REACTION OF MONOCHLOROACETIC ANHYDRIDE WITH 2-CYANOMETHYLAZINES

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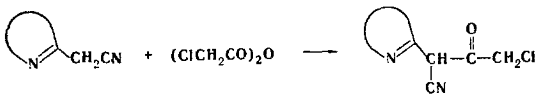
2-Cyanomethylpyridine (Ia) and 2-cyanomethylquinoline (Ib) are acylated by monochloroacetic anhydride at the carbon atom of the methylene group when an equimolar mixture of the starting reagents is refluxed for 30-60 min in benzene or toluene; the products are the corresponding α-chloro ketones [IIa, mp 157°C (from benzene), 89% yield; IIb, mp 196-197° (from toluene), 99% yield].

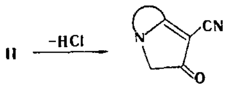


I

II

The UV spectrum of ketone IIa in ethanol contains three maxima at 240, 295, and 370 nm; this is in agreement with the data for ω-acetyl-2-cyanomethyl-pyridine – 238, 294, and 363 nm (in methanol) [1]. A singlet at 4.6 ppm from the protons of the methylene group is observed in the PMR spectra of II in $CDCl_3$.

When ketones II are heated in inert solvents such as halobenzenes, they undergo intramolecular cyclization accompanied by splitting out of a molecule of hydrogen halide to give 1-cyano-2-(3H)ketopyrroloazaheterocycles III [IIIa, mp 230-231°C (from propanol) 98% yield; IIIb, mp 270° (from nitromethane), 89% yield].



III

The formation of a pyrrole ring is confirmed by a positive Ehrlich test, as a result of which dyes (styryls) are formed. The PMR spectra of III do not contain the signals of a methylidyne proton but do contain the signal of two protons of a methylene group at 5.57 ppm. This makes it possible to assume that the products exist in form III rather than in the enol form. The absorption band of a nitrile group is observed in the IR spectra of III at 2205 cm^{-1}. Good results were obtained for II and III on analysis for nitrogen.

LITERATURE CITED

1. C. D. Gutsche and H.-W. Voges, J. Org. Chem., 32, No. 9, 2685 (1967).

T. G. Shevchenko Kiev State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, p. 1147, August, 1976. Original article submitted February 13, 1976.