2-(1-Benzyl-2-benzimidazolylamino)-3-chloro-1,4-naphthoquinone (IXb). This compound was obtained in 40% yield as violet prisms with mp 174-175° (from o-xylene). IR spectrum: 1670 and 1660 cm⁻¹ (CO). Found: C 69.7; H 3.7; Cl 8.6; N 11.6%. C₁₂H₁₆CIN₃O₂. Calculated: C 69.7; H 3.8; Cl 8.6; N 11.6%.

2-(4-Phenyl-2-thiazolylamino)-3-chloro-1,4-naphthoquinone (XI). This compound was obtained in 36% yield as violet prisms with mp 217-218° (from o-xylene). Found: C 62.2; H 3.4; Cl 9.5; N 7.8; S 8.5%. C₁₉H₁₁C₁N₂O₂S. Calculated: C 62.2; H 3.0; Cl 9.7; N 7.6; S 8.7%.

5-Ethylbenzimidazo[1,2-a]naphtho[2,3-d]imidazole-7,12-dione (X) Hydrochloride. A solution of 1.3 g (3.7 mmole) of IXa in 10 ml of glacial acetic acid was refluxed for 4 h, after which it was cooled, and the resulting precipitate was removed by filtration and washed with ether to give 0.7 g (77%) of X. IR spectrum: 1660 and 1643 cm⁻¹ (CO). Found: C 64.8; H 4.4; Cl 10.2%. C₁₉H₁₃N₃O₂Cl. Calculated: C 64.8; H 4.0; Cl 10.0%.

Di(2-benzothiazolyl) Disulfide. A 3.34-g (20 mmole) sample of 2-mercaptobenzothiazole was added to a hot solution of 2.14 g (10 mmole) of I in 40 ml of alcohol and 40 ml of dioxane, and the mixture was refluxed for 1 h. The initially dark-red solution became lighter, and colorless needles precipitated. The solution was cooled, and the precipitate was removed by filtration to give 1.5 g of a product with mp 182-184° (from dioxane containing alcohol). The product was insoluble in alkalis but soluble in dilute sulfuric acid. The IR spectrum did not contain the absorption bands of functional groups. The melting point was in agreement with the literature value [4], and the results of elementary analysis were in agreement with the values calculated for di(2-benzothiazolyl) disulfide. Found: C 51.0; H 2.6; N 8.7%. C₁₄H₁₄N₂S₂. Calculated: C 50.6; H 2.4; N 8.4%.

**LITERATURE CITED**


**SYNTHESIS AND PROPERTIES OF CYANOPYRROLES**

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A number of cyanopyrroles were synthesized. The nitrile group was created by treatment of pyrrolecarboxylic acids with p-toluenesulfonamide and phosphorus pentachloride. It was found that the pyrrole ring is rapidly N-methylated in the presence of diazomethane when it contains three electron-acceptor substituents.

One of the most complex problems that arise in the synthesis of heme a—the prosthetic group of cytochromoxidase—is the introduction of a formyl group in the 8 position of the macrocycle. The preparation of porphyrins with a nitrile group and their subsequent reduction to formylporphyrins may serve as a possible approach to the solution of this problem. A recently proposed method [1] makes it possible to selectively reduce the nitrile group in the presence of vinyl and keto groups, and this is particularly valuable in the synthesis of compounds similar to heme a.
In the present research we accomplished the synthesis of a number of cyanopyrroles that are intermediates in the preparation of porphyrins.

The starting 2-methyl-3-carbabenzyloxy-4-(\(\beta\)-carbethoxyethyl)-5-carbethoxypyrrrole (I) was oxidized to a pyrrolecarboxylic acid (II) by treatment with sulfuryl chloride and bromine.

\[
\text{C}_8\text{H}_7\text{CH}_2\text{O}_2\text{C} \quad \text{SO}_2\text{Cl}_2, \text{Br}_2 \quad \text{C}_8\text{H}_7\text{CH}_2\text{O}_2\text{C} \quad \text{H}_2\text{C}=\text{N} \quad \text{CO}_2\text{C}_2\text{H}_5
\]

Acid II was esterified in alcohol in the presence of acid catalysts (HCl, TsOH, and H_2SO_4), during which it was observed that the benzyl ester undergoes partial transesterification. The benzyl residue is replaced completely when acid II is refluxed in ethanol containing HCl for 3 h. The structure of tetraethyl ester III was confirmed by mass spectrometric data and also by the PMR spectrum, in which four triplets with intensities of three proton units each are present at 1.17-1.31 ppm, and four quartets with intensities of two proton units each are present at 4.06-4.31 ppm (this is in agreement with four carbethoxy groups).

In this connection, the subsequent esterification of acid II was carried out by means of diazomethane. The reaction mixture was vacuum distilled and subjected to hydrogenolysis over Raney nickel. The product was treated with p-toluenesulfonamide (tosyl amide) and phosphorus pentachloride and chromatographed with a column filled with silica gel. The yield of 3-cyano-4-(\(\beta\)-carbomethoxyethyl)-2-carbomethoxy-5-carbethoxypyrrrole (IV) was 40% based on carboxylic acid II.

In addition to the NH absorption bands at 3260 cm\(^{-1}\) and the absorption bands of ester groups at ~1740 and 1710 cm\(^{-1}\), the IR spectrum of pyrrole IV contains the characteristic frequency of the nitrile group at 2250 cm\(^{-1}\). Signals at 2.60 and 3.16 ppm, which correspond to the propionic acid residue, and two singlets at 3.61 and 3.92 ppm of two carbomethoxy groups are present in the PMR spectrum; the triplet at 1.33 ppm and the quartet at 4.35 ppm with an overall intensity of five proton units are affiliated with a carbethoxy group. The mass spectrum of pyrrole IV contains a molecular ion peak at m/e 308.

Chromatography of the reaction mixture gave, in addition to the chief product IV, a small amount of an N-methyl-substituted pyrrole (V). In contrast to major product IV, the IR spectrum of V does not contain an NH absorption band at ~3300 cm\(^{-1}\). In addition to the signals that are present in the PMR spectrum of pyrrole IV, the PMR spectrum of V contains a singlet at 4.17 ppm corresponding to a methyl group attached to the nitrogen atom. The mass spectrum contains a molecular ion peak with m/e 322.

The nitrogen atom is evidently alkylated in the esterification of acid II with gaseous diazomethane, as a result of which a small amount of the N-methyl derivative, which gives N-methylpyrrole V after hydrogenation and treatment with tosyl amide and phosphorus pentachloride, is formed along with the required methyl ester. In contrast to the available data [2], N-methylation occurs even on brief treatment of pyrrolecarboxylic acid II with diazomethane.

It should be noted that the method that we used to introduce a nitrile group into the pyrrole ring by treatment of the \(\beta\)-carboxy group with p-toluenesulfonamide and phosphorus pentachloride differs favorably from the known syntheses [2] with respect to the smaller number of steps and the higher yields.

Saponification of pyrrole IV with 2 N alkali gives a tricaboxylic acid (VI), which, as one should have expected, is an extremely stable compound and does not undergo decarboxylation even when it is heated to 260°. Iodination of VI also does not lead to removal of the carboxyl group. An \(\alpha,\alpha'\)-unsubstituted pyrrole, which was esterified with diazomethane to 3-cyano-4-(\(\beta\)-carbomethoxyethyl)pyrrole (VII), was obtained only when sodium and potassium acetates were used.

The absence of substituents in the 2 and 5 positions of the pyrrole ring follows from the PMR spectrum, which contains signals at 6.57 and 7.20 ppm, each with an intensity of one proton unit. The structure of pyrrole VII was also confirmed by mass spectrometric data.