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CHEMISTRY OF *meso*-FORMYLPORPHYRIN OXIMES. THE SYNTHESIS OF THE HETERO ANALOG OF AUSTRALOCHLORIN

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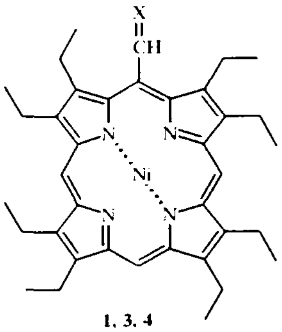
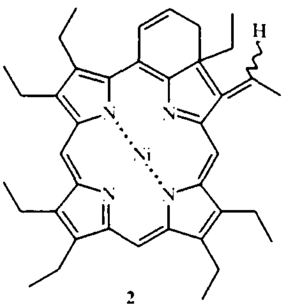
Recently we showed that nickel complex of *meso*-dimethylamino-1-propenyloctaethylporphyrin in the form of methiodide **1** is converted smoothly under the conditions of mild thermolysis (boiling in a solution in 1,2-dichloroethane) into an isomer of a new macrocycle **2**, which we named "australochlorin" [1]. This compound represents chlorin containing a conjugated six-membered ring and an exocyclic double bond. The supposed mechanism of transformation of compounds **1** into **2** involves the generation of an allyl carbocation, which is capable of deprotonating the α-CH group in the adjacent ethyl fragment with the formation of the final reaction products.

It is also known that aldoximes (both aliphatic and aromatic) in reaction with lead tetraacetate can give various reactive particles, including ions and radicals [2].

While studying the reactivity of aldoximes of the porphyrin series [3], we tried to use the given approach (the generation of reactive particles from the aldoxime by the action of lead tetraacetate) for the synthesis of the hetero analogs of australochlorin.



1, 3, 4



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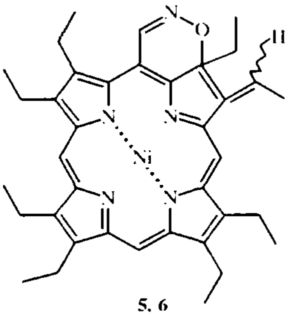

5, 6

1 X = $CHCH_2N^+Me_3I^-$
3 X = NOH
4 X = $N^+Me_2I^-$

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In fact, the treatment of a solution of nickel complex of *meso*-formyloctaethylporphyrin oxime **3** (obtained from the derivative **4** and hydroxylamine [3]) with lead tetraacetate (1.2 eq) in methylene chloride in the presence of an excess of triethylamine at room temperature for 5 min gives a mixture of two isomeric chlorins **5** and **6** with an overall yield of 77%.

The structure of the individual isomers **5** and **6** (hetero analogs of australochlorin) was determined on the basis of study of the ^{1}H NMR spectra and their comparison with those which we have already described for the individual isomers **2** [1].

Isomer 5. This isomer (the less polar during separation of the mixture on silica gel) was isolated with a yield of 47%. ^{1}H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm: 9.56; (1H, s, $C\underline{H}=N$); 9.07, 9.00, and 8.38 (3H, three s, *meso*-H); 6.96 (1H, q, J = 7.6 Hz, $=C\underline{H}CH_3$); 3.80-3.30 (12H, overlapping q, CH_2 of peripheral Et); 2.58 (3H, d, J = 7.6 Hz, $=CHC\underline{H}_3$); 2.05 and 1.60 (2H, m, CH_2 from ChlEt); 1.80-1.50 (18H, overlapping t, CH_3 of peripheral Et); 0.67 (3H, t, J = 7.4 Hz, CH_3 from ChlEt). UV spectrum (relative intensity, chloroform): 413 (13.5), 505 (1.0) 598 sh (1.5), 641 (6.3).

Isomer 6. This isomer (the more polar during separation of the mixture on silica gel) was isolated with a yield of 30%. ^{1}H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm: 9.53 (1H, s, $C\underline{H}=N$); 9.05-9.02 and 8.46 (3H, three s, *meso*-H); 6.62 (1H, q, J = 7.5 Hz, $=C\underline{H}CH_3$); 3.80-3.30 (12H, overlapping q, CH_2 of peripheral Et); 2.40 (3H, d, J = 7.5 Hz, $=CHC\underline{H}_3$); 1.80 and 1.30 (2H, m, CH_2 from ChlEt); 1.70-1.50 (18H, overlapping t, CH_3 of peripheral Et); 0.83 (3H, t, J = 7.3 Hz, CH_3 from ChlEt). The UV spectrum was identical with that of isomer **5**.

The transformation of aldoxime of the octaethylporphyrin series described in the present work is characteristic not only of nickel but also of copper, palladium, and platinum complexes.

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