.81, H 3.61; Found: C 68.85, H 3.58.

8-Chloro-4-naphthalenyl-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*]anthracen-6-one (7b). Yield (44%), pale yellow powder, m.p. 218-219 ^{o}C; IR: υ_{max} cm^{-1} 1640 (C=O); UV(THF): λ_{max} THF 324 nm, 283 nm, 238 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (1H, *d*, J=8.5, H-8"), 8.15 (1H, *d*, J_m=2.5Hz, H-7), 7.72 (2H, *m*, H-7",2"), 7.65 (1H, *d*, $J_{2,3}$=5.1Hz, H-2), 7.58 (1H, *dd*, $J_{m,o}$=2.6Hz, 9.0Hz, H-9), 7.47 (4H, *m*, H-3",4",5",6"), 7.41 (1H, *d*, J_o=9.0Hz, H-10), 6.95 (1H, *d*, $J_{3,2}$=5.1Hz, H-3), 6.62 (1H, *s*, H-4). MS: *m/z* 416 (M^+, 75%); Anal. Calcd. For $C_{24}H_{13}O_3ClS$ C 69.15, H 3.14; Found: C 69.13, H 3.18.

Photoirradiation of 6-chloro-3-(1-naphthylmethoxy)-2-(5-methylthienyl)-4*H*-chromen-4-one (2b). A deoxygenated solution of **2b** (200 mg, 0.00046 mol) in dry benzene (100 ml) on photolysis for 1h furnished **6b** and **8b**.

8-Chloro-2-methyl-4-naphthalenyl-3a,11b-dihydro-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*] anthraxcen-6-one (6b). Yield (20%), pale yellow powder, m.p. 208-209 ^{o}C; IR: υ_{max} cm^{-1} 1651 (C=O); UV(THF): λ_{max} THF 322 nm, 283 nm, 238 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (1H, *d*, J=8.5, H-8"), 8.21 (1H, *d*, J_m=2.6Hz, H-7), 7.70 (2H, *m*, H-7",2"), 7.60 (1H, *dd*, $J_{m,o}$=2.6Hz, 9.0Hz, H-9), 7.53 (4H, *m*, H-3",4",5",6"), 7.45 (1H, *d*, J_o=8.7Hz, H-10), 5.52 (1H, *d*, $J_{3,3a}$=2.5Hz, H-3), 5.32 (1H, *d*, $J_{4,3a}$=10.0Hz, H-4), 5.00 (1H, *d*, J_{11b3a}=8.1Hz, H-11b), 3.90 (1H, *d{dd}*, $J_{3a,3}$=2.1Hz, $J_{3a,11b}$=8.1, $J_{3a,4}$=10.0Hz, H-3a), 2.42 (3H, *s*, $C_{2'}$-CH_3); MS: *m/z* 432 (M^+, 56%); Anal. Calcd. For $C_{25}H_{17}O_3ClS$ C 69.36, H 3.96; Found: C 69.39, H 3.95.

8-Chloro-2-methyl-4-naphthalenyl-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*]anthracen-6-one (8b). Yield (40%), pale yellow powder, m.p. 220-221 ^{o}C; IR: υ_{max} cm^{-1} 1642 (C=O); UV(THF): λ_{max} THF 322 nm, 281 nm, 240 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (1H, *d*, J=8.5, H-8"), 8.15 (1H, *d*, J_m=2.5Hz, H-7), 7.72 (2H, *m*, H-7",2"), 7.57 (1H, *dd*, $J_{m,o}$=2.5Hz, 9.1Hz, H-9), 7.47 (4H, *m*, H-3",4",5",6"), 7.41 (1H, *d*, J_o=8.8Hz, H-10), 6.95 (1H, *d*, J_{allyl}=1.0Hz, H-3), 6.62 (1H, *J*=4.5Hz, H-4), 2.51 (3H, *s*, $C_{2'}$-CH_3); MS: *m/z* 430 (M^+, 65%); Anal. Calcd. For $C_{25}H_{15}O_3ClS$ C 69.68, H 3.51; Found: C 69.72, H 3.48.

Photoirradiation of 6-chloro-3-(methoxymethoxy)-2-(2-thienyl)-4*H*-chromen-4-one (1c). A deoxygenated solution of **1c** (200 mg, 0.00062 mol) in dry benzene (100 ml) on photolysis for 50 min furnished **5c** and **7c**.

8-Chloro-4-methoxy-3a,11b-dihydro-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*]anthracen-6-one (5c). Yield (12%), pale yellow powder, m.p. 165-167 ^{o}C; IR: υ_{max} cm^{-1} 1652 (C=O); UV(THF): λ_{max} THF 324 nm, 283 nm, 238 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (1H, *d*, J_m=2.4Hz, H-7), 7.58 (1H, *dd*, $J_{m,o}$=2.4Hz, 8.9Hz, H-9), 7.50 (1H, *d*, J_o=8.9Hz, H-10), 6.26 (1H, *dd*, $J_{2,3a}$=1.2Hz, $J_{2,3}$=6.0Hz, H-2), 5.56 (1H, *dd*, $J_{3,3a}$=2.4Hz, $J_{3,2}$=6.0Hz, H-3), 5.32 (1H, *d*, $J_{4,3a}$=3.0Hz, H-4), 4.92 (1H, *d*, $J_{11b,3a}$=10.0Hz, H-11b), 3.80 (1H, *d{dd}*, $J_{3a,3}$=2.3Hz, $J_{3a,11b}$=10.0, $J_{3a,4}$=3.0Hz, H-3a), 3.50 (3H, *s*, -O**CH$_3$**); MS: *m/z* 322 (M^+, 60%); Anal. Calcd. For $C_{15}H_{11}O_4ClS$ C 55.82, H 3.44; Found: C 55.85, H 3.46.

8-Chloro-4-methoxy-4*H*-5,11-dioxa-1-thia-cyclopenta[a]anthracen-6-one (7c). Yield (23%), pale yellow powder, m.p. 185-187 ^{o}C; IR: υ_{max} cm^{-1} 1642 (C=O); UV(THF): λ_{max} THF 320 nm, 283 nm, 238 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (1H, *d*, J_m=2.4Hz, H-7), 7.65 (1H, *d*, $J_{2,3}$=5.1Hz, H-2), 7.60 (1H, *dd*, $J_{m,o}$=2.4Hz, 9.0Hz, H-9), 7.50 (1H, *d*, J_o=9.0Hz, H-10), 7.17 (1H, *d*, $J_{3,2}$=5.1Hz, H-3), 6.29 (1H, *s*, H-4), 3.64 (3H, *s*, -O**CH$_3$**); MS: *m/z* 320 (M^+, 71%); Anal. Calcd. For $C_{15}H_9O_4ClS$ C 56.17, H 2.83; Found: C 56.20, H 2.86.

Photoirradiation of 6-chloro-3-(methoxymethoxy)-2-(5-methylthienyl)-4*H*-chromen-4-one (2c). A deoxygenated solution of **2c** (200 mg, 0.00060 mol) in dry benzene (100 ml) on photolysis for 50 min furnished **6c** and **8c**.

8-Chloro-4-methoxy-2-methyl-3a,11b-dihydro-4*H*-5,11-dioxa-1-thia-cyclopenta[*a*] anthracen-6-one (6c). Yield (10%), pale yellow powder, m.p. 173-174 ^{o}C; IR: υ_{max} cm^{-1} 1653 (C=O); UV(THF): λ_{max} THF 322 nm, 283 nm, 240 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (1H, *d*, J_m=2.6Hz, H-7), 7.58 (1H, *dd*, $J_{m,o}$=2.6Hz, 8.9Hz, H-9), 7.51 (1H, *d*, J_o=8.7Hz, H-10), 5.50 (1H, *d*, $J_{3,3a}$=2.4Hz, H-3), 5.35 (1H, *d*, $J_{4,3a}$=3.0Hz, H-4), 4.90 (1H, *d*, J_{11b3a}=10.0Hz, H-11b), 3.75 (1H, *d{dd}*, $J_{3a,3}$=2.2Hz, $J_{3a,11b}$=10.0, $J_{3a,4}$=3.0Hz, H-3a), 3.52 (3H, *s*, -O**CH$_3$**), 2.50 (3H, *s*, $C_{2'}$-CH_3); MS: *m/z* 336 (M^+, 53%); Anal. Calcd. For $C_{16}H_{13}O_4ClS$ C 57.06, H 3.89; Found: C 57.09, H 3.92.

8-Chloro-4-methoxy-2-methyl-4H-5,11-dioxa-1-thia-cyclopenta[a]anthracen-6-one (8c). Yield (20%), pale yellow powder, m.p. 190-191 ^{o}C; IR: υ_{max} cm^{-1} 1640 (C=O); UV(THF): λ_{max} THF 330 nm, 281 nm, 240 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (1H, *d*, J_m=2.4Hz, H-7), 7.65 (1H, *dd*, $J_{m,o}$=2.5Hz, 8.9Hz, H-9), 7.42 (1H, *d*, J_o=9.0Hz, H-10), 6.90 (1H, *d*, J_{allyl}=1.1Hz, H-3), 6.60 (1H, *J*=4.6Hz, H-4), 3.60 (3H, *s*, -O**CH$_3$**), 2.40 (3H, *s*, $C_{2'}$-CH_3); MS: *m/z* 334 (M^+, 72%); Anal. Calcd. For $C_{16}H_{11}O_4ClS$ C 57.40, H 3.31; Found: C 57.37, H 3.35.

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