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PHENYL-SUBSTITUTED PORPHYRINS. 1. SYNTHESIS OF *meso*-PHENYL-SUBSTITUTED PORPHYRINS

S. A. Syrbu, T. V. Lyubimova, and A. S. Semeikin

A method was developed for the synthesis of a series of meso-phenyl-substituted octaalkylporphyrins with various numbers of phenyl groups at various positions. Some of their properties were studied.

Keywords: octaalkylporphyrins, phenyl-substituted porphyrins.

At present their readily available synthetic analogs *meso*-(5,10,15,20)-tetraphenylporphyrins, produced by the condensation of pyrrole with benzaldehydes, are mainly used to study the properties of porphyrins. In certain cases, however, they are not very suitable since unlike natural porphyrins they do not have alkyl or pseudoalkyl substituents at the β-positions of the porphyrin ring whereas all the *meso* positions, on the other hand, are substituted. The octaalkylporphyrins that are closer to the natural materials are also not always convenient since they do not have substituents that can be used to "tie" the active groups for immobilization. Of great interest, therefore, are compounds that combine the advantages of these two types of porphyrins such as, for example, *meso*-substituted octaalkylporphyrins.

Fairly effective methods have now been developed for the synthesis of some such porphyrins by the condensation of α-unsubstituted pyrroles and their linear derivatives with benzaldehydes in the presence of acidic catalysts [1] (Scheme 1). By these methods we synthesized a series of monophenyl-substituted octaalkylporphyrins **2** and also symmetrical 5,15-diphenyl- and 5,10,15,20-tetraphenyloctaalkylporphyrins **4** and **6** (Tables 1 and 2).

Since *meso*-(5,10,15,20)-tetraphenyloctaalkylporphyrins have a distorted saddle-like structure and their physicochemical characteristics differ substantially from those of the usual flat porphyrins [2], it was of great interest to study the effect of the number of peripheral substituents on the properties of the porphyrins. However, there have not until now been any suitable methods for the synthesis of the least symmetrical 5,15-diphenyl- and 5,10,15-triphenyloctaalkylporphyrins (**4** and **5**). In all such methods difficultly obtainable starting compounds are used, and a mixture of porphyrins requiring separation is formed during the synthesis [3].

Starting from all the facts discussed above we developed a method for the synthesis of a series of *meso*-phenyl-substituted octaalkylporphyrins with various numbers of *meso*-phenyl groups at various positions on the basis of the acid-catalyzed condensation of a mixture of 3,4-dialkylpyrroles and 3,4-dialkyl-2-hydroxymethylpyrroles with benzaldehydes followed by oxidation of the obtained mixture of porphyrinogens with *p*-chloroanil (Scheme 2). The obtained mixture of porphyrins can be separated fairly easily and completely by successive column chromatography on aluminum oxide and silica gel. We carried out three series of

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Ivanovo State University of Chemistry and Technology, Ivanovo, Russia; e-mail: s_serg@isuct.ivanovo.su. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1464-1472, October, 2004. Original article submitted December 29, 2001.

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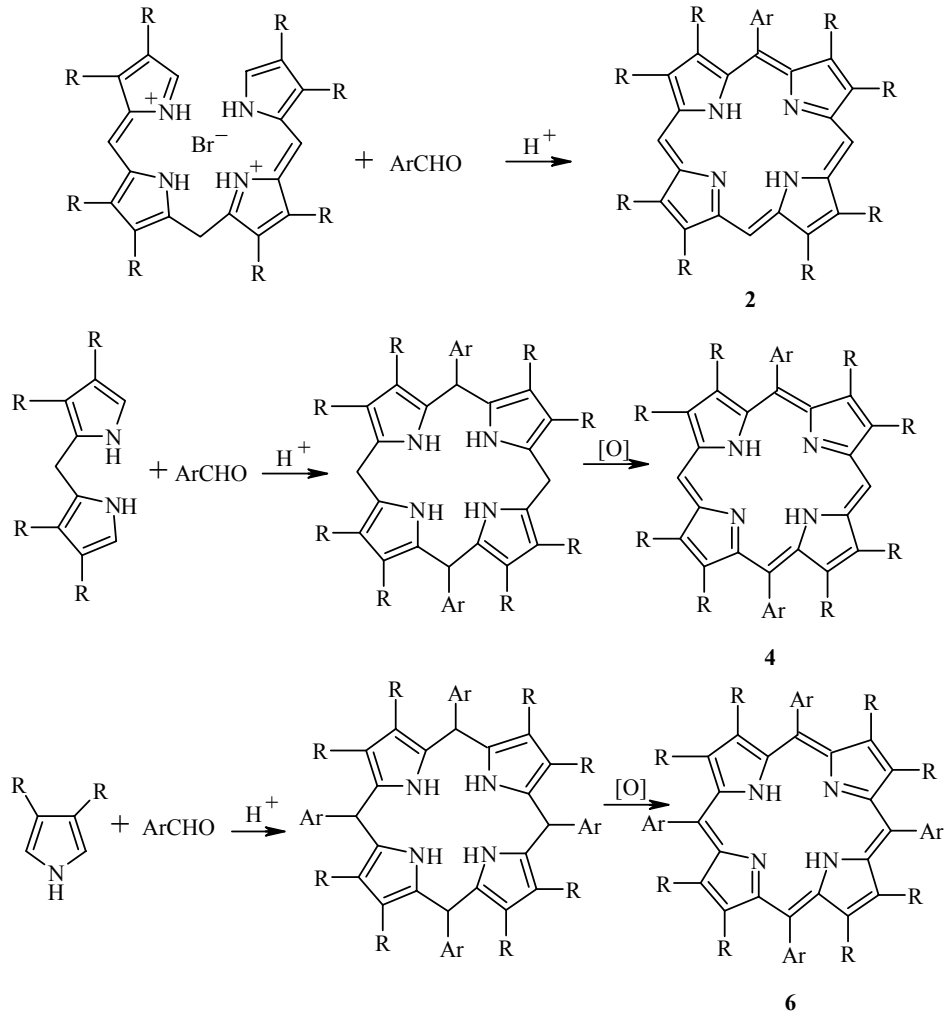
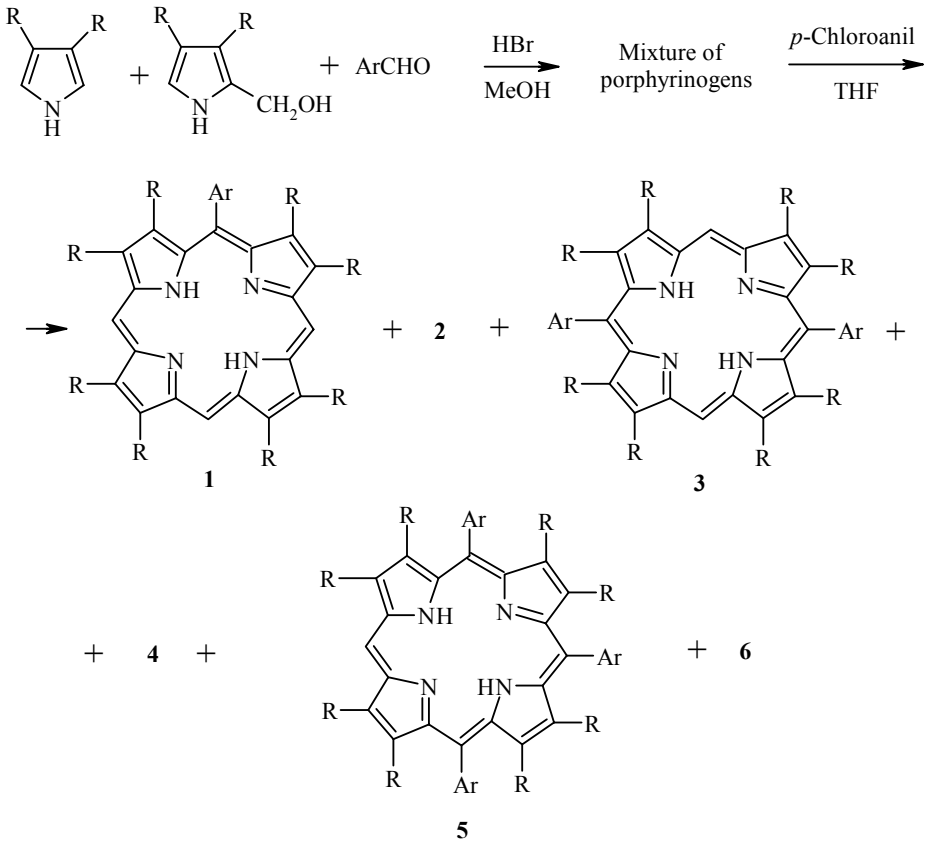
Scheme 1



reactions with various substituted pyrroles and benzaldehydes (Series 1: **1A**, R = Me, Ar = H; **2A-6A**, R = Me, Ar = Ph. Series 2: **1B**, R = Me, Ar = H; **2B-6B**, R = Me, Ar = 3,5-*t*-$Bu_2C_6H_3$. Series 3: **1C**, R = Et, Ar = H; **2C-6C**, R = Et, Ar = Ph).

During the synthesis we were unable to separate the mixture of octamethylporphyrin **1A** and 5,15-diphenyloctamethylporphyrin **3A** on account of their low solubility in the majority of organic solvents. It proved possible to separate these isomers as a result of the increased solubility of the *trans* isomer **3** with the introduction of *tert*-butyl groups into the benzene rings. For the separation of the porphyrins their mixture was first chromatographed on a short column with aluminum oxide (to separate the products from reduction of the *p*-chloroanil). Then, by repeated chromatography on aluminum oxide the mixture was separated into a "readily mobile fraction" containing monophenyl-, *trans*-diphenyl-, and octaalkylporphyrins (**2**, **3**, and **1** respectively) and a "poorly mobile fraction" containing *cis*-diphenyl-, triphenyl-, and tetraphenyloctaalkylporphyrins (**4**, **5**, and **6** respectively). The readily mobile fraction was separated into the individual porphyrins by further chromatography on silica gel, while the poorly mobile fraction was separated on aluminum oxide. The insoluble octamethylporphyrin **1A**, obtained in the first series of reactions, was purified by dissolving in a mixture of chloroform and 0.5% trifluoroacetic acid followed by precipitation of the porphyrin with the addition of

Scheme 2



triethylamine until the color of the solution changed. The yield and some properties of the synthesized porphyrins are given in Tables 1 and 2. Since some of the porphyrins have "blurred" ESR, the spectra of their protonated forms were recorded.

Although the yield of the individual porphyrins in this synthesis is lower than in their production according to Scheme 1 (Table 1), the proposed method makes it possible to obtain the previously unobtainable *cis*-diphenyl- and triphenyloctaalkylporphyrins **4** and **5**, especially as their yield can be increased by using different proportions of the 3,4-dialkylpyrrole, 3,4-dialkyl-2-hydroxymethylpyrrole, and the respective benzaldehyde (in our case 1:1:1). The reason for the different ratios of the yields of the porphyrins in all three series of reactions using the various substrates, when the statistical mixture of compounds **1**, **2**, **3**, **4**, **5**, and **6** in ratios of 1:4:2:4:4:1 should be obtained in all cases [4], is not clear.

Optimization of the structure of the synthesized porphyrins by molecular mechanics (HyperChem software, MM+ force field) showed that the distortion of the porphyrin ring increases with increase in the number of substituting groups (compounds **1** < **2** < **3** < **4** < **5** < **6**). Comparison of the physical characteristics of the obtained porphyrins also shows that with increase in the number of groups substituting the periphery of the porphyrin macrocycle the changes increase in the same order and are particularly marked in the transition from the *trans*-diphenyloctaalkylporphyrins **3** to their *cis* isomers **4** and then to the triphenyl- and tetraphenyloctaalkylporphyrins **5** and **6**. This shows up in a marked decrease of the mobility of the porphyrins on the sorbents, in the nonadditive bathochromic shift of all the bands in the electronic absorption spectra with change in the actual form of the spectra (Table 1), and in the downfield shift of the signals for the NH protons and the upfield shift of the signals for the *meso* protons and the signals for the β-alkyl substituents in the ^{1}H NMR spectra, due probably to decrease in the ring current of the macrocycle (Table 2).

TABLE 1. The Characteristics of *meso*-Phenyl-substituted Octaalkylporphyrins

Porphyrin	Empirical formula	Found, % / Calculated, %			R_f*	UV spectrum, λ_{max}, nm (log ε)						Yield, %*[2]
		C	H	N		I	II	III	IV	Soret	Solvent	
1	2	3	4	5	6	7	8	9	10	11	12	13
1A	$C_{28}H_{30}N_4$	79.6 / 79.9	7.1 / 6.9	13.3 / 13.1	—	620 (3.65)	568 (3.68)	535 (3.96)	500 (4.60)	400 (5.61)	$(Cl_2CH)_2$	34.8 (62.0)
						590 (3.90)	sh	548 (4.23)	—	401 (5.60)	$CHCl_3$–1% CF_3CO_2H	
1C	$C_{36}H_{86}N_4$	75.2 / 75.3	15.0 / 15.2	9.8 / 9.5	0.83 (A), 0.57 (B)	620 (3.74)	568 (3.86)	535 (4.04)	499 (4.15)	400 (5.25)	$CHCl_3$	4.0 (70.0)
2A	$C_{34}H_{34}N_4$	81.9 / 82.3	6.9 / 6.7	11.2 / 11.0	0.65 (A)	624 (3.45)	571 (3.81)	537 (3.85)	504 (4.16)	404 (5.26)	$CHCl_3$	4.0 (56.0)
						sh	559 (4.22)	sh	—	418 (5.53)	$CHCl_3$–1% CF_3CO_2H	
2B	$C_{38}H_{42}N_4$	82.3 / 82.7	7.6 / 7.4	10.1 / 9.9	0.58 (A)	624 (3.23)	571 (3.56)	537 (3.61)	504 (3.86)	405 (4.92)	$CHCl_3$	5.5 (38.2)
2C	$C_{42}H_{90}N_4$	77.5 / 75.8	13.9 / 14.0	8.6 / 8.2	0.87 (A), 0.47 (B)	624 (3.54)	573 (3.90)	538 (3.97)	505 (4.24)	405 (5.31)	$CHCl_3$	43.7 (62.0)
3A	$C_{40}H_{38}N_4$	83.6 / 83.5	6.7 / 6.6	9.7 / 9.9	0.75 (A)	627 (3.23)	575 (3.82)	542 (3.70)	508 (4.19)	409 (5.29)	$CHCl_3$	9.2*[3] (64.0)
						619 (3.87)	572 (4.12)	sh	—	430 (5.46)	$CHCl_3$–1% CF_3CO_2H	
3B	$C_{44}H_{46}N_4$	83.8 / 84.2	7.3 / 7.1	8.9 / 8.7	0.88 (A)	626 (3.38)	574 (3.89)	539 (3.78)	508 (4.25)	409 (5.36)	$CHCl_3$	8.5 (46.1)
3C	$C_{48}H_{94}N_4$	79.3 / 79.8	13.0 / 12.7	13.0 / 12.8	0.93 (A), 0.59 (B)	627 (3.30)	575 (3.87)	542 (3.76)	508 (4.25)	410 (5.35)	$CHCl_3$	7.9 (46.0)
4A	$C_{40}H_{38}N_4$	83.6 / 84.0	6.7 / 6.5	9.7 / 9.5	0.18 (A)	sh	586 (3.79)	sh	515 (4.17)	417 (5.25)	$CHCl_3$	4.9

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
4B	$C_{44}H_{46}N_4$	83.8 83.3	7.3 7.5	8.9 9.2	0.17 (A), 0.37 (C)	sh	582 (3.82)	sh	512 (4.20)	414 (5.29)	$CHCl_3$	3.5
4C	$C_{48}H_{94}N_4$	79.3 78.8	13.0 13.3	7.7 7.9	0.18 (A), 0.92 (D)	sh	578 (3.89)	sh	510 (4.25)	413 (5.39)	$CHCl_3$	12.4
5A	$C_{46}H_{42}N_4$	84.9 84.5	6.5 6.6	8.6 8.9	0.34 (C)	666 (3.32)	600 (3.74)	sh	528 (4.13)	430 (5.24)	$CHCl_3$	13.5
						sh	653 (4.24)	598 (3.99)	—	451 (5.40)	$CHCl_3$–1% CF_3CO_2H	
5B	$C_{50}H_{50}N_4$	84.9 85.4	7.2 7.0	7.9 7.6	0.19 (C), 0.87 (E)	668 (3.67)	597 (3.81)	sh	526 (4.16)	429 (5.28)	$CHCl_3$	36.0
5C	$C_{54}H_{98}N_4$	80.7 81.1	12.3 12.1	7.0 6.8	0.15 (A), 0.86 (D)	667 (3.79)	608 (3.91)	sh	534 (4.14)	438 (5.28)	$CHCl_3$	10.8
6A	$C_{52}H_{46}N_4$	85.9 85.6	6.4 6.5	7.7 7.9	0.16 (C)	694 (3.96)	602 (3.91)	—	553 (3.97)	454 (5.21)	$CHCl_3$–0.5% NEt_3	5.2 (65.0)
						687 (4.40)	sh	sh	—	466 (5.32)	$CHCl_3$–1% CF_3CO_2H	
6B	$C_{56}H_{54}N_4$	85.9 86.5	7.0 6.8	7.1 6.7	0.35 (E)	692 (3.72)	595 (3.95)	sh	549 (4.06)	450 (5.28)	$CHCl_3$–0.5% NEt_3	7.5 (44.0)
						700 (4.56)	sh	sh	—	473 (5.40)	$CHCl_3$–1% CF_3CO_2H	
6C	$C_{60}H_{102}N_4$	81.9 81.5	11.7 11.9	6.4 6.6	0.30 (D)	696 (3.75)	598 (3.82)	sh	551 (4.14)	452 (5.34)	$CHCl_3$–0.5% NEt_3	6.7 (31.2)
						691 (4.53)	sh	sh	—	471 (5.50)	$CHCl_3$–1% CF_3CO_2H	

* Eluent (solvent): benzene (A), benzene–hexane, 1:1 (B), benzene–methanol, 10:1 (C), benzene–methanol, 1:1 (D), benzene–methanol, 10:2 (E).

*[2] The yield of the porphyrins synthesized according to Scheme 1 is given in parentheses.

*[3] Mixture with octamethylporphyrin **1A**.

TABLE 2. The ^{1}H NMR Spectra of *meso*-Phenyl-substituted Octaalkylporphyrins

Porphyrin	Chemical shifts, δ, ppm					
	meso-H	Ar		R	NH	Solvent
		o-H	*m*-, *p*-H			
1A	10.74, s	—	—	3.68, s	-4.45, s	$CDCl_3$–CF_3CO_2H
1C	10.10, s	—	—	4.11, q; 1.92, t	-3.75, s	$CDCl_3$
2A	10.13, s; 9.92, s	8.02, m	7.75, m	3.58, s; 3.52, s; 2.46, s	-3.20, s; -3.30, s	$CDCl_3$
	10.50, s; 10.37, s	8.26, m	8.01, m	3.58, s; 3.32, s; 2.27, s	-2.99, s; -4.21, s	$CDCl_3$–CF_3CO_2H
2B	10.13, s; 9.91, s	7.89, s	7.80, s; 1.49, s (Bu)	3.61, s; 3.58, s; 3.52, s; 2.42 s	-3.25, s	$CDCl_3$
2C	10.18, s; 9.93, s	8.21, d	7.79, d; 7.66, t	4.12, m; 1.89, m; 2.78, m; 1.18, m	-3.02, s; -3.15, s	$CDCl_3$
3A	10.34, s	8.26, m	7.95, m	3.26, s; 2.27, s	-3.07, s	$CDCl_3$–CF_3CO_2H
3B	10.22, s	7.91, s	7.80, s; 1.50, s (Bu)	3.54, s; 2.46, s	-2.45, s	$CDCl_3$
3C	10.23, s	8.21, d	7.78, d; 7.67, t	4.09, q;9, t;2.79, q; 1.18, t	-2.08, s	$CDCl_3$
4A	9.79, s	8.13, m	7.76, m	3.49, s; 3.29, s; 2.08, s	1.46, s; -3.02, s	$CDCl_3$
	9.99, s	8.36, m; 8.28, m	7.97, m	3.17, s; 2.22, s; 1.81, s	-1.31, s; -2.23, s; -3.84, s	$CDCl_3$–CF_3CO_2H
4B	9.84, s	7.94, s	7.77, s; 1.49, s (Bu)	3.54, s; 3.40, s; 2.26, s; 2.10, s	1.25, s; -3.14, s	$CDCl_3$
4C	9.63, s	8.30, d	7.75, d; 7.67, t	3.92, q; 1.80, t; 3.80, q; 1.57, t; 2.65, q; 0.63, t; 2.25, q; 0.44, t	-2.72, br. s	$CDCl_3$
5A	9.56, s	8.22, m	7.72, m	3.25, s; 2.25, s; 1.95, s; 1.86, s	1.41, s; -2.35, s	$CDCl_3$
	9.79, s	8.36, m; 8.23, m	7.96, m	3.13, s; 2.24, s; 1.84, s; 1.81, s	-1.26, s; -2.47, s	$CDCl_3$–CF_3CO_2H
5B	9.64, s	7.99, s	7.74, s; 1.51, s (Bu)	3.30, s; 2.26, s; 1.97, s; 1.87, s	-2.45, s	$CDCl_3$
5C	9.45, s	8.32, m	7.71, m	3.75, q; 1.56, t; 2.70, q; 0.72, t; 2.25, m; 0.46, t; 0.37, t	-2.09, s	$CDCl_3$
6A	—	8.41, m	7.87, m	1.77, s	0.80, s	$CDCl_3$
	—	8.35, m	7.93, m	1.84, s	-1.14, s	$CDCl_3$–CF_3CO_2H
6B	—	8.13, s	7.70, s; 1.49, s (Bu)	1.82, br. s	0.84, s	$CDCl_3$
	—	8.22, s	7.90, s; 1.49, s (Bu)	1.79, s	-0.40, s	$CDCl_3$–CF_3CO_2H
6C	—	8.36, m	7.71, m	2.52, br. s; 0.47, br. s	—	$CDCl_3$
	—	8.46, m	7.88, m	2.42, q; 2.16, q; 0.17, t	-0.19, s	$CDCl_3$–CF_3CO_2H

The broadening and destructuring of the signals for the alkyl substituents and the NH protons in the ^{1}H NMR spectra of the tetraphenyloctaalkylporphyrins **6B** and **6C** is apparently due to the existence of several conformations, which change from one to the other at a rate close to the "proton relaxation" time. Protonation of the porphyrins excludes the possible existence of conformations on account of repulsion of the positive charges.

This leads to restoration of the fine structure in the ^{1}H NMR spectra of these porphyrins and to splitting of the components of the signal for the CH_2 protons of the ethyl groups in the porphyrin **6C** into two due to their nonequivalence. Interesting is the splitting of the signals for the *meta* and *para* protons of the phenyl rings in the ethyl derivatives of phenyl-substituted porphyrins, which is not observed in the tetraphenylporphyrins not substituted at the β position. There is also a strong downfield shift of the signals for the protons of the CH_3 fragments of the ethyl groups adjacent to the phenyl rings for the β-ethyl-substituted porphyrins, arising on account of the strong screening action of the ring current of the phenyl rings.

Thus, change in the number of peripheral substituents in the porphyrin ring (distortion of the macrocycle) can provide a tool for smooth adjustment of the physicochemical characteristics of porphyrins without significant change in the internal structure of the macrocycle.

At the present time the most interesting of the synthesized porphyrins are being studied by X-ray crystallographic analysis, and the kinetics of complexation and protonation in solutions are being investigated.

EXPERIMENTAL

The electronic absorption spectra were recorded on a Lambda 20 instrument. The ^{1}H NMR spectra were recorded on a Bruker AC-200 instrument at 200 MHz with HMDS as internal standard (δ 0.05 ppm). The individuality and purity of the compounds were established by TLC (Silufol).

3,4-Dialkyl-2-hydroxypyrroles. The compounds were synthesized by the reduction of 3,4-dialkyl-2-formylpyrroles with sodium borohydride by analogy with data in [5]. The latter were obtained by the formylation of 3,4-dimethylpyrrole [6] or 3,4-diethylpyrrole [7] by the Vilsmeier method [8]. The α-unsubstituted tetraalkylpyrrolylmethanes and octaalkylbiladienes-*a*,*c* were obtained from the corresponding 3,4-dialkyl-5-ethoxycarbonyl-2-methylpyrroles by methods similar to those described in [9].

Synthesis and Separation of the Mixture of *meso*-Phenyloctaalkylporphyrins. To a solution of 3,4-dialkyl-2-hydroxymethylpyrrole (13.6 mmol), 3,4-dialkylpyrrole (13.6 mmol), and benzaldehyde (13.6 mmol) in methanol (35 ml) in an inert atmosphere we added concentrated hydrobromic acid (1 ml). The mixture was stirred at room temperature for 4 h. The white precipitate of the porphyrinogens was filtered off, washed with methanol, and dissolved in THF (40 ml). To the obtained solution we added a solution of *p*-chloroanil (5 g, 20 mmol) in THF (50 ml), and we stirred the mixture for 5 h at ~20°C. The solvent was distilled under vacuum, and the residue was washed with 10% sodium hydroxide solution and with water and dried at room temperature to constant weight. The precipitate was dissolved in chloroform (200 ml) (when necessary the insoluble precipitate was filtered off) and chromatographed on a column (3 × 15 cm) with aluminum oxide of III activity, eluting the mixture of porphyrins with chloroform. The eluate was evaporated and rechromatographed on a column (2.5 × 50 cm) with aluminum oxide of III activity with chloroform as eluant. The mixture was separated into two fractions – a readily mobile fraction and a poorly mobile fraction. The readily mobile fraction was chromatographed on a column (2.5 × 60 cm) of silica gel (L 100/250) with benzene as eluant. For separation into the individual porphyrins the poorly mobile fraction was chromatographed on a column (2.5 × 60 cm) of aluminum oxide of III activity with chloroform as eluant. After evaporation of the eluates the porphyrins were finally precipitated with methanol (50 ml), filtered, and dried to constant weight at room temperature. The residue insoluble in chloroform was dissolved in a mixture of chloroform and 0.5% trifluoroacetic (50 ml) acid with subsequent precipitation of the porphyrin by the addition of triethylamine until the color of the solution had changed. The porphyrin was filtered off, washed with chloroform (50 ml), and dried to constant weight at ~20°C.

Series 1. From a mixture of 2-hydroxymethyl-3,4-dimethylpyrrole, 3,4-dimethylpyrrole, and benzaldehyde we obtained: A mixture of octamethylporphyrin **1A** and 5,15-diphenyloctamethylporphyrin **3A**, yield 360 mg; 5-phenyloctamethylporphyrin **2A**, yield 90 mg; 5,10-diphenyloctamethylporphyrin **4A**, yield 200 mg; 5,10,15-triphenyloctamethylporphyrin **5A**, yield 400 mg; 75,10,15,20-tetraphenyloctamethyl-porphyrin **6A**, yield 130 mg.

Series 2. From a mixture of 2-hydroxymethyl-3,4-dimethylpyrrole, 3,4-dimethylpyrrole, and 3,5-di-*tert*-butylbenzaldehyde we obtained: Octamethylporphyrin **1B**, yield 500 mg; 5-(3,5-di-*tert*-butylphenyl)octamethylporphyrin **2B**, yield 150 mg; 5,15-di(3,5-di-*tert*-butylphenyl)octamethylporphyrin **3B**, yield 460 mg; 5,10-di(3,5-di-*tert*-butylphenyl)octamethylporphyrin **4B**, yield 200 mg; 5,10,15-tri(3,5-di-*tert*-butylphenyl)octamethylporphyrin **5B**, yield 1600 mg; 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)octamethylporphyrin **6B**, yield 1600 mg.

Series 3. From a mixture of 3,4-diethyl-2-hydroxymethylpyrrole, 3,4-diethylpyrrole, and benzaldehyde we obtained: Octaethylporphyrin **1C**, yield 90 mg; 5-phenyloctaethylporphyrin **2C**, yield 1200 mg; 5,15-diphenyloctaethylporphyrin **3C**, yield 370 mg; 5,10-diphenyloctaethylporphyrin **4C**, yield 580 mg; 5,10,15-triphenyloctaethylporphyrin **5C**, yield 370 mg; 5,10,15,20-tetraphenyloctaethylporphyrin **6C**, yield 190 mg.

Octaethylporphyrins (1). To a solution of 3,4-dialkyl-2-hydroxymethylpyrrole (8.0 mmol) in methanol (10 ml) in an inert atmosphere we added concentrated hydrobromic acid (0.3 ml). The mixture was stirred at ~20°C for 2 h. The white precipitate of the porphyrinogen was filtered off, washed with methanol, and dissolved in THF (15 ml). To the obtained solution we added a solution of *p*-chloroanil (1.2 g, 5 mmol) in THF (50 ml), and we stirred the mixture for 5 h at ~20°C. The solvent was distilled under vacuum, and the residue was washed with a 10% solution of sodium hydroxide and with water and dried to constant weight at room temperature. The octamethylporphyrin **1A** (**1B**) was purified by reprecipitation from a mixture of chloroform and trifluoroacetic acid. Yield 520 mg. The octaethylporphyrin **1C** was isolated by column chromatography (2.5 × 60 cm) with aluminum oxide of III activity and with chloroform as eluant. Yield 750 mg.

5-Phenyloctaalkylporphyrins (2). A solution of octaalkylbiladiene-*a*,*c* (1.0 mmol), the respective benzaldehyde (10 mmol), and concentrated hydrobromic acid (1 ml) in ethanol (50 ml) was boiled for 4 h, iodine (0.26 g, 1 mmol) was then added, and the mixture was boiled for a further 15 min. The mixture was cooled and neutralized with a concentrated solution of ammonia (2 ml). The precipitate was filtered off, washed with ethanol, and dried. The porphyrins were dissolved in chloroform (100 ml) and chromatographed on a column (2.6 × 60 cm) of aluminum oxide of III activity with chloroform as eluent. The eluate was evaporated, the porphyrin was precipitated with methanol (30 ml), and after filtration it was dried to constant weight at ~20°C. 5-Phenyloctamethylporphyrin **2A**, yield 280 mg; 5-(3,5-di-*tert*-butylphenyl)octamethylporphyrin **2B**, yield 230 mg; 5-phenyloctaethylporphyrin **2C**, yield 380 mg.

5,15-Diphenyloctaalkylporphyrins (3). To a solution of the respective benzaldehyde (2.5 mmol) and *p*-toluenesulfonic acid (0.13 g, 6.0 mmol) in methanol (30 ml) in an inert atmosphere we added a solution of tetraalkyldipyrrolylmethane (2.5 mmol) in methanol (20 ml). The mixture was stirred at ~20°C for 3 h and kept overnight with cooling. The precipitated porphyrinogen was then filtered off, washed with methanol, and dissolved in THF (100 ml). To the obtained solution we added a solution of *p*-chloroanil (0.9 g, 3.75 mmol) in THF (50 ml), and we stirred the mixture at ~20°C for 4 h. The solvent was distilled under vacuum, and the residue was washed with a 10% solution of sodium hydroxide and with water and dried at ~20°C to constant weight. 5,15-Diphenyloctamethylporphyrin **3A** was purified by reprecipitation from a mixture of chloroform and trifluoroacetic acid. Yield 450 mg. 5,15-Di(3,5-*tert*-butylphenyl)octamethylporphyrin **3B** and 5,15-diphenyloctaethylporphyrin **3C** were purified by column chromatography (2.5 × 60 cm) of aluminum oxide with III activity with chloroform as eluent. Yield 460 mg and 400 mg respectively.

5,10,15,20-Tetraphenyloctaalkylporphyrins (6). To a solution of 3,4-dialkylpyrrole (9.0 mmol) and benzaldehyde (9.0 mmol) in methanol (50 ml) in an inert atmosphere we added concentrated hydrobromic acid (2 ml). The mixture was stirred at ~20°C for 4 h, and the white precipitate of the porphyrinogen was filtered off, washed with methanol, and dissolved in THF (40 ml). To the obtained solution we added a solution of *p*-chloroanil (1.9 g, 7.7 mmol) in THF (30 ml), and we stirred the mixture at ~20°C for 5 h. The solvent was distilled under vacuum, and the residue was washed with a 10% solution of sodium hydroxide and with water and dried to constant weight at ~20°C. The precipitate was dissolved in chloroform (100 ml) and chromatographed twice on a column (2.5 × 60 cm) of aluminum oxide of III activity with chloroform as eluent.

The eluate was evaporated, and the porphyrin was precipitated with methanol (30 ml), filtered off, and dried to constant weight at ~20°C. 5,10,15,20-Tetraphenyloctamethylporphyrin **6A**, yield 1.1 g. 5,10,15,20-Tetra(3,5-di-*tert*-butylphenyl)octamethylporphyrin **6B**, yield 1.2 g. 5,10,15,20-Tetraphenyloctaethylporphyrin **6C**, yield 0.6 g.

REFERENCES

1. O. Golubchikov (editor), *Advances in the Chemistry of Porphyrins* [in Russian], NII Khimii SPBGU, St. Petersburg (1997), Vol. 1, p. 52.
2. C. J. Medforth, M. D. Berber, and K. M. Smith, *Tetrahedron Lett.*, **31**, 3719 (1990).
3. Y. Aoyama, K. Saita, H. Toi, H. Ogoshi, and Y, Okamoto, *Tetrahedron Lett.*, **28**, 4853 (1987).
4. F. A. Walker, J. A. Barry, V. L. Balke, G. A. McDermott, M. Z. Wu, and P. F. Linde, *Electrochem. and Spectrochem. Studies of Biological Redox Components* (1981), p. 377.
5. G. P. Gurinovich, A. N. Sevchenko, and K. N. Solov'ev, *Spectroscopy of Chlorophyll and Related Compounds*, Nauka i Tekhnika, Minsk (1968), p. 52.
6. K. Ichimura, S. Ichikawa, and K. Imamura, *Bull. Chem. Soc. Jpn.*, **4**, 1157 (1976).
7. H. W. Whitlock and R. J. Hanauer, *J. Org. Chem.*, **33**, 2169 (1968).
8. A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1620 (1965).
9. N. S. Dudkina, E. M. Kuvshinova, and A. S. Semeikin, *Zh. Obshch. Khim.*, **68**, 2042 (1998).