A Novel Route to the Tetrabenzporphyrin System

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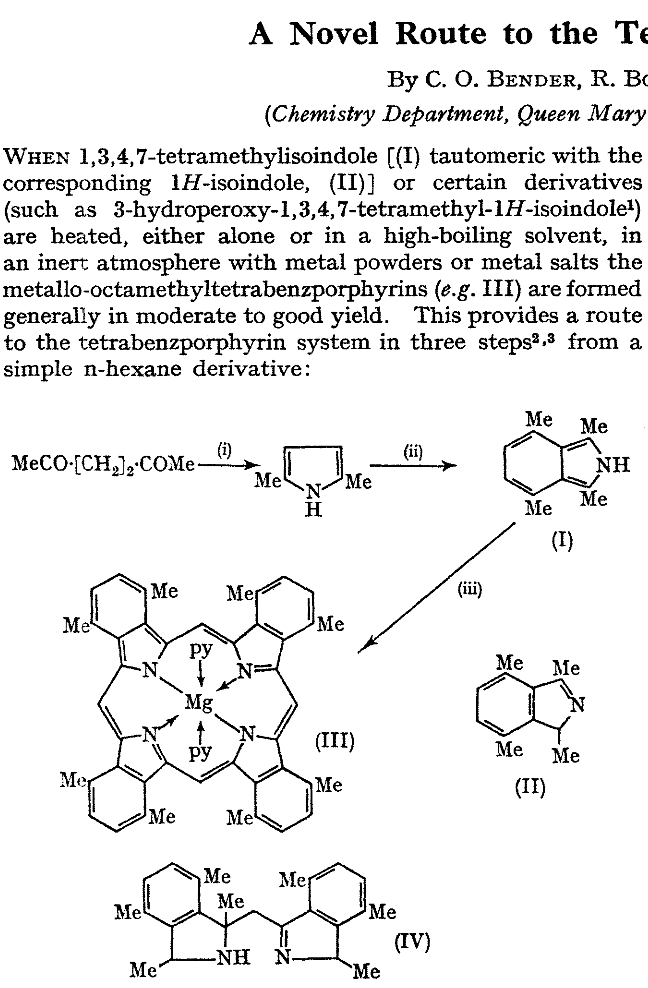
WHEN 1,3,4,7-tetramethylisoindole [(I) tautomeric with the corresponding 1*H*-isoindole, (II)] or certain derivatives (such as 3-hydroperoxy-1,3,4,7-tetramethyl-1*H*-isoindole[1]) are heated, either alone or in a high-boiling solvent, in an inert atmosphere with metal powders or metal salts the metallo-octamethyltetrabenzporphyrins (*e.g.* III) are formed generally in moderate to good yield. This provides a route to the tetrabenzporphyrin system in three steps[2,3] from a simple n-hexane derivative:



(i) $(NH_4)_2CO_3$, 81—86%; (ii) hexane-2,5-dione, 84%; (iii) (a) Mg, 400°, 3 hr., (b) pyridine (Soxhlet), 81%.

The complexes characterised include those of magnesium [bispyridine complex (III)], zinc (bispyridine complex), copper, nickel, and cobalt (pyridine bromide of Co^{III} complex). Demetallation of (III) with acid gave the parent base: oxidation of the latter with ceric sulphate by Linstead's procedure[4] suggested that four methine bridges were present and gave 3,6-dimethylphthalimide (62%) as the only product detected.

The octamethyltetrabenzporphyrin complexes were dark blue solids, generally highly crystalline, which did not melt below 300° and which were sparingly soluble in common organic solvents. Solutions of the parent base and of the zinc and magnesium complexes in pyridine were bright green, and emitted a scarlet fluorescence in u.v. light: on continued irradiation such solutions became yellow or colourless. The electronic spectra possessed strong absorptions in the 400 nm. (Soret) region and at ~600 nm. and, as expected for a porphyrin, the spectrum of the dication (and the metal complexes) was simpler than that of the free base (Figure). The free base in 1-chloronapthalene had maxima† [nm. ($\epsilon \times 10^{-3}$)] at λ 375 (14·1); 400 (35·2); 428 (173·4); 445 (236·3); 540 (3·4); 574i (12·6); 582 (14·9); 602i (13·4); 614 (32·6); 620i (52·6); 627 (83·0); and 674 (47·8). For comparison an analytical sample of tetrabenzporphyrin itself in the same solvent[5] had λ_{max} 367 (23); 392 (43); 421 (180); 437 (235); 476 (3·7); 493 (3·4); 530 (5·1); 572 (16); 609·5 (66); and 665 (50). The correspondence between the main absorption bands is good, the bathochromic shift in the present case being attributed to the alkyl groups; this effect has been observed before in the porphyrin series.[6]

The mass spectrum‡ of nickel octamethyltetrabenzporphyrin showed prominent peaks due to molecular ions: accurate mass measurement confirmed the molecular formula (Found: M^+, 678·2303. Calc. for $C_{44}H_{36}N_4{}^{58}Ni$:

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† Because of the difficulty in ensuring rapid and complete dissolution we regard these extinctions as minimum values.

‡ Dr. T. P. Toube, whom we thank for these measurements, informs us that the thermal stability of this type of compound makes its complete removal from the mass spectrometer a difficult and tedious operation.

678·2293). The doubly-charged molecular ions were also detected. N.m.r. spectra were complicated by the presence of a paramagnetic species. E.s.r. signals were recorded for the nickel complex both in the solid state and in pyridine solution.§ It is pertinent that the e.s.r. signal reported for the related system, phthalocyanine, was originally attributed[7] to a thermally attainable triplet species but recent work [8] has implicated a paramagnetic impurity.

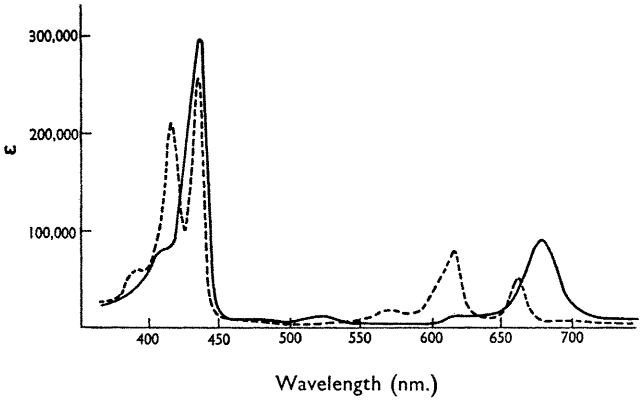

FIGURE. *Electronic spectra of octamethyltetrabenzporphyrin in trifluoroacetic acid* (——) *and in pyridine–2% trifluoroacetic acid* (- - -).

Structure (III) contains four carbon atoms fewer than the reactant molecules: we suppose that the 1*H*-isoindole (II) may undergo self-condensation to give products of type (IV), which at elevated temperatures, undergo dehydrogenation, dealkylation, and further condensation reactions to generate the highly stabilised macrocyclic system. The gases evolved during the reaction (methane, ethane, and propane) accord with the suggestion that the tertiary methyl group in (IV) is homolytically removed, while deep-red unstable intermediates, thought to be 1-(isoindol-1-ylmethylene)isoindole derivatives, have been isolated in certain reactions and are being examined.

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§ Magnesium tetrabenzporphyrin, prepared by a slight modification of Linstead's method (ref. 4) also shows an e.s.r. signal in pyridine solution. We thank Dr. K. D. Sales for the e.s.r. measurements.

[1] C. O. Bender and R. Bonnett, *Chem. Comm.*, 1966, 198.

[2] D. M. Young and C. F. H. Allen, *Org. Synth.*, Coll. Vol. 2, 1943, 219.

[3] C. O. Bender and R. Bonnett, *J. Chem. Soc.* (*C*), 1968, 3036. The yield quoted is that obtained before sublimation: *cf.* also H. Fletcher, *Tetrahedron*, 1966, **22**, 2481.

[4] P. A. Barrett, R. P. Linstead, F. G. Rundall, and G. A. P. Tuey, *J. Chem. Soc.*, 1940, 1079.

[5] Unpublished observations by Dr. Margaret Whalley. We are grateful to Professor J. A. Elvidge for bringing these results to our attention.

[6] *E.g.*, A. Stern and H. Wenderlein, *Z. phys. Chem.* (*Leipzig*), 1936, *A*, **175**, 405.

[7] F. H. Winslow, W. O. Baker, and W. A. Yager, *J. Amer. Chem. Soc.*, 1955, **77**, 4754.

[8] A. B. P. Lever, *J. Chem. Soc.*, 1965, 1821; H. A. O. Hill and M. M. Norgett, *J. Chem. Soc.* (*A*), 1966, 1476.