# SYNTHESIS OF AN ISOMER OF DEOXOPHYLLOERYTHROETIOPORPHYRIN

G. V. Ponomarev

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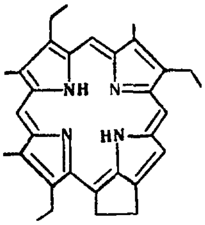
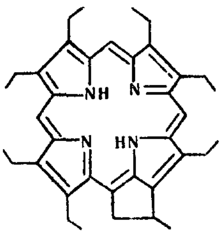
The presence in the porphyrin fractions of petroleum oils of a large amount of deoxophylloerythroetioporphyrin (I) and its homologs is the principal argument in favor of the biogenic (i.e., from chlorophyll or chlorobium chlorophyll) origin of petroporphyrins [1], since alternative pathways for the formation of porphyrins with a cyclopentane ring are not known. At the same time, very little study has been devoted to the physical and chemical properties of such compounds because of the difficulties involved in their preparation [2].

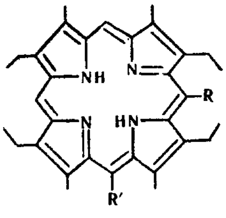
We have recently observed that Schiff bases of meso-formyloctaethylporphyrin are converted by thermolysis to a porphyrin with a methylcyclopentane ring (II). We assumed that in similar compounds the β-methyl groups adjacent to the meso substituent would, during thermolysis, possibly participate in the construction of an unsubstituted cyclopentane ring.



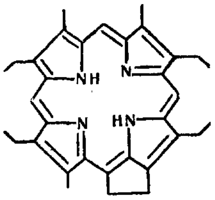
I



II



III, V



IV

In fact, when porphyrin III (R = H, R' = CH = NMe) is heated *in vacuo* at 285-290°C for 2.5 h, it is converted to porphyrin IV (45-55%), the electronic spectrum of which is identical to the spectrum of I [2]. PMR spectrum (250 MHz; CDCl$_3$ + 1% CF$_3$COOH), δ: 10.54 (1H), 10.46 (2H), meso-H; 5.63 (m, 2H) and 4.37 (m, 2H), cyclopentane ring CH$_2$CH$_2$; 4.09 (m, 8H), α-CH$_2$; 3.63 (3H), 3.60 (3H), 3.57 (3H), CH$_3$; 1.91 (3H), 1.71 (3H), 1.68 (3H), 1.66 (3H), all t, β-CH$_3$; −3.68 and −4.94 ppm (NH). Mass spectrum, m/z (relative intensity, %): 492 (M$^+$, 100), 477 (18). Porphyrin IV can be used as a model for the study of the physicochemical properties of I.

We accomplished the synthesis of a mixture of isomers III and V (R = CH = NMe, R' = H) in 85-90% yield by the method we developed in [3] on the basis of the Cu complex of etioporphyrin II. The mixture of isomers was separated by thin-layer chromatography, and their structures were proved by means of the PMR spectra. The amount of the more labile V isomer isolated was one fourth the amount of the III isomer. Since isomer V did not melt up to 320°C, and the bulk of the substance decomposed irreversibly during thermolysis at 340-350°C, and virtually no formation of the corresponding porphyrin with a methylcyclopentane ring was observed, the mixture of isomers III and V was used without prior separation for the production of porphyrin IV.

## LITERATURE CITED

1. J. Martin, E. Quirke, G. J. Shaw, P. D. Soper, and J. R. Maxwell, Tetrahedron, 36, 3261 (1980).
2. A. Chaudhry, P. S. Clezy, and A. H. Mirza, Aust. J. Chem., 33, 1095 (1980).
3. G. V. Ponomarev and G. B. Maravin, Khim. Geterotsikl. Soedin., No. 1, 85 (1977).

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