

1. PREPARATION OF TETRAKIS(4-AMINOPHENYL)PORPHIN

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UDC 547.979.733

Condensation of p-nitrobenzaldehyde with pyrrole in propionic acid with added acetic anhydride gave tetrakis(4-nitrophenyl)porphin (24%), by the reduction of which tetrakis(4-aminophenyl)porphin, which was also obtained by hydrolysis of tetrakis(4-acetamidophenyl)porphin, was synthesized.

Tetraphenylporphins that contain groups that are capable of further transformations (amino, hydroxy, etc.) in the phenyl rings are currently of interest. The diazotization of tetrakis(4-aminophenyl)porphin and replacement of the diazo group [1] may serve as an example of such transformations.

Tetraphenylporphins are obtained by condensation of pyrrole with benzaldehydes (the Rothmund reaction). The yields in this reaction depend substantially on the character of the substituent in the phenyl ring. Electron-acceptor substituents accelerate the reaction and increase the yields of tetraphenylporphins, whereas electron-donor substituents retard the reaction and decrease the yields; this is apparently due to preferred polymerization of pyrrole to give polypyrroles [2]. For this reason it has been proposed [3-5] that tetraphenylporphins with electron-donor groups be obtained by changing the nature of the electron-acceptor substituents in porphyrins. We set out to develop a method for the synthesis of tetrakis(4-nitrophenyl)porphin (I) with its subsequent reduction to tetrakis(4-aminophenyl)porphin (II) and to synthesize the latter by hydrolysis of tetrakis(4-acetamidophenyl)porphin.

Porphyrin I should be obtained in high yield in the condensation of pyrrole with p-nitrobenzaldehyde; however, it has been found [6] that it is obtained in only 7% yield in pyridine-acetic acid. We have shown that in propionic or acetic acid, I is obtained in 4 and 5% yields, respectively, but it is mixed with a large amount of difficult-to-separate polymeric products. The yield of porphyrin I was increased to 24% when acetic anhydride was added to the reaction mixture [7]. It can be separated from the polymeric products by means of dimethylformamide (DMF).

The nitro derivative was reduced almost quantitatively to amino derivative II with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in concentrated HCl. Amino derivative II was also obtained by hydrolysis of tetrakis(4-acetamidophenyl)porphin synthesized by the method of Treibs and Haberle [6].

EXPERIMENTAL

The electronic absorption spectra of the compounds were recorded with a Specord UV-vis spectrophotometer. The individuality of the compounds obtained was established by thin-layer chromatography (TLC) on Silufol.

Tetrakis(4-nitrophenyl)porphin (I). A 5.5-g (0.036 mole) sample of p-nitrobenzaldehyde was heated to the boiling point in a mixture of 6 ml (0.063 mole) of acetic anhydride and 150 ml of propionic acid, 2.5 ml (0.036 mole) of pyrrole was added, and the mixture was refluxed for 30 min. It was then cooled to room temperature and allowed to stand for 24 h. The resulting precipitate was removed by filtration, washed with hot water, and dried. The dry precipitate was mixed with 50 ml of DMF, and I was removed by filtration, washed successively with a small amount of DMF and hot water, and dried. For further purification I was recrystallized from pyridine to give 1.7 g (24%) of a product with R_f 0.54 [pyridine-decane (1:1)]. Electronic spectrum (in DMF), λ_{max} (log ϵ): 646 (3.53), 590 (3.69), 551 (3.83), 515 (4.10), 423 nm (5.33).

Ivanov Institute of Chemical Technology, Ivanovo 153460. Translated from *Khimiya Getrotsiklicheskih Soedinenii*, No. 10, pp. 1354-1355, October, 1982. Original article submitted December 28, 1981.

Tetrakis(4-aminophenyl)porphin (II). A) A 6-g (7.6 mmole) sample of I was stirred for 30 min with 300 ml of concentrated HCl, after which 26 g of SnCl₂·2H₂O was added, and the mixture was heated rapidly to 80°C and maintained at this temperature for 30 min. It was then cooled and diluted with 300 ml of water, and the precipitated hydrochloride of II was removed by filtration and dissolved in water. The aqueous solution was treated with ammonium hydroxide until the color of the mixture changed. The precipitated II was washed with water, dried, dissolved in chloroform, and chromatographed on silica gel using chloroform as the eluent. Evaporation of the eluate and crystallization of the residue from chloroform-hexane gave 4.74 g (93%) of II.

B) A 0.1-g sample of tetrakis(4-acetamidophenyl)porphin was dissolved by heating in 25 ml of 25% H₂SO₄, and the solution was heated to 70°C for 15 min. It was then cooled, and II was precipitated by the addition of ammonium hydroxide until the color of the mixture changed. The porphin was removed by filtration, washed with water, dried, and recrystallized from chloroform-hexane. The product had R_f 0.71 (methanol) and 0.47 [acetone-heptane (2:1)]. Electronic spectrum in benzene, λ_{max} (log ε): 658 (3.74), 598 (3.61), 563 (4.02), 523 (3.99), 492 (3.61), 421 nm (5.55).

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REACTION OF o-QUINONES OF THE BENZOFURAN AND INDOLE SERIES WITH ACETOACETIC ESTER AND ACETYLACETONE

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UDC 547.567.722.752

The reaction of o-quinones of the benzofuran and indole series with acetoacetic ester and acetylacetone in the presence of zinc chloride leads to derivatives of 4,5-dihydroxybenzofuran and 4,5-dihydroxyindole with acetoacetic ester and acetylacetone residues in the 7 position.

We have found that o-quinones of the benzofuran (I-III) and indole (IV-VI) series, like p-quinones [1, 2], react with keto enols (VII, VIII) in the presence of zinc chloride as the catalyst. However, o-quinones [3, 4] are considerably more reactive. Thus the reaction of keto enols with o-quinones takes place when the reactions are heated in alcohol for 10-15 min. The previously inaccessible 4,5-dihydroxybenzofuran (IX-XIII) and 4,5-dihydroxyindole (XIV-XVII) derivatives (Table 1) with acetoacetic ester and acetylacetone residues in the 7 position are formed in high yields as a result of this reaction.

Thus we proposed a new preparative method for the dihydroxyheterylation of keto enols.

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