SYNTHESIS OF 6H,7H-[1]BENZOPYRANO-[3,4-*c*][1]BENZOPYRAN-6,7-DIONES

E. M. Poronik, M. P. Shandura, and Yu. P. Kovtun

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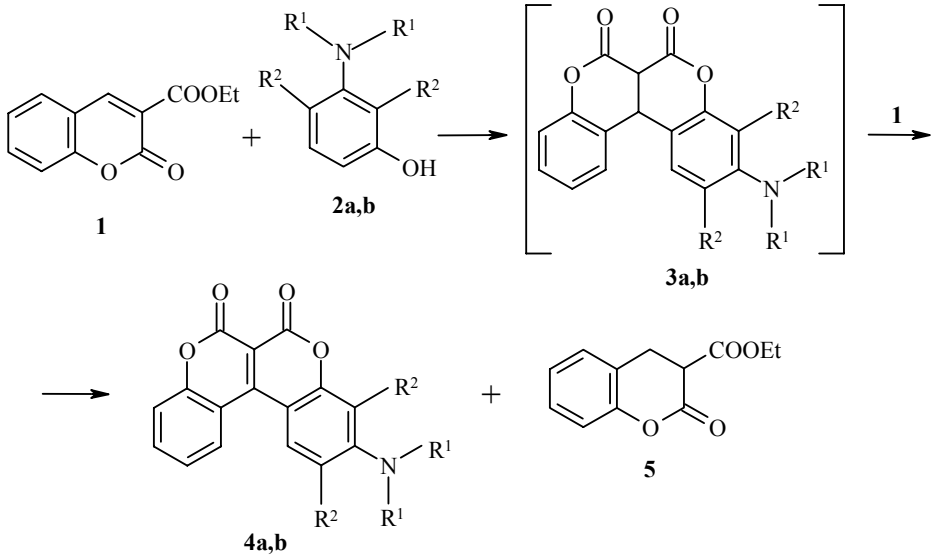
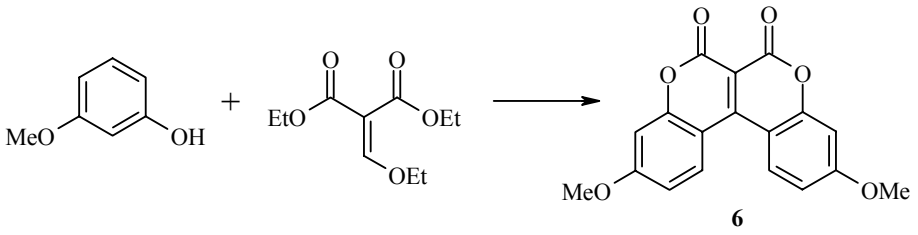
In an attempt to obtain compound **3a** by condensation of coumarin-3-carboxylic acid (**1**) with *m*-diethylaminophenol **2a**, from the reaction mixture we isolated, instead of the expected compound, an intensely fluorescent substance in 36% yield with a ^{1}H NMR spectrum corresponding to structure **4a**.



a R ^{1} = Et, R^2 = H, **b** R^{1}R^2 = $CH_2CH_2CH_2$

A compound of similar structure **6** was obtained earlier in a similar type of process [1]. The authors of that paper hypothesized that oxidation in the last step occurred by means of oxygen in the air.



Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev 02094; e-mail: yu_kovtun@svitonline.com. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 460-461, March, 2006. Original article submitted January 24, 2006.

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We have conducted additional studies of this cyclization, and we have determined that oxidation of the intermediates **3** does not occur by the action of oxygen in the air. Coumarinocoumarins **4** are also formed under an inert atmosphere. We found that in this reaction, coumarin **1** acts as an oxidizing agent. In the presence of 2 equivalents of compound **1**, the yield of compounds **4** increased approximately two-fold. The dihydrocoumarin **5** formed in this case was identified in the reaction mixture by TLC by comparing with the compound separately obtained by the procedure in [2]. The authors of [3] observed similar properties of coumarin as an oxidizing agent.

Compounds 4a,b were obtained by heating a mixture of coumarin **1** (10 mmol) and aminophenols **2a,b** (5 mmol) for 1.5 h at 140°C. After cooling, the solid residue was recrystallized from an appropriate solvent.

6H,7H-3-Diethylamino[1]benzopyrano[3,4-*c*][1]benzopyran-6,7-dione (4a). Yield 74%; mp 176-177°C (alcohol). The UV spectrum (Shimadzu UV-3100), $\lambda_{absorption}$ 455 nm (CH_3CN); (Varian Cary Eclipse), $\lambda_{emission}$ 550 nm (CH_3CN). ^{1}H NMR spectrum (300 MHz, CDC_3, TMS), δ, ppm (*J*, Hz): 1.27 (6H, t, *J* = 7.2, CH_3); 3.49 (4H, q, *J* = 7.2, NCH_2); 6.48 (1H, s, H-4); 6.71 (1H, d, *J* = 9.3, H-2); 7.33-7.38 (2H, m, H-9 + H-11); 7.65 (1H, t, *J* = 8.1, H-10); 8.05 (1H, d, *J* = 9.6, H-1); 8.20 (1H, d, *J* = 7.8, H-12). Found, %: C 71.60; H 5.13; N 4.21. $C_{20}H_{17}NO_4$. Calculated, %: C 71.63; H 5.11; N 4.18.

(6H,7H-[1]benzopyrano[3,4-*c*][1]benzopyran-6,7-dione)[2,3,4-*i,j*]-2,3,4,6,7,8-hexahydroquinolizine (4b). Yield 86%; mp >300°C (DMF). UV spectrum (Shimadzu UV-3100), $\lambda_{absorption}$ 480 nm (CH_3CN); (Varian Cary Eclipse), $\lambda_{emission}$ 583 nm (CH_3CN). ^{1}H NMR spectrum (300 MHz, CF_3COOD, TMS), δ, ppm (*J*, Hz): 2.52 (4H, br. s, $NCH_2\underline{CH_2}$); 3.32 (4H, br. s, $NCH_2CH_2\underline{CH_2}$); 3.87 (4H, br. s, $N\underline{CH_2}$); 7.65-7.80 (2H, m, H-9 + H-11); 8.03 (1H, t, *J* = 7.8, H-10); 8.42 (1H, s, H-1); 8.50 (1H, d, *J* = 7.8, H-12). Found, %: C 73.48; H 4.78; N 3.94. $C_{22}H_{17}NO_4$. Calculated, %: C 73.53; H 4.77; N 3.90.

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