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SHORT COMMUNICATIONS

Transformation of Hydroxyiminoacetoacetanilides in Sulfuric Acid

D. I. Ilyushkin, E. S. Semichenko, and G. A. Suboch

Siberian State Technological University, pr. Mira 82, Krasnoyarsk, 660049 Russia
e-mail: organic@scn.ru

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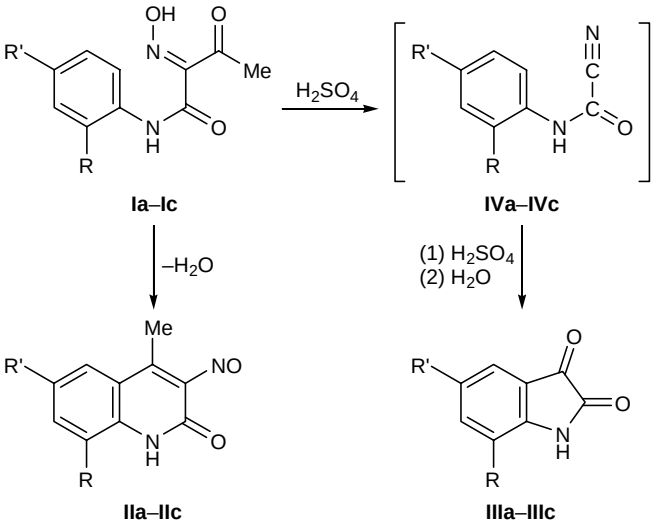
Cyclization of acetoacetanilides on heating in sulfuric acid underlies the general procedure for synthesis of quinolines according to Knorr [1]. However, there are no published data on the behavior of α-hydroxyimino-β-oxocarboxanilides under similar conditions.

We have found that heating of hydroxyiminoacetoacetanilides **Ia**–**Ic** in sulfuric acid, instead of the expected nitrosoquinolines **IIa**–**IIc**, leads to formation of isatins **IIIa**–**IIIc** in 14 to 44% yield. Presumably, Beckmann fragmentation of **Ia**–**Ic** gives cyanoformanilides **IVa**–**IVc** which are converted into the corresponding isatins. The low yields of **IIIa**–**IIIc** may be due to concurrent processes, e.g., transformation into phenyl isocyanate.

Anilide **Ia**–**Ic**, 0.0485 mol, was added over a period of 15 min under stirring to 20 ml (0.349 mol) of concentrated sulfuric acid heated to 75°C, maintaining the temperature below 85°C. The mixture was stirred for 20 min at 80–85°C, cooled, and poured onto 200 g of ice. The precipitate of isatin **IIIb** or **IIIc** was filtered off, while compound **IIIa** was isolated by extraction into chloroform (5×200 ml). The products were purified as follows. Crude isatin **IIIa**–**IIIc** was dissolved in an appropriate amount of 2 N aqueous sodium hydroxide, 0.1 g of charcoal was added, the mixture was stirred for 30 min at 80°C, a 1.5-fold amount of glacial acetic acid was added, and the mixture was filtered. Concentrated hydrochloric acid was added to the filtrate to precipitate compound **IIIa**–**IIIc**. Isatin (**IIIa**): yield 14%, yellow–red crystals, mp 203.5°C (from EtOH) [2]. 7-Methylisatin (**IIIb**): yield 44%, yellow–red crystals, mp 270°C (from EtOH); published data [3]: mp 268–270°C. 5,7-Dimethylisatin (**IIIc**): yield 14.4%, yellowish–red crystals, mp 247°C (from EtOH); published data [3]: mp 247–249°C.



I–**IV**, R = R' = H (**a**), R = Me, R' = H (**b**); R = R' = Me (**c**).

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using ethyl acetate–chloroform (1:3) as eluent; detection under UV light. The melting points of compounds **IIIa**–**IIIc** coincided with published data.

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