DEHYDROGENATION OF CERTAIN INDOLINE DERIVATIVES INTO INDOLES

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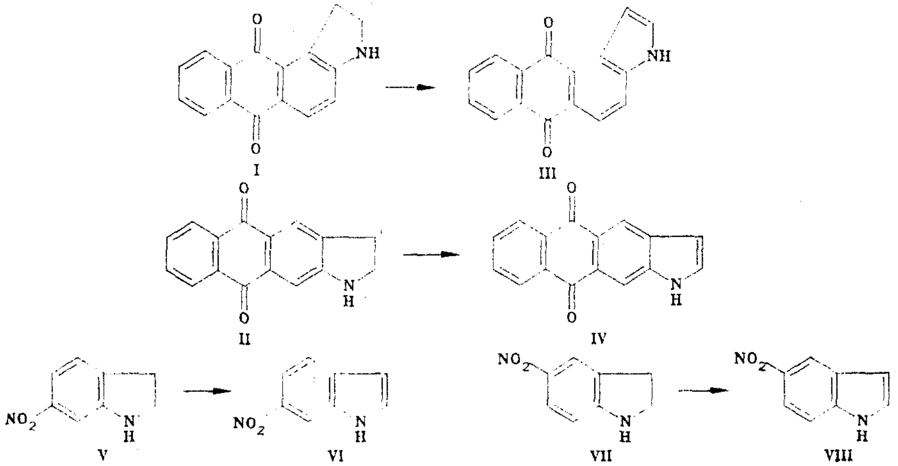
The dehydrogenation was studied of certain acceptor indoline derivatives in nitrobenzene, in the presence of cadmium, sodium, and potassium carbonates. A method has been proposed for a mild dehydrogenation of certain acceptor groups containing indoline derivatives in nitrobenzene, in the presence of potassium carbonate.

For the dehydrogenation of indoline derivatives to indole, most diverse dehydrogenating agents are used, which include 2,3-dicyano-4,5-dichloro-p-benzoquinone, a complex of $CuCl_2$ with pyridine, manganese dioxide, and others [1]. We studied the dehydrogenation of certain acceptor groups containing indoline derivatives by boiling in nitromethane or nitrobenzene in the presence of cadmium, sodium, and potassium carbonates.

On boiling in nitromethane in the presence of 1 mole of cadmium carbonate, the previously synthesized by us [2] naphtho[2,3-e]indoline-6,11-dione (I) and naphtho[2,3-f]indoline-5,10-dione (II) were converted in a quantitative yield into naphtho[2,3-e]indole-6,11-dione (III) and naphtho[2,3-f]indole-5,10-dione (IV). Replacement of cadmium carbonate by sodium or potassium carbonate did not influence the duration of the dehydrogenation reaction in nitromethane.

On boiling in nitromethane for 20 h in the presence of 1 mole of cadmium, sodium and, and potassium carbonates, 6-nitroindoline (V) was converted into 6-nitroindole (VI) in a 10% yield. Dehydrogenation of 5-nitroindoline (VII) under similar conditions could not be accomplished.

If instead of nitromethane, nitrobenzene was used as the solvent, the duration of the dehydrogenation reaction was considerably shortened. Thus, on boiling in nitrobenzene for 1 h in the presence of 1 mole of cadmium or sodium carbonate, compounds I and II were converted into compounds III and IV. When potassium carbonate was used, the time of the dehydrogenation reaction was reduced to 5 min. 6-Nitroindoline and 5-nitroindoline were boiled in nitrobenzene for 2 h in the presence of potassium carbonate and were converted into 6-nitroindole (VI) and 5-nitroindole (VIII) in a yield of 82 and 53%, respectively.



Thus, we proposed a method of mild dehydrogenation of certain acceptor groups containing indoline derivatives by boiling in nitrobenzene in the presence of potassium carbonate.

Compounds II, IV, VI, and VIII were identical according to IR, PMR, and mass spectra to previously obtained samples [2, 3]. The elemental analysis data corresponded to the calculated values.

It should be noted that the dehydrogenation of indoline to indole also proceeds readily under the above-described conditions.

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EXPERIMENTAL

The PMR spectra were run on a Bruker WP-200 SY spectrometer (in $CDCl_3$), using TMS as internal standard, the IR spectra on a UR-20 spectrophotometer with NaCl and LiF prisms (in mineral oil), rate of scanning 160, spectral width of the slit 4 cm^{-1}.

The mass spectra were obtained on a Varian MA 311A mass spectrometer, at an ionizing voltage of 70 eV, cathode emission current 1 mA, accelerating voltage 3 kV. The evaporation temperature of the samples was from 30 to 300°C in a linearly programmed regime. The course of the reaction and the purity of the compounds were monitored on plates with an immobilized Silufol UV-254 silica gel layer.

Naphtho[2,3-e]indole-6,11-dione (II, $C_{16}H_9NO_2$). A. A 0.09 portion (0.05 mmole) of cadmium carbonate was added to a solution of 0.12 g (0.5 mmole) of compound I in 50 ml of nitromethane, and the mixture was boiled for 10 h. The precipitate was filtered off, the filtrate was evaporated under vacuum, and the dione II was obtained in a yield of 0.11 g (92%). Mp 246°C (from alcohol).

B. A 0.07 g portion (0.5 mmole) of potassium carbonate was added to a solution of 0.12 g (0.5 mmole) of compound I in 5 ml of nitrobenzene and the mixture obtained was boiled for 5 min. The precipitate was filtered off. Compound II was separated from nitrobenzene by steam distillation in a yield of 0.10 g (83%), mp 246°C (from alcohol).

Naphtho[2,3-g]indole-5,10-dione (VI, $C_{16}H_9NO_2$) was obtained in a similar way as compound II by methods **A** and **B**. By method **A**, mp 320°C (from alcohol), yield 92%; by method **B**, mp 320°C (from alcohol), yield 83%.

6-Nitroindole (VI, $C_8H_6N_2O_2$). A 0.14 g portion (1.0 mmole) of potassium carbonate was added to a solution of 0.17 g (1 mmole) of indoline V in 5 ml of nitrobenzene and the mixture was boiled for 2 h. The precipitate was filtered. Compound VI was separated from nitrobenzene by steam distillation in a yield of 0.14 g (82%), mp 144-145°C (from alcohol).

5-Nitroindole (VIII, $C_8H_6N_2O_2$) was obtained in a similar way as compound VI in a yield of 53%, mp 141-142°C (from alcohol).

LITERATURE CITED

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