

SHORT  
COMMUNICATIONS

## A Simple Route to 2,6-Dihydronaphtho[1,2,3-*cd*]indol-6-ones

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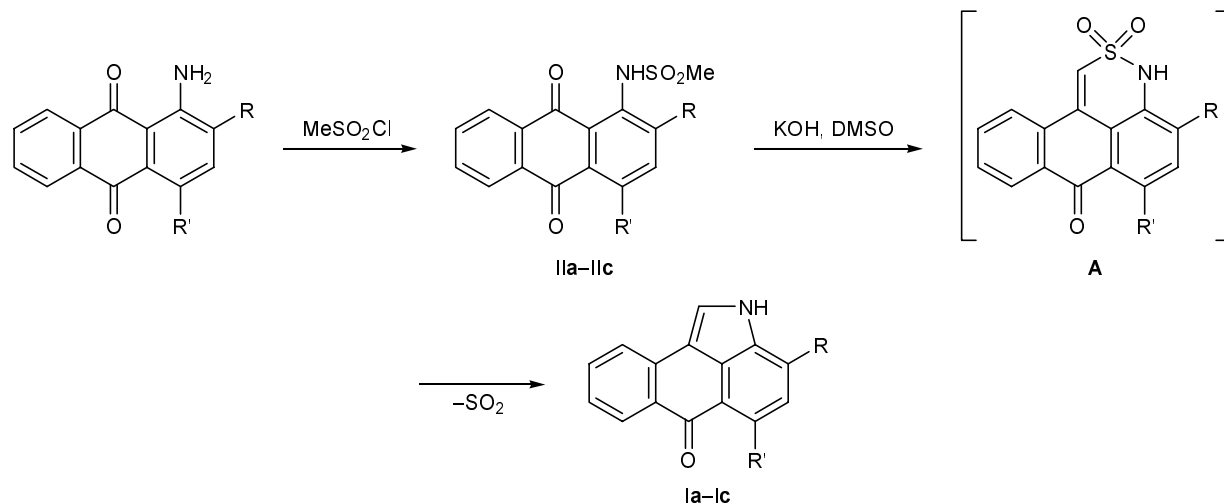
2,6-Dihydronaphtho[1,2,3-*cd*]indol-6-ones **Ia–Ic** exhibit luminescent properties and are suitable for practical purposes [1]; however, their application is restricted by relatively low accessibility. Previously known methods for the preparation of pyrrolanthrone (**Ia**) from 4-aminoanthrone and formic acid and from 1-amino-2,7-dihydro-3*H*-naphtho[1,2,3-*de*]indole [2] have recently been supplemented by the cyclization of *S,S*-disubstituted *N*-(9,10-dioxoanthracen-1-yl)sulfoximides [3].

We have found a simpler procedure for the synthesis of pyrrolanthrones **Ia–Ic** from *N*-(9,10-dioxoanthracen-1-yl)methanesulfonamides **Ila–Ilc** which are available from the corresponding 1-amino-9,10-anthraquinones. Presumably, this cyclization is an example of formation of a pyrrole ring [4] from unsaturated sultam ring; however, we failed to detect structure **A** by NMR spectroscopy when the transformation **Ila** → **Ia** was performed in DMSO-*d*<sub>6</sub> in an NMR ampule. We believe that the proposed procedure for the syn-

thesis of 2,6-dihydronaphtho[1,2,3-*cd*]indol-6-ones in combination with high activity of the pyrrole ring therein toward electrophilic reagents will be helpful in studying the properties of these compounds in more detail.

***N*-(9,10-Dioxoanthracen-1-yl)methanesulfonamide (Ila).** Methanesulfonyl chloride, 0.5 ml, was added to a solution of 1 g (4.45 mmol) of 1-amino-9,10-anthraquinone in 6 ml of nitrobenzene. The mixture was stirred for 20 h at 120°C and cooled to 15°C, and the precipitate was filtered off, washed with alcohol, and recrystallized from 1,4-dioxane. Yield 1.23 g (91%), mp 219°C. <sup>1</sup>H NMR spectrum, δ, ppm: 11.85 s (1H, NH), 8.18–8.24 m (2H), 7.92–8.02 m (5H), 3.30 s (3H, Me). Found, %: C 59.82; H 3.65; N 4.77. C<sub>15</sub>H<sub>11</sub>NO<sub>4</sub>S. Calculated, %: C 59.80; H 3.65; N 4.65.

***N*-(4-Hydroxy-9,10-dioxo-2-phenoxyanthracen-1-yl)methanesulfonamide (Ilb).** A mixture of 1 g (3.02 mmol) of 1-amino-4-hydroxy-2-phenoxy-9,10-anthraquinone and 4 ml of methanesulfonyl chloride



was heated for 8 h at 100°C. The mixture was cooled, and the precipitate was filtered off, washed with alcohol, and recrystallized from 1,4-dioxane. Yield 0.96 g (78%), mp 267–269°C. <sup>1</sup>H NMR spectrum, δ, ppm: 13.5 s (1H, OH), 11.4 s (1H, NH), 8.3 m (2H), 7.82 (2H), 7.47 m (2H), 7.24 m (2H), 7.33 m (1H), 6.51 s (1H), 3.40 s (3H, Me). Found, %: C 61.72; H 3.70; N 3.42. C<sub>21</sub>H<sub>15</sub>NO<sub>6</sub>S. Calculated, %: C 61.61; H 3.67; N 3.42.

**N-[2-(4-*tert*-Butylphenoxy)-4-hydroxy-9,10-dioxoanthracen-1-yl]methanesulfonamide (IIc)** was synthesized as described above for compound **IIb** from 1 g (2.58 mmol) of 1-amino-2-(4-*tert*-butylphenoxy)-4-hydroxy-9,10-anthraquinone. Yield 0.72 g (60%), mp 280–281°C. <sup>1</sup>H NMR spectrum, δ, ppm: 13.5 s (1H, OH), 11.4 s (1H, NH), 8.3 m (2H), 7.82 (2H), 7.47 m (2H), 7.25 m (2H), 6.50 s (1H), 3.50 s (3H, Me), 1.40 s (9H, *t*-Bu). Found, %: C 64.67; H 5.06; N 3.02. C<sub>25</sub>H<sub>23</sub>NO<sub>6</sub>S. Calculated, %: C 64.52; H 4.94; N 3.01.

**2,6-Dihydronaphtho[1,2,3-*cd*]indol-6-one (Ia).** Finely powdered KOH, 0.5 g (8.90 mmol), was added to a solution of 0.5 g (1.66 mmol) of compound **IIa** in 10 ml of DMSO. The mixture was stirred for 6 h at 110–115°C, cooled, and poured into 5% acetic acid (0–5°C, 200 ml). The precipitate was filtered off and recrystallized twice from benzene–ethanol (5:1). Yield 0.29 g (87%), mp 255–257°C. <sup>1</sup>H NMR spectrum, δ, ppm: 12.00 s (1H, NH), 8.45 br.s (1H, CH, pyrrole), 8.32 d (1H, *J* = 7.8 Hz), 8.12 d (1H, *J* = 7.8 Hz), 7.97 d (1H, *J* = 7.5 Hz), 7.88 d (1H, *J* = 7.5 Hz), 7.70 br.t (1H, *J* = 7.0 Hz), 7.52 br.t (1H, *J* = 7.5 Hz), 7.42 br.t (1H, *J* = 7.0 Hz). Found, %: C 82.17; H 4.14; N 6.38. C<sub>15</sub>H<sub>9</sub>NO. Calculated, %: C 82.19; H 4.14; N 6.39.

**5-Hydroxy-3-phenoxy-2,6-dihydronaphtho[1,2,3-*cd*]indol-6-one (Ib).** A mixture 0.5 g (1.22 mmol) of compound **IIb**, 10 ml of DMSO, and 0.5 g (8.90 mmol) of finely powdered potassium hydroxide was stirred for 6 h at 120°C. The mixture was cooled and poured into 5% acetic acid (0–5°C, 200 ml), and the precipitate was filtered off and recryst-

allized from toluene. Yield 0.39 g (77%), mp 289–291°C. <sup>1</sup>H NMR spectrum, δ, ppm: 11.80 s (1H, OH), 8.59 br.s (1H, NH), 8.53 d (1H, CH, pyrrole), 7.96 d (1H, *J* = 7.8 Hz), 7.83 d (1H, *J* = 3.5 Hz), 7.68 t (1H, *J* = 7.0 Hz), 7.45 m (3H), 7.29 t (1H, *J* = 7.2 Hz), 7.23 m (2H), 6.4 s (1H). Found, %: C 77.05; H 3.98; N 4.26. C<sub>21</sub>H<sub>13</sub>NO<sub>3</sub>. Calculated, %: C 77.06; H 3.98; N 4.28.

**3-(4-*tert*-Butylphenoxy)-5-hydroxy-2,6-dihydronaphtho[1,2,3-*cd*]indol-6-one (Ic)** was synthesized as described above for compound **Ib** from 0.5 g (1.07 mmol) of amide **IIc**. Yield 0.41 g (88%), mp 287–289°C. <sup>1</sup>H NMR spectrum, δ, ppm: 11.80 s (1H, OH), 8.65 br.s (1H, NH), 8.54 d (1H, CH, pyrrole), 7.95 d (1H, *J* = 7.8 Hz), 7.84 d (1H, *J* = 3.5 Hz), 7.68 t (1H, *J* = 7.0 Hz), 7.47 m (3H), 7.14 m (2H), 6.4 s (1H), 1.4 s (9H, *t*-Bu). Found, %: C 78.56; H 5.57; N 3.67. C<sub>25</sub>H<sub>21</sub>NO<sub>3</sub>. Calculated, %: C 78.33; H 5.48; N 3.65.

The <sup>1</sup>H NMR spectra were recorded on a Bruker DRX-500 instrument (500 MHz) from solutions in DMSO-*d*<sub>6</sub> using TMS as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol plates using toluene–acetone (10:1) as eluent.

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