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Porphyrins and Their Derivatives: XXII*. A New Product of Intramolecular Cyclization of 5,10,15,20-Tetraphenyl-2-formylporphyrin Copper Complex

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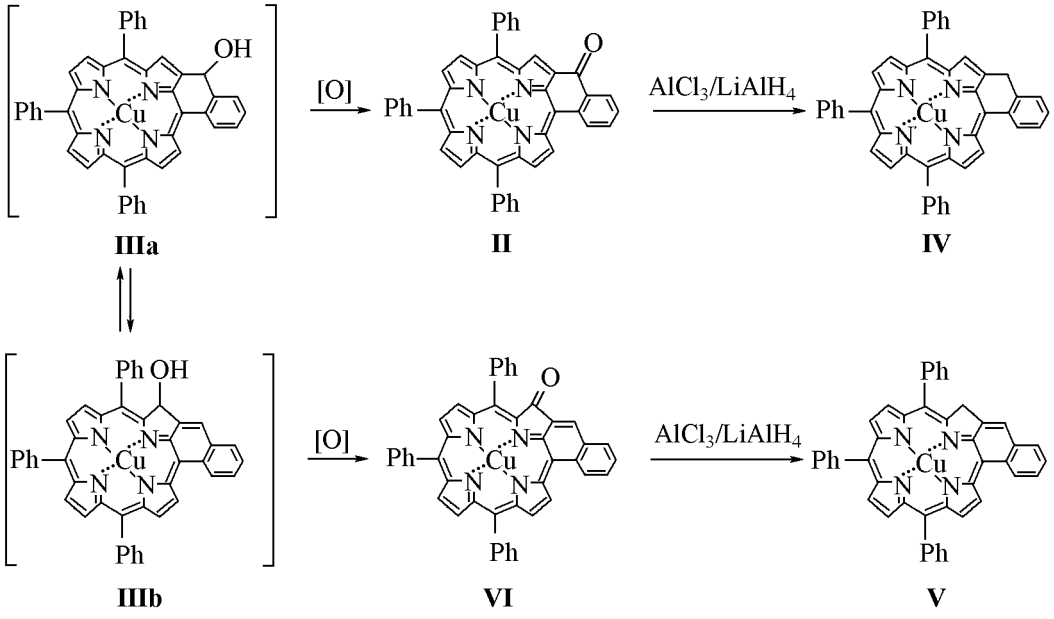
Abstract—The treatment at boiling of 5,10,15,20-tetraphenyl-2-formylporphyrin copper(II) with saturated solution of p-chloranil in benzene in the presence of 70% aqueous trifluoroacetic acid affords alongside verdin (16.7%) its isomer with a keto group located in the β-position of the macrocycle in 71% yield.

In 1980 attempting to demetallate with trifluoroacetic acid the 5,10,15,20-tetraphenyl-2-formylporphyrin copper complex (**I**) Henrick et al for the first time obtained verdin (**II**) in 0.1% yield and characterized it by means of X-ray diffraction study [2]. On formation of such compound reported Buchler [3] when he tried to prepare thioacetals of 5,10,15,20-tetra(4-methylphenyl)-2-formylporphyrin. In 38% yield verdin **II** was isolated by treating aldehyde **I** with trifluoroacetic acid in dichloromethane under inert atmosphere [4]. Compound **II** presumably formed by disproportionation of intermediate unstable alcohol **IIIa**. In 1944 similar transformations were thoroughly investigated on 5,10,15,20-tetra(3-methoxyphenyl)-2-formylporphyrin [5] and new products were revealed originating from so-called "abnormal double" intramolecular cyclization of the above formylporphyrin.

We showed before that the cyclization of aldehyde **I** in the presence of an oxidant (p-chloranil) afforded verdin (II) in up to 67% yield [6]. At reduction of verdin (II) with a system $AlCl_3$–$LiAlH_4$, 1 : 1, alongside compound **IV** arose a small amount of compound **V** (~4.8%) that possessed chlorin type of the electron absorption spectrum (λ_{max} 669 nm). In the presence of bases compound **IV** quantitatively underwent



* Communication XXI, see [1].

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rearrangement into porphyrin **V**. However since the reduction of verdin (**II**) occurred in the presence of acid ($AlCl_3$) we presumed that compound **V** arising as impurity originated from reduction of isomeric ketone **VI** that was present in the raw verdin (**II**).

When verdin (**II**) obtained along procedure [6] was subjected to thorough chromatographic investigation we detected therein a small impurity of another substance. We succeeded in isolation of the substance by means of column chromatography on silica gel with benzene–hexane, 3:1, as eluent. The yield of compound **VI** in the synthesis of verdin (II) was about 5%. The data of IR spectroscopy [ν(CO) 1694 cm^{-1}] and mass spectrometry (M^+ 701) evidenced that compound **VI** actually was isomeric to verdin (**II**) [ν(CO) 1647 cm^{-1} and M^+ 701].

Compounds **II** and **VI** readily underwent demetallation when treated with concn. sulfuric acid to afford free bases **VII** and **VIII** respectively. We previously erroneously believed that verdin (**II**) cannot be demetallate [6]. In chromatography on silica gel the free base **VIII** moves faster than the copper complex **VI**. Unlike that base **VII** is more polar than the corresponding complex **II**. Therefore the compounds **II** and **VI** is better to separate as free bases **VII** and **VIII**, and in the system chloroform–hexane the isomers are cleanly separated.

The location of the carbonyl group significantly affects the spectral characteristics of the isomeric ketones. The Soret band of copper complex **VI** undergoes blue shift nearly by 60 nm compared with verdin (**II**). At the same time in the visible region the most long-wave band of compound **VI** is shifted to the red side by 20 nm. In the ^1H NMR spectrum of ketone **VIII** the resonance of NH protons occurs at δ 0.425 ppm, and in the spectrum of verdin-base **VII** at δ –0.586 ppm

We first presumed that the best way to prepare ketone **VI** should be oxidation of compound **V** that might be quantitatively obtained from easily accessible porphyrin **IV**. However all our attempts to oxidize chlorin (**V**) [$PdCl_2$, $PdCl_2$–$Cu(OAc)_2$, ArO_3–2Py] afforded exclusively verdin (**II**).

Since the intramolecular cyclization of aldehyde **I** affords both isomers **II** and **VI** then between their precursors, unstable alcohols **IIIa** and **IIIb**, should exist an equilibrium. Therefore to direct the cyclization of aldehyde **I** to ketone **VI** the equilibrium should be shifted to prevailing formation of alcohol **IIIb**. This equilibrium is the most affected by the character and concentration of the oxidant. Apparently the electron deficiency of the macrocycle caused by its interaction with a π-acceptor (oxidant) facilitates the shift of the hydroxy group into the β-position of the porphyrin. We found that when the cyclization was carried out in benzene in the presence of 70% aqueous trifluoroacetic acid as catalyst the only suitable oxidant was p-chloranil, and at raising its concentration in the reaction mixture the yield of ketone **VI** increased.

As expected, the reduction of ketone **VI** in ether by the system $AlCl_3$–$LiAlH_4$, 1:1, afforded in 58% yield porphirin **V**, identical to that obtained at the rearrangement of reduced verdin (**IV**). Base **IX** obtained by reductive demetallation of complex **V** with a system $Cu(OAc)_2$–$NaBH_4$ [6] contained in the ^1H NMR spectrum a characteristic signal of chlorin protons at 5.11 ppm and abnormally broad resonance of the internal NH-protons (from –1.9 to –4.2 ppm).

EXPERIMENTAL

^1H NMR spectra were registered on spectrometers Bruker AM-250 and DPX-300 at operating frequencies 250.15 and 300.13 MHz respectively, solvent $CDCl_3$, internal reference TMS. Mass spectra were measured on MKh-1321 instrument with direct input of sample. Ionizing energy 70 eV, the temperature of ion source 220°C. IR spectra were recorded on spectrometer IKS-29 (LOMO, St. Petersburg) from KBr pellets. Electron absorption spectra were taken on spectrophotometer Specord M-40 in $CHCl_3$ (c 10^{-5} mol l^{-1}). TLC was carried out on Silufol UV-254 plates, eluents benzene and benzene–hexane, 3:1. Column chromatography was performed on silica gel L 40/100. The 5,10,15,20-tetraphenyl-2-formylporphyrin copper(II) was prepared as in [7].

2-Oxo-10,15,20-triphenylnaphtho[2,3,4-c,d]-porphynatocopper (VI) (β-ketone). To a mixture of 0.365 g of aldehyde **I**, 1.96 g *p*-chloranil, and 80 ml of benzene was added a solution of 8 ml of trifluoroacetic acid in 5 ml of water, and the mixture was boiled for 13 h. Then the reaction mixture was cooled, washed with water (2 × 100 ml), 2% solution of NaOH (2 × 100 ml), again with water, and the solvent was evaporated to dryness. The residue was dissolved in 10 ml of benzene, 3 ml of hexane was added, and the solution was charged into a column with silica gel (2 × 30 cm). Elution was carried out with benzene–hexane mixture, 3:1. Eluate containing compound **VI** was evaporated, the residue was crystallized from a mixture $CHCl_3$–CH_3OH, 1:5. Yield of ketone VI 0.247 g (71%). Electronic spectrum, λ_{max}, nm ($\log\varepsilon$): 404 (4.96), 468 (4.63), 489 (4.60), 609 (3.6), 664 (4.17), 718 (4.37).

The green verdin (**II**) zone was washed from the column after porphyrin **VI**. After crystallization we obtained 0.061 g (16.7%) of verdin (**II**).

2-Oxo-10,15,20-triphenylnaphtho[2,3,4-c,d]-porphyrin (VIII). In 3 ml of concn. H_2SO_4 was dissolved 0.03 g of ketone **VI**. After 10 min the brown-violet solution was poured at stirring into 100 ml of cold water and was neutralized with ammonia. The separated precipitate was filtered off, dried, dissolved in 2 ml of chloroform, 1 ml of hexane was added, and the solution was charged into chromatographic column packed with silica gel (1 × 10 cm). Eluent chloroform–hexane, 3:1. The green zone of porphyrin **VIII** was collected. The solvent was evaporated to dryness, the residue was crystallized from a mixture chloroform–methanol, 1:5. Yield 0.025 g (91%). Electronic spectrum, λ_{max}, nm ($\log\varepsilon$): 404 (4.96), 467 (4.60), 514 (4.40), 581 (3.76), 646 (4.05), 688 (4.23), 728 (4.30). ^{1}H NMR spectrum, δ, ppm: 9.19 d, 9.03 d, 8.52 d, 8.44 d, 8.26 d, 8.20 d (6H, β-pyrrole); 8.5 s (1H, bridge); 8.29 m, 8.13 m, 8.05 m (6H, *o*-phenyl); 7.9 t, 7.87 d, 7.84 d, 7.63 t (4H, phenyl); 7.72 m (9H, *m*-, ..-phenyl); 0.43 br.s (2H, NH). M^+ 640.

2-Oxo-10,15,20-triphenylnaphtho[1,2,3-e,f]-porphynatocopper (V). In 30 ml of anhydrous ether under argon was dissolved 0.21 g of ketone **VI**, 3.4 ml of 0.44 M $AlCl_3$ solution in ether was added, and after 2 min 4.8 ml of 0.31 M $LiAlH_4$ solution in ether. The mixture was stirred for 10 min at room temperature and excess reducing agent was quenched with 1 ml of ethyl acetate. Then 30 ml of 3% HCl solution was added, and the stirring was continued for another 10 min. The ether layer was separated, washed with water (2 × 30 ml), and then evaporated to dryness. The residue was dissolved in 10 ml of benzene, 8 ml of hexane was added, and the solution was charged into a chromatographic column packed with silica gel (2 × 15 cm). Eluent benzene–hexane mixture, 1:1. The green zone was collected, the solvent was evaporated, the dry residue was dissolved in 5 ml of chloroform, and 25 ml of hot heptane was added. The precipitated crystals were filtered off and dried. Yield of compound **V** 0.119 g (58%). Electronic spectrum, λ_{max}, nm ($\log\varepsilon$): 443 (5.37), 592 (4.28), 615 (4.39), 669 (4.80). M^+ 687.

10,15,20-Triphenylnaphtho[1,2,3-e,f]-porphyrin (IX) was prepared from complex **V** along procedure [6]. [6]. ^{1}H NMR spectrum, δ, ppm: 9.46 d, 9.01 d, 8.21 d, 8.07 d (6H, β-pyrrole); 8.45 s (1H, bridge); 8.27 m (3H, *o*-phenyl and β-pyrrole); 8.11 m (2H, β-pyrrole); 8.03 m (3H, *o*-phenyl and β-pyrrole); 7.94 t, 7.89 m, 7.76 t (4H, phenyl); 7.71 m (6H, *m*-, *p*-phenyl); 7.66 m (3H, *m*-, *p*-phenyl); 5.11 s (2H, β-pyrrole); –1.9 ÷ –4.2 br.s (2H, NH).

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