Chemistry of Heterocyclic Compounds, Vol. 37, No. 3, 2001

CHEMISTRY OF METAL COMPLEXES OF OXIMES OF *meso*-FORMYLPORPHYRINS. OXIDATIVE CYCLIZATION TO METAL COMPLEXES OF HYDROXY-1,2-OXAZINOCHLORINS

D. V. Yashunsky, Yu. V. Morozova, and G. V. Ponomarev

Keywords: hydroxy-1,2-oxazinochlorins, metal complexes, oximes of *meso*-formylporphyrins, phase-transfer hydrolysis.

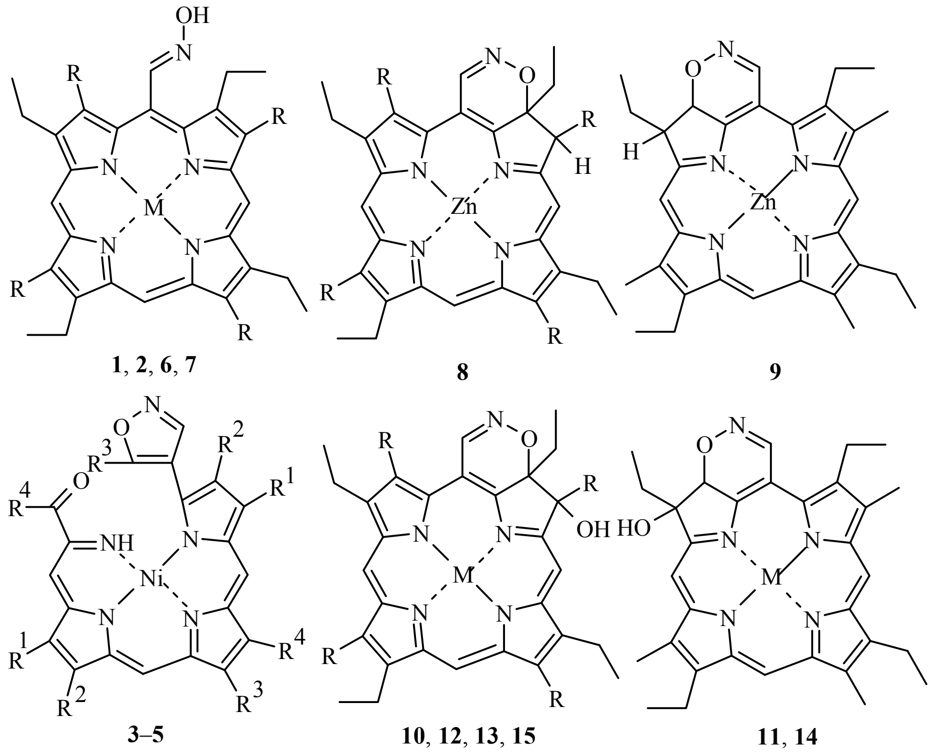
We described in [1] the conversion of nickel complexes of oximes of *meso*-formylporphyrins **1** (M = Ni, R = Me) or **2** (M = Ni, R = Et) under phase-transfer hydrolysis conditions (methylene chloride–water, several minutes at room temperature) to tripyrrolylisoxazoles **3-5**. The surprising capacity of nickel complexes to undergo oxidative opening of the porphyrin ring to a certain extent is also characteristic for some palladium complexes of porphyrin oximes. Zinc complexes of the oxime of *meso*-formyletioporphyrin-I **6** (M = Zn, R = Me) and octaethylporphyrin **7** (M = Zn, R = Et) behave quite differently. When a solution of complex **6** is vigorously stirred in methylene chloride with a small amount of water, after a few hours the starting complex is transformed to two major compounds in 2:1 ratio, and the transformation is accompanied by a change in the color of the solution from red to green. Their electronic spectra were practically identical, and in addition to a Soret band contained an intense band in the 630 nm region, typical of metal complexes of chlorins.

The only possible variant of the conversion of oxime **6** to derivatives of the chlorin series is formation of isomeric 1,2-oxazinochlorins **8** (M = Zn, R = Me) and **9**. But from mass spectral data for the isolated chlorins, it followed that these compounds differ from the starting oxime **1** by 16 au, which corresponded to addition of one oxygen atom to the cyclization products. In our opinion, the probable intermediate chlorins **8** and **9** undergo hydroxylation *via* a peroxide mechanism to stable hydroxychlorins **10** (M = Zn, R = Me) and **11** (M = Zn). Oxidation of benzochlorins to hydroxybenzochlorins *via* a similar mechanism was observed when the Ni complex of β-*meso*-(2-formylvinyl)deuteroporphyrin-IX was treated in concentrated sulfuric acid [2] (Scheme).

Obviously using a symmetric oxime **7** (M = Zn, R = Et) as the starting material led to formation of a single reaction product: hydroxy-1,2-oxazinochlorin **12** (M = Zn, R = Et). The zinc complexes **10**, **11**, or **12** obtained in this way may be easily demetallated under mild conditions (shaking a chloroform solution with a 1 M solution of hydrochloric acid) to the corresponding free bases. In this case, the total yield for the transformation of zinc complexes **6** or **7** to the free bases **13** + **14** (M = 2H, R = Me) or to **15** (M = 2H, R = Et) is ~50%.

Institute of Biomedical Chemistry, Russian Academy of Medical Sciences, Moscow 119832; e-mail: gelii@main.ibmh.msk.su. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 405-407, March, 2001. Original article submitted November 2, 2000.

Scheme



3 $R^1 = R^3 = Me$, $R^2 = R^4 = Et$; **4** $R^1 = R^3 = Et$, $R^2 = R^4 = Me$;
5 $R^1 = R^2 = R^3 = R^4 = Et$

The observed conversion of oximes to hydroxy-1,2-oxazinochlorins is general. Similar results were obtained when using as the starting materials the copper, palladium, and platinum complexes of oximes of such *meso*-formylporphyrins as etioporphyrin-II and coproporphyrin-I.

REFERENCES

1. G. V. Ponomarev, Yu. V. Morozova, and D. V. Yashunskii, *Khim. Geterotsikl. Soedin.*, 277 (2000).
2. M. G. H. Vicente and K. M. Smith, *J. Org. Chem.*, **56**, 4407 (1991).