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CHEMISTRY OF OXIMES OF *meso*-FORMYLPORPHYRINS. OPENING OF THE PORPHYRIN MACROCYCLE INTO TRIPYRROLYL-ISOXAZOLES. THE REVISED STRUCTURE OF "ISOPHLORINS"

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In a previous report we described the conversion of the nickel complex of the oxime of *meso*-formyletioporphyrin-I (**1**) under interphase hydrolysis conditions (methylene chloride and water, several minutes at room temperature) into two basic brownish yellow compounds to which we ascribed the structures of the isomeric "isophlorins" **2** and **3** [1] on the basis of their electronic (absence of Soret bands in the 400 nm region and a broad band at 700-800 nm) and ^{1}H NMR spectra (retention of the overall number of protons in both the *meso*-proton region and in the region of the peripherae β,β'-pyrrolyl substituents analogous to those of the starting oxime **1**) (Scheme 1).

Unfortunately the electron impact mass spectra of compounds **2** and **3** were complex and defied logical interpretation, and the molecular ion peaks were of low intensity and differed by 4 a.u. from the theoretical values. In the mass spectra of porphyrins examples are quite commonly encountered in which $[M + 1]^+$, $[M + 2]^+$, and even $[M + 3]^+$ peaks have been observed in place of the molecular ions, but there has been no theoretical explanation for this fact.

However the chemical ionization and MALDI mass spectra of these compounds, that we have named "isophlorins", always differ by 4 a.u. on the high side from the molecular mass of the initial oxime. In this case such a change in molecular mass is possible only under conditions in which one of the pyrrole carbon atoms, which is not directly bonded to protons, is replaced by an oxygen. Thus there are signs that the assignment of the "isophlorin" structure to the brownish yellow products of the oxime transformation is incorrect.

To establish the structure of the "isophlorins" and to exclude the formation of isomeric reaction products we have carried out directed syntheses of the two oximes **4** and **5** from the nickel complex of etioporphyrin-II by a known method [3]. The oximes **4** and **5** were then shaken for a short while in a mixture of methylene chloride and water, and we isolated in about 50% yield the yellow brown compounds **6** and **7** by column chromatography of the reaction mixture. These compounds had electronic and mass spectra identical to those of the so-called "isophlorins" which we had isolated previously from the transformation of oxime **1** [1].

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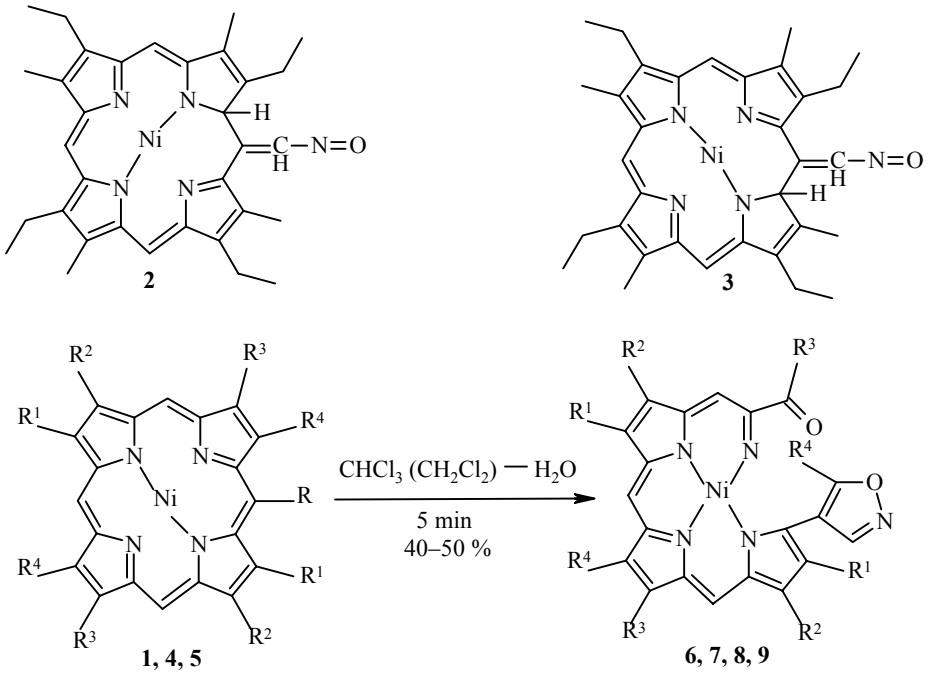
Scheme 1



1 R = H; **4**, **5** R = CH=NOH; **1**, **8** $R^1 = R^3 = Me$; $R^2 = R^4 = Et$; **4**, **6** $R^1 = R^4 = Et$; $R^2 = R^3 = Me$; **5**, **7** $R^1 = R^4 = Me$; $R^2 = R^3 = Et$; **9** $R^1 = R^3 = Et$; $R^2 = R^4 = Me$

The IR spectrum of compound **4** has an intense band at 1682 cm^{-1} which indicates the presence of a carbonyl oxygen. An analysis of its ^{13}C NMR spectrum leads to the conclusion that it is an α,β-conjugated carbonyl group (196.3 ppm). Moreover C-H correlation experiments permit the assignment of the broad singlet at 7.0 ppm in the ^1H NMR spectrum to a proton on a heteroatom (NH or OH). Nevertheless, despite the presence of much spectroscopic information for the isolated yellow brown compounds, we were only able to draw a final conclusion on their structures on the basis of X-ray crystallographic data* on compound **6** as tripyrrolylisoxazoles. Consequently tripyrrolylisoxazole **7** is formed from oxime **5**, and the isomers **8** and **9**, and not the "isophlorins" **2** and **3**, from oxime **1**.

It remains astonishing that under such mild conditions it is possible for a whole cascade of reactions to occur, apparently including closing of a 1,2-oxazine ring, oxidation of a β-pyrrole carbon atom, rupture of the β,β'-bond of a pyrrole ring, and rearrangement of a 1,2-oxazine ring into a 1,2-oxazol ring with elimination of an α-pyrrole carbon atom. It must be noted that the observed formation of linear polypyrrole compounds during such facile hydrolytic opening of a porphyrin macrocycle is a obvious case which changes to a considerable degree our ideas about the especial stability of the porphyrin aromatic system.

The present studies of the reactivity of oximes of *meso*-porphyrins shows their inexhaustible synthetic possibilities, demonstrated by their many, often unexpected, transformations. Variation of the peripheral surroundings, the central metal in the complex, and the nature of the reagent, permit the direction of the reaction to the formation of desirable compounds – nitriles [3], a heteroanalog of australochlorin [4], or tripyrrolylisooxazole.

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* The X-ray structural analysis was carried at the Center for X-ray Structural Investigation, Institute of Organoelement Chemistry, Russian Academy of Science.

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