Photo-rearrangements of some 3-allyloxy-2-phenyl-chromones: Synthesis of vinyl substituted benzopyronopyrans

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Abstract: Photochemical reactions of some 3-allyloxy-2-phenylchromones have been studied. Photoreactions of the compounds afforded substituted pyronopyran derivatives through the 1,4-biradicals.

Keywords: Photo-cyclisation; H-abstraction; allyloxychromones; photoreactivity

1. Introduction

The photochemical H-abstraction in the carbonyl compounds has become an important area of research in organic chemistry to synthesize numerous exotic carbocyclic and heterocyclic products which are very difficult to obtain under the thermal routes. 1-11 3-Alkoxy-2-aryl-chromones are the substrates that undergo easy intramolecular H-abstraction by the photo excited carbonyl chromophore to provide cyclised products. 12-17 In the recent past, we have reported the phototransformations of some 3-alkoxychromones 18-20 where photoreactions occur through intramolecular H-abstraction to furnish angular tetracyclic compounds. In the present study, we wish to report the results of our investigations upon the photolysis of chromones 4a-4f. The major interest behind this study was to synthesize vinyl substituted pyrane derivatives.

2. Results and Discussion

Figure 1. 6-chloro-3-hydroxychromones

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The chromones 4a-4f used in this study were obtained from the O-alkylation of the 3-hydroxy compounds 1-3 with an appropriate alkylation agent (like 3-chloro-2-methylpropene and 1-chloro-3-methyl-2-butene) in the presence of freshly ignited K₂CO₃/dry acetone and Bu₄N⁺T as phase transfer catalyst (PTC). The use of PTC in these syntheses not only expedited the reaction but also improved the yields of 3-alkoxychromones. The crude chromones were subjected to column chromatography (60-120 mesh) and recrystallization from MeOH afforded hydroxy compounds obtained through the retro-Diels Alder cleavage of the pyrone moiety.

Thus, these are formed by the loss of a hydrogen molecule from the starting chromones. It shows that only reorganisation has taken place during the photochemical reaction of these chromones. The mass spectra of the photoproducts also exhibit the ion at m/z 154/156 which is always preferred equatorial disposition in cyclohexane.

Regarding the major feature of the ¹H NMR (400MHz) spectrum of 5a, are the resonating signals due to H-1, 3, 4, 5, 4a & 2a which appeared at δ 6.85 (1H, br s), 5.81 (1H, dd), 5.71 (1H, d), 4.52 (1H, d), 3.60 (1H, d) and 2.81 (2H, m) respectively. In a double resonance experiment, irradiation of the doublet at 4.52 converted the doublet at 3.60 to singlet and conversely the irradiation of doublet at 3.60 converted the doublet at 4.52 to singlet. Other photoproducts 5b-5f also represented similar kind of spectral pattern. The stereochemical features of the dihydrophenyl compounds 5a-5f were deduced from the correlation between dihedral angle (φ) and coupling constant (J). The hydrogen atoms at C-4a and C-5 were disposed cis to each other having coupling constant J₄a.₅=11Hz and dihedral angle φ~0°. Here, pyran ring C is present in the pseudo chair form and R' group at C-5 occupies pseudo equatorial disposition which is not without precedent because the heavier group always prefers equatorial disposition in cyclohexane.

The mass spectra of the dihydro compounds 5a-5f exhibit the molecular ion (m/z) at the same value as that of the starting compound. It shows that only reorganisation has taken place during the photoreaction. But aromatic compounds 6a-6f produce molecular ion at a value two mass unit less than the starting chromones. Thus, these are formed by the loss of a hydrogen molecule from the starting chromone. The mass spectra of the photoproducts also exhibit the ion at m/z 154/156 which is obtained through the retro-Diels Alder cleavage of the pyrone moiety.

**Scheme 1.** Photolysis of chromones
Mechanistically, these phototransformations could be ascribed to the easy intramolecular H-abstraction from C3-OCH2- groups by the photoexcited carbonyl chromophores through the six membered cyclic transition state that produced 1,4-biradicals 7a-7f. These intermediates underwent further cyclisation followed by [1,7]-H migration to yield dihydrocyclised products 5a-5f while loss of H2 molecule resulted in the oxidised compounds 6a-6f (Scheme 2).

3. Conclusion

This photochemical study represents a general and greener method for the synthesis of some novel vinyl substituted benzopyronopyrane derivatives without using any specific and toxic reagent.

4. Experimental Section

4.1. General

Melting points reported are uncorrected. IR spectra were recorded on a Perkin Elmer spectrometer using KBr pellets and UV-Vis spectra on Elico SL-164 spectrometer. 1H NMR spectra were recorded on a 400 MHz Bruker spectrometer using TMS as internal standard. The mass spectra were recorded on Schimatzu QP-5000. TLC plates were coated with silica gel G suspended in MeOH-CHCl3. Silica gel (100-200 mesh) was used for column chromatography.

4.2. Synthesis of 3-allyloxychromones 4a-4c

4.2.1. 6-Chloro-3-(2-methylprop-1-enyloxy)-2-phenyl-4H-chromen-4-one (4a)

A suspension of 6-chloro-3-hydroxy-2-phenyl-4H-chromen-4-one21-23 1 (2.7 g, 0.01 mol), 3-chloro-2-methylpropene (0.91 g, 0.01 mol), freshly ignited K2CO3 (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 product that was
percolated through a column of silica-gel (60-120 mesh) using petroleum ether-benzene (1:1) as eluent and that was further crystallized from EtOH to afford 4a.

4a: Yield (2.6 g, 81%); off white powder; m.p. 88-89°C; IR (KBr): 1641 cm⁻¹ (C=O); UV-Vis (THF): nm 341, 322, 240; ¹H NMR (CDCl₃): δ 8.22 (1H, d, J₆=2.6Hz, H-5), 8.09 (2H, m, H-2’, 6’), 7.62 (1H, dd, J₆m=2.5, 8.8Hz, H-7), 7.51 (3H, m, H-3’, 4’, 5’), 7.50 (1H, J₆=8.9Hz, H-8), 5.19 (2H, br s, H-α,β), 4.71 (2H, s, H-α,β), 1.92 (3H, s, C₂″-CH₃); MS: m/z 326 (M⁺, 100%), 271 (37.4), 243 (42.3), 215 (25.5), 172 (32.3), 154 (40.0), 110 (28.5). Anal. Calcd. for C₁₉H₁₅O₃Cl: C, 69.84; H, 4.63. Found: C, 69.88; H, 4.59%.

4.2. 6-Chloro-3-(2-methylprop-1-enyloxy)-2-(4-methylphenyl)-4H-chromen-4-one (4b)

The chromone 4b was synthesized by reacting 2²¹-²³ (2.85 g, 0.01 mol) with 3-chloro-2-methylpropene (0.91 g, 0.01 mol) under similar conditions as described for 4a.

4b: Yield (2.65 g, 78%); off white powder; m.p. 95-96°C; IR (KBr): 1635 cm⁻¹ (C=O); UV-Vis (THF): nm 338, 317, 252; ¹H NMR (CDCl₃): δ 8.20 (1H, d, J₆=2.5Hz, H-5), 8.03 (2H, AA’ part of AA’XX’ system, quasi d, J=7.3 Hz, H-2’, 6’), 7.61 (1H, dd, J₆m=2.5, 8.9Hz, H-7), 7.45 (1H, d, J₆=8.8Hz, H-8), 7.30 (2H, XX’ part of AA’XX’ system, quasi d, J=7.3 Hz, H-3’, 5’), 5.21 (1H, br s, H-α), 5.02 (1H, H-β), 4.71 (2H, s, H-α,β), 1.86 (3H, s, C₂″-CH₃), 2.44 (3H, s, Cα’-C₃H₃); MS: m/z 340 (M⁺, 100%), 285 (23.2), 257 (32.7), 229 (35.4), 186 (87.0), 154 (48.2). Anal. Calcd. for C₂₀H₁₇O₃Cl: C, 70.49; H, 5.03. Found: C, 70.46; H, 4.99%.

4.2.3. 6-Chloro-3-(2-methylprop-1-enyloxy)-2-(4-methoxyphenyl)-4H-chromen-4-one (4c)

The chromone 4c was synthesized by reacting 3²¹-²³ (3.0 g, 0.01 mol) with 3-chloro-2-methylpropene (0.91 g, 0.01 mol) under similar conditions as used for 4a.

4c: Yield (2.8 g, 80%); off white powder; m.p. 84-85°C; IR (KBr): 1638 cm⁻¹ (C=O); UV-Vis (THF): nm 342, 326, 255; ¹H NMR (CDCl₃): δ 8.19 (1H, d, J₆=2.4Hz, H-5), 8.12 (2H, AA’ part of AA’XX’ system, quasi d, J=8.9Hz, H-2’, 6’), 7.60 (1H, dd, J₆m=2.4, 9.0Hz, H-7), 7.53 (1H, d, J₆=9.0Hz, H-8), 7.05 (2H, XX’ part of AA’XX’ system, quasi d, J=7.5Hz, H-3’, 5’), 5.23 (2H, br s, H-α,β), 4.78 (2H, s, H-α,β), 3.93 (3H, s, C₄″-OC₂H₃); MS: m/z 356 (M⁺, 100%), 301 (27.0), 273 (36.7), 245 (28.2), 202 (22.5), 154 (51.0), 110 (53.3). Anal. Calcd. for C₂₀H₁₇O₄Cl: C, 67.32; H 4.80. Found: C, 67.35; H, 4.36%.

4.3. Photolysis of 3-allyloxychromones 4a-4c

4.3.1. Photolysis of 6-Chloro-3-(2-methylprop-1-enyloxy)-2-phenyl-4H-chromen-4-one (4a)

A deoxygenated solution of 4a (200 mg, 0.61 mmol) in dry benzene (200 mL) was photolysed with light from a 125 W mercury arc lamp in a pyrex reactor under nitrogen atmosphere for 45 minutes. The progress of reaction was monitored by TLC. The solvent was distilled out under reduced pressure to obtain a dark gummy viscous mass, which was chromatographed over a column of silica gel (100-200 mesh) packed in petroleum ether-benzene (2:3). Elution of column with benzene-EtOAc (3:1) gave starting compound 4a (20%, co-TLC & m.m.p.), and two new compounds 5a and 6a.

5a: Yield (36 mg; 18%); light yellow powder; m.p. 163-164°C; IR (KBr): 1654 cm⁻¹ (C=O); UV-Vis (THF): nm 335, 285, 255; ¹H NMR (CDCl₃): δ 8.22 (1H, d, J₆=2.5Hz, H-8), 7.56 (1H, dd, J₆m=2.5, 8.9Hz, H-10), 7.50 (1H, d, J₆=8.9Hz, H-11), 6.85 (1H, br s, H-1), 5.81 (1H, dd, J₆=2.1Hz, J₆m=10.1Hz, H-3), 5.71 (1H, d, J₆=10.0Hz, H-4), 5.10 (2H, d, J₆=1.4Hz, H-α,β), 4.52 (1H, d,
Photolysis of 6-Chloro-3-(2-methylprop-1-enyloxy)-2-(4-methoxyphenyl)-4H-chromen-4-one (4b)

The benzene solution of 4b (200 mg, 0.58 mmol) was photolysed under similar conditions as described for 4a. The photolysate on chromatographic separation afforded two new compounds 5b and 6b.

5b: Yield (30 mg 15%); light yellow powder; m.p. 168-170°C; IR (KBr): 1656 cm\(^{-1}\) (C=O); UV-Vis (THF): \(\lambda\) 341, 290, 252; \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.23 (1H, d, J\(_{ax,5}\)=2.5Hz, H-8), 7.65 (1H, dd, J\(_{m,o}\)=2.5, 8.9Hz, H-10), 7.51 (1H, d, J\(_{o}=8.9Hz\), H-11), 6.80 (1H, br s, H-1), 5.50 (1H, br s, H-4), 5.45 (1H, d, J\(_{5,4a}=11.0Hz\), H-5), 5.11 (2H, d, J\(_{allyl}=1.4Hz\), H-\(\alpha,\beta\)), 3.50 (1H, d, J\(_{4a,5}=11.2Hz\), H-4a), 2.15 (3H, s, C\(_3\)-CH\(_3\)), 2.90 (2H, m, H-2a) 1.94 (3H, s, C\(_1\)-CH\(_3\)); MS: \(m/z\) 340 (M\(^+\), 75%), 285 (37.5), 257 (22.0), 229 (23.2), 186 (100), 154 (41.1), 126 (66.3), 110 (25.2). Anal. Calcd. for C\(_{20}\)H\(_{16}\)O\(_2\): C, 70.49; H, 4.93.

Found: C, 70.46; H, 4.99%.

6b: Yield (65 mg 33%); light yellow powder; m.p. 208-210°C; IR (KBr): 1637 cm\(^{-1}\) (C=O); UV-Vis (THF): \(\lambda\) 338, 274, 245; \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.18 (1H, d, J\(_{ax,5}\)=2.4Hz, H-8), 7.76 (1H, d, J\(_{o}=8.0Hz\), H-1), 7.60 (1H, dd, J\(_{m,o}=2.6.8Hz\), H-10), 7.55 (1H, d, J\(_{o}=9.0Hz\), H-11), 6.98 (2H, m, H-2,4), 5.20 (2H, d, J\(_{allyl}=1.2Hz\), H-\(\alpha,\beta\)), 5.00 (1H, s, H-5), 2.25 (3H, s, C\(_3\)-CH\(_3\)), 1.89 (3H, s, C\(_1\)-CH\(_3\)); MS: \(m/z\) 338 (M\(^+\), 90%), 184 (54.0), 154 (34.6), 144 (19.3), 126 (29.7), 110 (100). Anal. Calcd. for C\(_{20}\)H\(_{14}\)O\(_2\): C, 70.90; H, 4.46. Found: C, 70.92; H, 4.43%.

4.3.3. Photolysis of 6-Chloro-3-(2-methylprop-1-enyloxy)-2-(4-methoxyphenyl)-4H-chromen-4-one (4c)

The benzene solution of 4c (200 mg, 0.00056 mol) was photolysed under similar conditions as described for 4a. The chromatographic work up of photolysate provided the two new compounds 5c and 6c.

5c: Yield (28 mg 14%); light yellow powder; m.p. 160-162°C; IR (KBr): 1657 cm\(^{-1}\) (C=O); UV-Vis (THF): \(\lambda\) 331, 281, 251; \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.20 (1H, d, J\(_{ax,5}\)=2.6Hz, H-8), 7.55 (1H, dd, J\(_{m,o}=2.4.8.9Hz\), H-10), 7.45 (1H, d, J\(_{o}=9.0Hz\), H-11), 6.71 (1H, br s, H-1), 5.25 (1H, br s, H-4), 5.15 (2H, d, J\(_{allyl}=1.4Hz\), H-\(\alpha,\beta\)), 4.50 (1H, d, J\(_{\gamma,\delta}=10.6Hz\), H-5), 4.00 (1H, d, J\(_{\gamma,\delta}=11.0Hz\), H-4a), 3.80 (3H, s, C\(_3\)-OCH\(_3\)), 2.75 (2H, m, H-2a) 1.80 (3H, s, C\(_1\)-CH\(_3\)); MS: \(m/z\) 356 (M\(^+\), 70%), 301 (33.1), 273 (34.5), 245 (22.0), 202 (100), 154 (27.1), 126 (18.9), 110 (47.9). Anal. Calcd. for C\(_{20}\)H\(_{17}\)O\(_4\): C, 67.32; H 4.80. Found: C, 67.35; H, 4.36%.
6c: Yield (62 mg 31%); light yellow powder; m.p. 200-202 °C; IR (KBr): 1643 cm⁻¹ (C=O); UV-Vis (THF): nm 341, 276, 249; ¹H NMR (CDCl₃): δ 8.24 (1H, d, J₈=2.4Hz, H-8), 7.80 (1H, d, J₈=8.6Hz, H-1), 7.57 (1H, dd, J₈=m=2.5, 8.9Hz, H-10), 7.40 (1H, d, J₈=8.9Hz, H-11), 6.98 (1H, dd, J₈=m=2.4, 8.6Hz, H-2), 6.72 (1H, d, J₈=m=2.3Hz, H-4), 5.12 (2H, d, J₈=1.2Hz, H-α,β), 4.95 (1H, s, H-5). 3.87 (3H, s, C₃-OC₃H₃), 1.88 (3H, s, C₁'-CH₃); MS: m/z 354 (M⁺, 65%), 200 (26.1), 160 (36.7), 126 (39.4), 110 (100). Anal. Calcd. for C₂₀H₁₅O₄Cl: C, 67.71; H, 4.26. Found: C, 67.68; H, 4.30%.

4.4. Synthesis of 3-allyloxychromones 4d-4f

4.4.1. 6-Chloro-3-(3-methylbut-2-enyloxy)-2-phenyl-4H-chromen-4-one (4d)

The chromone 4d was synthesized by reacting 1⁻²¹⁻²³ (2.7 g, 0.01 mol) with 1-chloro-3-methyl-2-butene (1.1 g, 0.01 mol) under similar conditions as applied for 4a.

4d: Yield (2.6 g, 77%); off white powder; m.p. 95-96 °C; IR (KBr): 1644 cm⁻¹ (C=O); UV-Vis (THF): nm 345, 325, 251; ¹H NMR (CDCl₃): δ 8.18 (1H, d, J₈=m=2.6Hz, H-5), 8.10 (2H, m, H-2', 6'), 7.62 (1H, dd, J₈,m,o=2.4, 8.9Hz, H-7), 7.53 (3H, m, H-3',4',5'), 7.51 (1H, d, J₈,o=9.0Hz, H-8), 5.61 (1H, bt, J=7.0 Hz, H-2''), 4.85 (2H, d, J₈=6.9Hz, H-1''), 1.78 (6H, br s, C₃''-(CH₃)₂); MS: m/z 340 (M⁺, 95%), 271 (26.4), 248 (33.7), 215 (33.7), 186 (21.2), 154 (36.1), 110 (100). Anal. Calcd. for C₂₀H₁₇O₃Cl: C, 70.49; H, 5.03. Found: C, 70.51; H, 5.01%.

4.4.2. 6-Chloro-3-(3-methylbut-2-enyloxy)-2-(4-methylphenyl)-4H-chromen-4-one (4e)

The chromone 4e was synthesized by reacting 2⁻²¹⁻²³ (2.85 g, 0.01 mol) with 1-chloro-3-methyl-2-butene (1.1 g, 0.01 mol) under similar conditions as used for 4a.

4e: Yield (2.9 g, 82%); off white powder; m.p. 101-102°C; IR (KBr): 1639 cm⁻¹ (C=O); UV-Vis (THF): nm 332, 315, 254; ¹H NMR (CDCl₃): δ 8.20 (1H, d, J₈=m=2.4Hz, H-5), 8.00 (2H, AA' part of AA'XX' system, quasi d, J=8.8 Hz, H-2',6'), 7.61 (1H, dd, J₈,m,o=2.6, 8.9Hz, H-7), 7.50 (1H, d, J₈,o=9.0Hz, H-8), 7.33 (2H, AA' part of AA'XX' system, quasi d, J=8.8 Hz, J₈,o=8.5Hz, H-3',5'), 5.61 (1H, bt, J=7.0 Hz, H-2''), 4.85 (2H, d, J₈=6.9Hz, H-1'''), 1.82 (6H, br s, C₃''-(CH₃)₂), 2.39 (3H, s, C₅-C₃H₃); MS: m/z 354 (M⁺, 95%), 285 (43.0), 257 (47.3), 229 (23.1), 200 (22.9), 154 (45.5), 110 (33.3). Anal. Calcd. for C₂₁H₁₉O₃Cl: C, 71.08; H, 5.40. Found: C, 71.12; H, 5.43%.

4.4.3. 6-Chloro-3-(3-methylbut-2-enyloxy)-2-(4-methoxyphenyl)-4H-chromen-4-one (4f)

The chromone 4f was synthesized by reacting 3⁻²¹⁻²³ (3.0 g, 0.01 mol) with 1-chloro-3-methyl-2-buten-1 (1.1 g, 0.01 mol) under similar conditions as used for 4a.

4f: Yield (2.9 g, 80%); off white powder; m.p. 92-93°C; IR (KBr): 1638 cm⁻¹ (C=O); UV-Vis (THF): nm 342, 322, 252; ¹H NMR (CDCl₃): δ 8.21 (1H, d, J₈=m=2.6Hz, H-5), 8.16 (2H, dd, J₈,o=1.2,9.0Hz, H-2', 6'), 7.63 (1H, dd, J₈,m,o=2.4,8.7Hz, H-7), 7.51 (1H, d, J₈,o=9.0Hz, H-8), 7.03 (2H, dd, J₈,m,o=2.6,8.8Hz, H-3', 5'), 5.66 (1H, dd, J₈=1.1,7.0Hz, H-2''), 4.81 (2H, d, J₈=6.8Hz, H-1''), 1.81 (6H, br s, C₃''-(CH₃)₂), 3.90 (3H, s, C₄-OC₃H₃); MS: m/z 370 (M⁺, 100%), 301 (41.0), 273 (26.3), 245 (33.2), 216 (55.0), 154 (25.7), 110 (64.1). Anal. Calcd. for C₂₁H₁₅O₄Cl: C, 68.02; H 5.16. Found: C, 67.99; H, 5.19%.
4.5. Photolysis of 3-allyloxychromones 4d-4f

4.5.1 Photolysis of 6-Chloro-3-(3”-methylbut-2”-enyloxy)-2-phenyl-4H-chromen-4-one (4d)

The benzene solution of 4d (200 mg, 0.58 mmol) was photolysed under similar conditions as described for 4a. The chromatographic separation of photolyse yielded two new compounds 5d and 6d.

5d: Yield (34 mg; 17%); light yellow powder; m.p. 171-172°C; IR (KBr): 1652 cm\(^{-1}\) (C=O); UV-Vis (THF): nm 332, 298, 261; \(^1^H\) NMR (CDCl\(_3\)): \(\delta\) 8.20 (1H, d, \(J_m=2.5\) Hz, H-8), 7.62 (1H, dd, \(J_m,o=2.6,9.0\)Hz, H-1), 7.50 (1H, d, \(J_o=8.9\) Hz, H-11), 6.85 (1H, br s, H-1), 5.35 (1H, d, \(J_{1',5}=6.5\) Hz, H-1’), 5.85 (1H, dd, \(J_{3,2a}=2.0\) Hz, \(J_{3,4}=10.0\) Hz, H-3), 5.70 (1H, d, \(J_{4,3}=10.0\) Hz, H-4), 4.50 (1H, d, \(J_{5,4a}=11.0\) Hz, H-5), 3.60 (1H, d, \(J_{4a,5}=11.0\) Hz, H-4a), 2.80 (2H, m, H-2a) , 1.81 (6H, s, C\(_{2'}-(CH_3)_2\) ); MS: \(m/z\) 340 (M\(^+\), 64%), 271 (32.0), 243 (21.5), 186 (36.7), 154 (9.8), 126 (47.8), 110 (100). Anal. Calcd. for C\(_{20}\)H\(_{17}\)O\(_3\)Cl: C, 70.49; H, 5.03. Found: C, 70.51; H, 5.01%.

6d: Yield (70 mg; 35%); light yellow solid; m.p. 214-215°C; IR (KBr): 1643 cm\(^{-1}\) (C=O); UV-Vis (THF): nm 342, 292, 240; \(^1^H\) NMR (CDCl\(_3\)): \(\delta\) 8.28 (1H, d, \(J_m=2.6\) Hz, H-8), 8.04 (1H, d, \(J_{m,o}=8.9\) Hz, H-11), 7.57 (1H, d, \(J_o=8.9\) Hz, H-11), 7.52-7.55 (3H, m, H-2, 3, 4), 6.15 (1H, d, \(J_{1',5}=6.8\) Hz, H-1’), 4.85 (1H, d, \(J_{4,3}=6.5\) Hz, H-5), 1.85 (6H, s, C\(_2'-(CH_3)_2\) ); MS: \(m/z\) 338 (M\(^+\), 70%), 184 (100), 154 (28.7), 126 (24.4), 110 (90). Anal. Calcd. for C\(_{20}\)H\(_{15}\)O\(_3\)Cl requires C, 70.90; H, 4.46. Found: C, 70.94; H, 4.50%.

4.5.2. Photolysis of 6-Chloro-3-(3”-methylbut-2”-enyloxy)-2-(4-methylphenyl)-4H-chromen-4-one (4e)

The benzene solution of 4e (200 mg, 0.00056 mol) was photolysed under similar conditions as described for 4a. The photolysate on chromatographic separation afforded two new compounds 5e and 6e.

5e: Yield (32 mg; 16%); light yellow powder; m.p. 175-176°C; IR (KBr): 1650 cm\(^{-1}\) (C=O); UV-Vis (THF): nm 330, 285, 250; \(^1^H\) NMR (CDCl\(_3\)): \(\delta\) 8.19 (1H, d, \(J_m=2.5\) Hz, H-8), 8.04 (1H, d, \(J_m,o=2.3,\) 8.6Hz, H-1), 7.62 (1H, dd, \(J_m=2.4\) Hz, \(J_m,o=2.6,8.9\) Hz, H-10), 7.51 (1H, d, \(J_o=8.9\) Hz, H-11), 6.80 (1H, br s, H-1), 5.50 (1H, br s, H-4), 5.45 (1H, d, \(J_{1',5}=6.9\) Hz, H-1’), 5.25 (1H, d, \(J_{5,4a}=11.3\) Hz, H-5), 5.15 (1H, d, \(J_{4,3}=6.9\) Hz, H-1”), 3.50 (1H, d, \(J_{4a,5}=11.3\) Hz, H-4a), 2.30 (3H, s, C\(_3-C\)H\(_3\)), 2.90 (2H, m, H-2a) , 1.73 (6H, s, C\(_2'-(CH_3)_2\) ); MS: \(m/z\) 354 (M\(^+\), 90%), 285 (33.2), 257 (37.7), 200 (29.3), 200 (67.4), 154 (53.7), 126 (31.2), 110 (100). Anal. Calcd. for C\(_{21}\)H\(_{19}\)O\(_3\)Cl: C, 71.08; H, 5.40. Found: C, 71.12; H, 5.43%.

6e: Yield (68 mg; 34%); light yellow powder; m.p. 220-221°C; IR (KBr): 1643 cm\(^{-1}\) (C=O); UV-Vis (THF): nm 341, 280, 238; \(^1^H\) NMR (CDCl\(_3\)): \(\delta\) 8.26 (1H, d, \(J_m=2.6\) Hz, H-8), 7.76 (1H, d, \(J_o=3.0\) Hz, H-1), 7.64 (1H, dd, \(J_m,o=2.5,\) 8.9Hz, H-10), 7.52 (1H, d, \(J_o=9.0\) Hz, H-11), 6.98 (2H, m, H-2, 4), 6.15 (1H, d, \(J_{1',5}=7.0\) Hz, H-1’), 5.15 (1H, d, \(J_{5,1}=6.2\) Hz, H-5), 2.25 (3H, s, C\(_3-C\)H\(_3\)), 1.84 (6H, s, C\(_2'-(CH_3)_2\) ); MS: \(m/z\) 352 (M\(^-\), 100%), 198 (21.1), 154 (57.7), 126 (75.3), 110 (31.7). Anal. Calcd. for C\(_{21}\)H\(_{17}\)O\(_3\)Cl: C, 71.49; H, 4.86. Found: C, 71.53; H, 4.90%.
4.5.3. Photolysis of 6-Chloro-3-(3’”-methylbut-2”-enyloxy)-2-(4-methoxyphenyl)-4H-
chromen-4-one (4f)

The benzene solution of 4f (200 mg, 0.00054 mol) was photolysed under similar conditions as
described for 4a. The chromatographic work up of photolysate provided the two new compounds 5f
and 6f.

5f: Yield (36 mg; 18%); light yellow powder; m.p. 178-180°C; IR (KBr): 1655 cm⁻¹ (C=O); UV-Vis
(THF): nm 335, 285, 253; ¹H NMR (CDCl₃): δ 8.18 (1H, d, Jₘₙ=2.5Hz, H-8), 7.55 (1H, dd, Jₘₙ=8.9Hz,
H-10), 7.45 (1H, d, Jₘₙ=8.9Hz, H-11), 6.71 (1H, br s, H-1), 5.29 (1H, d, J₁’,₅=6.9Hz, H’₁), 5.25
(1H, br s, H-4), 4.50 (1H, d, J₅₄ₐ’=10.9Hz, H-5), 4.10 (1H, d, J₄α₅ₐ’=11.2Hz, H-4a), 3.80 (3H, s, C₃-OC₃H₃),
2.36 (2H, s, H-2a), 1.77 (6H, s, C₂’-(CH₃)₂); MS: m/z 370 (M⁺, 100%), 301 (44.2), 273 (22.1),
245 (35.3), 216 (56.4), 154 (29.1), 110 (76.3). Anal. Calcd. for C₂₁H₁₉O₄Cl: C, 68.02; H, 5.16. Found: C, 67.99;
H, 5.19%.

6f: Yield (74 mg; 37%); light yellow powder; m.p. 224-225°C; IR (KBr): 1642 cm⁻¹ (C=O); UV-Vis
(THF): nm 345, 273, 245; ¹H NMR (CDCl₃): δ 8.19 (1H, d, Jₘₙ=2.4Hz, H-8), 7.80 (1H, d, Jₙₒ=8.6Hz,
H-1), 7.57 (1H, dd, Jₘₙ=2.4,8.8Hz, H-10), 7.40 (1H, d, Jₙₒ=8.9Hz, H-11), 6.98 (1H, dd, Jₘₙ=2.4,
8.6Hz, H-2), 6.72 (1H, d, Jₙₒ=2.3Hz, H-4), 6.15 (1H, d, J₅ₑ=7.0Hz, H’₁), 5.20 (1H, d, J₅ₙ=6.8Hz, H-5),
3.87 (3H, s, C₃-OC₃H₃), 1.83 (6H, s, C₂’-(CH₃)₂); MS: m/z 368 (M⁺, 85%), 214 (33.7), 160 (45.2),
154 (24.0), 126 (28.7), 110 (100). Anal. Calcd. for C₂₁H₁₇O₄Cl: C, 68.39; H, 4.65. Found: C, 68.39; H,
4.62%.

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