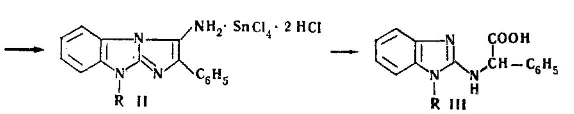

I-III a R = CH_3; b R = $C_6H_5CH_2$

The structure of III was shown by means of a series of reactions (methylation with diazomethane, decarboxylation, conversion into the 2,2'-azo derivative of benzimidazole under the action of sodium hypochlorite [2]) and was confirmed by IR spectra. The spectrum of the methyl ester of **IIIa** has the band of carbonyl absorption (1739 cm^{-1}) in the spectrum of free **IIIa** this is strongly shifted in the low-frequency direction (1655 and 1352 cm^{-1}), which shows the possibility of a betaine structure [3].

2-(α-Carboxybenzylamino)-1-methylbenzimidazole (IIIa). Small needles with mp 220° C (decomp., water), soluble in dilute alkalies and DMFA. Found, %: C 68.12; H 5.32; N 15.05. Calculated for $C_{16}H_{15}N_3O_2$, %: C 68.31; H 5.38; N 14.94. **Methyl ester of IIIa.** Needles with mp 150–151° C. Found, %: C 68.94; H 5.52; N 14.40. Calculated for $C_{17}H_{17}N_3O_2$, %: C 69.14; H 5.80; N 14.23.

2-(α-Carboxybenzylamino-2-benzylbenzimidazole (IIIb). Mp 246° C((DMFA and water). Found, %: C 73.68; H 5.60; N 11.83. Calculated for $C_{22}H_{19}N_3O_2$, %: C 73.93; H 5.36; N 11.76. **Methyl ester of IIIb.** Mp 166–167° C (from butanol). Found, %: C 74.48; H 5.80; N 11.47. Calculated for $C_{23}H_{21}N_3O_2$, %: C 74.36; H 5.70; N 11.32.

REFERENCES

1. A. M. Simonov and V. A. Anisimova, KhGS [Chemistry of Heterocyclic Compounds], **4**, 1102, 1968.
2. A. F. Pozharskii, E. A. Zvezdina, and A. M. Simonov, KhGS [Chemistry of Heterocyclic Compounds], **3**, 185, 1967.
3. S. Takahashi and H. Kano, J. Org. Chem., **30**, 1118, 1965.

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SYNTHESIS OF ALKYL-SUBSTITUTED PORPHYRINOGENS

G. V. Ponomarev, R. P. Evstigneeva, and N. A. Preobrazhenskii

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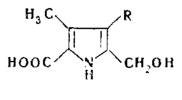
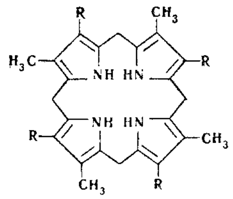
Porphyrinogens are hexahydroporphyrins in which the four pyrrole rings are connected by methylene bridges. They are intermediate in the biosynthesis of heme and chlorophyll [1,2]. One of the methods of synthesis of the simple porphyrins with alkyl substituents, in broad outline analogous to the polymerization of porphobilinogen, is the condensation in an acid medium of 5-carboxy-2-hydroxymethylpyrroles [3]. We have shown that the heating of the pyrroles **I** and **II** in the dark at 50–60° C in a mixture of methanol and acetic acid for 15–20 min and in methanol with a small amount of HCl, HBr, or CF_3COOH for 1.5–2 min in an atmosphere of argon, leads to the porphyrinogens **III** and **IV** respectively, which are isolated from the solution in the form of large faintly colored prismatic needles. Octamethylporphyrinogen (yield 57%) does not melt below 250° C and is sparingly soluble in organic solvents. Found, %: C 78.32; H 8.80; N 13.35. Calculated for $C_{28}H_{36}N_4$, %: C 78.50; H 8.41; N 13.09. Etioporphyrinogen (yield 92%) decomposes on being heated above 100° C. Found, %: C 79.21; H 9.38; N 11.80. Calculated for $C_{32}H_{44}N_4$, %: C 79.33; H 9.1; N 11.57.



I R = CH_3; II R = C_2H_5



III R = CH_3; IV R = C_2H_5

In the crystalline state, the porphyrinogens are stable in the air for several days, and in ethanolic solution in the dark they do not decompose nor undergo transition into porphyrins during several hours. By the photooxidation of the porphyrinogens in various solvents and using metal acetates, we have obtained porphyrins and the corresponding metal complexes with high yields.

REFERENCES

1. D. Mauzerall and S. Granick, J. Biol. Chem., **232**, 1141, 1958.
2. D. Mauzerall, J. Am. Chem. Soc., **82**, 2601, 1960.
3. W. Siedel and F. Winkler, Ann., **554**, 162, 1943.

5 July 1968 Lomonosov Moscow Institute of Precision Chemical Engineering