NEW REARRANGEMENT IN THE INDOLE SERIES

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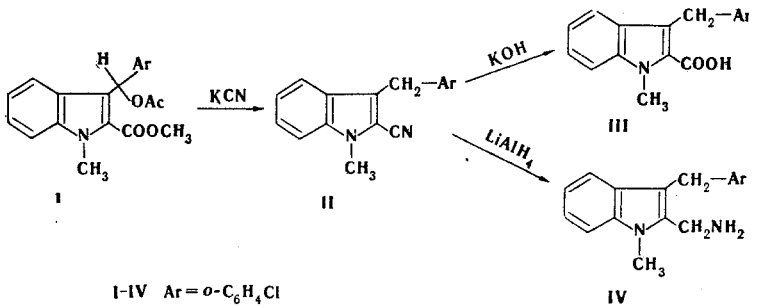
A new oxidative rearrangement of 3-(α-methylaminobenzyl)indole to 2-cyano-3-benzoylindole by treatment with KCN in air was discovered in 1972 [1] and studied in detail in [2]. In contrast to what was described in [1, 2], we have found that treatment of indole I, which contains an α-acetoxybenzyl group in the 3 position [3], with KCN in alcohol gives 1-methyl-2-cyano-3-benzylindole (II) (mp 108°) in 85% yield and is not accompanied by oxidation. Di(3-indolyl)phenylmethane is formed as a side product.



I

II

III

I-IV Ar = o-C_6H_4Cl

IV

The PMR spectrum of II contains signals of aromatic protons (8 H, 7.3 ppm), of an N—CH_3 group (s 3H, 3.98 ppm), and a CH_2 group (s, 2H, 4.51 ppm). The IR spectrum does not contain CO bands but does contain bands of stretching vibrations of a C≡N group (2250 cm^{-1}). Acid III (mp 220°) was obtained when nitrile II was refluxed for 10 h in ethylene glycol with KOH in a stream of nitrogen. IR spectrum: 1680 cm^{-1} (COOH). Reduction of nitrile II with $LiAlH_4$ in ether gives 1-methyl-2-aminomethyl-3-benzylindole (IV) in 75% yield; the product was isolated in the form of the hydrochloride (mp 254°) and hydrosulfate (mp 215°) salts. The resistance of nitrile II to oxidation is apparently explained by the presence of a substituent attached to the nitrogen atom. The introduction of a cyano group in the reaction with 1-methyl-2-carboxy-3-(α-chlorobenzyl)indole required more severe conditions and gave a product in low yield (15%).

All of the isolated compounds gave one spot on the thin-layer chromatogram in a cyclohexane—ethyl acetate system (3:1) and had a satisfactory elementary analysis.

LITERATURE CITED

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3. N. A. Kogan and M. I. Vlasova, Khim. Geterotsikl. Soedin., 1003 (1974).

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