LETTERS TO THE EDITOR

3-NITRO-4-CHLOROCOUMARIN-DEPENDENT SYNTHESIS OF CARBOXYLIC ACID ANHYDRIDES

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The synthesis of 3-nitro-4-acetoxycoumarin by the reaction of 3-nitro-4-chlorocoumarin (I) and sodium acetate in aqueous ethanol was described in [1]. However, no data on the chemical behavior of this compound, in which the ester group is activated by the overall electron-acceptor effect of the carbonyl and nitro groups, are available. In studying the thiolation of chlorocoumarin I we observed that S-containing coumarins that are capable of hydrolysis cannot be isolated from the reaction mixture and that chlorocoumarin I itself, which is stable in moist media, is rapidly hydrolyzed in the presence of added weak bases, including sodium acetate [2]. In special experiments on the reaction of equimolar amounts of chlorocoumarin I and benzoate we were unable to detect the expected ester in the reaction mixture. Another possible reaction product — benzoyl chloride — also was not detected. At the same time, carrying out the reaction of condensing agent I with two molar equivalents of carboxylates makes it possible to obtain anhydrides in high yields under mild conditions; the anhydrides are easily separated by filtration from a second reaction product — water soluble 3-nitro-4-hydroxycoumarin salt II.



Regeneration of chlorocoumarin I from the recovered 3-nitro-4-hydroxycoumarin (III) is achieved in almost quantitative yield by reaction with phosphorus oxychloride [3].

A 0.36-ml (4.44 mmole) sample of pyridine or 0.38 g (4.44 mmole) of NaHCO₃ was added to a suspension of 0.89 g (4.4 mmole) of p-bromobenzoic acid in a solution of 0.60 g (2.2 mmole) of I in 3.5 ml of DMF or DMSO, and the mixture was heated at 60°C with stirring for 8 min. It was then cooled to 18-20°C and, after 10 min, diluted with 15 ml of cold water. The p-bromobenzoic acid anhydride was removed by filtration, washed with water, and air dried to give a product with mp 218-220°C (mp 219.4-220°C [4]). IR spectrum (KBr): ν 3095, 3062, 3035 (=CH); 1784, 1721 (C=O); 1584 cm⁻¹ (Ar). The yield was 0.85 g (100%). The aqueous filtrate was acidified to pH 2 with concentrated HCl, and the precipitated hydroxycoumarin III, with mp 176-177°C [mp 177°C (dec.) [5]], was removed by filtration. The yield was 0.39 g (85%).

Benzoic, cinnamic, 1-naphthylacetic, diphenylacetic, and p-nitrobenzoic acid anhydrides were similarly obtained in 82-94% yields.

LITERATURE CITED

- 1. M. Siddiq, P. F. G. Praill, and A. W. Khan, J. Chem. Soc. Pakistan, 5, 73 (1983).
- 2. É. A. Parfënov and L. D. Smirnov, Khim. Geterotsikl. Soedin., No. 8, 1032 (1991).
- 3. V. L. Savel'ev, O. S. Artamonova, and V. A. Zagorevskii, Khim. Geterotsikl. Soedin., No. 3, 316 (1976).
- 4. K. Kikukawa, K. Kono, K. Nagira, F. Wada, and T. Matsuda, Tetrahedron Lett., 21, 2877 (1980).
- 5. C. F. Hübner and K. P. Link, J. Am. Chem. Soc., 67, 99 (1945).

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