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SHORT COMMUNICATIONS

Synthesis of 1-Alkylamino-3*H*-naphtho-[1,2,3-*de*]quinoline-2,7-diones

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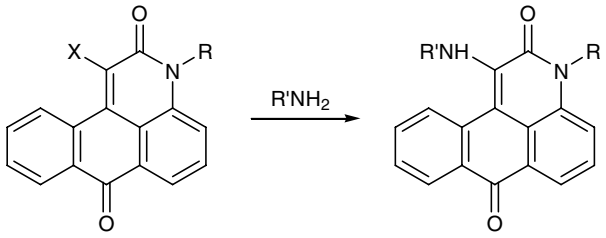
1-Alkylamino-3*H*-naphtho[1,2,3-*de*]quinoline-2,7-diones **I** exhibit luminescence properties [1]. Known methods for the synthesis of these compounds are based on nucleophilic replacement of hydrogen or chlorine atom or nitro or sulfo group in the corresponding 1-substituted 3*H*-naphtho[1,2,3-*de*]quinoline-2,7-diones **Ia**–**Id** (Scheme 1) [2–4].

Scheme 1.



Ia–Id **IIa–IId**

R = Me, X = H (**a**), O_2N (**b**); R = H, X = SO_3Na (**c**), Cl (**d**); R' = Alk, Ar.

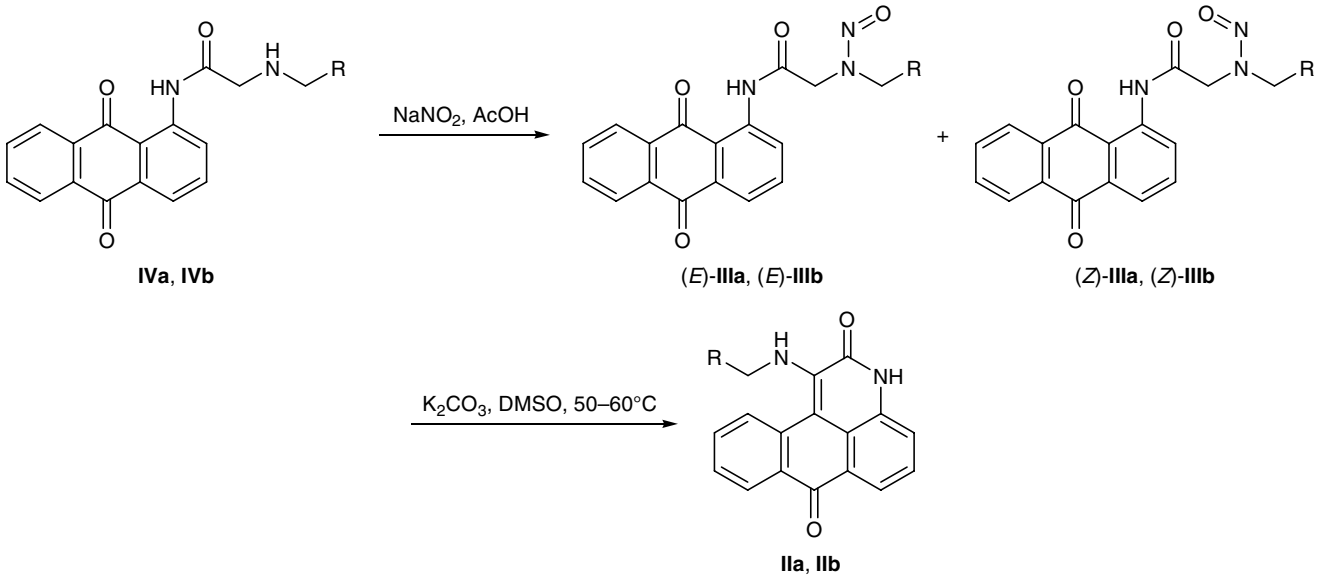
However, initial compounds **Ia**–**Id** are difficultly accessible, and the yields of the target alkylamino derivatives are often poor. The alkylation of 1-amino-3*H*-naphtho[1,2,3-*de*]quinoline-2,7-dione (**I**, R = H, X = NH_2) does not give compounds **II** but involves the endocyclic nitrogen atom [5].

We have found that readily available 1-(*N*-nitroso-*N*-alkylaminoacetamido)-9,10-anthraquinones **IIIa** and **IIIb** undergo cyclization to alkylaminonaphthoquinolines **IIa** and **IIb** under mild conditions (Scheme 2). Presumably, the intramolecular ring closure is followed by elimination of the nitroso group, for analogous cyclization of the precursors of nitrosamines **IIIa** and **IIIb**, 1-(alkylaminoacetamido)-9,10-anthraquinones **IVa** and **IVb**, does not occur under similar conditions. The reaction is also accompanied by decomposition of nitrosamines **IIIa** and **IIIb** with formation of 1-amino-9,10-anthraquinone which was detected by TLC in the reaction mixture.

It is known that electron-withdrawing substituents in the acetylamino group of acetylaminoanthraquinones facilitate their cyclization to the corresponding 3*H*-naphtho[1,2,3-*de*]quinoline-2,7-diones [6]. In the ^{1}H NMR spectra of both *E* and *Z* isomers of **IIIa** and **IIIb**, singlets from the methylene protons are displaced downfield by 1.2–2.0 ppm relative to the corresponding signals of 1-(alkylaminoacetamido)-9,10-anthraquinones **IVa** and **IVb**, so that they appear approximately in the same region as the methylene proton signal of 1-chloroacetylamino-9,10-anthraquinone (δ 4.55 ppm). The *N*-nitrosoalkylamino groups in **IIIa** and **IIIb** are stronger electron acceptors than chlorine atom, and this factor is likely to favor the cyclization of **III** into **II**.

1-Ethylamino-3*H*-naphtho[1,2,3-*de*]quinoline-2,7-dione (IIa). A mixture of 0.58 g (1.7 mmol) of compound **IIIa**, 8 ml of dimethyl sulfoxide, 1.5 g of anhydrous sodium sulfate, and 1 g of potassium carbonate was stirred for 1 h at 60°C. The mixture was cooled and poured onto 100 g of ice, the precipitate was filtered off and treated with 6 ml of benzene at 60–70°C, the mixture was cooled, and the precipitate was filtered off. This procedure was repeated once more. Yield 0.50 g (70%), mp 270–273°C. UV spectrum (DMF), λ_{max}, nm (log ε): 345 (3.80), 445 (4.20) (cf. [4]). ^{1}H NMR spectrum, δ, ppm: 1.06 t (3H, CH_3, J = 7 Hz), 3.05 m (2H, CH_2), 7.50–7.62 m and 7.98–8.07 m (7H, H_{arom}), 8.28 m (1H, NH), 12.40 s (1H, NH). Found, %: C 73.84; H 4.79; N 9.32. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.48; H 4.82; N 9.65.

Scheme 2.



IVa, **IVb** (*E*)-**IIIa**, (*E*)-**IIIb** (*Z*)-**IIIa**, (*Z*)-**IIIb**

IIa, **IIb**

R = Me (**a**), Ph (**b**).

1-Benzylamino-3*H*-naphtho[1,2,3-*de*]quinoline-2,7-dione (IIb) was synthesized in a similar way from 1.5 g (4.2 mmol) of compound **IIIb**, 15 ml of DMSO, 2 g of Na_2SO_4, and 2 g of K_2CO_3. Yield 1 g (75%), mp 280–283°C. UV spectrum (DMF), λ_{max}, nm (logε): 345 (3.70), 445 (4.17). ^{1}H NMR spectrum, δ, ppm: 4.32 d (2H, CH_2, J = 7 Hz), 7.01–7.18 m (5H, C_6H_5), 7.90 t (1H, NH, J = 8 Hz), 7.50–7.51 m and 8.00–8.40 m (7H, H_{arom}), 12.35 s (1H, NH). Found, %: C 78.01; H 4.41; N 8.15. $C_{23}H_{16}N_2O_2$. Calculated, %: C 78.40; H 4.54; N 7.95.

***N*-(9,10-Dioxo-9,10-dihydroanthracen-1-yl)-2-[ethyl(nitroso)amino]acetamide (IIIa).** Sodium nitrite, 0.8 g (11 mmol), was added under stirring at 20–22°C to a solution of 1.23 g (4 mmol) of compound **IVa** in 30 ml of acetic acid. After 30–40 min, the precipitate was filtered off and washed with water (10 ml), ethanol (10 ml), and diethyl ether (10 ml). Yield 1.20 g (89%), mp 134–136°C. According to the ^{1}H NMR data (taking into account that signals of *E* isomers appear in a weaker field [7]), compound **IIIa** was a mixture of *Z* and *E* isomers at a ratio of 3:1. ^{1}H NMR spectrum, δ, ppm: 1.06 t (0.76H, CH_3, J = 8 Hz); 1.45 t (2.25H, CH_3, J = 8 Hz); 3.70 q (0.5H, C**H**$_2$CH$_3$, *Z* isomer, J = 8 Hz); 4.40 q (1.5H, C**H**$_2$CH$_3$, *E* isomer, J = 8 Hz); 4.57 s (1.5H, $COCH_2$, *Z* isomer); 5.31 s (0.5H, $COCH_2$, *E* isomer); 7.85–8.20 m, 8.18–8.26 m, and 8.86–8.95 m (7H, H_{arom}); 12.09 s (0.75H, NH, *Z* isomer); 12.15 s (0.25H, NH, *E* isomer). Found, %: C 64.40; H 4.33; N 11.95. $C_{18}H_{15}N_3O_4$. Calculated, %: C 64.09; H 4.45; N 12.46.

2-[Benzyl(nitroso)amino]-*N*-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide (IIIb). Sodium nitrite, 1.2 g (17 mmol), was added under stirring at 20–22°C to a solution of 3.00 g (7.5 mmol) of compound **IVb** in 50 ml of acetic acid. The product was isolated as described above for **IIIa**. Yield 2.80 g (87%) (a mixture of *Z* and *E* isomers at a ratio of 1:2), mp 178–180°C. ^{1}H NMR spectrum, δ, ppm: 4.48 s (1.32H, C**H**$_2$Ph, *E* isomer); 4.91 s (0.66H, C**H**$_2$Ph, *Z* isomer); 5.30 s (0.66H, $COCH_2$, *Z* isomer); 5.59 s (1.32H, $COCH_2$, *E* isomer); 7.40–7.52 m, 7.89–7.97 m, 8.23–8.30 m, and 8.79–8.90 m (12H, H_{arom}); 12.01 s (0.75H, NH, *Z* isomer); 12.20 s (0.25H, NH, *E* isomer). Found, %: C 69.17; H 4.25; N 10.44. $C_{23}H_{17}N_3O_4$. Calculated, %: C 69.17; H 4.26; N 10.52.

***N*-(9,10-Dioxo-9,10-dihydroanthracen-1-yl)-2-(ethylamino)acetamide (IVa).** A mixture of 2.00 g (6.6 mmol) of 2-chloro-*N*-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide, 30 ml of dioxane, and 5 ml of 70% aqueous ethylamine was heated for 2 h at 60°C. After cooling, the yellow precipitate was filtered off and purified by recrystallization from ethanol. Yield 1.63 g (79%), mp 138–140°C. ^{1}H NMR spectrum, δ, ppm: 1.19 t (3H, CH_3, J = 6 Hz); 2.66 q (2H, C**H**$_2$CH$_3$, J = 6 Hz); 3.25 br.s (1H, N**H**CH$_2$); 3.37 br.s (2H, C**H**$_2$NH); 7.83–7.92 m, 8.13–8.21 m, and 9.10–9.12 m (7H, H_{arom}); 12.10–13.60 br.s (1H, NHCO). Found, %: C 70.42; H 5.07; N 8.72. $C_{18}H_{16}N_2O_3$. Calculated, %: C 70.12; H 5.19; N 9.09.

The ^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer from solutions in DMSO-d_6

using tetramethylsilane as internal reference. The UV spectra were measured on a Helios ε spectrophotometer. The progress of reactions and the purity of products were monitored by TLC on Silufol plates (toluene–acetone, 10:1). 2-Chloro-*N*-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide was synthesized by the procedure described in [8].

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