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Porphyrins and Their Derivatives: XXVI.* Synthesis and Properties of 2-(3-Butenyl)-5,10,15,20-tetraphenylporphyrin

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Abstract—2-[2-(1,3-Dioxolan-2-yl)vinyl]-5,10,15,20-tetraphenylporphyrin and its copper complex were reduced into the corresponding ethyldioxolanes by diimide generated in the system hydrazine hydrate – air oxygen – pyridine. The hydrolysis of the obtained ethyldioxolanes results in the formylethyl derivatives that react with the methylenetriphenylphosphorane to form 2-(3-butenyl)-5,10,15,20-tetraphenylporphyrin and its copper complex.

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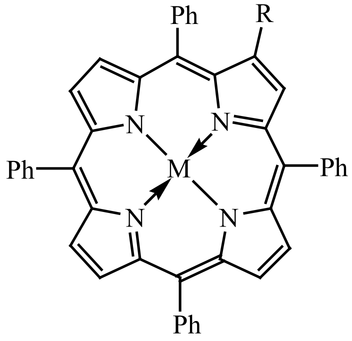
Porphyrin-containing complexes are widely used as catalysts of various reactions and as new specialty materials [2, 3]. We formerly demonstrated that the homopolymerization was impossible for 2-vinyl-5,10,15,20-tetraphenylporphyrin, 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin, and their copper, zinc, and nickel complexes whereas the copolymerization of these porphyrin monomers with styrene, methyl methacrylate, and acrylonitrile afforded polymers with low content of macrocyclic fragments [4–6].



Ia, Ib–VIa, VIb

CH_2CH_2CHO (**IV**), $CH_2CH_2CH_3$ (**V**), $CH_2CH_2CH{=}CH_2$; (**VI**); M = 2H (**a**), Cu (**b**).

It apparently originates from the steric screening of the vinyl group in the above mentioned porphyrins and by the specific inhibiting effect of the porphyrin macrocycle [4]. Inasmuch as the degree of copolymerization of 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin and its metal complexes is higher that that of 2-vinyltetraphenylporphyrin and its chelates the possible way to increase the content of the porphyrin fragments in copolymers may consist in removing the vinyl group to a larger distance from the macrocycle in the porphyrin monomers.

We report here on the synthesis of derivatives of *meso*-tetraphenylporphyrin containing in the β-position of the pyrrole ring a butenyl substituent with a terminal double bond.

As initial compounds we used vinyldioxolanes **Ia** and **Ib** that had been obtained in [7] by Wittig reaction of 2-formyltetraphenylporphyrin and its copper complex with 1,3-dioxolan-2-ylmethylenetriphenylphosphorane but had not been isolated in the individual state. The purification of the crude dioxolanes **Ia** and **Ib** we first carried out by chromatography on aluminum oxide using for elution a mixture benzene – tetrachloromethane, 1 : 1.5 (for free base) and 1 : 2 (for copper complex). The best yield of porphyrin **Ia** was 71%, of its copper complex **Ib**, 68%. It was further found that the free aldehydes **IIa** and **IIb** obtained by hydrolysis of crude dioxolanes **Ia** and **Ib** in a two-phase system benzene – water in the presence of iodic acid in contrast to dioxolanes were readily purified by chromatography on silica gel. The acetalization of aldehydes **IIa** and **IIb** with ethylene

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* For Communication XXV, see [1].

glycol in the mixture benzene–dioxane, 1 : 1, in the presence of *p*-toluenesulfonic acid with the azeotropic removal of the formed water gave dioxolanes **Ia** and **Ib** in the yields 75 and 78% respectively. The addition to the reaction mixture at the end of the azeotropic acetalization of triethyl orthoformate and the subsequent distillation of the formed ethanol resulted in the increase in the yield of vinyldioxolane **Ia** to 89%, and of copper complex **Ib,** to 91%. Vinyldioxolane **Ia** according to its ^{1}H NMR spectrum was a mixture of *cis*- and *trans*-isomers which we failed to separate by chromatography.

The exocyclic double bond of vinyldioxolanes **Ia** and **Ib** was not hydrogenated by the system $NaBH_4$–Pd/C, and in the copper complex **Ib** also by systems $NaBH_4$–$PdCl_2$, $NaBH_4$–$NiCl_2 \cdot 6H_2O$ in various solvent mixtures (THF–methanol, THF–ethanol, dioxane–2-propanol) both at room temperature and at boiling.

The hydrogenation of the α,β-unsaturated aldehydes **IIa** and **IIb** by the system formic acid–Pd/C at 50°C proceeded very slow giving trace amounts of aldehydes **IVa** and **IVb** and propylporphyrins **Va** and **Vb**, reduction product of both the double bond and the aldehyde group. The boiling resulted in fast conversion of aldehydes **IIa** and **IIb** into propylporphyrins **Va** and **Vb,** after 3 h of boiling their yield attained 78 and 77% respectively.

On boiling the solutions of vinyldioxolanes **Ia** and **Ib** and hydrazine hydrate in THF or dioxane in the presence of Pd/C ethyldioxolanes **IIIa** and **IIIb** formed in trace amounts and also their derivatives with hydrogenated cryptoolefin bonds, the corresponding chlorins and bacteriochlorins. The hydrogenation did not occur in the inert atmosphere, and in the presence of air oxygen the yields of ethyldioxolanes **IIIa** and **IIIb** grew with lowering temperature and at room temperature were close to the yields obtained in the absence of Pd/C. Evidently in the latter case the reduction occurred under the action of diimide formed by the oxidation of hydrazine.

The diimide reduction of the cryptoolefin bonds of the porphyrin macroring, in particular, of the tetraphenylporphyrin and a number of its metal complexes was well known [8–10], but the hydrogenation by diimide of exocyclic multiple bonds of porphyrins was described in some early publications on conversion of the vinyl groups in the natural porphyrins and chlorines into ethyl groups [11–13].

We investigated the reduction of vinyldioxolanes **Ia** and **Ib** by diimide generated in the systems hydrazine hydrate – air oxygen in THF, dioxane, and pyridine varying the reaction temperature from ambient to the boiling point of the mixture. We also investigated the system tosylhydrazine – potassium carbonate in boiling pyridine, hydrazine hydrate – 30% hydrogen peroxide in pyridine. At the use of the system hydrazine hydrate – air oxygen the heating, aeration, introducing catalytic quantities of copper (at the reduction of copper complex **Ib**) resulted in shortening of the reaction time and in decrease of the yield of the target products **IIIa** and **IIIb**. It is evidently due to the decrease in the regioselectivity of the diimide hydrogenation and the increase in the degradation of the porphyrin macrocycle.

It was found that the reduction of vinyldioxolane **Ib** with the system hydrazine hydrate (50-fold molar excess) – air oxygen in pyridine at room temperature within 10 days resulted in a complete consumption of the initial porphyrin and in the formation of ethyldioxolane **IIIb** in 70% yield and its chlorin derivative in 9–11% yield. The oxidation of the latter with *p*-chloranil in boiling toluene raised the yield of ethyldioxolane **IIIb** to 81%.

Unlike the copper complex of vinyldioxolane **Ib** free base **Ia** was slowly (14 days) reduced by the system hydrazine hydrate (50-fold molar excess) – air oxygen in pyridine, and the process was unselective: even at room temperature alongside the exocyclic double bond actively occurred the reduction of the cryptoolefin bonds of the macrocycle providing a mixture of chlorin and bacteriochlorin derivatives of porphyrin **IIIa**. The dehydrogenation of the mixture with *p*-chloranil in boiling toluene resulted in porphyrin **IIIa** in 76% yield.

The diimide reduction of vinyldioxolanes **Ia** and **Ib** in THF or dioxane proceeded with lower yields (45–53% after the treatment with *p*-chloranil in toluene) and slower (14–17 days) than in pyridine. The boiling in toluene with *p*-chloranil is the optimum method of conversion of the mentioned chlorin and bacteriochlorin derivatives into porphyrins **IIIa** and **IIIb**. This reaction did not occur in benzene, was very slow in the boiling dioxane, and in *o*-xylene the duration of dehydrogenation was three times shorter, the yield of ethyldioxolane **IIIa** was 63%, of its copper complex **IIIb**, 56%.

The reduction of vinyldioxolanes **Ia** and **Ib** with the system tosylhydrazine–K_2CO_3 in boiling pyridine under inert atmosphere after treatment of the reduction products with *p*-chloranil in boiling toluene gave ethyldioxolane **IIIa** in up to 70% yield and copper complex **IIIb** in up to 73% yield. The use of the system hydrazine hydrate–30% solution of hydrogen peroxide resulted in the decrease in the yield of ethyldioxolanes **IIIa** and **IIIb** to 7–29% (after *p*-chloranil treatment).

Ethyldioxolanes **IIIa** and **IIIb** proved to be considerably stable against hydrolysis, and the aldehydes **IVa** and **IVb** were readily oxidized by air oxygen. Dioxolane **IIIa** was hydrolyzed in the mixture of trifluoroacetic acid with 20% sulfuric acid, 3 : 1, aldehyde **IVa** was obtained in 83% yield. Aldehyde **IVb** was obtained in 85% yield by hydrolysis of dioxolane **IIIb** in the mixture benzene–water in the presence of trifluoroacetic and iodic acids.

The reaction of aldehydes **IVa** and **IVb** with the methylenetriphenylphosphorane generated *in situ* from the corresponding iodide by the action of potassium carbonate complex with 18-crown-6 in boiling benzene furnished the target butenylporphyrins **VIa** and **VIb** in 80% and 87% yield respectively.

The copper complexes **IIIb** and **VIb** cleanly underwent demetallation with the system $NaBH_4$–$Cu(CH_3COO)_2$ in the mixture THF–methanol giving free bases **IIIa** and **VIa** in 87 и 88% yield respectively.

EXPERIMENTAL

^{1}H NMR spectra were registered on spectrometers Bruker DPX-300 and DPX-400 at operating frequencies 300.13 and 400.447 MHz, internal reference TMS, solvent $CDCl_3$. Mass spectra FAB were recorded on an instrument VC 7070 EQ. The ion desorption was performed with a beam of xenone atoms with the energy 8 kV from the matrix of a solution of the studied compound in 3-nitrobenzyl alcohol. The precise mass of molecular ions was evaluated at the resolution of the mass spectrometer equal 10000. Electron absorption spectra were measured on a spectrophotometer Specord M-40 in benzene (c 10^{-6}–10^{-4} mol l^{-1}). TLC was carried out on Silufol and Alufol plates, the column chromatography was performed using silica gel L 40/100 and aluminum oxide of the III grade of activity. The crude vinyldioxolanes **Ia** and **Ib** were prepared by scaled procedures [4].

2-(2-Formylvinyl)-5,10,15,20-tetraphenylporphyrin (IIa). To a solution of 1.007 g (1.41 mmol) of crude vinyldioxolane **Ia** in 100 ml of benzene was added a solution of 1.919 g (8.42 mmol) of iodic acid in 50 ml of water, and the mixture was boiled for 1.5 h in an argon atmosphere under vigorous stirring. Then the reaction mixture was cooled, neutralized with 5% water solution of sodium carbonate, the organic layer was separated, washed with water, and evaporated to dryness. The residue was dissolved in toluene and applied to a column (4 × 50 cm) packed with silica gel, eluent toluene. The fraction containing formylporphyrin **IIa** was evaporated to dryness, the residue was recrystallized from the mixture chloroform–methanol, 1 : 5. Yield 0.652 g (69%), R_f 0.25 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 433 (5.36), 524 (4.24), 565 (3.81), 605 (3.72), 662 (3.56). ^{1}H NMR spectrum, δ, ppm: –2.73 br.s, –2.59 br.s (2H, NH), 6.07 d.d (J 8.25, 10.45 Hz), 6.85 d.d (J 7.50, 15.5 Hz), 6.99 d (J 15.5 Hz), 7.35 d.d (2H, CH=CH, J 1.8, 10.45 Hz), 7.76 m (12H, *m-, p*-phenyl), 8.023 d.t, 8.11 d.t (J 1.5, 6.5 Hz), 8.19 m (8H, *o*-phenyl), 8.83 m, 8.99 s (7H, β-pyrrole), 10.24 d, 9.20 d (1H, CHO). Mass spectrum: m/z 669.791 $[M + 1]^+$.

2-(2-Formylvinyl)-5,10,15,20-tetraphenyl-porphyrinatocopper (IIb) was similarly obtained from 1.005 g (1.30 mmol) of crude vinyldioxolane **Ib** in 100 ml of benzene, 1.766 g (7.75 mmol) of iodic acid in 50 ml of water. Yield 0.711 g (75%), R_f 0.32 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 433 (5.34), 549 (4.23), 592 (3.99). Mass spectrum: m/z 730.313 $[M]^+$.

2-[2-(1,3-Dioxolan-2-yl)vinyl]-5,10,15,20-tetraphenylporphyrin (Ia). A solution of 0.693 g (1.04 mmol) of aldehyde **IIa**, 1.15 ml (1.28 g, 20.7 mmol) of ethylene glycol, 0.404 g (2.12 mmol) of *p*-toluenesulfonic acid monohydrate in a mixture of 150 ml of benzene and 150 ml of dioxane was boiled in a device equipped with a Dean-Stark trap for 7 h. Then to the solution was added 0.43 ml (0.384 g, 2.59 mmol) of triethyl orthoformate, the mixture was boiled for 2 h, and the solution was distilled off till bp 90°C. On cooling 1.005 g (7.27 mmol) of potassium carbonate was added, and the mixture was stirred at room temperature for 24 h. The dispersion was filtered, the precipitate was washed with benzene on the filter, the combined filtrates were evaporated to dryness, the residue was dissolved in benzene, filtered through a bed (5 cm) of aluminum oxide, the filtrate was evaporated to the minimum volume and crystallized from the mixture benzene–methanol, 1:3. Yield 0.657 g (89%), R_f 0.36 (Alufol, eluent benzene–tetrachloromethane, 1 : 2). Electronic spectrum, λ_{max} (log ε): 425 (5.56), 520 (4.35), 555 (3,93), 597 (3.82), 653 (3.52). ^{1}H NMR spectrum, δ, ppm: –2.68 br.s, –2.72 br.s (2H, NH), 3.95 m (4H, CH_2–CH_2-dioxolane), 5.08 d (1H, CH-dioxolane), 6.42 d, 6.31 d.d, 5.72 d, 5.58 d.d (2H, CH=CH-*trans,* J 15.6, 6 Hz, CH=CH-*cis*, J 7.2, 6 Hz), 7.76 m (12H, *m-, p*-phenyl), 8.20 m, 8.10 m, (8H, *o*-phenyl), 8.93 s, 8.79 m (7H, β-pyrrole). Mass spectrum: m/z 713.844 $[M + 1]^+$.

2-[2-(1,3-Dioxolan-2-yl)vinyl]-5,10,15,20-tetraphenylporphyrinatocopper (Ib) was similarly prepared from 0.710 g (0.97 mmol) of aldehyde **IIb**, 1.08 ml (1.207 g, 19.4 mmol) of ethylene glycol, 0.01 g (0.05 mmol) of *p*-toluenesulfonic acid monohydrate, 0.40 ml (0.36 g, 2.43 mmol) triethyl orthoformate in a mixture of 150 ml of benzene and 150 ml of dioxane. Yield 0.685 g (91%), R_f 0.44 (Alufol, eluent benzene–tetrachloromethane, 1 : 2). Electronic spectrum, λ_{max} (log ε): 423 (5.65), 548 (4.60). Mass spectrum: *m/z* 774.366 $[M]^+$.

2-[2-(1,3-Dioxolan-2-yl)ethyl]-5,10,15,20-tetraphenylporphyrin (IIIa). A solution of 0.502 g (0.70 mmol) of vinyldioxolane **Ia** and 1.71 ml (1.763 g, 35.2 mmol) of hydrazine hydrate in 40 ml of pyridine was maintained for 14 days in the dark in contact with air at 20°C. Then the reaction mixture was poured in a solution of 5 g of ammonim chloride in 800 ml of water, the separated precipitate was filtered off, washed with water, dried for 4 h at 120°C, dissolved in 150 ml of toluene, 2.592 g (10.5 mmol) of *p*-chloranil was added, and the mixture was boiled for 50 h. On cooling to the reaction mixture was added a solution of 25.127 g (0.45 mol) of potassium hydroxide in 100 ml of water, and the mixture was vigorously stirred at room temperature for 8 ч, then the organic layer was separated, washed with water (3 × 100 ml), passed through a bed of aluminum oxide (3 cm), evaporated to dryness, the residue was dissolved in a minimum volume of the mixture benzene– tetrachloromethane, 1 : 2, and applied to a column (3.5 × 50 cm) packed with silica gel. Elution with the same solvent mixture, the fraction containing dioxolane **IIIa** was evaporated to dryness, the residue was recrystallized from the mixture chloroform–methanol, 1 : 5. Yield 0.383 g (76%), R_f 0.20 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 420 (5.66), 515 (4.36), 549 (3.95), 592 (3.90), 648 (3.79). ^{1}H NMR spectrum, δ, ppm: –2.78 br.s (2H, NH), 2.20 m (2H, β-CH_2), 3.00 t (2H, α-CH_2), 3.89 m (4H, CH_2–CH_2-dioxolan), 4.80 t (1H, CH-dioxolane), 7.75 m (12H, *m-, p*-phenyl), 8.20 m, 8.11 m (8H, *o*-phenyl), 8.85 s, 8.79 d, 8.74 d, 8.66 s, 8.60 d (7H, β-pyrrole). Mass spectrum: *m/z* 715.860 $[M + 1]^+$.

2-[2-(1,3-Dioxolan-2-yl)ethyl]-5,10,15,20-tetraphenylporphyrinatocopper (IIIb) was obtained similarly from 0.542 g (0.70 mmol) of copper complex **Ib**, 1.7 ml (1.752 g, 35.0 mmol) of hydrazine hydrate in 40 ml of pyridine within 10 days. The reduction products were boiled for 26 h with 1.353 g (5.50 mmol) of *p*-chloranil in 150 ml of toluene, on cooling the solution was stirred with a solution of 17.815 g (0.32 mol) of potassium hydroxide in 100 ml of water for 8 h at room temperature. The product was subjected to chromatography on silica gel, eluent benzene–tetrachloromethane, 1 : 1. Yield 0.440 g (81%), R_f 0.28 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 418 (5.75), 540 (4.18). Mass spectrum: *m/z* 776.382 $[M]^+$.

2-(2-Formylethyl)-5,10,15,20-tetraphenylporphyrin (IVa). A solution of 0.401 g (0.56 mmol) dioxolane **IIIa** in a mixture of 60 ml of trifluoroacetic acid and 20 ml of 20% water solution of sulfuric acid was stirred for 3 h at room temperature under an argon atmosphere, then it was poured into a solution of 2.464 g (23.2 mmol) of sodium carbonate in 800 ml of water. The separated precipitate was filtered off, washed with water, dried for 4 h at 110°C, then it was dissolved in a minimum volume of the mixture benzene– tetrachloromethane, 1 : 1, and applied to a column (3.5 × 40 cm) packed with silica gel. Elution with the same solvent mixture, the fraction containing aldehyde **IVa** was evaporated to dryness, the residue was recrystallized from the mixture chloroform–methanol, 1 : 5. Yield 0.312 g (83%), R_f 0.30 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 418 (5.67), 514 (4.31), 550 (3.83), 588 (3.78), 647 (3.51). ^{1}H NMR spectrum, δ, ppm: –2.77 br.s (2H, NH), 2.90 m (2H, β-CH_2), 3.22 t (2H, α-CH_2), 7.74 m (12H, *m-, p*-phenyl), 8.20 m, 8.12 m, (8H, *o*-phenyl), 8.84 s, 8.81 d, 8.76 d, 8.63 d, 8.58 s (7H, β-pyrrole), 9.69 t (1H, CHO). Mass spectrum: *m/z* 671.807 $[M + 1]^+$.

2-(2-Formylethyl)-5,10,15,20-tetraphenyl-porphyrinatocopper (IVb. A solution of 0.405 g (0.52 mmol) of dioxolane **IIIb** in 40 ml of benzene was boiled for 12 h with a solution of 1.919 g (8.42 mmol) of iodic acid and 5 ml (7.445 g, 65.3 mmol) of trifluoroacetic acid in 20 ml of water at viorous stirring under an argon atmosphere. The mixture was neutralized with 20% water solution of sodium carbonate, the benzene layer was separated, washed with water, and evaporated to dryness. The residue it was dissolved in a minimum volume of the mixture benzene– tetrachloromethane, 1 : 1, and applied to a column (3.5 × 50 cm) packed with silica gel. Elution with the same solvent mixture, the fraction containing aldehyde **IVb** was evaporated to dryness; the residue was recrystallized from the mixture chloroform–methanol, 1 : 5. Yield 0.325 g (85%), R_f 0.39 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 418 (5.76), 548 (4.45). Mass spectrum: *m/z* 732.329 $[M]^+$.

2-Propyl-5,10,15,20-tetraphenylporphyrin (Va). A mixture of 0.212 g (0.32 mmol) of porphyrin **IIa** and 0.212 g of 5%-ного Pd/C in 50 ml of formic acid was boiled for 2 h, Pd/C was filtered off, washed on the filter with formic acid, then with THF. The combined filtrates were poured into 500 ml of water, neutralized with 10% water solution of sodium carbonate. The separated precipitate was filtered off, washed with water, dried for 5 h at 120°C, dissolved in a minimum volume of the mixture benzene–hexane, 1 : 1, and this solution was applied to a column (2.5 × 30 cm) packed with silica gel. Elution with the mixture benzene–hexane, 1 : 1, the fraction containing propylporphyrin **Va** was evaporated to dryness, the residue was recrystallized from the mixture chloroform–methanol, 1 : 5. Yield 0.162 g (78%), R_f 0.81 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 420 (5.61), 516 (4.23), 550 (3.73), 592 (3.72), 651 (3.52). ^{1}H NMR spectrum, δ, ppm: –2.78 br.s (2H, NH), 0.85 t (3H, CH_3), 1.80 m (2H, β-CH_2), 2.79 t (2H, α-CH_2), 7.73 m (12H, *m-*, *p*-phenyl), 8.20 m, 8.10 m (8H, *o*-phenyl), 8.86 s, 8.79 m, 8.73 d, 8.63 m (7H, β-pyrrole). Mass spectrum: *m*/*z* 657.824 $[M + 1]^+$.

2-Propyl-5,10,15,20-tetraphenylporphyrinatocopper (Vb) was obtained similarly from 0.210 g (0.29 mmol) of aldehyde **IIb**, 0.210 g of 5% Pd/C in a mixture of 50 ml of formic acid and 50 ml of dioxane. The reaction products were subjected to chromatography on a column (2.5×50 cm) packed with silica gel, eluent benzene–hexane, 1.5:1. Yield 0.159 g (77%), R_f 0.93 (Silufol, eluent benzene–tetrachloromethane, 1 : 1). Electronic spectrum, λ_{max} (log ε): 416 (5.71), 540 (4.23). Mass spectrum: *m*/*z* 718.346 $[M]^+$.

2-(3-Butenyl)-5,10,15,20-tetraphenylporphyrin (VIa). A mixture of 0.503 g (0.75 mmol) of porphyrin **IVa**, 1.516 g (3.75 mmol) g of methyltriphenylphosphonium iodide, 1.036 g (7.50 mmol) of potassium carbonate, and 0.05 g (0.19 mmol) of 18-crawn-6 in 70 ml of benzene was boiled under an urgon atmosphere for 10 h, then the mixture was cooled, filtered through a bed of aluminum oxide (3 cm), concentrated to the volume of 40 ml, 40 ml of tetrachloromethane was added, and the solution was applied to a column (3.5×40 cm) packed with silica gel, eluent benzene–tetrachloromethane, 1 : 1. The fraction containing butenylporphyrin **VIa** was evaporated to dryness, the residue was recrystallized from the mixture chloroform–methanol, 1 : 5. Yield 0.401 g (80%), R_f 0.81 (Silufol, eluent benzene). Electronic spectrum, λ_{max} (log ε): 419 (5.63), 515 (4.19), 550 (3.76), 591 (3.72), 648 (3.51). ^{1}H NMR spectrum, δ, ppm: –2.78 br.s (2H, NH), 2.55 q (2H, β-CH_2, *J* 7.2 Hz), 2.93 t (2H, α-CH_2, *J* 7.8 Hz), 4.91 m (2H, CH_2-vinyl), 5.74 m (1H, CH-vinyl), 7.73 m (12H, *m-*, *p*-phenyl), 8.20 m, 8.11 d (8H, *o*-phenyl), 8.82 s, 8.75 d, 8.70 m, 8.62 s, 8.57 d (7H, β-pyrrole). Mass spectrum: *m*/*z* 669.834 $[M + 1]^+$.

2-(3-Butenyl)-5,10,15,20-tetraphenylporphyrinatocopper (VIb) was similarly obtained from 0.546 g (0.75 mmol) of aldehyde **IVb**, 1.51 g (3.73 mmol) of methyltriphenylphosphonium iodide, 1.030 g (7.45 mmol) of potassium carbonate, and 0.05 g (0.19 mmol) of 18-crawn-6 in 70 ml of benzene. Yield 0.474 g (87%), R_f 0.92 (Silufol, eluent benzene– tetrachloromethane, 1:1). Electronic spectrum, λ_{max} (log ε): 417 (5.72), 548 (4.37). Mass spectrum: *m*/*z* 730.357 $[M]^+$.

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