

## A convenient one pot synthesis of substituted and unsubstituted 2, 4-diaryl-5-oxo-5,6,7,8-tetrahydro-2-chromens

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Anhydrous zinc chloride catalysed reactions of arylideneacetophenones **2a-c** give 2, 4-diaryl-5-oxo-5, 6, 7, 8-tetrahydro-2-chromens **4a-c** with 1, 3-cyclohexanedione. Under similar conditions arylideneacetophenones **2a-b** and **2d-f** react with 5, 5-dimethyl-1, 3-cyclohexanedione (dimedone) yielding 7, 7-dimethyl-2, 4-diaryl-5-oxo-5, 6, 7, 8-tetrahydro-2-chromens **4d-h**.

In continuation to our previous work<sup>1</sup> on the synthesis of 7, 7-dimethyl-2, 4-diphenyl-5-oxo-5, 6, 7, 8-tetrahydro-2-chromen **4i**, we now report the synthesis of five more 2, 4-diaryl-7, 7-dimethyl-5-oxo-5, 6, 7, 8-tetrahydro-2-chromens **4d-h** and three 2, 4-diaryl-5-oxo-5, 6, 7, 8-tetrahydro-2-chromens **4a-c** without methyl substituents in the 7-position. Of these eight compounds six seem to be new and the remaining two **4d-e** have been prepared using glacial acetic acid in presence of phosphorous pentoxide by Ahluwalia *et al*<sup>2</sup>.

The formation of compounds **4a-h** may be explained by the initial formation of a 1:1 adduct **3**<sup>3</sup> which presumably underwent cyclisation (**Scheme 1**).

This mechanistic pathway is supported by the fact that a 1:1 adduct **3**<sup>3</sup> which we had previously isolated from a base catalysed reaction was subsequently converted to the chromen structure **4i**<sup>1</sup>. A similar two step synthesis of such compounds was also reported by Ahluwalia *et al*<sup>2</sup>.

The condensation of **1** (R=H) with 1-(4-chlorophenyl)-3-phenyl-2-propene-1-one **2a** in toluene and *n*-heptane in presence of anhyd. zinc chloride at refluxing temperature gave a white crystalline solid. In its mass spectrum, a peak was observed at *m/z* 336 (*M*<sup>+</sup>). The <sup>1</sup>H NMR spectrum of this compound **4a** showed besides usual signals, two doublets at δ 4.51 (d, *J*=4.87 Hz, 1H, H-4) and 5.69 (d, *J*=4.87 Hz, 1H, H-3) and <sup>13</sup>C NMR showed signals at δ 197.20 (C-5), 166.03 (C-2), 145.91 (C-9), 144.99 (C-10), 113.78 (C-3), 37.07 (C-4), 35.26 (C-6), 27.72 (C-8), 20.41 (C-7), on the basis of which it was assigned the structure 2-(4-chloro)phenyl-4-phenyl-5-oxo-5, 6, 7, 8-tetrahydro-2-chromen **4a**. Similarly **1** (R=CH<sub>3</sub>) on

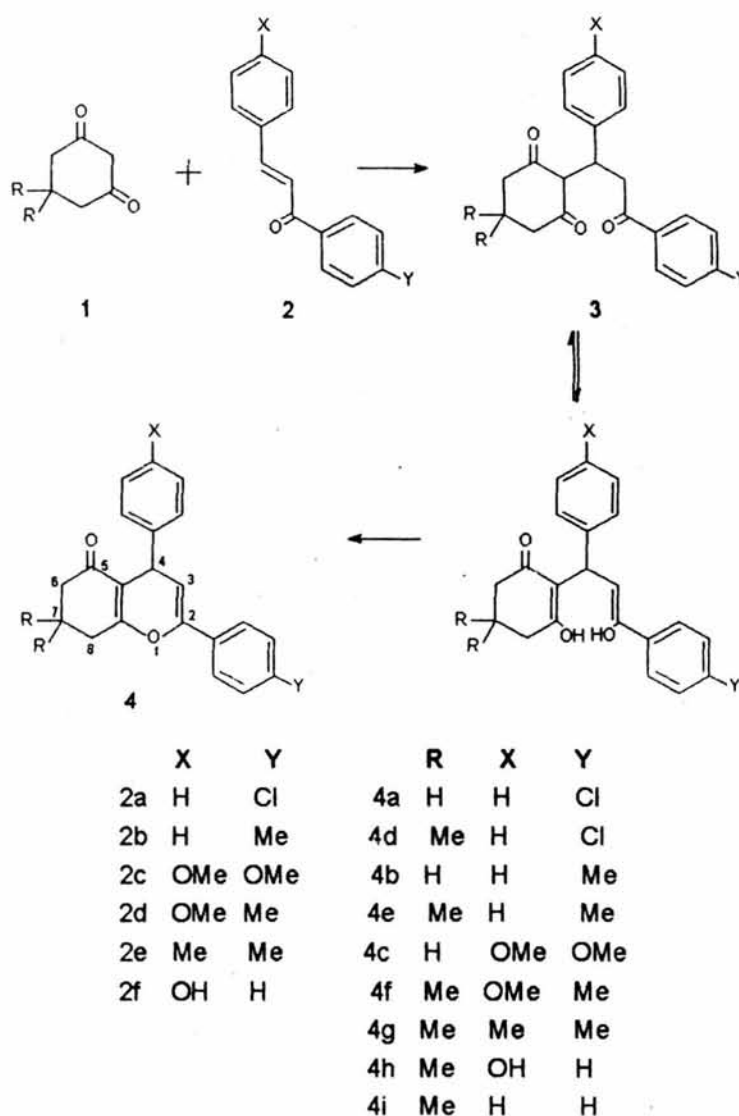
condensation with other arylideneacetophenones (**2a-b**, **2d-f**) afforded the tetrahydro-2-chromen (**4d-h**, **Scheme I**). The structures of all these compounds were assigned on the basis of their spectral data and elemental analysis.

### Experimental Section

Melting points are uncorrected. IR spectra were recorded as KBr pellet using SHIMADZU IR-470 infrared spectrophotometer in the range of 4000-400cm<sup>-1</sup>, <sup>1</sup>H-NMR spectra in CDCl<sub>3</sub> on a JEOL JNM LA400 at 500MHz using TMS as internal standard (chemical shifts in δ, ppm), <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> at 125.65 MHz and mass spectra in the JEOL JMS-HX 110A spectrophotometer. All the compounds gave satisfactory C and H analyses.

1-(4-chlorophenyl)-3-phenyl-2-propene-1-one<sup>4,5</sup> **2a**, 1-(4-methylphenyl)-3-phenyl-2-propene-1-one<sup>6</sup> **2b**, 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propene-1-one<sup>7</sup> **2d**, 1, 3-bis-(4-methylphenyl)-2-propene-1-one<sup>8,9</sup> **2e** and 1-phenyl-3-(4-hydroxy phenyl)-2-propene-1-one<sup>10</sup> **2f** were prepared following literature method. The reactions described in the present paper were carried out following a general procedure.

**General procedure.** To a solution of **1** (R=H/CH<sub>3</sub>) (0.015 to 0.025 mole) and arylideneacetophenone **2a-f** (0.015 to 0.025 mole) in anhyd. zinc chloride (0.30 to 0.50g) was added toluene/benzene (25 mL) and *n*-heptane (25 to 50mL) and the reaction mixture was refluxed for 30 hr under Dean-Stark attachment. The reaction mixture was cooled, neutralized by 5% aq. NaHCO<sub>3</sub> solution, and extracted with ether (4×25mL). The ether extract was washed with water until the washings were neutral to pH = 7.0 which was then



Scheme I

dried over anhyd.  $\text{Na}_2\text{SO}_4$  and evaporated in *vacuo*. A solid mass obtained was recrystallised. The compounds (**4a-b**, **4e-g**) were recrystallised from mixed solvents, chloroform and pet ether (40-60°) and compounds (**4c-d** and **4h**) from neat ethanol. The solvents used in TLC for the compound **4a** is neat chloroform; chloroform and pet ether (40-60°) in the ratio 9:1 for the compounds **4b** and **4c**; chloroform and pet ether (40-60°) in the ratio 5:1 for the compounds **4f** and **4g**; chloroform and pet ether (40-60°) in the ratio 2:3 for the compound **4d**; ethyl acetate and pet ether (60-80°) in the ratio 1:1 for the compound **4c** and ethyl acetate and chloroform in the ratio 1:3 for the compound **4h**.

**2 - (4 - chloro) phenyl - 4 - phenyl - 5 - oxo - 5, 6, 7, 8 - tetrahydro-2-chromen 4a.** Yield 44%; m. p.

153 - 54°C;  $R_f$  0.57; IR : 1655 (C=O in conjugation), 1640 (C=C), 1610, 1595 (phenyl);  $^1\text{H}$  NMR:  $\delta$  2.04 (s, 2H, H-7), 2.39 (s, 2H, H-6), 2.69 (s, 2H, H-8), 4.51 (d,  $J=4.87\text{Hz}$ , 1H, H-4), 5.69 (d,  $J=4.87\text{Hz}$ , 1H, H-3), 7.3-7.5 (m, 9H, aromatic protons);  $^{13}\text{C}$  NMR:  $\delta$  197.20 (C-5), 166.03 (C-2), 144-99 (C-10), [134.47, 131.43, 128.62, 128.44, 128.14, 126.64, 125.75 (aromatic carbons)], 113.78 (C-3), 37.07 (C-4), 35.26 (C-6), 27.72 (C-8), 20.41 (C-7); MS:  $m/z$  336 ( $\text{M}^+$ ). Anal. Found : C, 74.73; H, 5.11. Calcd for  $\text{C}_{21}\text{H}_{17}\text{O}_2\text{Cl}$ : C, 75.0; H, 5.05%. 2, 4 - Dinitrophenylhydrazone derivative had m.p. 168-70°C.

**2 - (4 - methyl) phenyl - 4 - phenyl - 5 - oxo - 5, 6, 7, 8 - tetrahydro-2-chromen 4b.** Yield 47%; m. p. 131-32°C;  $R_f$  0.50; IR : 1642 (C=O in conjugation),

1620 (C=C), 1540 (phenyl);  $^1\text{H NMR}$  :  $\delta$  1.54 (s, 3H,  $-\text{C}_6\text{H}_4\text{-CH}_3$ ), 2.17 (s, 2H, H-7), 2.38 (s, 2H, H-6), 2.67 (s, 2H, H-8), 4.51 (d,  $J = 5.12\text{Hz}$ , 1H, H-4), 5.65 (d,  $J = 5.12\text{Hz}$ , 1H, H-3), 7.27 - 7.50 (m, 9H, aromatic protons);  $^{13}\text{C NMR}$ :  $\delta$  197.35 (C-5), 166.30 (C-2), 146.94 (C-9), 145.39 (C-10), [138.74, 130.20, 129.12, 128.52, 128.21, 126.50, 124.41 (aromatic carbons)], 113.88 (C-3), 37.12 (C-4), 35.24 (C-6), 27.79 (C-8), 21.24 ( $-\text{C}_6\text{H}_4\text{-CH}_3$ ), 20.45 (C-7); MS:  $m/z$  316 ( $\text{M}^+$ ). Anal. Found : C, 82.07; H, 6.32. Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_2$ : C, 83.0; H, 6.32%.

**2, 4 - bis - (4 - methoxyphenyl) - 5 - oxo - 5, 6, 7, 8 - tetrahydro-2-chromen 4c.** Yield 52%; m. p. 80-81°C;  $R_f$  0.76; IR: 1650 (C=O in conjugation), 1600 (C=C), 1510 (phenyl);  $^1\text{H NMR}$  :  $\delta$  2.10 (s, 3H,  $\text{OCH}_3$ ), 4.44 (d,  $J = 5.12\text{ Hz}$ , 1H, H-4), 5.55 (d,  $J = 5.12\text{ Hz}$ , 1H, H-3), 7.25 - 7.78 (m, 8H, aromatic protons);  $^{13}\text{C NMR}$ :  $\delta$  197.40 (C-5), 165.99 (C-2), 146.56 (C-9), 143.75 (C-10), [137.79, 131.36, 130.04, 129.15, 127.81, 125.67 (aromatic carbons)], 113.76 (C-3), 55.35 ( $\text{OCH}_3$ ), 55.28 ( $\text{OCH}_3$ ), 37.08 (C-4), 34.29 (C-6), 27.72 (C-8), 20.41 (C-7); MS:  $m/z$  362 ( $\text{M}^+$ ). Anal. Found : C, 75.82; H, 6.13. Calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_4$ : C, 75.80; H, 6.64%.

**7,7 - Dimethyl - 2 - (4 - chlorophenyl) - 4-phenyl - 5 - oxo - 5, 6, 7, 8 tetrahydro-2-chromen 4d:** Yield 56%; m.p. 175-76°C;  $R_f$  0.40; IR: 1645 (C=O in conjugation), 1614 (C=C), 1547 (phenyl);  $^1\text{H NMR}$  :  $\delta$  1.06 (s, 3H,  $\text{CH}_3$ ), 1.13 (s, 3H,  $\text{CH}_3$ ), 2.24 (s, 2H, H-6), 2.54 (s, 2H, H-8), 4.48 (d,  $J = 5.12\text{Hz}$ , 1H, H-4), 5.69 (d,  $J = 5.12\text{Hz}$ , 1H, H-3), 7.29 - 7.52 (m, 9H, aromatic protons);  $^{13}\text{C NMR}$ :  $\delta$  197.05 (C-5), 164.31 (C-2), 145.83 (C-9), 144.96 (C-10), [134.56, 131.43, 128.60, 128.09, 126.63, 125.72 (aromatic carbons)], 112.48 (C-3), 50.87 (C-6), 41.41 (C-8), 35.37 (C-4), 32.11 (C-7), 29.12 (C-7  $\text{CH}_3$ ), 27.65 (C-7  $\text{CH}_3$ ); MS:  $m/z$  363 ( $\text{M}^+$ ). Anal. Found: C, 74.26; H, 5.67. Calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_2\text{Cl}$ : C, 75.92; H, 5.50%. 2, 4 - Dinitrophenylhydrazone derivative had m.p. 159-60°C.

**7, 7 - Dimethyl - 2 - (4-methylphenyl)-4-phenyl - 5 -oxo - 5, 6, 7, 8 - tetrahydro-2-chromen 4e.** Yield 58%; m. p. 162-63°C;  $R_f$  0.51; IR: 1640 (C=O in conjugation), 1610 (C=C), 1500 (phenyl);  $^1\text{H NMR}$  :  $\delta$  1.05 (s, 3H,  $\text{CH}_3$ ), 1.12 (s, 3H,  $\text{CH}_3$ ), 2.22 (s, 2H, H-6), 2.35 (s, 3H,  $-\text{C}_6\text{H}_4 - \text{CH}_3$ ), 2.54 (s, 2H, H-8), 4.48 (d,  $J = 4.87\text{Hz}$ , 1H, H-4), 5.64 (d,  $J = 4.87\text{ Hz}$ , 1H, H-3), 7.3 - 7.48 (m, 9H, aromatic protons) ;  $^{13}\text{C NMR}$  :  $\delta$  197.17 (C-5), 164.55 (C-2), 146.83 (C-9), 145.35 (C-10), [138.69, 130.20, 129.08, 128.35, 126.46, 124.37 (aromatic carbons)], 112.56 (C-3), 50.92 (C-6), 41.48

(C-8), 35.35 (C-4), 32.10 (C-7), 29.13 (C-7  $\text{CH}_3$ ), 27.65 (C-7  $\text{CH}_3$ ), 21.22 ( $-\text{C}_6\text{H}_4 - \text{CH}_3$ ); MS:  $m/z$  358 ( $\text{M}^+$ ). Anal. Found C, 83.02; H, 6.95. Calcd. for  $\text{C}_{24}\text{H}_{24}\text{O}_2$ : C, 83.70; H, 6.98%. 2, 4 - Dinitrophenylhydrazone derivative had m. p. 165-68°C.

**7, 7 - Dimethyl - 5 - oxo - 2 (4 - methylphenyl) - 4- (4 - methoxyphenyl) - 5, 6, 7, 8 - tetrahydro-2-chromen 4f.** Yield 51%; m. p. 132-33°C;  $R_f$  0.52; IR: 1641 (C=O in conjugation), 1618 (C=C), 1500 (phenyl);  $^1\text{H NMR}$  :  $\delta$  1.04 (s, 3H,  $\text{CH}_3$ ), 1.12 (s, 3H,  $\text{CH}_3$ ), 2.22 (s, 2H, H-6), 2.35 (s, 3H,  $-\text{C}_6\text{H}_4\text{-CH}_3$ ), 2.53 (s, 2H, H-8), 3.75 (s, 3H,  $\text{OCH}_3$ ), 4.43 (d,  $J = 4.87\text{ Hz}$ , 1H, H-4), 5.63 (d,  $J = 4.87\text{ Hz}$ , 1H, H-3), 7.24 - 7.48 (m, 8H, aromatic protons);  $^{13}\text{C NMR}$ :  $\delta$  197.28 (C-5), 164.31 (C-2), 158.17 (C-9), 146.73 (C-10), [138.64, 137.68, 130.25, 129.16, 124.34 (aromatic carbons)], 112.79 (C-3), 55.18 ( $\text{OCH}_3$ ), 50.95 (C-6), 41.46 (C-8), 34.43 (C-4), 32.10 (C-7), 29.13 (C-7  $\text{CH}_3$ ), 27.64 (C-7  $\text{CH}_3$ ), 21.22 ( $-\text{C}_6\text{H}_4\text{-CH}_3$ ), MS:  $m/z$  346 ( $\text{M}^+$ ). Anal. Found : C, 79.56; H, 6.93. Calcd. for  $\text{C}_{25}\text{H}_{26}\text{O}_3$ : C, 80.21; H, 6.95%.

**7, 7 - Dimethyl - 2, 4 bis (4 - methylphenyl) - 5 - oxo - 5, 6, 7, 8- tetrahydro-2-chromen 4g.** Yield 54%; m. p. 144.46°C;  $R_f$  0.51; IR: 1642 (C=O in conjugation), 1620 (C=C), 1500 (phenyl);  $^1\text{H NMR}$  :  $\delta$  1.05 (s, 3H,  $\text{CH}_3$ ), 1.12 (s, 3H,  $\text{CH}_3$ ), 2.22 (s, 2H, H-6), 2.28 (s, 3H -  $\text{C}_6\text{H}_4\text{-CH}_3$ ), 2.35 (s, 3H, -  $\text{C}_6\text{H}_4 - \text{CH}_3$ ); 2.53 (s, 2H, H-8), 4.43 (d,  $J = 5.12\text{ Hz}$ , 1H, H-4), 5.63 (d,  $J = 5.12\text{ Hz}$ , 1H, H-3), 7.25 - 7.47 (m, 8H, aromatic protons);  $^{13}\text{C NMR}$ :  $\delta$  197.21 (C-5), 164.44 (C-2), 146.67 (C-9), 142.47 (C-10), [138.62, 135.99, 130.25, 129.06, 128.02, 124.34 (aromatic carbons)], 112.64 (C-3), 50.94 (C-6), 41.48 (C-8), 34.94 (C-4), 32.10 (C-7), 29.13 (C-7  $\text{CH}_3$ ), 27.69 (C-7  $\text{CH}_3$ ), 21.22 ( $-\text{C}_6\text{H}_4\text{-CH}_3$ ), 21.02 ( $-\text{C}_6\text{H}_4\text{-CH}_3$ ); MS:  $m/z$  358 ( $\text{M}^+$ ). Anal. Found: C, 83.54; H, 7.30. Calcd. for  $\text{C}_{25}\text{H}_{26}\text{O}_2$ : C, 83.79, H, 7.26%.

**7, 7 - Dimethyl - 2 - phenyl - 4 (4-hydroxyphenyl)- 5-oxo- 5, 6, 7, 8 -tetrahydro-2-chromen 4h.** Yield 55%; m. p. 188-90°C;  $R_f$  0.60; IR: 1670 (C=O in conjugation), 1640 (C=C), 1585, 1505 (phenyl);  $^1\text{H NMR}$ : 1.05 (s, 3H,  $\text{CH}_3$ ), 1.12 (s, 3H,  $\text{CH}_3$ ), 2.24 (s, 2H, H-6), 2.54 (s, 2H, H-8), 4.42 (d,  $J = 5.12\text{ Hz}$ , 1H, H-4), 5.69 (d,  $J = 5.12\text{Hz}$ , 1H, H-3), 7.31 - 7.59 (m, 9H, aromatic protons);  $^{13}\text{C NMR}$ :  $\delta$  198.48 (C-5), 165.13 (C-2), 154.80 (C-9), 146.54 (C-10), [136.78, 132.94, 129.24, 128.70, 124.40 (aromatic carbon)] 112.85 (C-3), 50.92 (C-6), 41.48 (C-8), 34.48 (C-4), 32.21 (C-7), 29.02 (C-7  $\text{CH}_3$ ), 27.65 (C-7  $\text{CH}_3$ ); MS:  $m/z$  364

(M<sup>+</sup>). 2, 4 - Dinitrophenylhydrazone derivative, m p 124-26°C.

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