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The Photochemical Synthesis of 1- and 3-Acetylphenoxazines

Short Communication

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1- and 3-Acetylphenoxazine were prepared by the photochemical reaction of 10-acetylphenoxazine.

(Keywords: Acetylphenoxazines; Photochemistry)

Photochemische Synthese von 1- und 3-Acetylphenoxazinen
(Kurze Mitteilung)

1- und 3-Acetylphenoxazin wurden durch photochemische Reaktion aus 10-Acetylphenoxazin dargestellt.

Although many workers have reported synthetic methods of a variety of phenoxazine known to exhibit pharmacological activities[1–3], the recorded synthetic methods are considerably tedious[4–6]. 2-Acetylphenoxazine was easily prepared by the acetylation of phenoxazine using *Friedel-Crafts* type reaction[7], but the corresponding 1- and 3-homologs have not been prepared. On the other hand, photochemistry has provided versatile routes to the preparation of many compounds, which are difficult to be prepared by any other methods. In this paper, this interesting photochemical technique has been applied to the preparation of 1- and 3-acetylphenoxazines.

In this experiment, an ultraviolet light from a 5 Watt low-pressure mercury lamp was used. A methanol solution of 10-acetylphenoxazine (**1**) was irradiated in a nitrogen atmosphere at 5° for 5 h. The photo-

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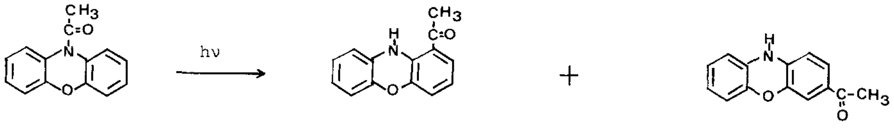
products obtained were chromatographed on silica gel and recrystallized from benzene.

1-Acetylphenoxazine (**2**) and 3-acetylphenoxazine (**3**) were synthesized by the photochemical reaction of **1** in 25% and 13% yields, respectively. The presence of a small amount of some unidentified products in the reaction mixture was detected by TLC. The structures of the photoproducts were fully supported by microanalytical results and spectral data.



1 2 3

$\delta_2 = 7.18$ $j_{23} = 7.2$
$\delta_3 = 6.50$ $j_{24} = 2.2$
$\delta_4 = 6.69$ $j_{34} = 7.0$
$\delta = 2.50$ (3 H, CH_3)
$\delta = 9.76$ (1 H, NH)

$\delta_1 = 6.53$ $j_{12} = 8.2$
$\delta_2 = 7.41$ $j_{14} = 0.0$
$\delta_4 = 7.16$ $j_{24} = 1.9$
$\delta = 2.42$ (3 H, CH_3)
$\delta = 8.00$ (1 H, NH)

The present report offers a facile method for the photochemical synthesis of 1- and 3-acylphenoxazines from readily available starting material.

Experimental

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

10-Acetylphenoxazine (**1**) was obtained according to the reported method[8]. TLC (solvent: benzene) *Rf*(**1**) = 0.14.

Acetylphenoxazine (**2**, **2**)

A solution of 10-acetylphenoxazine (1.0 g, 0.004 mol) in methanol (430 ml) was irradiated in a quartz glass tube from outside by means of 5 Watt low-pressure mercury arc lamp in a nitrogen atomosphere through a 7 cm-thick layer of cold water (0–5°) for 5 h. After the removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column using benzene as an eluent and recrystallized from benzene.

Compound **2** gave yellow crystals; m.p. 156°; yield 25%; TLC *Rf* = 0.74.
IR (KBr): 1638 cm^{-1} (C=O).
MS: *m*/e = 225 (M^+). $C_{14}H_{11}NO_2$ (225.2).
Compound **3** gave yellow crystals; m.p. 186°; yield 13%; TLC *Rf* = 0.08.
IR (KBr): 1647 cm^{-1} (C=O).
MS: *m*/e = 225 (M^+). $C_{14}H_{11}NO_2$ (225.20).

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