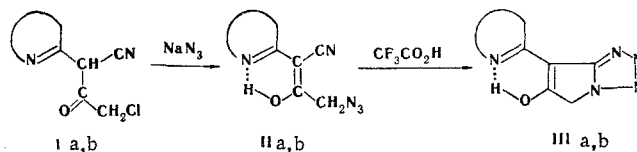


SYNTHESIS OF 6-HYDROXYPYRROLOTETRAZOLES

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We have previously [1] obtained 2-(2-pyridyl)-3-keto-4-chlorobutyronitrile (Ia) by acylation of 2-cyanomethylpyridine with monochloroacetic anhydride. 2-(2-Benzimidazolyl)-3-keto-4-chlorobutyronitrile [Ib, mp 278-279° (from n-propanol), 84% yield] is formed under the same conditions. These halo ketones react readily with sodium azide in aqueous dimethylformamide (DMF), during which 2-(2-hetaryl)-3-keto-4-azidobutyronitrile enols (II) [IIa, mp 158-159° (dec., from propanol), 83% yield; IIb, mp > 320° (from propanol), 99% yield] are formed.



In addition to the absorption band of a nitrile group at 2195-2200 cm^{-1} , the band of an azido group at 2120-2122 cm^{-1} is observed in the IR spectra of II. The PMR spectrum of IIa in deuterodimethyl sulfoxide, contains, in addition to the corresponding multiplets of the protons of a pyridine ring, a signal from two protons of a methylene group at 4.60 ppm and a broad signal from a chelated enolic proton at 15-16 ppm.

The azides obtained in this research are decomposed by mineral acids at room temperature with nitrogen evolution. However, when II are treated with trifluoroacetic acid at -15° , they are smoothly converted to the previously unknown 6-hydroxy-7-(2-hetaryl)pyrrolotetrazaoles III [IIIa, mp 233° (deg., from DMF), 93% yield; IIIb, mp > 320° (from DMF), 89% yield]. The IR spectra of III differ qualitatively from the spectra of II; specifically, they do not contain the absorption bands of nitrile and azido groups, whereas elementary analysis for nitrogen confirms the empirical formula of pyrrolotetrazaoles III. In addition to signals of aromatic protons, a two-proton singlet of a methylene group at 5.1-5.3 ppm is observed in the PMR spectra of III in trifluoroacetic acid.

Good results of analysis for nitrogen were obtained for all of the new compounds.

LITERATURE CITED

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