A Novel Conversion of Porphyrins into Chlorins

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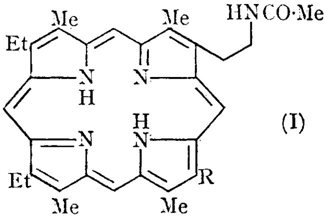
NORMALLY chlorins are not easily formed from porphyrins,[1] but conversion of a meso-substituted porphyrin into a purpurin (*i.e.*, a complex chlorin) is a key step in Woodward's synthesis of chlorophyll.[2] We now report a somewhat related reaction of a much simpler system, in which the chlorin chromophore is generated by intramolecular electrophilic attack at a β-position of the porphyrin nucleus under remarkably mild conditions.[3] It should be noted that electrophilic substitution of fully β-alkylated porphyrins usually occurs at the *meso*-positions.[4]

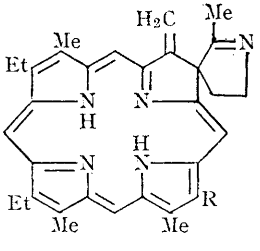
When the acetamidoethylporphyrins (Ia and Ib)[5] were warmed with phosphoryl chloride in pyridine, the colour changed in a few minutes from red to green and the chlorins (IIa and IIb)[6] could be isolated in good yield (spectroscopic data indicated almost quantitative conversion). Their electronic spectra showed the intense long-wavelength peak characteristic of chlorins, a Soret band, and several smaller peaks [(IIa) λ_{max} (CH_2Cl_2) 399, 495, 528, 598, 648 mμ (log ϵ, 5·29, 4·05, 4·12, 3·59, 4·47)]. Analysis of their proton magnetic resonance (100 Mc./sec. in $CDCl_3$) showed that these chlorins had the structures (IIa) and (IIb); in particular, the uncoupled geminal protons of the exocyclic methylene group gave singlets at τ 3·27 and 4·34 while the four meso-protons of (IIa) gave singlets at 0·31 [two protons, resolved in the case of (IIb)], 0·67 and 1·45. These structures were confirmed by the mass spectra, which exhibited intense molecular ions and $M-41$ peaks (due to loss of MeCN, metastable peak); (IIb) also showed a large $M-72$ peak (due to loss of CH_2·NH·CO·Me) like the porphyrins (Ia) and (Ib).

Hydrogenation of chlorin (IIa) with palladised charcoal and triethylamine[7] gave quantitatively a



(I)

(a) R=Et
(b) R=[CH₂]₂·NH·CO·Me



(II)

dihydro-derivative, the proton magnetic resonance spectrum of which lacked signals for olefinic protons, possessed a doublet (three protons) at τ 7·95, corresponding to the new methyl group and a new multiplet (one proton) at τ 5·70. The meso-protons gave a normal chlorin pattern, *viz.*, τ 0·31 (two protons), 1·27, 1·45, showing that the unusual location of one signal at τ 0·67 in the spectrum of (IIa) is due to the neighbouring olefinic group. The electronic spectrum of this dihydro-compound was also that of a typical chlorin [λ_{max} (CH_2Cl_2) 390, 498, 518, 588, 638 mμ (log ϵ, 5·18, 4·02, 3·51, 3·50, 4·32)]. Its mass spectrum showed the expected shift of two mass units and also a notable increase in the intensity of the $M-15$ peak, due to "benzylic" cleavage of the new methyl group.[8] The partially reduced $\beta\beta\beta'$-trialkylated portion of this molecule has a noteworthy resemblance to certain features of the vitamin B_{12} system, and it may be biogenetically significant that it is produced by electrophilic attack at an occupied β-position, followed by reduction.

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[1] H. Fischer and A. Stern "Die Chemie des Pyrrols", Akademische Verlag, Leipzig, 1940, Vol. II, Part I, p. 144.

[2] R. B. Woodward, *Angew. Chem.*, 1960, **72**, 658; R. B. Woodward, W. A. Ayer, J. M. Beaton, F. Bickelhaupt, R. Bonnett, P. Buchsacher, G. L. Closs, H. Dutler, J. Hannah, F. P. Hauck, S. Itô, A. Langemann, E. Le Goff, W. Leimgruber, W. Lwowski, J. Sauer, Z. Valenta, and H. Volz, *J. Amer. Chem. Soc.*, 1960, **82**, 3800.

[3] An interesting conversion of porphyrins into oxo-chlorins by oxidative rearrangement has been described by R. Bonnett, D. Dolphin, A. W. Johnson, D. Oldfield, and G. F. Stephenson, *Proc. Chem. Soc.*, 1964, 371.

[4] H. Voigt, Dissertation, Braunschweig, 1964; A. W. Johnson and D. Oldfield, *J. Chem. Soc.*, 1965, 4303; R. Bonnett and G. F. Stephenson, *J. Org. Chem.*, 1965, **30**, 2791.

[5] These compounds were prepared by variants of the MacDonald method (G. P. Arsenault, E. Bullock, and S. F. MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 4384) as intermediates in syntheses of vinylporphyrins for spectroscopic studies.

[6] Good microanalyses of these compounds and of the dihydro-derivative of (IIa) were obtained.

[7] Experiment carried out by Mr. K. M. Smith.

[8] A. H. Jackson, G. W. Kenner, K. M. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, 1965, **21**, 2913.