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CHEMISTRY OF OXIMES OF *meso*-PORPHYRIN METAL COMPLEXES. SYNTHESIS OF CHLORINE WITH FUSED 1,2-OXAZOCINE RING

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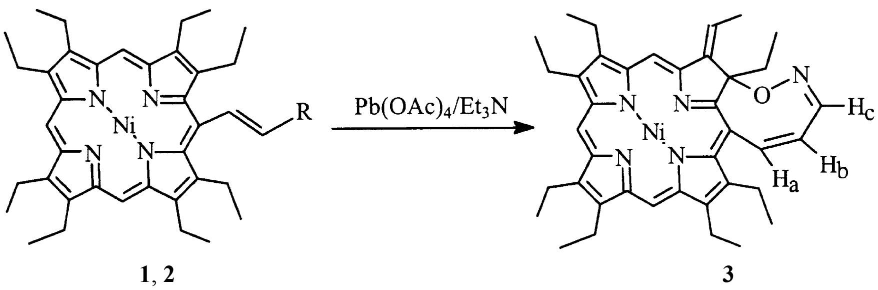
Intramolecular cyclizations of vinylogs of various *meso*-substituted porphyrins yield chlorine structures with fused exocycles. Thus, cyclization of *meso*-alkoxycarbonylvinylporphyrins leads to purpurins with five-membered exocycles [1], while metalloporphyrins with substituents such as CH=CH–CHO, $CH=CHCH_2OH$, and $CH=CHCH_2NMe_2$ form benzochlorines with five-membered exocycles [2-4].

Taking account of the tendency of metal complexes of *meso*-porphyrin oximes to undergo cyclization to yield oxazinochlorines found in our previous work [5, 6], we studied the possibility of such transformations of the corresponding vinylog, namely, the oxime of *meso*-*trans*-formylvinyloctaethylporphyrin (**1**).



1, **2** **3**

1 R = CH=NOH, **2** R = CHO

Porphyrin **1** was obtained in quantitative yield as a mixture of the *syn* and *anti* isomers in the reaction of the corresponding *meso*-*trans*-formylvinylporphyrin (**2**) [2] with hydroxylamine hydrochloride in pyridine at room temperature. Chromatographic separation on a silica gel column gave the mobile and polar isomers as pure compounds in 3:2 ratio. ^1H NMR spectrum on a Bruker WM-400 spectrometer (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz) of the more mobile isomer of **1**: 9.41 and 9.39 (2H, 1H, two s, *meso*-H); 9.15 (1H, d, *J* = 15.8, C$\underline{H}$–CH–CH=N); 8.22 (1H, d, *J* = 9.8, CH=CH–C$\underline{H}$=N); 5.51 (1H, dd, CH=C$\underline{H}$–CH=N); 3.84-3.76 (16H, overlapping q, $8CH_2CH_3$); 1.77, 1.76, 1.70 and 1.67 (24H, four t, *J* = 7.4, $8CH_2CH_3$). Mass spectrum (Reflex, Bruker MALDI): M^+ 660.23. Electronic spectrum on a Hewlett Packard HP 8453 spectrometer ($CHCl_3$), λ_{max}, nm (I_{rel}, %): 404 (8.85), 525 (1.0), 563 (1.18).

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^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz) of the less mobile isomer of **1**: 9.41 and 9.40 (2H, 1H, two s, *meso*-H); 9.17 (1H, d, *J* = 15.7, C$\underline{H}$=CH–CH=N); 7.50 (1H, d, *J* = 10.3, CH=CH–C$\underline{H}$=N); 6.04 (1H, dd, CH=C$\underline{H}$–CH=N); 3.84-3.76 (16H, overlapping q, $8CH_2CH_3$); 1.77, 1.75, 1.70 and 1.68 (24H, four t, *J* = 7.9, $8CH_2CH_3$). Electronic spectrum ($CHCl_3$), λ_{max}, nm (I_{rel}, %): 404 (9.65), 525 (1.0), 562 (1.24).

Treatment of oxime **1** as a mixture of *syn* and *anti* isomers by lead tetraacetate in the presence of triethylamine in dichloroethane at 0°C over 10-15 min with subsequent chromatographic separation led to **3** in 30% yield as the result of oxidative cyclization as a single isomer relative to the *exo*-ethylidene bond.

Electronic spectrum of **3** ($CHCl_3$), λ_{max}, nm (I_{rel}, %): 441 (3.9), 640 (1.0), 693 (1.2) shows a significant bathochromic shift of about 50 nm of all the bands relative to the spectra of the nickel complexes of standard chlorines. ^{1}H NMR spectrum of chlorine **3** ($CDCl_3$), δ, ppm (*J*, Hz): 8.80, 8.67 and 8.35 (1H, 1H, 1H, all s, *meso*-H); 8.09 (1H, d, *J* = 11.8, H_a); 7.46 (1H, d, *J* = 6.9, H_c); 5.97 (1H, dd, H_b); 6.55 (1H, q, *J* = 5.9, =C$\underline{H}$–CH_3); 3.76-3.36 (12H, overlapping q, $6CH_2CH_3$); 3.28 and 2.74 (2H, two dq, *J* = 6.75, *J* = 14.0, CH_2CH_3, chlorine); 2.58 (3H, d, =CH–CH_3); 1.70-1.16 (18H, overlapping t, $6CH_2CH_3$); 0.39 (3H, t, CH_2CH_3, chlorine). This spectrum agrees completely with the proposed structure and unequivocally indicates inversion of the C=C double bond (*J* = 11.8 Hz) in the exocycle formed. Mass spectrum (MALDI): 658.2 (M + H). Found, %: C 70.92; H 6.80; N 10.35. $C_{39}H_{45}N_5NiO$. Calculated, %: C 71.13; H 6.89; N 10.64.

Thus, we have found that, similar to metal complexes of *meso*-formaldoximeporphyrins, their vinylogs (**1**) also are capable of cyclization. This is the first example of a macrocycle with a condensed eight-membered exocycle in the chemistry of tetrapyrrole compounds.

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