

SYNTHESIS OF THE PARENT COMPOUND OF ISOBACTERIOCHLORINS -

A DIMINUTION OF THE  $\pi$ -SYSTEM OF PORPHINS

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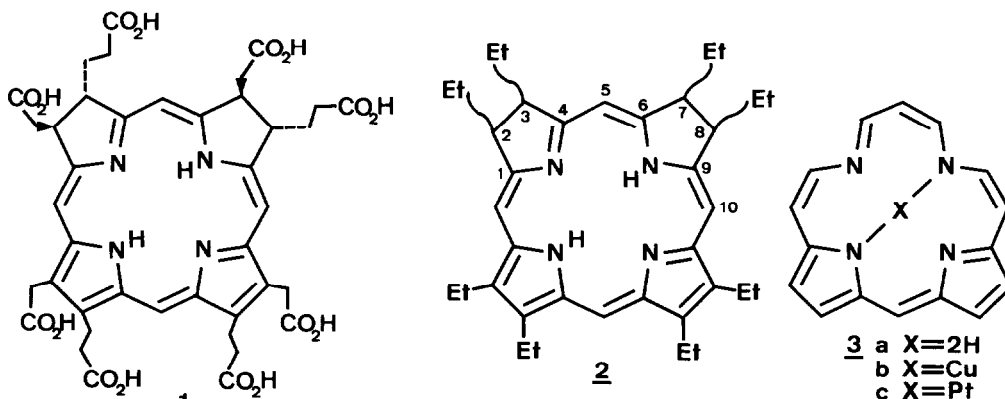
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Abstract: A four step synthesis of 1,4;6,9-bisdesethenophorphin 3 proceeding via the intermediates 4, 5 and 6 is presented. The spectral properties of 3 indicate close similarities to porphyrins and isobacteriochlorins.

Partially hydrogenated porphyrins are wide-spread in nature. Chlorins and bacteriochlorins, which have been known for many years, have been investigated thoroughly from a chemical as well as a biochemical point of view<sup>1)</sup>. Recently isobacteriochlorins have attracted attention. Sirohydrochlorin 1, which is the first naturally occurring derivative, has been isolated by L.M. Siegel e. al.<sup>2)</sup> and seems to be an important intermediate in the biosynthesis of vitamin B<sub>12</sub><sup>3)</sup>.

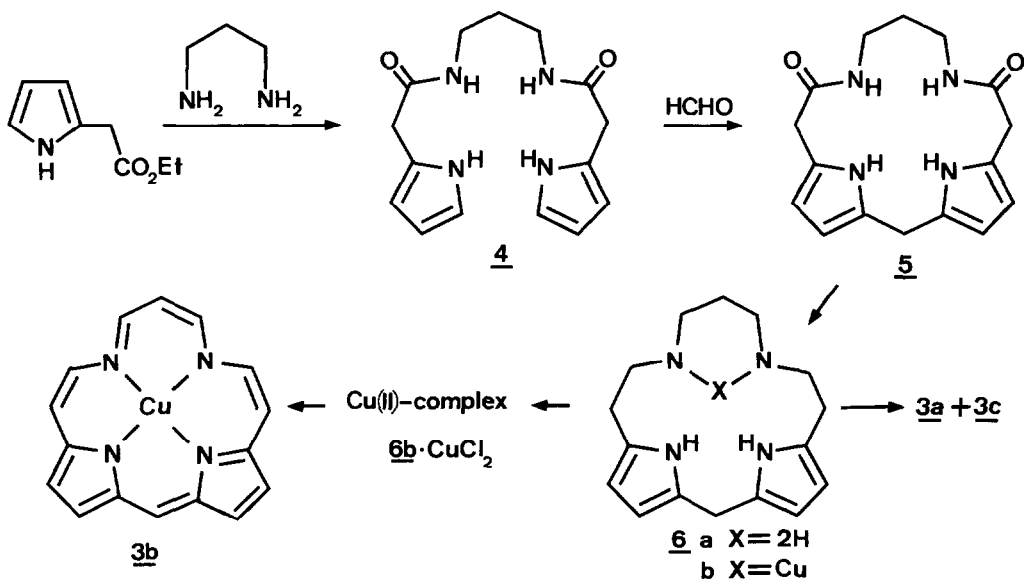
Several isobacteriochlorin derivatives have been synthesized<sup>4)</sup>. The stereoisomers 2 were obtained from octaethylporphin by a reduction-isomerization sequence<sup>5)</sup>.



We report the synthesis of the parent compound 3 of isobacteriochlorins which, containing the  $\pi$ -system of a tetrahydroporphin, is free from substituents and the 1,4;6,9-positioned etheno-bridges favouring a planar structure of porphin and its derivatives.

A 96% yield of the diamide 4<sup>6)</sup> was obtained from a neat mixture of 1 mmol ethyl pyrrole-2-acetate and 2 mmol 1,3-diaminopropane after four weeks at room temperature. Ring closure with formaldehyde (1 mmol 4, 7.6 ml aqueous 35% HCHO, 90 ml EtOH, 3.5 h reflux) gave 26% 5<sup>6,7)</sup> as a crystalline, colourless and fairly stable compound.

Attempts to dehydrogenate 5 or its iminoether<sup>8)</sup>, e.g. at the meso position between the pyrrole rings, failed. Reaction of 5 with diisobutylaluminiumhydride (toluene, N<sub>2</sub>-atmosphere, 2 h at 40-45°C) gave 75% of the Diamine 6a<sup>6)</sup> which is quite sensitive to air. A stable Cu(II)-complex 6b·CuCl<sub>2</sub><sup>6,9)</sup> was formed in a reaction of 6a with copper(II)chloride in aqueous ammonia (60%).



After many unsuccessful attempts we finally were able to dehydrogenate 6b using platinum dioxide in boiling xylene (6-8 h). A 3% yield of 3b<sup>6)</sup> was obtained as a red, crystalline and paramagnetic compound. The structure of 3b follows from the ESR-<sup>10)</sup> and UV-spectrum [CHCl<sub>3</sub>:  $\lambda = 384$  nm ( $\lg \epsilon: 4.99$ , Soret-band); 527 (4.04); 566 (4.36)] which may be compared with those of

Cu(II)-porphyrins<sup>11)</sup>.

A dehydrogenation of 6a with platinum dioxide in xylene gave 3a in very poor yield<sup>12)</sup>. The seven signals of the <sup>1</sup>H NMR-spectrum (in CDCl<sub>3</sub>) at 9.65 ppm (2H), 9.26 (2H), 8.89 (1H), 8.37 (2H), 7.97 (2H), 7.75 (2H) and 7.00 (1H) prove 3a to be a diatropic compound. The UV-spectrum [CHCl<sub>3</sub>: λ = 352 (sh, 4.2), 367 (6.25), 458 (sh, 0.4), 489 (sh, 0.65), 526 (0.95, 566 (1) and 612 (0.1) · relative intensities given] resembles that of isobacteriochlorins<sup>4)</sup>. A Pt(II)-complex 3c<sup>12)</sup> has been obtained as a by-product of the reaction, the structure of which is in agreement with the mass spectrum<sup>13)</sup>.

The UV- and <sup>1</sup>H NMR-spectrum of 3a point to a planar or nearly planar structure. No exact conclusion, however, can be drawn at the moment concerning the conformation of this compound.

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- 6) Satisfactory elemental analyses were obtained for all new compounds. High resolution mass spectra have been made from 6a, 3b.
- 7) The actual yield of 5 is higher. We have not been able so far to separate 5 completely from polymeric by-products.
- 8) A similar reaction was applied in the synthesis of azacyclooctatetraenes: L.A.Paquette, J.Am.Chem.Soc. 90, 3897 (1968).
- 9) The structure of the crystalline Cu(II)-complex 6b·CuCl<sub>2</sub> is not known. The mass spectrum is in accordance with 6b: m/e = 335/333 (2.4%/6.2%, M<sup>+</sup>, <sup>65</sup>Cu/<sup>63</sup>Cu), 334/332 (10%/20%, M<sup>+</sup>-1), 331 (5.2%), 330 (3.3%), 329 (6.2%), 272 (8.6%), 272 (38.2%), 270 (100%, M<sup>+</sup>-Cu).
- 10) 3b: g = 2.1196, |a<sub>Cu</sub>| = 85.5 G; Copper octaethylisobacteriochlorin <sup>4f</sup>): g = 2.1073, |a<sub>Cu</sub>| = 90 G. We thank Prof. Sustmann for recording the spectrum.
- 11) J.H.Fuhrhop, D.Mauzerall, J.Am.Chem.Soc. 91, 4174 (1969); K.M.Smith, Porphins and Metalloporphins, Elsevier, Amsterdam 1975, p. 25, 187-190.
- 12) No analysis could be made therefore. UV-spectrum (CHCl<sub>3</sub>): 378 nm (4.53, relat. intensity), 483 (sh, 0.58), 504 (1.00, "α"-band), 549 (3.97, "β"-band).
- 13) MS: m/e = 454/455/456/458 (97%/100%/75%/21%, M<sup>+</sup>, <sup>194</sup>Pt/<sup>195</sup>Pt/<sup>196</sup>Pt/<sup>198</sup>Pt), 457 (15%, <sup>196</sup>Pt<sub>M+1</sub>).

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