1-Methyltetradehydrocorrins

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IN a recent Communication,[1] we described a stepwise synthesis of porphyrins (*e.g.* I), whereby the formation of the macrocycle was accomplished by heating the dihydrobromide of a 1,19-dideoxy-1-bromo-19-methylbiladiene-ac (*e.g.* II). It has now been found that when the same biladiene salt is treated with base in presence of nickel ions it cyclises smoothly (70%) to the nickel tetradehydrocorrin (III), possibly by the mechanism shown. The product is a neutral complex and the proposed structure is supported by analysis and the existence in the n.m.r. spectrum of a band at τ 8·52 (3 protons) which corresponds to the angular methyl group and which is absent from the spectrum of the parent biladiene salt. When the nickel complex (III) is treated with perchloric acid it forms a crystalline salt (IV) in which the protons of the angular methyl group now appear at τ 9·38 in the n.m.r. spectrum. This protonation is reversed by basification. The visible spectrum of (IV) corresponds to that of the nickel complex of the 1,19-dimethyltetradehydrocorrin (V), which has been prepared[2] by cyclisation of the corresponding 1,19-dideoxy-1,19-dimethylbiladiene-ac, and which also shows bands in the n.m.r. spectrum about τ 9·34 corresponding to the protons of the angular methyl groups. The high τ values for these protons in the complexes (IV) and (V) may be caused by the shielding of the methyl groups by the peripheral double bonds of the adjacent ring,

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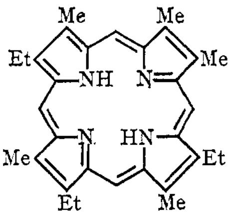
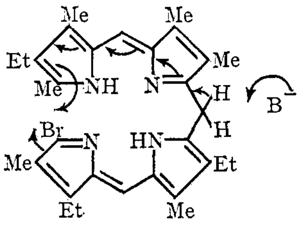
[1] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *Chem. Comm.*, 1965, 232.

[2] D. Dolphin, R. L. N. Harris, A. W. Johnson and I. T. Kay, *Proc. Chem. Soc.*, 1964, 359.

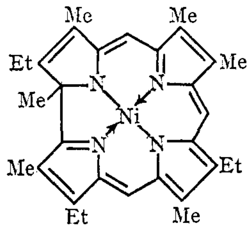
i.e. the shielding of the 1- or 19-methyl groups by the 2,3- or 17,18-double bonds respectively. Examination of models suggests that such an interaction could not exist in the nickel complex (III), and in its n.m.r. spectrum as well as those of vitamin B_{12}[3] and synthetic corrins,[4] there are no bands above τ 9. The existence of linear tetrapyrroles (II) which can give rise either to porphyrins (I) or to derivatives (III) containing the 1-methylcorrin skeleton has obvious bearings on the mode of biogenesis and the chemical synthesis of vitamin B_{12}, and these features are at present under investigation.



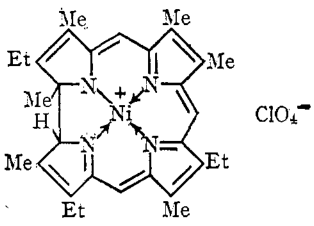
(I)



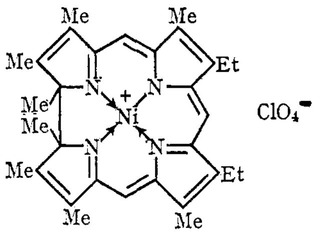
(II)



(III)



(IV)



(V)

(*Received, June 29th,* 1965; *Com.* 407.)

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[3] H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc.*, 1965, 2859.

[4] A. Eschenmoser, E. Bertele, H. Boos, J. D. Dunitz, F. Elsinger, I. Felner, H. P. Gribi, H. Gschwend, E. F. Meyer, M. Pesaro, and R. Scheffold, *Angew. Chem., Internat. Edn.*, 1964, **3**, 490.