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Synthesis of 6*H*-Naphtho[1,2,3-*cd*]indol-6-ones

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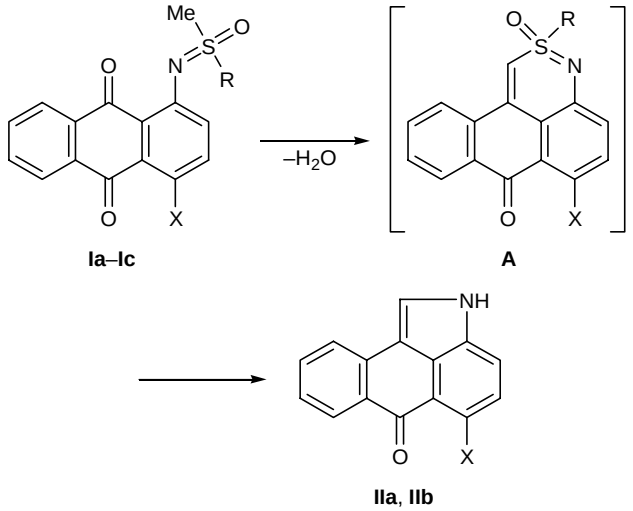
Abstract—*S*,*S*-Dimethyl- and *S*-methyl-*S*-phenyl-*N*-(9,10-anthraquinon-1-yl)sulfoximides are converted into 6*H*-naphtho[1,2,3-*cd*]indol-6-ones on heating in polar aprotic solvents.

6*H*-Naphtho[1,2,3-*cd*]indol-6-ones (pyrrolanthrones) are luminophors [1]. Pyrrolanthrone having no substituent in the pyrrole fragment is synthesized by heating difficultly accessible 4-aminoanthrone in formic acid or by ring contraction of 1-diazoanthrapyridone [2]. Pyrrolanthrones substituted at the nitrogen or pyrrole carbon atom can be prepared by heating 1-chloro-9,10-anthraquinone with N-substituted α-amino acids in boiling higher alcohols in the presence of copper(I) salts or by thermolysis of 1-(dialkylamino)anthraquinones [3].

We have found that heating of substituted *N*-(9,10-anthraquinon-1-yl)sulfoximides **Ia**–**Ic**, which are obtained by the procedure reported in [4], in dimethyl sulfoxide in the presence of potassium carbonate or in tetrahydrofuran in the presence of potassium hydroxide results in formation of pyrrolanthrones **IIa** and **IIb** in nearly quantitative yield. Presumably, initially formed cyclic sulfoximide **A** undergoes fragmentation (probably, with participation of water liberated in the first stage; Scheme 1); the structure of the other products thus formed was not determined.

Scheme 1.



Ia–**Ic** **A** **IIa**, **IIb**

I, X = H, R = Me (**a**), Ph (**b**); X = Cl, R = Ph (**c**);
II, X = H (**a**), Cl (**b**).

EXPERIMENTAL

The ^{1}H NMR spectra were obtained on a Bruker DRX-500 spectrometer (500 MHz) in DMSO-d_6 using tetramethylsilane as internal reference. The IR spectra were recorded on a Specord M-80 instrument in KBr. The molecular weight of compound **IIa** was determined by mass spectrometry on a Finnigan MAT Inkos instrument (70 eV). The progress of reactions and the purity of products were monitored by TLC on Silufol plates using toluene–acetone (10:1) as eluent.

6*H*-Naphtho[1,2,3-*cd*]indol-6-one (IIa). *a*. To a solution of 0.65 g (2.2 mmol) of sulfoximide **Ia** in 50 ml of DMSO we added under stirring at 100°C 0.7 g (5 mmol) of K_2CO_3. After 2 min, the mixture was poured into 300 ml of 5% acetic acid cooled to 0–5°C. The bright yellow precipitate was filtered off, dried, and recrystallized from chloroform. Yield 0.44 g (95%), mp 251–252°C. IR spectrum, ν, cm^{-1}: 3472 (NH), 1645 (C=O). ^{1}H NMR spectrum, δ, ppm: 12.00 s (1H, NH), 8.45 s (1H, 1-H), 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 82.18; H 4.14; N 6.39. M^+ 219. $C_{15}H_9NO$. Calculated, %: C 82.192; H 4.14; N 6.392. *M* 219.

b. To a solution of 0.79 g (2.2 mmol) of sulfoximide **Ib** in 15 ml of THF we added 0.7 g (12.5 mmol) of potassium hydroxide in 15 ml of ethanol. The mixture was heated for 5 min at 60–65°C and poured into 300 ml of 5% acetic acid cooled to 0–5°C. The precipitate was filtered off and recrystallized from chloroform. Yield 0.47 g (99%), mp 252°C.

5-Chloro-6*H*-naphtho[1,2,3-*cd*]indol-6-one (IIb). To a solution of 0.26 g (6.6 mmol) of sulfoximide **Ic** in 20 ml of DMSO we added under stirring at 90–100°C 0.3 g (2.2 mmol) of K_2CO_3. After 5 min, the mixture was poured into 100 ml of 5% acetic acid cooled to 0–5°C. The precipitate was filtered off and recrystallized from toluene. Yield 0.195 g (90%), mp 312–314°C. ^{1}H NMR spectrum, δ, ppm: 12.13 s (1H, NH), 8.49 s (1H, 1-H), 8.30 d (1H, *J* = 8.0 Hz), 8.11 d (1H, *J* = 7.8 Hz), 7.84 d (1H, *J* = 8.0 Hz), 7.71 br.t (1H, *J* = 7.0 Hz), 7.47 d (1H, *J* = 8.0 Hz), 7.43 br.t (1H, *J* = 7.0 Hz). Found, %: C 71.07; H 3.18; N 5.53. $C_{15}H_8ClNO$. Calculated, %: C 70.95; H 3.18; N 5.60.

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