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CHEMISTRY OF *meso*-FORMYLPORPHYRIN OXIMES. ISOMERIZATION TO ISOPHLORINS

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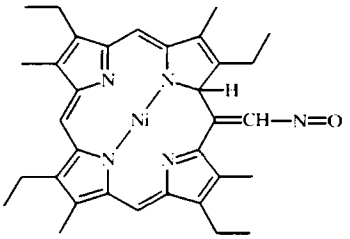
In the previous communication we described the unusual transformation of *meso*-formylporphyrin oximes with high yields into the corresponding *meso*-cyanoporphyrins in the presence of tetrabutylammonium hydroxide [1].

During investigation of the chemical characteristics of *meso*-formylporphyrin oximes we found that solutions of the Ni^{+2}, Cu^{+2}, and Pd^{+2} complexes of oximes of the *meso*-formylporphyrin series in chloroform or methylene chloride change color from the traditional red to brown-yellow when shaken with water. In some cases the addition of an aqueous solution of sodium bicarbonate accelerates this process. Conversely, shaking with dilute hydrochloric acid does not lead to any transformations in the oximes. In the electronic spectrum of the reaction mixture the Soret band gradually decreases, which indicates a process leading to disruption of the chain of conjugation in the 18-π-membered porphyrin macrocycle. Thus, agitation of a solution of nickel complex of *meso*-formyletioporphyrin-I **1** in methylene chloride for 15-30 min in the presence of water led after chromatographic separation of the reaction products on silica gel in methylene chloride to two main reaction products with yields of 40-50%. They had almost identical electronic spectra, a characteristic feature of which was a strong and very broad absorption band in the region of 700-800 nm, while in the UV part of the spectra there were several bands just as broad and comparable in intensity with the long-wave band. By analyzing the ^1H NMR spectra and mass spectra we established that the compounds were the isomeric products from the transformation of



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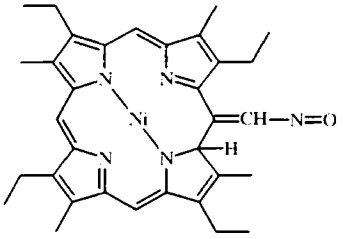

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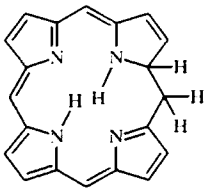

4,5-dihydroporphin
(isophlorin)

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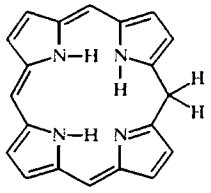

5,22-dihydroporphin
(phlorin)

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oxime **1** to new heterocycles **2, 3**, which can be assigned to derivatives of *exo*-methyleneisophlorin. (By isophlorin we mean derivatives of 4,5-dihydroporphyrin **4**, in contrast to the classical phlorins, i.e., 5,22-dihydroporphyrins **5** [2].) Since the ratio of isomer **2** more mobile on silica gel and the less mobile isomer **3** amounts to 1:3, it can be concluded that the direction of isomerization of *meso*-oxime is greatly affected by the peripheral environment, i.e., by the size and composition of the adjacent β-pyrrole substituents; the nature of the metal complex is also important.

Compounds **2, 3** are stable and do not undergo any further transformations in organic solvents (chloroform, benzene, DMF, pyridine) or during chromatography on silica gel. Consequently, the isomerization of porphyrin oximes to isophlorins is irreversible.

The discovered transformation is characteristic only of the metal complexes of *meso*-formylporphyrin oximes. The isomerization to isophlorin is extremely sensitive to the presence of one or the other central atom. In some cases a completely different process occurs. The corresponding free bases of *meso*-formylporphyrin oximes are stable under these conditions and do no enter into such rearrangement.

REFERENCES

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