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LETTERS TO THE EDITOR

RECYCLIZATION OF 3-ETHOXYCARBONYL-BENZO[*c*]PYRILIUM SALTS BY PRIMARY AMINES

S. L. Bogza[1], O. V. Rozhkov[2], N. M. Bogdan[2], K. I. Kobrakov[1], and V. I. Dulenko[2]

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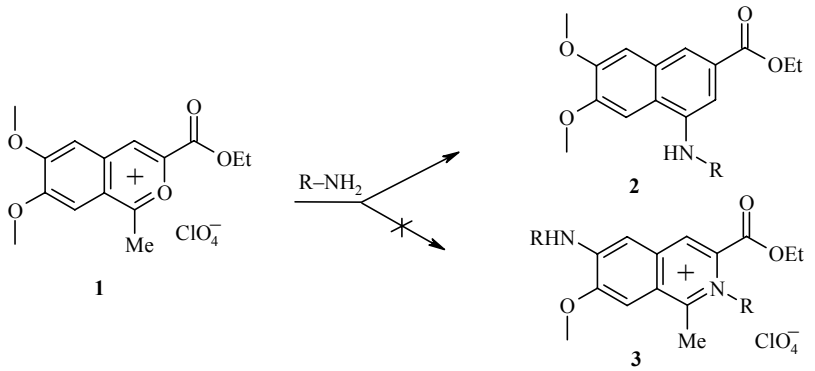
We have already reported various pathways in the conversion of 1,3-dialkyl-4-ethoxycarbonylbenzo[*c*]pyrilium perchlorates [1, 2]. In a continuation of a study of the effect of the functional substituent in the heterocyclic ring on the recyclization of the benzo[*c*]pyrilium cation, we investigated the reaction of 3-ethoxycarbonylbenzo[*c*]pyrilium salt (**1**) with primary amines. The synthesis and reactions of this salt were reported by Dorofeenko and Korobkova [3].

We have found that the action of primary amines leads to one of the possible pathways for the conversion of perchlorate **1**, namely, the formation of esters of 4-(R-amino)-6,7-dimethoxy-2-naphthoic acid (**2a-c**) in 58-73% yield. Products of the recyclization or substitution of the 6-methoxy group such as **3** were not found, although the technique used for work up of the reaction mixture [2] was designed for the isolation of such compounds. Ketols similar to those obtained by Brovchenko and Kuznetsov [4] in the reaction of 3-carboxybenzo-[*c*]pyrilium salts with secondary amines, which proceeds with the elimination of CO_2, were also not found.

Comparison of the results of the transformations of 3- and 4-ethoxycarbonylbenzo[*c*]pyrilium salts in the presence of aliphatic and arylalkyl amines shows that transfer of the ethoxycarbonyl group from $C_{(4)}$ to $C_{(3)}$ reduces the possibility of the nucleophilic substitution of the methoxy group at $C_{(6)}$ of the benzo[*c*]pyrilium cation [2]. The reactions of salt **1** are limited to recyclization of the pyran ring, which should lead to greater yields of naphthalene derivatives **2**.



1 **2** **3**

2 a R = CH_2Ph; **b** R = Bu; **c** R = (2-furyl)methyl

[1] A. N. Kosygin Moscow State Textile University, 117918 Moscow, Russia; e-mail: serge_z@yahoo.com.
[2] L. M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk, Ukraine. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 840-841, June, 2002. Original article submitted January 16, 2002.

The ^{1}H NMR spectra were taken on a Varian Gemini spectrometer at 200 MHz.

Ethyl Ester of 4-Benzyl-6,7-dimethoxy-2-naphthoic Acid (2a) was obtained in 73% yield; mp 148-149°C. IR spectrum in nujol mull, ν, cm^{-1}: 3410 (N–H), 1710 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 1.27 (3H, t, *J* = 7.0, CH_3); 3.87 (3H, s, OCH_3); 3.95 (3H, s, OCH_3); 4.24 (2H, q, *J* = 7.0, CH_2); 4.52 (2H, d, *J* = 4.9, CH_2); 6.79 (1H, s, H arom); 6.94 (1H, t, *J* = 4.9, NH); 7.24 (1H, t, *J* = 7.3, H arom); 7.31 (2H, t, *J* = 7.3, H arom); 7.38 (1H, s, H arom); 7.42 (2H, d, *J* = 7.3, H arom); 7.63 (1H, s, H arom); 7.71 (1H, s, H arom). Found, %: C 72.1; H 6.15; N 3.9. $C_{22}H_{23}NO_4$. Calculated, %: C 72.3; H 6.34; N 3.83.

Ethyl Ester of 4-Butylamino-6,7-dimethoxy-2-naphthoic Acid (3b) was obtained in 58% yield; mp 111-112°C. IR spectrum in nujol mull, ν, cm^{-1}: 3400 (N–H), 1710 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 1.02 (3H, t, *J* = 7.3, CH_3); 1.43 (3H, t, *J* = 7.0, CH_3); 1.53 (2H, m, *J* = 7.3, CH_2); 1.80 (2H, m, *J* = 7.3, CH_2); 3.36 (2H, t, *J* = 7.3, CH_2); 4.00 (3H, s, OCH_3); 4.05 (3H, s, OCH_3); 4.41 (2H, q, *J* = 7.0, CH_2); 7.03 (1H, s, H arom); 7.17 (1H, d, *J* = 1.4, H arom); 7.19 (1H, s, H arom); 7.91 (1H, d, *J* = 1.4, H arom). Found, %: C 69.8; H 7.2; N 4.1. $C_{19}H_{25}NO_4$. Calculated, %: C 69.95; H 7.34; N 4.07.

Ethyl Ester of 6,7-Dimethoxy-4-furfurylamino-2-naphthoic Acid (2c) was obtained in 66% yield; mp 133-134°C. IR spectrum in nujol mull, ν, cm^{-1}: 3410 (N–H), 1705 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 1.42 (3H, t, *J* = 7.5, CH_3); 3.97 (3H, s, OCH_3); 4.03 (3H, s, OCH_3); 4.42 (2H, q, *J* = 7.5, CH_2); 4.55 (2H, s, CH_2); 6.38 (2H, s, H arom); 7.06 (1H, s, H arom); 7.19 (1H, s, H arom); 7.27 (1H, s, H arom); 7.43 (1H, s, H arom); 7.95 (1H, s, H arom). Found, %: C 68.5; H 5.65; N 3.95. $C_{20}H_{21}NO_5$. Calculated, %: C 68.6; H 5.76; N 3.8.

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