CHEMISTRY OF *meso*-FORMYLPORPHYRIN OXIMES. AN ELEGANT SYNTHESIS OF *meso*-CYANOPORPHYRINS

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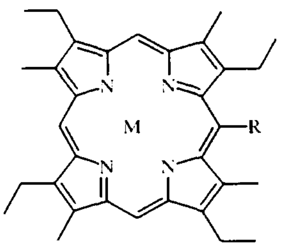
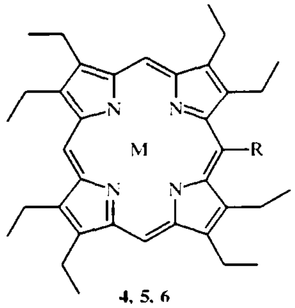
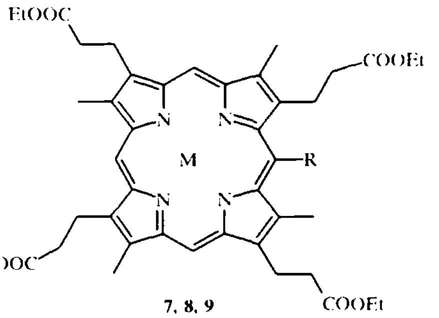
The traditional method for the synthesis of *meso*-porphyrins is to heat the corresponding oximes of *meso*-formylporphyrins in acetic anhydride in the presence of hydroxylamine hydrochloride. (For greater detail, see the review [1].) In a special investigation devoted to study of this reaction it was shown that various compounds can form, depending on the temperature and the heating time, and mainly through the transformation of the intermediate acetoxyoxime. In some cases the acetoxyoximes are so stable that even prolonged heating in acetic anhydride leads to only a small yield of the cyanoporphyrins [3]. In connection with the difficulty of producing *meso*-cyanoporphyrins there is hardly any information in the literature on the chemical properties of such compounds with the exception of hydrolysis in sulfuric acid [2, 4].



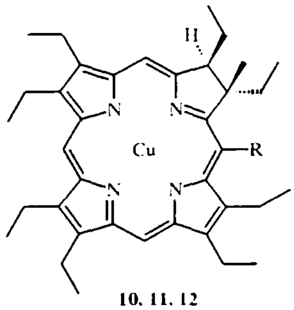
1, 2, 3
M = 2H, Ni, Cu



4, 5, 6
M = Ni, Pd, Pt



7, 8, 9
M = Ni, Cu, Pd



10, 11, 12

1, 4, 7, 10 R = $CH=N^+Me_3I^-$; 2, 5, 8, 11 R = $CH=NOH$; 3, 6, 9, 12 R = CN

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In the present communication we propose a completely new approach to the synthesis of *meso*-cyanoporphyrins, which can be applied successfully to the synthesis both of free porphyrin bases and of their metal complexes and also of labile derivatives such as chlorins.

We found that the treatment of solutions of the *meso*-formylporphyrin oximes in methylene chloride at room temperature with 5-10-fold amount (on the amount of the porphyrin) of $Bu_4N^+OH^-$ led after 10-15 min to new compounds, the structure of which according to the IR spectra (ν_{CN} 2200 cm^{-1}) and also to the ^1H NMR, mass, and electronic spectra corresponded to *meso*-cyanoporphyrins.

Thus, the corresponding nitriles **3, 6, 9, 12** were obtained with yields of 80-90% from porphyrins **2, 5, 8** and octaethylchlorin **11**. In turn, the initial oximes **2, 5, 7, 11** were obtained with high yields not by the traditional method (by heating the corresponding *meso*-formylporphyrins with hydroxylamine in aqueous pyridine) but by the method we developed for the production of Schiff bases [5], i.e., by treating the corresponding imino salts (methiodides of the Schiff bases) **1, 4, 7, 10** with hydroxylamine hydrochloride for several minutes at room temperature in pyridine solution.

The ability that we observed for the oximes of *meso*-formylporphyrins to be easily converted into the corresponding *meso*-cyanoporphyrins is only one of the reactions that we discovered with the oximes of *meso*-formylporphyrins (chlorins), leading to the production of the most widely varied new compounds – porphyrins, chlorins, isobacteriochlorins, and isophlorins.

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