

SHORT  
COMMUNICATIONSSynthesis of 2-Aroylmethylidene-6-hydroxy-  
2,3-dihydroindol-3-ones

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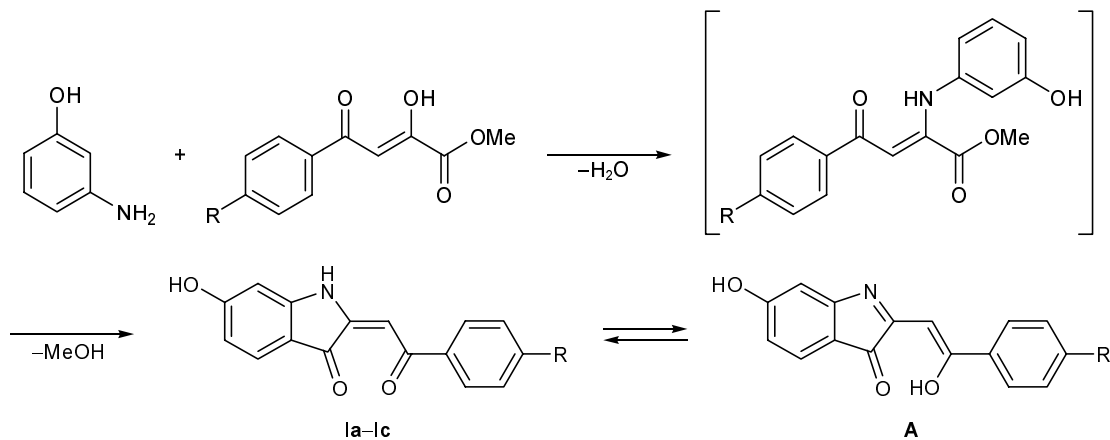
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Methyl 4-aryl-2,4-dioxobutanoates are known to react with aromatic amines to give methyl 4-aryl-2-aryl-amino-4-oxobut-2-enoates as a result of attack by the amine at the  $\alpha$ -carbonyl group [1]. This reaction was thoroughly studied using kinetic methods [2] and was shown to produce almost no by-products, regardless of the substituent in the aromatic amine [3] and solvent nature [4]. We have found that the reaction of methyl 4-aryl-2,4-dioxobutanoates with 3-aminophenol in boiling acetic acid (reaction time 1–2 h) leads to formation of 2-arylmethylidene-6-hydroxy-2,3-dihydroindol-3-ones **Ia–Ic** (Scheme 1). Presumably, the primary condensation product, methyl 4-aryl-2-(3-hydroxyphenylamino)-4-oxobut-2-enoate, undergoes intramolecular ring closure to the 2,3-dihydroindol-3-one heterocyclic system.

Compounds **Ia–Ic** are red crystalline substances which are soluble in DMSO and DMF. Their IR spectra contain absorption bands due to stretching vibrations of the carbonyl group in position 3 of the indole

ring ( $1650\text{--}1660\text{ cm}^{-1}$ ), ketone carbonyl group conjugated with the double bond ( $1630\text{--}1640\text{ cm}^{-1}$ ), and hydroxy group ( $3060\text{--}3070\text{ cm}^{-1}$ ). In the  $^1\text{H NMR}$  spectra of **Ia–Ic** we observed a signal at  $\delta$  7.33–7.40 ppm from the olefinic proton, a number of aromatic proton signals in the  $\delta$  region 7.0–8.3 ppm, OH proton signal at  $\delta$  10.20–10.30 ppm, and a strongly broadened signal at  $\delta$  13.80 ppm. The presence of the latter indicates that compounds **Ia–Ic** can exist in the enol form (**A**). Compound **Ia** showed in the mass spectrum the molecular ion peak with  $m/z$  265  $[M]^+$  and fragment ion peaks with  $m/z$  77  $[\text{Ph}]^+$  and 105  $[\text{PhCO}]^+$  which are consistent with the assumed structure.

**6-Hydroxy-2-(2-oxo-2-phenylethylidene)-2,3-dihydro-1H-indol-3-one (Ia)**. A mixture of 0.01 mol of 3-aminophenol and 0.01 mol of methyl 2,4-dioxo-4-phenylbutanoate in 10 ml of acetic acid was heated for 1 h under reflux. The mixture was then kept for 4–5 h at room temperature, and the precipitate was filtered off and recrystallized from acetic acid. Yield 1.0 g



(32%), mp >300°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660 (CO), 1620 (COC=C), 3060 (OH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 7.40 s (1H, CH=), 10.36 s (1H, OH), 8.44 d (1H, 5-H,  $J = 9.0$  Hz), 8.18 d (2H, *o*-H,  $J = 8.0$  Hz), 8.15 s (1H, 7-H), 7.32 d (1H, 4-H,  $J = 9.0$  Hz), 7.1 d (2H, *m*-H,  $J = 8.0$  Hz). Found, %: C 72.30, 72.55; H 4.06, 4.28; N 5.15, 5.39.  $\text{C}_{16}\text{H}_{11}\text{NO}_3$ . Calculated, %: C 72.42; H 4.17; N 5.27.

Compounds **Ib** and **Ic** were synthesized in a similar way.

**6-Hydroxy-2-[2-(4-methylphenyl)-2-oxoethylidene]-2,3-dihydro-1H-indol-3-one (Ib)**. Yield 2.9 g (88%), mp >300°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1650 (CO), 1630 (COC=C), 3060 (OH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 7.33 s (1H, CH=), 10.20 s (1H, OH), 8.50 d (1H, 5-H,  $J = 9.0$  Hz), 8.15 s (1H, 7-H), 7.25 d (1H, 4-H,  $J = 9.0$  Hz), 8.20 d (2H, *o*-H,  $J = 8.0$  Hz), 7.35 d (2H, *m*-H,  $J = 8.0$  Hz). Found, %: C 73.20, 73.02; H 4.79, 4.55; N 5.11, 5.02.  $\text{C}_{17}\text{H}_{13}\text{NO}_3$ . Calculated, %: C 73.11; H 4.67; N 5.06.

**6-Hydroxy-2-[2-(4-methoxyphenyl)-2-oxoethylidene]-2,3-dihydro-1H-indol-3-one (Ic)**. Yield 1.84 g (53%), mp >300°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1650 (CO), 1630 (COC=C), 3080 (OH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 7.33 s (1H, CH=), 10.30 s (1H, OH), 13.80 s (1H, NH), 8.46 d (1H, 5-H,  $J = 9.0$  Hz), 8.22 d (2H,

*o*-H,  $J = 8.0$  Hz), 8.19 s (1H, 7-H), 7.21 d (1H, 4-H,  $J = 9.0$  Hz), 7.11 d (2H, *m*-H,  $J = 8.0$  Hz). Found, %: C 69.01, 69.24; H 4.35, 4.53; N 4.64, 4.88.  $\text{C}_{17}\text{H}_{13}\text{NO}_4$ . Calculated, %: C 69.12; H 4.44; N 4.76.

The IR spectra were recorded on a Specord-80 spectrophotometer from samples dispersed in mineral oil. The  $^1\text{H}$  NMR spectra were measured on Mercury-300 and Bruker DRX-500 instruments at 300.056 and 500.13 MHz, respectively, using DMSO- $d_6$  as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT Incos 50 spectrometer.

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