A Three-stage Synthesis of a Nickel Corrin Perchlorate from Pyrrolic Intermediates

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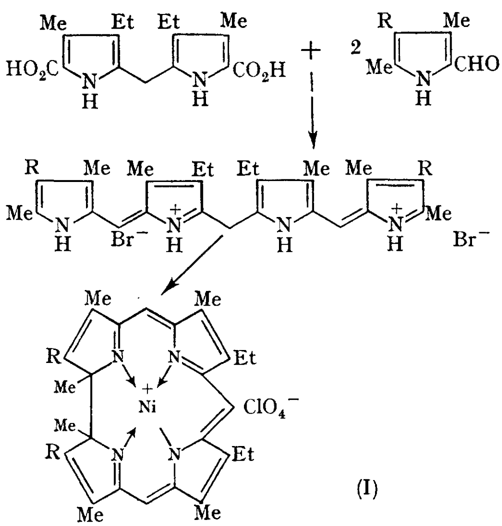
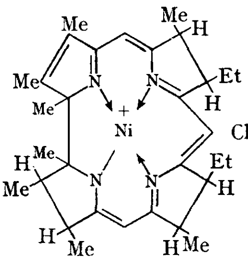
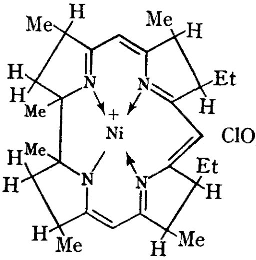
WE have described[1] the hydrogenation of nickel 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin perchlorate (I; R = Me) in presence of Raney nickel, when the corresponding monodehydrocorrin (II) was isolated as an orange-yellow perchlorate, the remaining $\beta\beta$-double bond in ring A probably resisting hydrogenation for steric reasons. In order to alleviate the crowding caused by the proximity of the 1, 2, 18, and 19 methyl groups, nickel 8,12-diethyl-1,3,7,13,17,19-hexamethyltetradehydrocorrin perchlorate (I; R = H) has been prepared by cyclisation of 1,19-dideoxy-8,12-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide in the usual manner. The 1,19-dideoxybiladiene-ac salt was itself obtained by condensation of 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid with two equivalents of 3,5-dimethyl-2-formylpyrrole. When the tetradehydrocorrin salt (I; R = H) was hydrogenated at 160° and 100 atmospheres in presence of freshly prepared Raney nickel, a yellow amorphous product was obtained



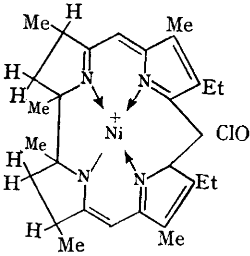
(I)



(II)



(III)



(IV)

which was isolated as the perchlorate. An examination of the n.m.r spectrum showed that all the $\beta\beta$-double bonds had been reduced (no methyl singlets below τ 8). This product is the nickel corrin salt (III). The *meso*-protons corresponded to two sharp singlets at τ 3·93 (1H) and 4·04 (2H). The visible spectrum contained maxima at 245, 306, 319, and 435 mμ; log ϵ 4·17, 4·32, 4·33, and 4·05 respectively, with inflections at 253, 268, 398, 415, and 450 mμ; log ϵ, 4·09, 3·97, 3·89, 3·98, and 4·00. These figures are similar to those quoted by Eschenmoser[2] for a synthetic nickel 1,8,8,13,13-pentamethylcorrin perchlorate, the n.m.r. spectrum of which showed singlets corresponding to the *meso*-protons at τ 3·97 (1H) and about 3·85 (2H). Our convenient synthesis of a nickel corrin salt comprises only three stages from readily available pyrrolic intermediates. Experiments to test the generality of the method are currently in progress.

An interesting reaction of the synthetic nickel corrin perchlorate (III) has been observed when it was heated with ethanolic potassium hydroxide solution in air for a short while. A deep purple crystalline compound was rapidly formed which showed an ultraviolet and visible spectrum similar in shape to that of a nickel tetradehydrocorrin salt[1] but with a general hypsochromic shift. Examination of the n.m.r. spectrum suggests that dehydrogenation had occurred in rings B and C and that the product is nickel 8,12-diethyl-1,3,7,13,17,19-hexamethyl-7,12-didehydrocorrin perchlorate (IV). The n.m.r. spectrum showed signals at 2·86 (s; 1 *meso*-H), 3·13 (s; 2 *meso*-H), 7·12 (q; 4H of 2 methylenes attached to unsaturated carbon), 7·6 (s; 6H of 2 methyls attached to unsaturated carbon) and a complex signal between τ 8·3 and 8·8 which has not been interpreted (protons of β-methyl groups attached to saturated carbon methyl groups and methyls of β-ethyl groups). A similar case of dehydrogenation caused by base in the presence of oxygen has been reported recently by Barton and Jones.[3]

Satisfactory analyses have been obtained for all of the above compounds. When an alkaline solution of the nickel corrin salt (III) was treated with methyl iodide in the absence of oxygen, an orange-yellow methylated derivative was obtained which was not dehydrogenated by air in presence of alkali, as evidenced by the failure to show the pronounced colour change. The structure of this product is under investigation.

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[1] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 30.

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

[3] D. H. R. Barton and D. W. Jones, *J. Chem. Soc.*, 1965, 3563.