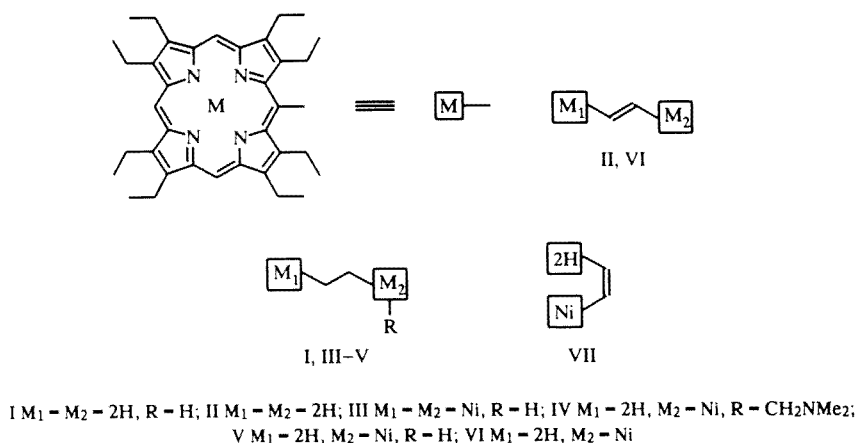


NEW ASPECTS OF THE OXIDATION REACTION OF ETHANEBISPORPHYRINS. SYNTHESIS OF MONONICKEL COMPLEXES OF CIS- AND TRANSETHYLENE-BISOCTAETHYLPORPHYRIN

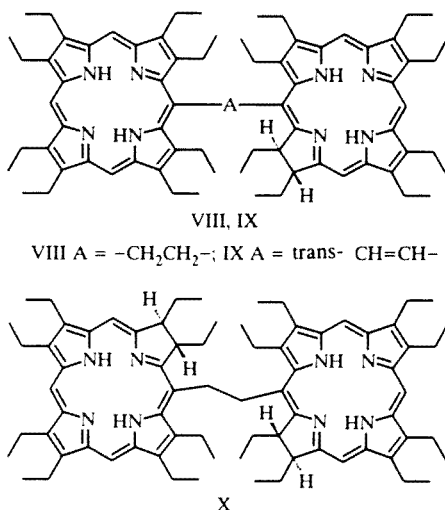
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The previously found [1] unusual conversion of ethanebisporphyrins of the type I to trans-ethylenebisporphyrins of the type II by the action of fatty acids assumed that the product of the monoprotection of both porphyrin nuclei was the primary intermediate according to the data existing at that time. Such an assumption was confirmed by the impossibility of the conversion to the desired ethylenes using strong acids (the diprotection at both porphyrin nuclei), as well as the inertness of the bisnickel complex of the type III under the conditions of the oxidation reaction (acetic acid, 80°C). It was shown later that the introduction of the meso-substituent (at the positions 5 or 10) into one of the porphyrin rings renders it possible to perform the oxidation reaction for derivatives of the type IV [2]. It was thereby assumed that both the free porphyrin part, as well as the part being the substituted nickel complex, were subjected to the monoprotection, whereby the positive charge was localized on the functional group of the substituent in the given case.



In the present work, we communicate a new reaction for the oxidation of 1-(meso-octaethylporphyrinyl)-2-(meso-octaethylporphyrinatonicke)ethane (V) [3] to the ethylene derivatives (VI) and (VII). This leads us to believe that the monoprotection of only one nucleus in the bisporphyrin molecule is required as the initial stage of the oxidation to ethylenebisporphyrins. The conversion of the dimer (V), indicated above, proceeds by the heating in acetic acid at 100°C for 6 h. The chromatographic separation of the reaction mixture on silica gel thereby resulted in the isolation of 42% of the unreacted ethane (V), 45% of the trans-ethylene (VI) [4], and 5% of the cis-ethylene (VII). The formation of the last proceeds on account of the thermal isomerization of the trans-isomer (VI) under the conditions for carrying out the oxidation reaction; this was confirmed independently by the heating of the pure trans-isomer (VI) in acetic acid at 100°C for 6 h. The resulting ratio of the trans- and cis-isomers, (VI) and (VII), (5:2 as determined from the PMR spectral data of the reaction mixture),

differs markedly from the ratio of 9:1 obtained by the chromatographic separation of the products of the oxidation of the ethane (V). This was associated with the chromatographic instability of the cis-isomer (VII), the conversion of which to the more stable trans-isomer (VI) on silica gel was noted previously [4].



The PMR spectrum of (VII) (CDCl_3 , 300 MHz) is as follows: 9.67 ppm, 9.00 ppm, 8.50(2) and 7.77(2) ppm (6H, s, meso-H), 9.50 and 9.33 ppm (2H, d, $J = 11$ Hz, $\text{CH}=\text{CH}$), 4.33-2.65 ppm (32H, all q, CH_2CH_3), 2.00-0.65 ppm (48H, all t, CH_2CH_3), and -2.10 ppm (2H, broad s, NH of porphyrin). For the UV spectrum, see [4].

The assumption of the requirement for the monoprotonation (at the nitrogen atom near to the meso-substituent) of only one nucleus in the bisporphyrin molecule as the initial stage of oxidation to ethylenebisporphyrins is confirmed indirectly by the ready conversion of the ethane-dimer (VIII) (obtained as a by-product in the demetallation of the known copper complex of the dimer (X) [5]) to the trans-ethylene dimer (IX). Here, only the monoprotonation (of the type indicated above) of the porphyrin nucleus probably occurs since the ethanebischlorine (X) does not give the ethylene derivative as the oxidation product under analogous conditions, and only undergoes degradation.

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