Chemistry of Heterocyclic Compounds, Vol. 41, No. 4, 2005

METHOD FOR PREPARATIVE SYNTHESIS OF 4-DIALKYLAMINO-2-HYDROXYACETOPHENONE

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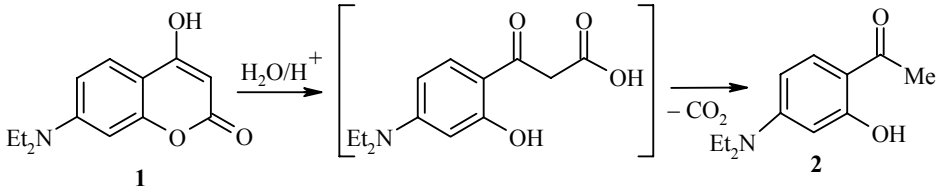
Keywords: 1-(4-diethylaminophenyl-2-hydroxy)ethanone, 7-diethylamino-4-hydroxychromen-2-one, decarboxylation.

Opening of the 4-hydroxycoumarin ring by mineral acids followed by decarboxylation has been known for a long time [1], but this reaction has not been important for preparative synthesis of the corresponding acetophenones. In most cases, there are more successful methods for obtaining the target compounds, and furthermore the indicated conversion usually occurs in low yields and is accompanied by considerable tar formation.

4-Dialkylamino-2-hydroxyacetophenones can be obtained by a Fries rearrangement of the corresponding acetoxy derivatives [2], but in this case (due to the considerable tar formation) the yield of acetophenone is low (about 15%) and it is a rather complicated task to separate and purify it.



1 **2**

For the example of the N-diethyl derivative, we have shown that cleavage of the ring in the readily accessible 7-dialkylamino-4-hydroxycoumarins **1** [3] when treated with mineral acids is a preparative synthesis method for the target acetophenones **2**.

1-(4-Diethylamino-2-hydroxyphenyl)ethanone (2, R = Et). A solution of 7-diethylamino-4-hydroxycoumarin (**1**) (40 g, 0.172 mol) in 30% H_2SO_4 (340 ml) was heated for 5 h at 125°C (until evolution of carbon dioxide stopped). The reaction mixture was neutralized with ammonium hydroxide and extracted with methylene chloride; the extract was dried with magnesium sulfate and evaporated down, and the residue was recrystallized from hexane. Yield of acetophenone **2** 32 g (90%); mp 42-44°C. ^{1}H NMR spectrum (Varian VXR-300, 300 MHz, $CDCl_3$, TMS, δ, ppm (*J*, Hz)): 1.20 (6H, t, *J* = 6.9, $2CH_3$); 2.47 (3H, s, CH_3CO); 3.39 (4H, q, *J* = 6.6, $2NCH_2$); 6.07 (1H, s, H-3); 6.18 (1H, d, *J* = 9.3, H-5); 7.51 (1H, d, *J* = 9.3, H-6).

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