Formation of Nickel Tetradehydrocorrins and Porphins from Linear Tetrapyrroles of Varied Oxidation Level

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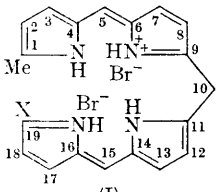
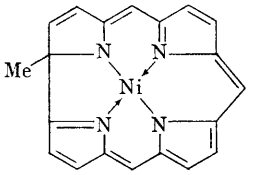
WE have shown that the β-octa-alkyl substituted linear tetrapyrrolic derivatives of 1-bromo-1,19-dideoxy-19-methylbiladiene-ac dihydrobromides (I; X = Br) can be cyclised to porphins when they are heated in *o*-dichlorobenzene[1,2] or even, in certain cases, kept in dimethyl sulphoxide and pyridine at room temperature.[2] The same 1,19-dideoxybiladiene-ac salts (I; X = Br) can also be cyclised to 1-methyltetradehydrocorrin nickel complexes (II) when they are treated with a base

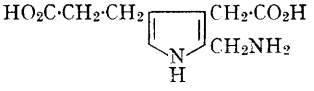
in presence of nickel ions in the absence of air.[3] These cyclisations of a single linear tetrapyrrole recall the biogeneses of the porphins and the cobalamins, both of which are derived from the same pyrrolic intermediate, porphobilinogen (III).



(I)



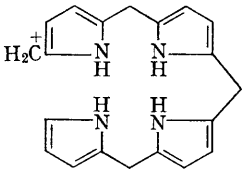
(II)



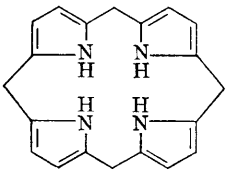
(III)

In order to improve the analogy with the naturally occurring compounds, we have prepared 1,19-dideoxy-1-methylbiladiene-ac dihydrobromides (I; X = H) and we have shown that these compounds also yield porphins when they are heated in *o*-dichlorobenzene. Thus 1,19-dideoxy-8,12-diethyl-1,2,3,7,13,17,18-heptamethylbiladiene-ac dihydrobromide gave 8,12-diethyl-2,3,7,13,17,18-hexamethylporphin in 33% yield after aerating and heating the *o*-dichlorobenzene solution at 100° for 14 hr. When the same biladiene-ac salt was treated with piperidine and nickel acetate in methanolic solution in air it was converted to nickel 8,12-diethyl-1,2,3,7,13,17,18-heptamethyltetradehydrocorrin[3] (56%).

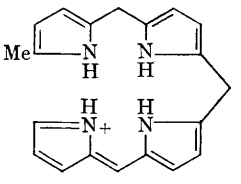
A possible point of divergence in the biosyntheses of porphins and cobalamins is the 1,19-dideoxybilane ion (IV; with appropriate β-substituents), which could cyclise to the porphyrinogen (V), known to be a precursor of the porphins, or alternatively rearrange to a 1,19-dideoxy-1-methylbilene salt (*e.g.*, VI), which might cyclise under the influence of heavy metal ions, to derivatives of corrin. The ability of bilenes to undergo cyclisation to tetradehydrocorrins has been demonstrated by the cyclisation (62%) of (VII) to (VIII).



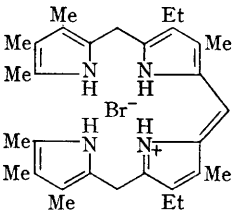
(IV)



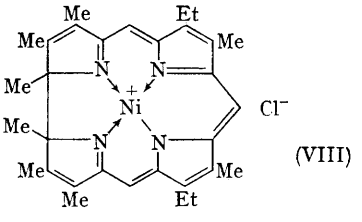
(V)



(VI)



(VII)



(VIII)

(*Received, April 20th*, 1967; *Com.* 379.)

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[2] P. Bamfield, R. L. N. Harris, A. W. Johnson, I. T. Kay, and K. W. Shelton, *J. Chem. Soc.* (*C*), 1966, 1436.
[3] R. L. N. Harris, A. W. Johnson and I. T. Kay, *Chem. Comm.*, 1965, 355.
[4] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1961, 2418.