filtrate was evaporated to give 6.3 g (40%) of 1,3-diphenyl-5,5-dioxo-3a,4,6,6a-tetrahydrothieno[3,4-c]pyrazole with mp 247-249° (from acetone). IR spectrum (KBr): 2900, 2800 (CH_2, CH), 1680 (C=N), 1280, 1150 cm^{-1} (SO_2).

The results of elementary analysis for C, H, N, and S were in agreement with the calculated values.

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ORIENTATION OF MESO-FORMYLATION IN METAL COMPLEXES OF ETIOPORPHYRIN-1

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It has recently been shown [1, 2] that the introduction of a second formyl group in the meso position of the porphyrin ring is possible in the Vilsmeier formylation of cobalt and copper complexes of octalkylporphyrins. It has been assumed [1] that a mixture of positional isomers of meso-diformyletioporphyrins is formed in the formylation of the Co complex of etioporphyrin, but the isolation and establishment of the structures of the individual compounds have not been accomplished. Attempts to carry out the reaction under similar conditions with the Co complex of octaethylporphyrin were unsuccessful because of the formation of a complex mixture of unidentifiable products [2]. However, only the meso-formyl- and α,γ-diformyloctaethylporphyrins were isolated and completely identified in the case of formylation of the Cu complex of octaethylporphyrin, on the basis of which conclusions were drawn regarding the direction of electrophilic substitution at the meso-carbon atoms in the porphyrin molecules.

We have established that the corresponding α,γ-diformyl- (I), α,β-diformyl- (II), and α,γ,β-triformyletioporphyrin (III) complexes are formed in 70-80% overall yields in the reaction of the Cu and Ni complexes of etioporphyrins for 3-4 h and of its Co complex for 5-10 min with $POCl_3$/DMF in dichloroethane at 50-60°. After demetallation of the complexes by treatment with concentrated sulfuric acid, the mixture of free phorphyrins was separated into individual compounds by means of thin-layer chromatography (TLC) on a loose layer of silica gel, and their structures were proved by means of their PMR and mass spectra. From the mass-spectral data for III it can be concluded that a small amount of $\alpha,\beta,\gamma,\delta$-tetraformyletioporphyrin, which is present in a sample of porphyrin III as an impurity, is also formed in the reaction.

The yields and ratios of the formylporphyrins formed are approximately identical in the case of all of the investigated etioporphyrin complexes. Thus porphyrin I was obtained in 25-30% yield, II was obtained in 43-46% yield, and III was obtained in 3-4% yield. The introduction of a second formyl group in the adjacent meso position of the porphyrin ring is consequently more preferable than introduction in the opposing position. This fact indicates the necessity for review and refinement of the theoretical concepts regarding the orientation of electrophilic substitution in the porphyrin series.

A characteristic feature of the electronic spectra of porphyrins II and III is the practically complete disappearance of the traditional (for porphyrins) four bands in the visible region and pronounced broadening of the "Soret band"; this indicates considerable distortion of the plane of the porphyrin ring of these compounds. Thus, for II, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$) in chloroform: 427 (102), 609 (7.3), 683 sh (5.12); for III, 431 (103), 630 (7.35), 694 sh (5.27). The spectrum of porphyrin I [λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 411.5 (190), 512 (7.05), 550 sh (6.2), 581 (7.34), 646 (5.15), and 666 sh (4.0)] coincides practically completely with the literature data [2] for α,γ-diformyletioporphyrin [λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 410 (126), 509 (6.76), 549 sh (6.02), 578 (6.92), and 646 (4.78)].

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NEW METHOD FOR THE SYNTHESIS OF PYRROQUINOLINES

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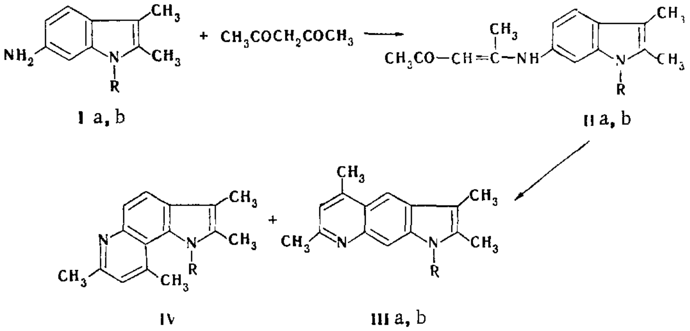
It has been found that the reaction of substituted 6-aminoindoles with 1,3-diketones in neutral media gives 3-(indolylamino)vinyl ketones, which, under the influence of strong acids, are cyclized to substituted pyrroquinolines with linear or angular fusion of the rings (see the diagram below).



I-III a R=H; b R=CH$_3$; IV R=H

The primary formation of one or the other isomer, i.e., the direction of the cyclization, depends basically on the steric requirements of the substituent attached to the pyrrole nitrogen atom of the indole.

Thus, when 4-[(2,3-dimethyl-6-indolyl)amino]pent-3-en-2-one (IIa, R=H), obtained by refluxing aminoindole Ia in excess acetylacetone (30 min), is heated in trifluoroacetic acid (for 1 h), it gives a mixture of two isomeric pyrroquinolines; the linear isomer (IIIa) and the angular isomer (IV) in a ratio of 4 : 1. 4,6,8,9-Tetramethylpyrro[3,2-g]quinoline (IIIa) was separated by recrystallization from ethanol and had mp 252-253°. The PMR spectrum (of a solution in dimethyl sulfoxide–acetone) contains three singlets of 3-H, 5-H, and 8-H protons (6.9, 7.68, and 7.85 ppm). 2,4,8,9-Tetramethylpyrro[2,3-f]quinoline (IV) was isolated preparatively on a loose thick layer of aluminum oxide and had mp 219-220°. The PMR spectrum (of a solution in the same solvent) contains a 3-H singlet (7.06 ppm) and two doublets of ortho-coupling 6-H (7.67 ppm, $J_{6,7}$=8 Hz) and 7-H (7.46 ppm, $J_{7,6}$=8 Hz) protons. Under the same conditions, 4-[(1,2,3-trimethyl-6-indolyl)amino]pent-3-en-2-one (IIb, R=CH$_3$) forms only linear 1,4,6,8,9-pentamethylpyrro[3,2-g]quinoline (IV) with mp 184-185°. The aromatic region in the spectrum of IIIa.

The results of elementary analysis (for C and H) and the molecular weight (obtained by mass spectrometry) for IIIa,b and IV were in agreement with the calculated values.

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