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A NEW SYNTHESIS OF *trans*-1,2-BIS(*trans*-OCTAETHYL-CHLORIN-20-YL)ETHYLENE

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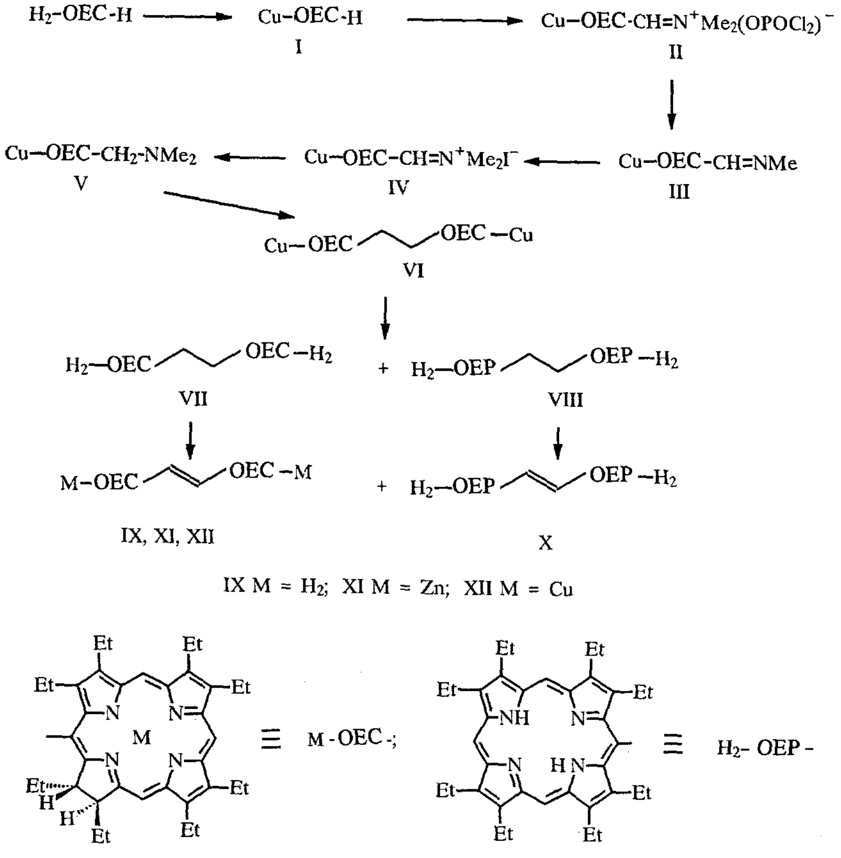
In light of two general reactions in porphyrin chemistry discovered in our laboratory, namely, the dimerization of *meso*-dimethylaminomethylporphyrins upon their heating in lower iodoalkanes to give ethane—bisporphyrins [1, 2] and the spontaneous oxidation of ethane—bisporphyrins to give *trans*-ethylene-bisporphyrins in solutions of acetic and other fatty acids [3-6], we undertook a study of the possibility of analogous transformations for chlorine compounds in order to obtain a suitable model of a photosynthetic "special pair."

The synthesis of the dimers was carried out starting from *trans*-ocatethylchlorine (OEC) according to the following scheme:



Copper complex I is readily formylated by the Vilsmeier reaction in a solution of dichloroethane or methylene chloride at 20°C to give intermediate phosphorus complex II, which, was treated without separation with 25% aqueous methylamine to give Schiff base III in 80-85% yield. Heating complex II in iodomethane for 30 min leads to crystalline iodomethylate IV, which, after removal of the solvent, was treated with a solution of $NaBH_4$ in methanol for 5 min. Removal of the solvent and chromatographic purification on a silica gel column using 9:1 chloroform—acetone as the eluent gave complex V in 70-75% overall yield relative to complex I. Heating complex V in iodomethane for 1 h at reflux, removal of the solvent, and

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chromatographic purification of the reaction products on a silica gel column with chloroform as the eluent leads to the more mobile dimer VI in 70-75% yield. Demetallation of complex VI in 9:1 H_2SO_4—CF_3CO_2H for 20 [sic] leads to a 2:1 mixture of dimers VII and VIII, whose structures were indicated by electron spectroscopy and mass spectrometry as well as comparison with samples obtained according to our previous procedure [3] and Smith [7]. The formation of porphyrin dimer VIII upon the demetallation of complex VI is a consequence of the partial oxidation of the chlorine macrocycles to give porphyrin rings upon demetallation in H_2SO_4—CF_3CO_2H [7]. Since dimers VII and VIII differ only slightly in their chromatographic mobility, they were oxidized by heating for 1 h in acetic acid at 50-60°C to give a mixture of ethylene—bischlorine IX and ethylene—bisporphyrin X in quantitative yield. This mixture was separated by chromatography on a column packed with silica gel (40×100 μm) using 9:1 chloroform—acetone as the eluent. Chlorine dimer IX had lower mobility on silica gel than porphyrin dimer X. Heating dimer IX with zinc and copper acetates in chloroform—methanol gave corresponding complexes XI and XII. The structures of dimers IX, XI, and XII were supported by their mass spectra. The conformation of chlorine dimer IX will be studied by PMR spectroscopy and reported separately.

The electronic spectra of *trans*-ethylene-bisporphyrins have a series of characteristic features [4, 8]. In particular, *trans*-ethylene—bisporphyrins are protonated to give a species with a strong band at 500-508 nm with greater intensity than the Soret band and a broad, strong band in the vicinity of 750 nm. Splitting of the Soret band into two components is found for the copper and zinc complexes of *trans*-ethylene-bisporphyrins. Similar spectral changes were found in the electronic spectra of chlorine derivatives IX, XI, and XII.

Dimer IX. UV spectrum, λ_{max} (relative intensity): 412 (5.0), 465 (2.97), 502 sh (1.11), 543 (0.54), 620 (0.54), 656 (1.0), 670 sh nm (0.97); in chloroform + CF_3CO_2H: 389 (2.52), 497 (3.78), 700 (1.0), 748 sh nm (0.83).

Complex XI. UV spectrum, λ_{max} (relative intensity): 406 (4.63), 419 (4.80), 469 (1.83), 538 (0.43), 577 (0.49), 639 nm (1.0).

Complex XII. UV spectrum, λ_{max} (relative intensity): 400 sh (3.98), 414 (4.31), 468 (2.35), 530 (0.57), 567 (0.59), 628 nm (1.0).

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