NEW METHOD FOR THE PREPARATION OF δ-CARBOLINE DERIVATIVES

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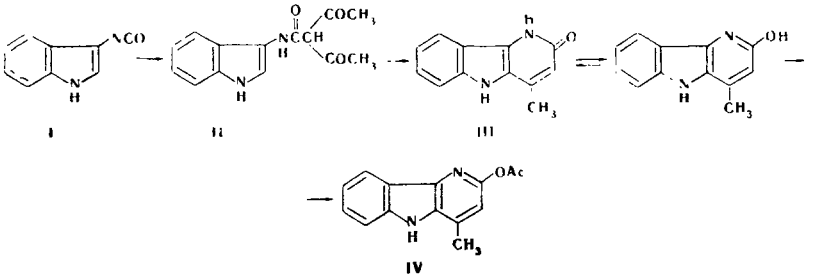
We have found a new method for the synthesis of difficult-to-obtain δ-carbolines [1] starting from 3-indolyl isocyanate (I) [2] and β-dicarbonyl compounds (acetylacetone and acetoacetic and malonic esters).

Thus 3-(2-acetyl-1,3-dioxobutylamino)indole (II, mp 152-153°), obtained by reaction of I with sodium acetylacetonate, is readily cyclized to 2-hydroxy-4-methyl-5H-pyrido[2,3-b]indole (III, mp 303-305°) when it is heated in alkali (94% yield) or treated with concentrated hydrochloric acid (in 72% yield, hydrochloride mp 318-320°).

The UV spectrum of an alcohol solution of III contains, in addition to absorption bands in the short-wave region of the spectrum characteristic for indole [λ_{max} 220 and 268 nm (log ε 4.31 and 3.83)], a long-wave absorption band [λ_{max} 328 nm (log ε 3.93)].



I II III

IV

The PMR spectrum of a solution of III in $(CD_3)_2SO$ has the following signals characteristic for δ-carbolines: at 8.08 (d, 1H, 9-H) [3], 6.29 (s, 1H, 3-H), 2.45 (s, 3H, CH_3), 11.36 (s, 1H, NH), and 7.04-7.52 ppm (m, 3H, 6-H, 7-H, and 8-H).

Compound III gives a red coloration with $FeCl_3$ and forms salts with mineral acids; it forms an O-acetyl derivative (IV, mp 215-216°) when it is heated in acetic anhydride. The chemical shifts of the protons in the PMR spectrum of a solution of IV in $(CD_3)_2SO$ have the same value as in the PMR spectrum of III; the only difference is that the singlet of the 3-H proton is at weaker field at 7.03 ppm. The absorption band of a carbonyl group appears at 1780 cm^{-1} ($OCOCH_3$) in the IR spectrum of a mineral oil suspension of IV.

The structures of the compounds obtained were confirmed by data from the IR, UV, and mass spectra and also by the results of elementary analysis.

LITERATURE CITED

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