Pyrrolyl- and Indolyl(1,3-dioxo-2-indanylidene)acetonitriles (IIa-e). A solution of 0.5 mmole of reaction product I in 50 ml of acetonitrile was irradiated from above with the full light of the UV lamp, which was situated at a distance of 10 cm from the surface of the solution. The corresponding dye, which precipitated in the form of a finely crystalline substance, was removed periodically by filtration and was recrystallized from acetonitrile. Irradiation was carried out for 20-30 h until I was converted almost completely to the dye, which was verified by chromatography. The dyes were obtained in 44-61% yields.

LITERATURE CITED

PYRROLOINDOLES.
6.* NEW SYNTHESIS OF 1H,5H-PYRROLO[2,3-f]INDOLE AND 3H,6H-PYRROLO[3,2-e]INDOLE

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Ethyl pyruvate 1-acetyl-5-indolinylhydrazone was obtained by diazotization of 1-acetyl-5-aminoindoline with subsequent reduction of the diazonium salt and condensation of the hydrazine with ethyl pyruvate. A mixture of hydrogenated derivatives of linear and angular pyrroloindoles is formed as a result of cyclization of the hydrazone in polyphosphoric acid esters. Subsequent hydrolysis, decarboxylation, and dehydrogenation lead to 1H,5H-pyrrolo[2,3-f]indole and 3H,6H-pyrrolo[3,2-e]indole.

Unsubstituted linear pyrroloindoles are difficult to obtain, and little study has therefore been devoted to them. The literature contains only two reports describing the synthesis of 1H,5H-pyrrolo[2,3-f]indole (I) [2] and 1H,7H-pyrrolo[3,2-f]indole (II) [3], which were obtained by closing of two pyrrole rings with the benzene ring. Pyrroloindole II is formed only as an impurity in angular 1H,6H-pyrrolo[2,3-e]indole (III) in the cyclization of the corresponding hydrazone obtained from m-phenylenediamine (with subsequent hydrolysis and decarboxylation) [3]. Only angular 3H,6H-pyrrolo[3,2-e]indole (IV) was synthesized by the same method when p-phenylenediamine was used as the starting amine [4]. Pyrroloindole I is obtained as the principal product in the cyclization of 2,5-bis(β-aminoethyl)hydrazine hydrobromide (with subsequent dehydrobromination [2]. However, the difficulty with which starting hydrazine V is obtained, the large number of steps, and the low overall yield make this method unsuitable for the synthesis of pyrroloindole I.

*See [1] for Communication 5.
We have accomplished a new synthesis of linear pyrroloindole I via an alternative scheme, viz., by rearrangement of the pyrrole ring to an indoline ring.

For the synthesis of hydrazine VII, 5-amino-N-acetylindoline VI was diazotized by the usual method with subsequent reduction of the diazonium salt with stannous chloride. However, the isolation of the hydrazine in individual form presented considerable difficulties and was accompanied by great losses, and hydrazine VII was therefore condensed without isolation with ethyl pyruvate to give a mixture of syn and anti isomers of hydrazone VIII (in 80% yield). A characteristic bathochromic shift of 22 nm, which is in good agreement with the literature data [5], is observed in the UV spectra of the syn form. In the IR spectra of the syn isomer the absorption band of the carbonyl group is shifted 70 cm⁻¹ to the low wave-number region as compared with the absorption band of the carbonyl group for the anti isomer. A weak-field shift of the proton of the NH group tied up in an intramolecular hydrogen bond (12.0 ppm) is observed in the PMR spectrum of the syn isomer. Unfortunately, the signal of the NH group of the anti isomer is not observed in the spectrum in view of exchange broadening. However, as expected, the chemical shift of the 4-H proton differs substantially for the anti (7.64 ppm) and syn (7.07 ppm) isomers.

An alcohol solution of hydrogen chloride, a solution of sulfuric acid in acetic acid, and polyphosphoric acid esters were used as cyclizing agents for the indolization of hydrazone VIII; the best results (73%) were obtained in the case of polyphosphoric acid esters. According to the PMR spectral data, two isomers, viz., angular ester IX and linear ester X in a ratio of 1:4, are formed as a result of the cyclization of hydrazone VIII.

All attempts to separate the mixture obtained were unsuccessful. However, for identification we were able to isolate ester X by column chromatography.

Three signals that are split due to small spin–spin coupling constants, the greatest of which $J_{13} = 2$ Hz, are observed in the PMR spectrum for linear isomer X in the aromatic region, whereas the AB system that is characteristic for the ortho protons of the benzene ring is observed in the spectrum of angular isomer IX (see the experimental section).

Attempts to separate acids XI and XII, as well as their N-acetylated derivatives, were also unsuccessful, and the mixture of acids XI and XII was therefore also subjected to dehydrogenation–decarboxylation in the presence of Pd on carbon, as a result of which we obtained a mixture of pyrroloindoles I and IV in a ratio of 1:1, which was separated by column chromatography. The structures of pyrroloindoles I and IV were established on the basis of the results of elementary analysis and the NMR and IR spectral data and by comparison with the literature data [2, 4].

This disparity in the ratio of cyclization products IX and X and the isolated pyrroloindoles I and IV is evidently explained by the lower thermal stability of linear pyrroloindole I and its intermediates as compared with angular pyrroloindole IV.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of alcohol solutions of the compounds were recorded with a