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CONVENIENT METHOD FOR SYNTHESIS OF 6-(N,N-DIETHYLAMINO)-9-(2-CARBOXYPHENYL)-1,2,3,4-TETRAHYDROXANTHYLIUM PERCHLORATE

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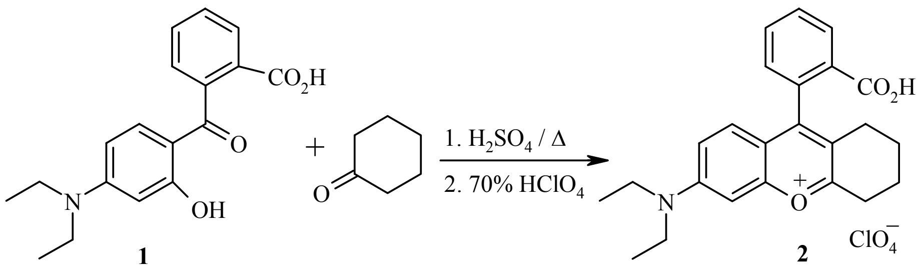
Goal-directed search for new dyes absorbing in the near IR range of the spectrum is an important problem in polymethine dye chemistry [1]. A major method for solving this problem is to search for new heterocyclic rings for assembling polymethine dyes.

Some 6-(N,N-dialkylamino)-1,2,3,4-tetrahydroxanthylium salts are used as starting materials for synthesis of fluorescent polymethine dyes absorbing in the near IR region [2]. Generally synthesis of such compounds is a multistep and labor-intensive process, while the yields of the target products are insignificant [2]. At the same time, derivatives of 6-(N,N-dialkylamino)-1,2,3,4-tetrahydroxanthylium derivatives substituted at the position 9 have not been described in the literature.

With the aim of obtaining new derivatives of this heterocyclic system, we have studied cyclocondensation of the easily prepared 2-hydroxy-4-(N,N-diethylamino)-(2-carboxy)benzophenone (**1**) and cyclohexanone. We found that carrying out the reaction in concentrated H_2SO_4 makes it possible to obtain the target compound **2** in rather high yield, and the isolation and purification processes are significantly simplified.

Benzophenone **1** is obtained from phthalic anhydride and 3-(N,N-diethylamino)phenol according to the procedure in [3].

The proposed synthesis method allows us to obtain compound **2** in good yield. Furthermore, this method is based on using accessible and inexpensive starting materials, which makes it promising for further application.



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Freshly distilled cyclohexanone (6.6 ml, 63.7 mmol) was added dropwise to concentrated H_2SO_4 (70 ml) cooled down to 0°C. Then compound **1** (10 g, 32 mmol) was added in portions with vigorous stirring. The reaction mixture was held for 1-1.5 h at 90°C, cooled down, and poured onto ice (300 g). 70% perchloric acid (7 ml) was added to the solution formed. The precipitate was filtered off, washed with cold water (100 ml), and recrystallized from acetic acid (25 ml). Yield 9.7 g (67%); mp 214-216°C (decomp.). ^{1}H NMR spectrum (Bruker AC-250, 250 MHz, acetone-d_6/TMS), δ, ppm (*J*, Hz): 1.36 (6H, t, $J = 7.14$, $N–CH_2\underline{CH_3}$); 1.81 (2H, m, CH_2); 2.0 (2H, m, CH_2); 2.31 (2H, m, CH_2); 3.2 (2H, m, CH_2); 3.78-3.87 (4H, q, $J = 7.14$, $N–\underline{CH_2}CH_3$); 7.19-7.22 (1H, m, H_{Ph}); 7.26 (1H, s, 5-H); 7.39-7.46 (2H, m, H_{Ar}); 7.81-7.97 (3H, td, $J = 7.6$, $J = 1.34$, H_{Ph}); 8.35-8.38 (1H, d, $J = 8.8$, 7-H). Found, %: C 60.8; H 5.7; N 3.1. $C_{24}H_{26}ClNO_7$. Calculated, %: C 60.6; H 5.5; N 2.9.

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