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SHORT COMMUNICATIONS

# Cyclocondensation of Ethyl Nitroacetate with 2-Hydroxybenzaldehydes

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Coumarins having a nitrogen-containing substituent in the 3-position are known to exhibit biological activity. For example, 3-nitrocoumarin inhibits phospholipase C in pathogenic yeasts *Candida albicans* [1]. This compound is prepared by hydrolysis of 3-nitro-2*H*-chromen-2-imine which is obtained by cyclocondensation of nitroacetonitrile with salicylaldehyde in the presence of methylamine [2]. The synthesis of 3-nitrocoumarin by nitration of unsubstituted coumarin with nitric acid involves difficulties, for the nitration occurs at the benzene ring; only in concentrated nitric acid, the corresponding dinitro derivative having one nitro group in the 3-position is formed [3].

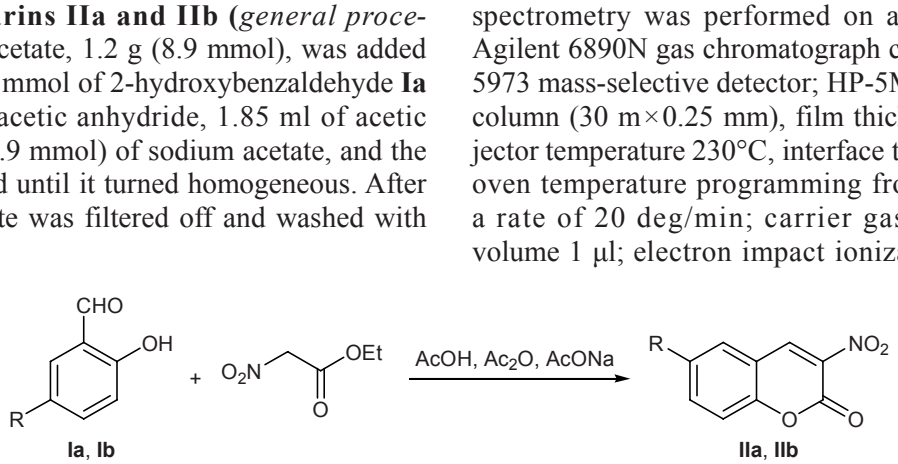
While studying cyclocondensations of 2-hydroxybenzaldehydes **Ia** and **Ib** with ethyl nitroacetate in a mixture of acetic acid with acetic anhydride we succeeded in isolating 3-nitrocoumarin (**IIa**) and 6-bromo-3-nitrocoumarin (**IIb**); the latter compound was previously unknown.

**3-Nitrocoumarins IIa and IIb (***general procedure***).** Ethyl nitroacetate, 1.2 g (8.9 mmol), was added to a mixture of 8.9 mmol of 2-hydroxybenzaldehyde **Ia** or **Ib**, 3.35 ml of acetic anhydride, 1.85 ml of acetic acid, and 0.73 g (8.9 mmol) of sodium acetate, and the mixture was heated until it turned homogeneous. After 24 h, the precipitate was filtered off and washed with water and ethanol.

**3-Nitro-2*H*-chromen-2-one (IIa).** Yield 0.46 g (30%), yellow prisms, mp 143°C (from ethanol) [1]. $^1$H NMR spectrum, δ, ppm: 7.64 m (2H, $H_{arom}$), 7.90 m (1H, $H_{arom}$), 8.05 d (1H, $H_{arom}$), 9.25 s (1H, 4-H). Mass spectrum, *m*/*z* ($I_{rel}$, %): 191 (63) $[M]^+$, 161 (7), 133 (29), 105 (6), 89 (100), 63 (33).

**6-Bromo-3-nitro-2*H*-chromen-2-one (IIb).** Yield 0.48 g (20%), yellow prisms, mp 200°C. $^1$H NMR spectrum, δ, ppm: 7.40 d ($H_{arom}$), 7.85 d ($H_{arom}$), 8.14 d ($H_{arom}$), 9.05 s ($H_{arom}$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 270 (100) $[M]^+$, 240 (18), 210 (20), 135 (5), 166 (100), 117 (10), 88 (60), 75 (100), 62 (32).

The $^1$H NMR spectra were recorded from solutions in DMSO-$d_6$ on a Bruker Avance DRX-200 spectrometer (200 MHz). The progress of reactions and the purity of products were monitored by thin-layer chromatography on PTSKh-AF-V Sorbfil plates (Krasnodar, Russia) using toluene as eluent; spots were visualized under UV light. Gas chromatography–mass spectrometry was performed on a Hewlett–Packard Agilent 6890N gas chromatograph coupled with an HP 5973 mass-selective detector; HP-5MS quartz capillary column (30 m×0.25 mm), film thickness 0.33 μm; injector temperature 230°C, interface temperature 270°C, oven temperature programming from 70 to 280°C at a rate of 20 deg/min; carrier gas helium; sample volume 1 μl; electron impact ionization, 70 eV; total




**Ia**, **Ib** **IIa**, **IIb**

R = H (**a**), Br (**b**).

ion current registration. The data acquisition parameters were set using standard Autotune program.

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