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The Photochemical Synthesis of 6-Acyl-5*H*-benzo[a]phenoxazin-5-ones

Short Communication

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6-Acyl-5*H*-benzo[a]phenoxazin-5-ones were prepared by the photochemical reaction of 5*H*-benzo[a]phenoxazin-5-one with aldehydes.

(Keywords: 5H-Benzo[a]phenoxazin-5-one; 6-Propionyl-5H-benzo[a]-phenoxazin-5-one)

Die photochemische Synthese von 6-Acyl-5H-benzo[a]phenoxazin-5-onen (Kurze Mitteilung)

Die Titelverbindungen wurden mittels photochemischer Reaktion von 5*H*-Benzo[a]phenoxazin-5-onen mit Aldehyden hergestellt.

Although many workers have reported synthetic methods of a variety of benzophenoxazones which are known to possess pharmacological activities[1–3], the recorded synthetic methods are tedious[4–8]. On the other hand, photochemistry has provided versatile routes to many compounds which are difficult to be prepared by any other methods. We now wish to report a novel route for the photochemical synthesis of 5*H*-benzo[a]phenoxazin-5-one derivatives.

Upon irradiation of benzene solution of 5*H*-benzo[a]phenoxazin-5-one (**1**) and aldehydes (**2a**, **b**) in a Pyrex vessel using 100 Watt high-pressure mercury lamp, 6-acyl-5*H*-benzo[a]phenoxazin-5-ones (**3a**, **b**) were obtained. The structures of **3a** and **3b** were fully supported by microanalytical results and spectral data. In particular, the NMR spectrum of **1** ($CDCl_3$) exhibited a characteristic singlet at 6.30 ppm due to the olefinic proton, but those of the photoproducts **3a**, **b** of **1** with **2a**

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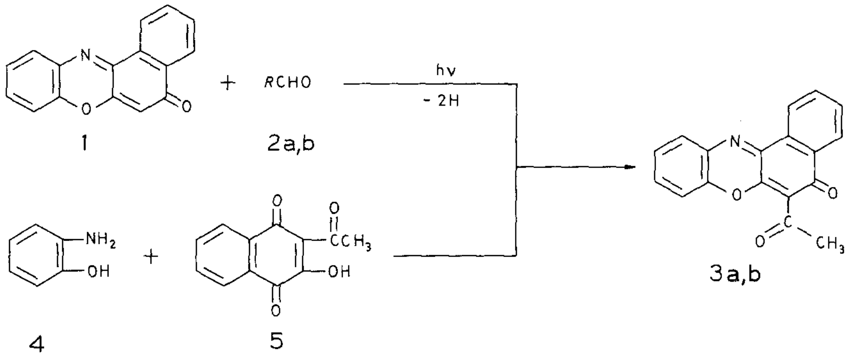

a: $R = CH_3$
b: $R = C_2H_5$

and **2 b** did not show a characteristic singlet at 6.30 ppm. Therefore, the photochemical addition did occur at the 6-position of **1**. Furthermore, the photoproduct **3 a** was identified by direct comparison with a sample prepared by an alternate route. This route involves the condensation of 2-aminophenol (**4**) with 2-acetyl-3-hydroxy-1,4-naphthoquinone (**5**) in an aqueous acetic acid. The latter compound was obtained in nine steps from 1,4-naphthoquinone[9].

The present report offers a facile method for the photochemical synthesis of 6-acyl-5*H*-benzo[a]phenoxazin-5-ones from readily available starting material.

Experimental

Melting points were determined on a Yanagimoto micromelting apparatus and are uncorrected. The infrared spectra were recorded on a Jasco DS 701 G spectrometer. Nuclear magnetic resonance spectra were determined on a Hitachi R-20 B spectrometer using tetramethylsilane as an internal reference. Mass spectra were determined on a Hitachi M-52 spectrometer.

6-Acetyl-5 H-benzo[a]phenoxazin-5-one (**3 a**)

Method (A)

A benzene solution (50 ml) of **1** (0.005 mol) and **2 a** (0.03 mol) was irradiated in a Pyrex glass tube for 20 h from outside by means of 100 Watt high-pressure mercury arc lamp in a nitrogen atmosphere through a 7 cm-thick layer of cold water (0-5°) and then bubbled with air for several minutes. After the removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column using cyclohexane-benzene (1:1) as an eluent. The photoproduct **3 a** thus obtained was further purified by recrystallization from ethanol.

Compound **3a** gave yellow crystals; M.p. 203°; yield 52%.

IR (KBr): 1618 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): 2.60 (s, 3H, CH_3 group), 7.09-7.85 (m, 6H, arom.), 8.07-8.29 (m, 1H, arom.), 8.47-8.67 (m, 1H, arom.).

MS: *m*/*s* = 289 (M^+).

$C_{18}H_{11}O_3N$ (289.3). Calcd. C 74.73, H 3.83, N 4.84.
Found C 74.75, H 3.72, N 4.85.

Method (B)

A mixture of **4** (0.0004 mol) and **5** (0.0009 mol) in 5 ml of 90% aqueous acetic acid was heated at 100 °C for 2 h. After the removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column using cyclohexane-benzene (1:1) as an eluent. The crude product was further purified by recrystallization from ethanol and identified (M.p., mixed M.p., IR, ^{1}H-NMR, and MS) as **3a**. Yield 45%.

6-Propionyl-5H-benzo[a]phenoxazin-5-one (**3b**)

The compound **3b** was prepared by photochemical reaction of **1** with **2b** in analogy to **3a**.

Compound **3b** gave yellow crystals; M.p. 177°; yield 62%.

IR (KBr): 1619 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): 0.99-1.33 (t, 3H, CH_3 group), 2.49-2.94 (q, 2H, CH_2 group), 6.96-7.78 (m, 6H, arom.), 8.01-8.30 (m, 1H, arom.), 8.41-8.68 (m, 1H, arom.).

MS: *m*/e = 303 (M^+).

$C_{19}H_{13}O_3N$ (303.3). Calcd. C 75.24, H 3.32, N 4.62.
Found C 75.24, H 3.51, N 4.63.

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