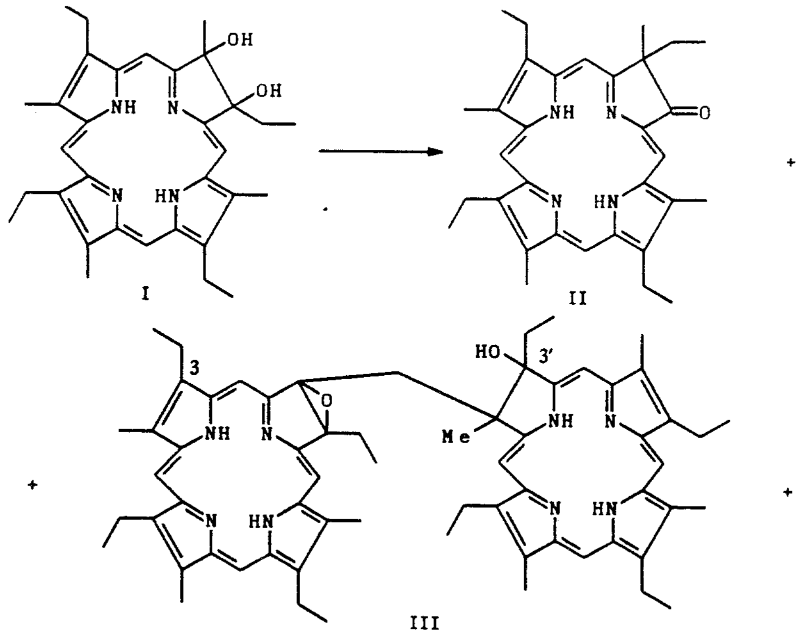
UNUSUAL TRANSFORMATIONS OF vic-DIHYDROXYCHLORINS IN ACETYLACETONE IN THE PRESENCE OF ZINC ACETATE: FIRST SYNTHESIS OF BISCHLORINS, DIACETYLCYCLOPROPYLCHLORINS, AND meso-DIACETYLMETHYLOCTAETHYLPORPHYRIN

G. V. Ponomarev and A. M. Shul'ga

In the presence of acids bis(dihydroxychlorins) may undergo various transformations — from the pinacol rearrangement in strong acids [1], the regioselectivity of which depends on the migrational activity of the peripheral substituents, to the formation of various porphyrins in the presence of weak or dilute acids [2] or on heating in vacuo [3].

We assumed that the use of CH acids in place of the traditional mineral or organic acids would make it possible to detect the development of intermediate carbonium ions and lead to the formation of new chlorins. Previously, in the case of meso-aminomethylporphyrins, we have shown that CH acids in the presence of $Zn(OAc)_2$ readily form products of nucleophilic addition to the intermediate carbonium ions with the formation of a carbon—carbon bond [4].

In fact, heating (20 min at 90°C) 100 mg of etioporphyrin-1 diol (I) and 700 mg of $Zn(OAc)_2$ in 4 ml of acetylacetone leads, after removal of the solvent in vacuo, demetallation in concentrated HCl, and subsequent chromatographic separation of the reaction products with a column packed with silica gel [chloroform—acetone (95:5)], to the formation of three principal substances (in the order of elution): 18 mg of etio ketone II, 25 mg of etiochlorin dimer III, and 20 mg of diacetylcyclopropylchlorin IV. The structures of II-IV were established by means of their PMR and mass spectra. The accurate assignment of all of the signals in the PMR spectra was made using the nuclear Overhauser effect. The most characteristic feature of the PMR spectrum of dimer III is the presence of signals of methyl protons of three ethyl groups in the 3, 8, and 3′ positions (at high field) at −1.04, 0.05, and 0.08 ppm, respectively, which attests to the mutual effect of the ring currents of the adjacent macrocycles on the chemical shifts of the peripheral substituents.



I

II

III

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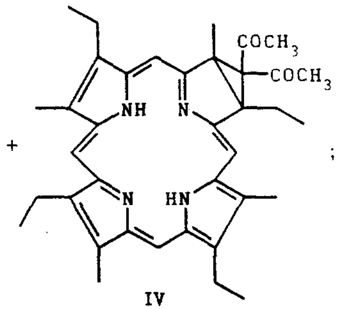

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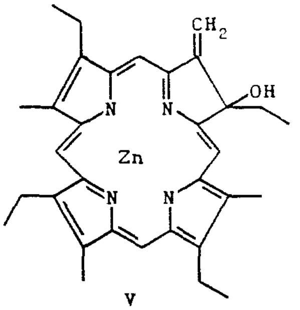

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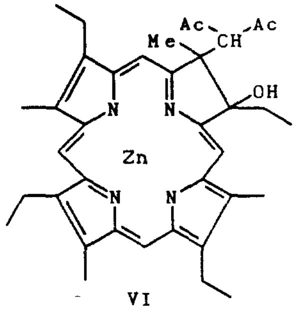

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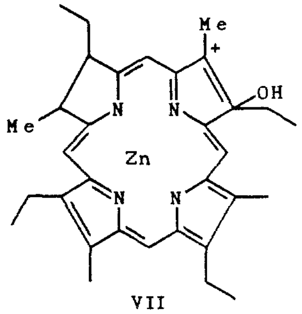
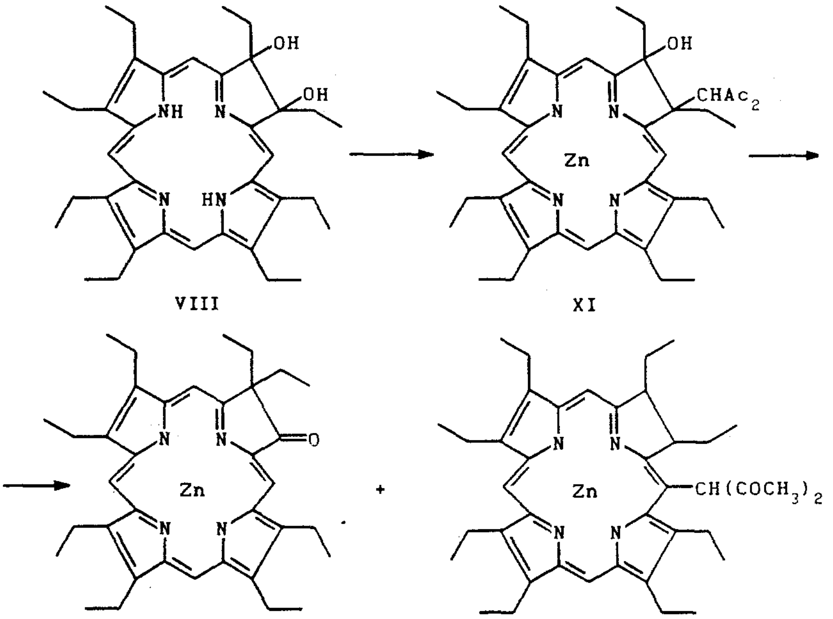


VII



VIII XI IX X

The observed phenomenon of dimerization of vic-dihydroxychlorins is general in character when there is a geminal methyl group next to a hydroxy group in the diol. The production of chlorins III and IV can be explained by the formation of intermediate complexes V and VI from carbonium ion VII. Similar products were isolated in the treatment of vic-dihydroxycoproporphyrin-1 tetraethyl ether.

Under similar conditions octaethylporphyrin diol VIII is converted in quantitative yield to 1:1 zinc complexes of keto-octaethylporphyrin (IX) and meso-diacetylmethyloctaethylporphyrin (X), which attests to a completely new specificity of the rearrangement of intermediate XI, which is probably due to both electronic and steric factors.

Consequently, the observed formation of dimeric chlorins from the corresponding carbonium ions is yet another confirmation of the dimerization that is characteristic for porphyrins that are capable of giving carbonium ions in an acidic medium [5, 6].

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NEW REACTION INVOLVING OXIDATIVE C-PHOSPHORYLATION OF PYRIDINE BY PHOSPHINE

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Extremely valuable tripyridylphosphines can be synthesized only by C-phosphorylation of metallated pyridines by chlorophospines [1-4]. We have established for the first time that tripyridylphosphine is formed in close-to-quantitative yield in the oxidative C-phosphorylation of pyridine by phosphine. A pyridine solution of CuX_2 ($X = Cl, OAc$) at 20-50°C rapidly absorbs phosphine even from a dilute gaseous PH_3—Ar mixture ($< 1\%$ PH_3) via the reaction

$$3C_5H_5N + PH_3 + 6CuX_2 \longrightarrow (2\text{-}C_5H_4N)_3P + 6CuX + 6HX \qquad (1)$$

The tri(2-pyridyl)phosphine is formed without side products under these conditions. The addition of water gives rise to a side reaction involving oxidative hydroxylation. Reaction (1) is accelerated by copper(I) ions. The rate constant of the reaction in excess pyridine at 25°C is $1.2 \cdot 10^2$ mole^2/liter^2·sec. The spent solution, which contains Cu(I) ions, is regenerated instantaneously by oxygen and is used repeatedly for reabsorption of PH_3. According to the results of potentiometric studies and data from the UV spectra, pyridine complexes of Cu(I) and Cu(II) dominate in CuX_2—CuX—Py solutions. It was demonstrated by the CNDO method that the incorporation of Py in the coordination sphere and an increase in the positive charge of the phosphine complex of copper(II) lead to deprotonation of phosphine with the formation of a phosphide ion as a consequence of the marked increase in the energies of the bonds between the central atom and the phosphorus atom of PH_3, as well as between the hydrogen atoms of PH_3 and the ligands. In the coordinated pyridine the N and m-C atoms bear negative charges, while the o- and p-C atoms bear positive charges. The coordinated X ligands and the central atom form strong bonds with the pyridine hydrogen atoms in the ortho positions. The remaining pyridine hydrogen atoms do not create bonds with the ligands and the Cu(II) ion. The bonds between the ligands are primarily ionic, while the bonds between the central atom and the ligands are covalent.

Reaction (1) includes the key steps

$$Cu_2X_3(PH_3)(C_5H_5N) \rightleftarrows Cu_2X_2(PH_2)(C_5H_5N) + HX \qquad (2)$$

$$Cu_2X_2(PH_2)(C_5H_5N) \longrightarrow Cu_2X_2(H)(C_5H_4NPH_2) \qquad (3)$$

$$Cu_2X_2(H)(C_5H_4NPH_2) \longrightarrow Cu + HX + C_5H_4NPH_2 + CuX \qquad (4)$$

$$Cu + CuX_2 \rightleftarrows 2CuX \qquad (5)$$

Copper(II) phosphide is formed via an electrophilic substitution mechanism with the nucleophilic assistance of (2). The tripyridylphosphine is formed as a result of nucleophilic addition of the phosphide ion to the o-C atom [(2) and (3)] with the subsequent elimination of copper(II) hydride, which decomposes to Cu and HX (4). Monovalent copper accumulates

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