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NOVEL METHOD FOR N-ALKYLATION OF A PYRIDONE RING

E. N. Elizbarashvili[1], I. V. Lagvilava[1], and Sh. A. Samsoniya[2]

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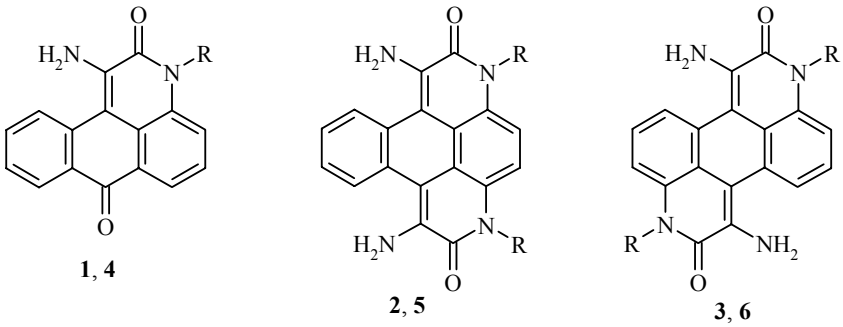
Anthrapyridone compounds are valuable fluorescent dyes; they are obtained from 1-aminoanthraquinones by acylation and cyclization [1]. Methods have been described for obtaining N-alkyl-substituted anthrapyridones which include introducing alkyl groups into the initial 1-aminoanthraquinone [2].

In this letter, we report the possibility of direct N-alkylation of the pyridone ring of pyridone-containing compounds by reacting alkyl halides (using ethyl bromide as an example) with 1-aminoanthrapyridone (**1**) in an aqueous alkaline suspension, in the presence of benzyltrimethylammonium chloride as a phase transfer catalyst. Similar results were obtained for alkylation of 1,8-diamino-3,6-dihydrodibenzo[*f,l,m,n*]-2,9-phenanthroline-2,7-dione (**2**) and 1,7-diamino-3,9-dihydrobenzo[1,2,3-*d,e*:4,5,6-*d'e'*]diquinoline-2,8-dione (**3**) using a two-fold excess of the alkyl halides. The corresponding ethyl-substituted compounds **4-6** were also isolated and characterized.



1, **4** **2**, **5** **3**, **6**

1– 3 R = H, **4–6** R = Et

The IR spectra were recorded on a Specord M-80 in KBr disks; the UV spectra were recorded on an SF-26 spectrophotometer in ethanol. The ^{1}H NMR spectra were obtained on a Bruker WP-200 (200 MHz) in DMSO-d_6 with TMS as the standard. The course of the reactions and the purity of the compounds were monitored and the R_f values were also determined on Silufol UV-254 plates.

General Alkylation Procedure. A suspension of 1-aminoanthrapyridone (5 g, 0.02 mol) and benzyltrimethylammonium chloride (0.1 g) in water (50 ml) was heated (~100°C) while gradually adding a 50% sodium hydroxide solution (40 ml). The reaction mixture changed color from yellowish-brown to violet. After a homogeneous mass was obtained, ethyl bromide (0.022 mol) was added and the mixture was heated for another 1.5-5 h (monitored by TLC). After the reaction went to completion, the mixture was cooled down, water (100 ml) was added, and the mixture was neutralized with 3% hydrochloric acid. The crystals that precipitated were filtered out and dried in air and then recrystallized from ethanol.

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[1] Georgian Technical University, Tbilisi 0175; e-mail: elizbarashvili@gtu.ge. [2] Iv. Javakhishvili Tbilisi State University, Tbilisi 0128, Georgia; e-mail: shsam@wanex.net. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1868-1869, December, 2005. Original article submitted May 17, 2005.

In alkylation of compounds **2** and **3**, ethyl bromide (0.044 mol) was added and the 50% sodium hydroxide solution was replaced by pyridine (50 ml).

1-Amino-3-ethyl-3H-naphtho[1,2,3-*d,e*]quinoline-2,7-dione (4). Yield 5 g (86%); mp 360-362°C (ethanol), R_f 0.158 (2:1 toluene–ether). IR spectrum, ν, cm^{-1}: 3470, 3310 (NH_2); 1695, 1680 (C=O). UV spectrum, λ_{max}, nm (log ε): 480 (4.04). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.98 (3H, t, *J* = 6.9, $CH_2\underline{CH_3}$); 2.99 (2H, s, NH_2); 3.43 (2H, q, *J* = 6.9, $\underline{CH_2}CH_3$); 7.22-7.78 (7H, m, H_{arom}). Found, %: C 74.50; H 4.90; N 9.62. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.47; H 4.86; N 9.65.

1,8-Diamino-3,6-diethyl-3,6-dihydrodibenzo[*f,l,m,n*]-2,9-phenanthroline-2,7-dione (5). Yield 1.78 g (24%); mp 384-386°C, R_f 0.405 (2:1 toluene–ethanol). IR spectrum, ν, cm^{-1}: 3480, 3330 (NH_2); 1690 (C=O). UV spectrum, λ_{max}, nm (log ε): 260 (4.32), 480 (4.58). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.88 (6H, t, *J* = 7.0, $CH_2\underline{CH_3}$); 2.69 (4H, s, NH_2); 3.418 (4H, q, *J* = 7.0, $\underline{CH_2}CH_3$); 7.14-7.30 (6H, m, H_{arom}). Found, %: C 70.90; H 5.40; N 15.00. $C_{22}H_{20}N_4O_2$. Calculated, %: C 70.95; H 5.41; N 15.04.

1,8-Diamino-3,9-diethyl-3,9-dihydrobenzo[1,2,3-*d,e*:4,5,6-*d'e'*]diquinoline-2,8-dione (6). Yield 1.86 g (25%); mp 389-390°C, R_f 0.156 (3:1 toluene–ethyl acetate). IR spectrum, ν, cm^{-1}: 3465, 3320 (NH_2); 1690 (C=O). UV spectrum, λ_{max}, nm (log ε): 356 (4.44), 463 (4.46). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.97 (6H, t, *J* = 7.0, $CH_2\underline{CH_3}$); 2.60 (4H, s, NH_2); 3.418 (4H, q, *J* = 7.0, $\underline{CH_2}CH_3$); 7.07-7.26 (6H, m, H_{arom}). Found, %: C 70.90; H 5.40; N 15.00. $C_{22}H_{20}N_4O_2$. Calculated, %: C 70.95; H 5.41; N 15.04.

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