

$J_{AB} = 16.5$  Hz), 6.48-7.30 (3H, m, 5-H, 6-H, 8-H), 8.06 ppm (1H, br., NH). Found, %: N 9.8.  $C_{19}H_{15}BrN_2O$ . Calculated, %: N 9.5.

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#### PORPHYRINS.

##### 20.\* INTERACTION OF 2-FORMYL-5,10,15,20-TETRAPHENYLPORPHYRIN WITH CH ACIDS

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UDC 547.749.04

The reactions of 2-formyl-5,10,15,20-tetraphenylporphyrin (Ia) with nitromethane and of its Cu complex (Ib) with nitromethane, malonic acid, and its esters have been investigated. On interacting porphyrins (Ia,b) with nitromethane in AcOH/BuNH<sub>2</sub> the 2-(2-nitrovinyl)porphyrins (IIa,b) were formed, in liquid NH<sub>3</sub> the nitroalcohols (IIIa,b) were formed, and in DMF/BuNH<sub>2</sub> the dinitro derivatives (IVa,b) were formed. The interaction of porphyrin (Ib) with malonic acid and its esters led to the corresponding condensation products in high yield.

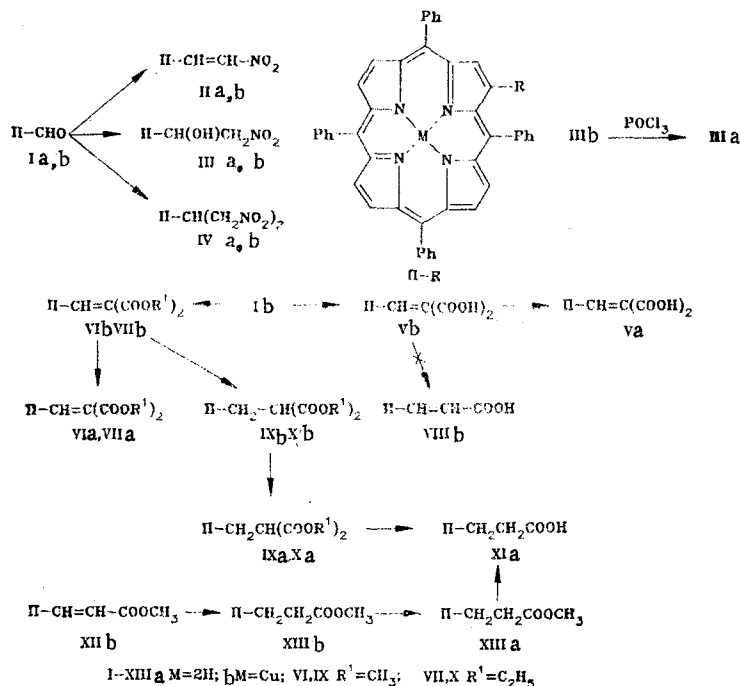
The substance 5,10,15,20-tetraphenylporphyrin is one of the simplest and most widely investigated porphyrins in numerous catalytic processes. With the aim of designing accessible catalysts containing immobilized metalloporphyrin we have effected the synthesis of functionally substituted derivatives of tetraphenylporphyrin which may be used for immobilization on various carriers.

We consider the following route the most promising for obtaining functional derivatives of tetraphenylporphyrin. First, a formyl group was introduced into the tetraphenylporphyrin in the  $\beta$ -pyrrole position, and then various reactions were effected on it which led to a compound with an active functional group such as carboxyl. Such compounds may readily be used for covalent addition to various carriers.

The introduction of a formyl group into the tetraphenylporphyrin molecule by the Vilsmeier reaction has been investigated in sufficient detail and occurs in practically quantitative yield. It was shown in [2, 3] that 2-formyl-5,10,15,20-tetraphenylporphyrin (Ia) interacted readily with phosphoranes by the Wittig reaction forming derivatives of acrylic acid. It was established in the present study that porphyrin (Ia) and its Cu complex (Ib) reacted readily with CH acids with the formation of various functionally substituted derivatives of tetraphenylporphyrin.

\*For Communication 19 see [1].

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskih Soedinenii, No. 7, pp. 936-940, July, 1985. Original article submitted January 26, 1984; revision submitted October 2, 1984.



At first we investigated the interaction of compounds (Ia) and (Ib) with the classical CH acid nitromethane. It was assumed that 2-(2-nitrovinyl)-5,10,15,20-tetraphenylporphyrin (IIa) and its Cu complex (IIb) could be obtained in this way. Previously nitrovinylporphyrins were obtained by the nitration of the corresponding  $\beta$ -vinylporphyrins [4]. It turned out that different compounds were formed depending on the reaction conditions. Nitroalcohols (IIIa,b) were formed on condensation of porphyrins (Ia,b) in liquid ammonia. Since demetallation of complex (IIIb) by the usual method (by treatment with concentrated H<sub>2</sub>SO<sub>4</sub>) led to decomposition of the substance, the new method of demetallation from [5] was used, viz., solution of complex (IIIb) in phosphorus oxychloride previously treated with a small quantity of water. Porphyrin (IIIa) was obtained by this method in 50% yield. Derivatives (IIIa,b) were converted into porphyrin (IIa) in 40% yield on heating in POCl<sub>3</sub>/H<sub>2</sub>O.

Nitrovinyl derivatives (IIa,b) were readily formed on condensing porphyrins (Ia,b) with nitromethane in AcOH.

Carrying out the reaction of porphyrins (Ia,b) with nitromethane by heating in DMF led to the dinitro derivatives (IVa,b) also in high yield. These experiments showed that porphyrin (Ia) possessed the classical properties of aromatic aldehydes.

On interacting complex (Ib) with malonic acid and its methyl and ethyl esters, the Cu complexes of 2-(2,2-dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin (Vb), 2-(2,2-dimethoxycarbonylvinylyl)-5,10,15,20-tetraphenylporphyrin (VIb), and 2-(2,2-diethoxycarbonylvinylyl)-5,10,15,20-tetraphenylporphyrin (VIIb) were obtained, the demetallation of which gave the corresponding porphyrins (Va-VIIa).

Under the conditions of the condensation 2-(2-carboxyvinyl)-5,10,15,20-tetraphenylporphyrin (VIIIb) was not formed.

It was discovered by us that dicarboxyvinyl derivatives (VIb) and (VIIb) were readily reduced by LiAlH<sub>4</sub> in THF at -10°C to the Cu complex of 2-(2,2-dimethoxycarbonylethyl)-5,10,15,20-tetraphenylporphyrin (IXb) and 2-(2,2-diethoxycarbonylethyl)-5,10,15,20-tetraphenylporphyrin (Xb), the demetallation of which gave 2-(2,2-dimethoxycarbonylethyl)-5,10,15,20-tetraphenylporphyrin (IXa) and 2-(2,2-diethoxycarbonylethyl)-5,10,15,20-tetraphenylporphyrin (Xa), respectively. The saponification of porphyrins (IXa) and (Xa) by boiling with aqueous KOH in pyridine with simultaneous decarboxylation led to 2-(2-carboxyethyl)-5,10,15,20-tetraphenylporphyrin (XIa).

An alternative synthesis of porphyrin (XIa) seemed of interest. 2-(2-Methoxycarbonylvinylyl)-5,10,15,20-tetraphenylporphyrin (XIIb) was synthesized by the known procedure of [2].

We succeeded in reducing the double bond in (XIIb) with sodium borohydride in the presence of NiCl<sub>2</sub> using the reduction method indicated in [6].

The obtained Cu complex of 2-(2-methoxycarbonyl-ethyl)-5,10,15,20-tetraphenylporphyrin (XIIIb) was demetallated to 2-(2-methoxycarbonyl-ethyl)-5,10,15,20-tetraphenylporphyrin (XIIIa) saponification of which gave a quantitative yield of porphyrin (XIa) which itself was the starting material for the synthesis of polymeric systems containing covalently bonded porphyrins.

#### EXPERIMENTAL

Electronic spectra in chloroform (spectra of porphyrins Va and Vb in DMF, of XIIIa in benzene) were taken on a Specord-40 instrument. IR spectra were obtained on a Perkin-Elmer 180 instrument (in KBr disks), PMR spectra on a Bruker WM-360 instrument (in CDCl<sub>3</sub>, spectrum of Va in DMSO-D<sub>6</sub>), internal standard was TMS, the multiplet signals of the o-, m-, and p-protons of the phenyl substituents are not shown. Mass spectra were taken on a Varian MAT-311 instrument. The mass spectra of copper complexes are shown for the signal of the <sup>63</sup>Cu isotope. Porphyrins were separated by TLC in a binder-free layer on 20 × 20 cm plates of L 5/40 μm silica gel in the systems chloroform-hexane 3:1 (A), 2.5:1 (B), 2:1 (C), chloroform-methanol 10:0.1 (D), benzene-acetone 10:0.1 (E). Data of R<sub>f</sub> are shown for system B on Silufol plates.

2-(2-Nitrovinyl)-5,10,15,20-tetraphenylporphyrin (IIa). A. A suspension of complex (Ib) (100 mg: 0.142 mmole) in a mixture of glacial acetic acid (20 ml), nitromethane (4 ml), and butylamine (5 ml) was boiled for 1 h, cooled to 0°C, the precipitated crystals were filtered off, washed with water, dried, chromatographed in system C, crystallized from a mixture of chloroform-hexane, and complex (IIb) (101 mg: 95%) was obtained with R<sub>f</sub> 0.64. UV spectrum, λ<sub>max</sub> (ε × 10<sup>-3</sup>): 394 (57.8), 436 (120.8), 554 (14.2), 601 nm (14.0). IR spectrum: 1630 (C=C), 1525, 1340 cm<sup>-1</sup> (NO<sub>2</sub>). Mass spectrum, m/z (%): 746 (M<sup>+</sup> 100). Found, %: C 73.4, H 4.1, N 9.1. C<sub>46</sub>H<sub>29</sub>CuN<sub>5</sub>O<sub>2</sub>. Calculated, %: C 73.9, H 3.9, N 9.3.

Complex (IIb) (100 mg: 0.134 mmole) was dissolved in a mixture of POCl<sub>3</sub> (5 ml) and H<sub>2</sub>O (0.5 ml) at 0°C, after 30 min the mixture was poured onto ice (200 g), neutralized with aqueous ammonia to pH 7, extracted with chloroform (3 × 50 ml), the extract was washed with water (300 ml), dried, evaporated under vacuum, the residue chromatographed in system B, crystallized from chloroform-hexane, and porphyrin (Ia) (86 mg: 93%) was obtained. UV spectrum, λ<sub>max</sub> (ε · 10<sup>-3</sup>): 436 (122.5), 530 (14.6), 572 (5.0), 608 (4.8), 668 nm (4.9). IR spectrum: 1627 (C=C), 1525, 1335 cm<sup>-1</sup> (NO<sub>2</sub>). Mass spectrum, m/z (%): 685 (M<sup>+</sup> 67), 653 (100), 638 (58), 626 (30), 614 (15). PMR spectrum: 9.00-8.72 (7H, m, β-H), 4.31-4.13 (2H, m, -CH=CH-NO<sub>2</sub>), -2.54 ppm (2H, s, NH). Found, %: C 80.3, H 4.8, N 10.4. C<sub>46</sub>N<sub>5</sub>N<sub>5</sub>O<sub>2</sub>. Calculated, %: C 80.6, H 4.6, N 10.4.

B. Porphyrin (IIa) was obtained from porphyrin (Ia) in 68% yield similarly to method A.

2-(2-Nitro-1-hydroxyethyl)-5,10,15,20-tetraphenylporphyrin (IIIa). A. Liquid ammonia (100 ml) was poured after 10 min into a solution of complex (Ib) (100 mg: 0.142 mmole) and nitromethane (10 ml) in chloroform (100 ml). After 10 h the chloroform solution was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated, and complex (IIIb) (112 mg: 94%) was separated chromatographically in system A having R<sub>f</sub> 0.11. UV spectrum, λ<sub>max</sub> (ε · 10<sup>-3</sup>): 417, (456.7), 541 nm (20.1). IR spectrum: 3570 (OH), 1560, 1356 cm<sup>-1</sup> (NO<sub>2</sub>). Found, %: C 71.9, H 4.2, N 9.4. C<sub>46</sub>H<sub>31</sub>CuN<sub>5</sub>O<sub>2</sub>. Calculated, %: C 72.2, H 4.1, N 9.2. Complex (IIIb) (100 mg: 0.131 mmole) was dissolved in a mixture of POCl<sub>3</sub> (5 ml) and H<sub>2</sub>O (0.5 ml) at 0°C, after 30 min the mixture was poured onto ice (200 g), neutralized with aqueous ammonia to pH 7, the product was extracted with chloroform (3 × 50 ml), the chloroform solution was washed with water (300 ml), evaporated under vacuum, the residue chromatographed in system A, crystallized from chloroform-hexane, and porphyrin (IIIa) (37 mg: 40%) R<sub>f</sub> 0.09 was obtained. UV spectrum: λ<sub>max</sub> (ε · 10<sup>-3</sup>): 421 (425.1), 518 (19.7), 552 (7.5), 594 (6.0), 649 nm (4.1). IR spectrum: 3570 (OH), 1565, 1355 cm<sup>-1</sup> (NO<sub>2</sub>). PMR spectrum: 9.04-8.68 (7H, m, β-H), 5.56-2.53 (1H, q., J = 8.8 Hz, J = 2.4 Hz, -CH(OH)CH<sub>2</sub>NO<sub>2</sub>), 4.79-4.60 (2H, o, J = 14.2 Hz, -CH(OH)CH<sub>2</sub>NO<sub>2</sub>), 3.08-3.04 (1H, d, J = 3 Hz, -CH(OH)CH<sub>2</sub>NO<sub>2</sub>), -2.75 ppm (2H, s, NH). Found, %: C 78.6, H 4.5, N 10.1. C<sub>46</sub>H<sub>33</sub>N<sub>5</sub>O<sub>3</sub>. Calculated, %: C 78.5, H 4.7, N 9.9.

B. Porphyrin (IIIa) was obtained from porphyrin (Ia) in 90% yield by a method similar to A.

2-[Bis(nitromethyl)methyl]-5,10,15,20-tetraphenylporphyrin (IVa). A. A mixture of DMF (50 ml), nitromethane (4 ml), butylamine (5 ml), and complex (Ib) (200 mg; 0.284 mmole) was kept for 2 h at 100°C, cooled, chloroform (100 ml) was added, the mixture was poured into water (1 liter), the chloroform layer was separated, washed with 20% AcOH, with water, dried, evaporated, the residue chromatographed in system C, crystallized from chloroform-hexane, and complex (IVb) (190 mg; 83%) of R<sub>f</sub> 0.37 was obtained. UV spectrum, λ<sub>max</sub> (ε·10<sup>-3</sup>): 418 (451.5), 542 nm (19.1). IR spectrum: 1570, 1350 cm<sup>-1</sup> (NO<sub>2</sub>). Mass spectrum, m/z (%): 807 (M<sup>+</sup> 68), 748 (42), 729 (24), 716 (66), 701 (100.) Found, %: C 69.8, H 4.0, N 10.5. C<sub>47</sub>H<sub>32</sub>CuN<sub>5</sub>O<sub>3</sub>. Calculated, %: C 69.8, H 4.1, N 10.4. Complex (IVb) (200 mg; 0.248 mmole) was dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> (100 ml) at 0°C, and after 30 min was poured onto ice (300 g), neutralized with aqueous ammonia to pH 7, extracted with chloroform (3 × 50 ml), the extract dried, evaporated, and porphyrin (IVa) (169 mg; 92%) of R<sub>f</sub> 0.28 was separated chromatographically in system C. UV spectrum, λ<sub>max</sub> (ε·10<sup>-3</sup>): 422 (406.7), 518 (17.2), 553 (6.0), 594 (5.0), 651 nm (3.9). IR spectrum: 1555, 1345 cm<sup>-1</sup> (NO<sub>2</sub>). Mass spectrum, m/z (%): 746 (M<sup>+</sup> 100), 654 (40), 640 (12). PMR spectrum: 8.84-8.65 (7H, m, β-H), 4.94, 4.86 (2H, J = 13.6 Hz, -CH-CH<sub>2</sub>NO<sub>2</sub>)<sub>2</sub>, 4.53 (1H, J = 6.6 Hz, J = 6.6 Hz, -CH(CH<sub>2</sub>NO<sub>2</sub>)<sub>2</sub>), -2.75 ppm (2H, s, NH). Found, %: C 75.8, H 4.8, N 11.3. C<sub>47</sub>H<sub>34</sub>N<sub>6</sub>O<sub>2</sub>. Calculated, %: C 75.6, H 4.6, N 11.3.

B. Porphyrin (IVa) was obtained from porphyrin (Ia) in 78% yield by a method similar to A.

2-(2,2-Dicarboxyvinyl)-5,10,15,20-tetraphenylporphyrin (Va). A mixture of complex (Ib) (200 mg; 0.284 mmole), malonic acid (500 mg; 4.79 mmole), pyridine (10 ml), and piperidine (2 ml) was heated at 100°C for 1 h, cooled to room temperature, diluted with water (200 ml), the precipitated solid was separated, washed with 20% AcOH, with water, dried, and chromatographed in system D. Complex (Vb) (203 mg; 87%) was obtained. The product remained at the origin in chromatographic system B. UV spectrum, λ<sub>max</sub> (ε·10<sup>-3</sup>): 419 (348.0), 543 nm (15.8). IR spectrum: 1710, 1680 (C=O), 1620 cm<sup>-1</sup> (C=C).

Porphyrin (Va) was obtained in 89% yield by the demetallation of complex (Vb). UV spectrum, λ<sub>max</sub> (ε·10<sup>-3</sup>): 421 (347.2), 517 (17.2), 552 (6.4), 594 (5.1), 649 nm (3.0). IR spectrum: 1715, 1680 (C=O), 1620 cm<sup>-1</sup> (C=C). Mass spectrum, m/z (%): 728 (M<sup>+</sup> 15), 684 (100). PMR spectrum: 8.89-8.76 (7H, m, β-H), 7.34 (1H, s, -CH=C(CO<sub>2</sub>H)<sub>2</sub>), -2.86 ppm (2H, s, NH).

2-(2,2-Diethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (VIIa). A mixture of complex (Ib) (800 mg; 1.14 mmole), DMF (10 ml), piperidine (10 ml), and diethyl malonate (1 ml 6.25 mmole) was heated at the boiling point for 1 h, cooled, diluted with water (300 ml), the precipitated solid was filtered off, washed with 20% AcOH (100 ml), with water, dried, chromatographed in system A, and crystallized from a mixture of chloroform-hexane. Complex (VIIb) (850 mg; 91%) of R<sub>f</sub> 0.19 was obtained. UV spectrum, λ<sub>max</sub> (ε·10<sup>-3</sup>): 425 (362.3), 547 (24.2), 586 nm (9.3). IR spectrum: 1730, 1705 (C=O), 1620 cm<sup>-1</sup> (C=C). Found, %: C 73.8, H 4.5, N 6.8. C<sub>52</sub>H<sub>38</sub>CuN<sub>4</sub>O<sub>4</sub>. Calculated, %: C 73.8, H 4.5, N 6.6.

Porphyrin (VIIa) of R<sub>f</sub> 0.16 was obtained in 96% yield by the demetallation of complex (VIIb) with phosphorus oxychloride. UV spectrum, λ<sub>max</sub> (ε·10<sup>-3</sup>): 427 (347.5), 522 (23.9), 559 (7.5), 599 (7.2), 656 nm (5.2). IR spectrum: 1720, 1690 (C=O), 1615 cm<sup>-1</sup> (C=C). Mass spectrum, m/z (%): 784 (M<sup>+</sup> 100). Found, %: C 79.3, H 5.0, N 7.3. C<sub>52</sub>H<sub>40</sub>N<sub>4</sub>O<sub>4</sub>. Calculated, %: C 79.6, H 5.1, N 7.1.

2-(2,2-Dimethoxycarbonylvinyl)-5,10,15,20-tetraphenylporphyrin (VIa) was synthesized from dimethyl malonate analogously to porphyrin (VIIa). The yield of complex (VIb) of R<sub>f</sub> 0.17 was 90%. UV spectrum λ<sub>max</sub> (ε·10<sup>-3</sup>): 427 (196.4), 548 (16.6), 588 nm (7.5) IR spectrum: 1735, 1715 (C=O), 1620 cm<sup>-1</sup> (C=C). Mass spectrum, m/z (%): 817 (M<sup>+</sup> 100). Found, %: C 73.2, H 4.2, N 7.2. C<sub>50</sub>H<sub>34</sub>CuN<sub>4</sub>O<sub>4</sub>. Calculated, %: C 73.4, H 4.2, N 7.1.

Porphyrin (VIa) of R<sub>f</sub> 0.14 was obtained in 96% yield by the demetallation of complex (VIb) with phosphorus oxychloride. UV spectrum, λ<sub>max</sub> (ε·10<sup>-3</sup>): 429 (154.0), 457 (13.3), 524 (4.3), 599 (4.1), 657 nm (3.0). IR spectrum: 1735, 1715 (C=O), 1620 cm<sup>-1</sup> (C=C). Mass spectrum, m/z (%): 756 (M<sup>+</sup> 100). PMR spectrum: 8.82-8.73 (7H, m, β-H), 7.54 (1H, s, -CH=C(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 3.74 (3H, s, CH<sub>3</sub>), 3.62 (3H, s, CH<sub>3</sub>), -2.75 ppm (2H, s, NH). Found, %: C 79.3, H 4.6, N 7.7. C<sub>50</sub>H<sub>36</sub>N<sub>4</sub>. Calculated, %: C 79.4, H 4.8, N 7.4.

2-(2-Methoxycarbonylethyl)-5,10,15,20-tetraphenylporphyrin (XIIIa). A. A mixture (2 g; 2.63 mmole) of the isomers of compound (XIIb) was dissolved in THF (100 ml), a solution of

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (20 mg) in methanol (50 ml) was added, the mixture cooled to  $-10^\circ\text{C}$ , and  $\text{NaBH}_4$  (150 mg) was added with stirring. After 20 min, water (50 ml) was poured in, the solid filtered off, washed with water, the porphyrin was extracted with chloroform (400 ml), dried, evaporated, and chromatographed in system B. Complex (XIIIb) (1.9 g: 95%) was obtained, demetallation of which with phosphorus oxychloride gave porphyrin (XIIIa) (1.83 g: 96%) of  $R_f$  0.34. UV spectrum,  $\lambda_{\text{max}}$  ( $\epsilon \cdot 10^{-3}$ ): 421 (347.7), 515 (18.5), 548 (5.83), 591 (5.0), 649 nm (3.56). IR spectrum  $1740 \text{ cm}^{-1}$  (C=O). Mass spectrum,  $m/z$  (%): 700 ( $M^+$  100). PMR spectrum: 8.85-8.60 (7H, m,  $\beta$ -H), 3.63 (3H, s,  $-\text{CH}_2\text{CH}_2\text{COOCH}_3$ ), 3.24-3.16 (2H, t,  $J = 8 \text{ Hz}$ ,  $-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ), 2.86-2.78 (2H, t,  $J = 8 \text{ Hz}$ ,  $-\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ), -2.78 ppm (2H, s, NH). Found, %: C 82.3, H 5.3, N 7.8.  $\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_2$ . Calculated, %: C 82.3, H 5.2, N 8.0.

B.  $\text{LiAlH}_4$  (40 mg) was added with stirring to a solution of porphyrin (VIIb) (100 mg: 0.118 mmole) in absolute THF (50 ml) cooled to  $-10^\circ\text{C}$ . After 15 min, 5% HCl (100 ml) was poured in, the precipitated solid was filtered off, washed with water (200 ml), and dried. Complex (Xb) (98 mg: 97%) was obtained, after demetallation of which with phosphorus oxychloride and chromatography in system A porphyrin (Xa) (94 mg: 96%) of  $R_f$  0.20 was isolated. UV spectrum,  $\lambda_{\text{max}}$  ( $\epsilon \cdot 10^{-3}$ ): 420 (528.6), 516 (20.8), 552 (7.2), 592 (6.1), 647 nm (3.4). IR spectrum:  $1735 \text{ cm}^{-1}$  (C=O). Mass spectrum,  $m/z$  (%): 786 ( $M^+$  100%). PMR spectrum: 8.83-8.56 (7H, m,  $\beta$ -H), 4.19-3.93 (2H, m,  $-\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_3)_2$ ), 3.99-3.83 (1H, t,  $-\text{CH}_2\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_3)_2$ ), 3.54-3.48 (4H, m,  $-\text{CH}_2\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_3)_2$ ), 1.14-1.06 (6H, m,  $-\text{CH}_2\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_3)_2$ ), -2.79 ppm (2H, s, NH). Found, %: C 79.4, H 5.2, N 7.4.  $\text{C}_{52}\text{H}_{42}\text{N}_4\text{O}_4$ . Calculated, %: C 79.4, H 5.4, N 7.1.

Aqueous 50% KOH solution (1 ml) was poured into a solution of porphyrin (Xa) (500 mg: 0.636 mmole) in pyridine (30 ml), the mixture was boiled for 2 h, cooled, 20% AcOH (200 ml) added, the precipitated solid was filtered off, washed with 20% AcOH, with water, dried, chromatographed in system D, and porphyrin (XIa) (407 mg: 93%) was isolated. The UV, IR, PMR, and mass spectra of the methyl ester obtained from porphyrin (XIa) were in agreement with those given above for porphyrin (XIIIa). Porphyrin (XIa) was obtained from porphyrin (XIIIa) in 98% yield by saponification under analogous conditions.

The authors are grateful to A. A. Yaroslavov for assistance in taking the UV spectra.

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