COUPLED ACYLATION OF AMINES DEPENDENT ON 3-NITRO-4-CHLOROCOUMARIN

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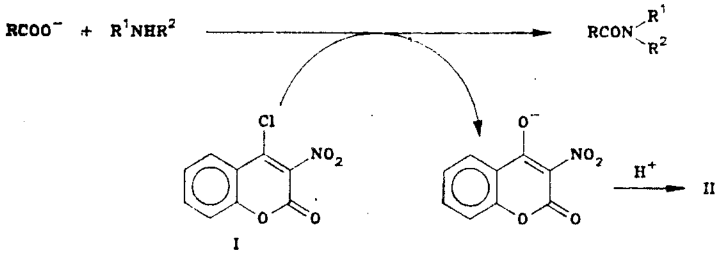
We found that 3-nitro-4-chlorocoumarin (I) can be utilized for the acylation of primary and secondary amines with salts of carboxylic acids on a preparative scale.



The mixture of 1 equivalent of 3-nitro-4-chlorocoumarin (I) and 2 equivalents of the inorganic salt of the carboxylic acid in dry DMF or DMSO [1.5-2.5 ml for 1 mmole of the coumarin (I)] is stirred for 15 min at 18-20°C. Then, 1 equivalent of the primary or secondary amine is added, and the mixture is stirred for 30 min more. The reaction mixture is diluted with excess water, and the precipitated N-acyl derivative is filtered off or extracted with a suitable extractant; it is recrystallized if necessary. The aqueous solution is acidified with concentrated hydrochloric acid until the pH 2 is reached, and the 3-nitro-4-hydroxycoumarin (II) is filtered off.

In this way, the N-benzoyl derivatives of aniline, β-naphthylamine, p-toluidine, N-diphenylacetylmorpholine, N-(β-phenylacryloyl)butylamine, and acetanilide (the yield 63%) were obtained in yields of 73-88%. The substitution of the aprotic polar solvent of benzene leads to a loss of selectivity; the yield of the acylation product falls using pyridine. It is impossible to utilize the ammonium salts of carboxylic acids for the acylation in view of the high contamination of the reaction product with 3-nitro-4-aminocoumarin, but it is convenient to introduce the combination of the free carboxylic acid with pyridine or sodium bicarbonate into the reaction.

The initial chlorocoumarin (I) is regenerated almost quantitatively by the method of [1] from the 3-nitro-4-hydroxycoumarin (II), which is recovered in 75-90% yield.

LITERATURE CITED

1. V. L. Savel'ev, O. S. Artamonova, and V. A. Zagorevskii, *Khim. Geterotsikl. Soedin.*, No. 3, 316 (1976).

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