Synthesis of Corroles, Tetradehydrocorrins, and Porphyrins from 1,19-Di-iodo- and 19-Iodo-1-methyl-1,19-dideoxybiladienes-a,c

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Summary 1,19-Di-iodo-1,19-dideoxybiladienes-a,c bearing acetic and propionic acid residues at the β-positions have been prepared for the first time, and transformed into corroles and aza-porphyrins whose substitution pattern corresponds to those of uroporphyrin III and 12-decarboxyuroporphyrin III; nickel tetradehydrocorrins and porphyrins are available from the corresponding 1-methyl-19-iodo-compounds.

CORROLES bearing more than two functionalised alkyl side-chains at the β-positions have not been reported previously. In particular, groups which are bulkier than methyl at the C-2 and C-18-positions thwart photocyclisation of 10,24-dihydro-(21*H*)-bilins (1,19-dideoxybiladienes-a,c),[1] so that sterically hindered corrole derivatives are not accessible by this procedure. A more promising method seems to be the thermal cyclisation of 1,19-dibromo-10,24-dihydro-(21*H*)-bilins[2] although no example is known of its application to the synthesis of compounds bearing substituents other than alkyl groups on rings A and D (*cf.* formula **10**).

We now report, for the first time, the synthesis of the more reactive 1,19-di-iodo-10,24-dihydro-(21*H*)-bilin dihydrobromides (**8a**)† and (**8b**)† whose substitution patterns correspond to that of uroporphyrin III and 12-decarboxyuroporphyrin III respectively, as well as their transformations into the new corroles (**10a**)† and (**10b**).† On the other hand, the nickel 1-methyl-tetradehydrocorrin (**11**) could be obtained by non-oxidative base-induced cyclisation of the 19-iodo-1-methyl-10,24-dihydro(21*H*)-bilin dihydrobromide (**9a**)† in the presence of nickel ions (*cf.* ref. 3).

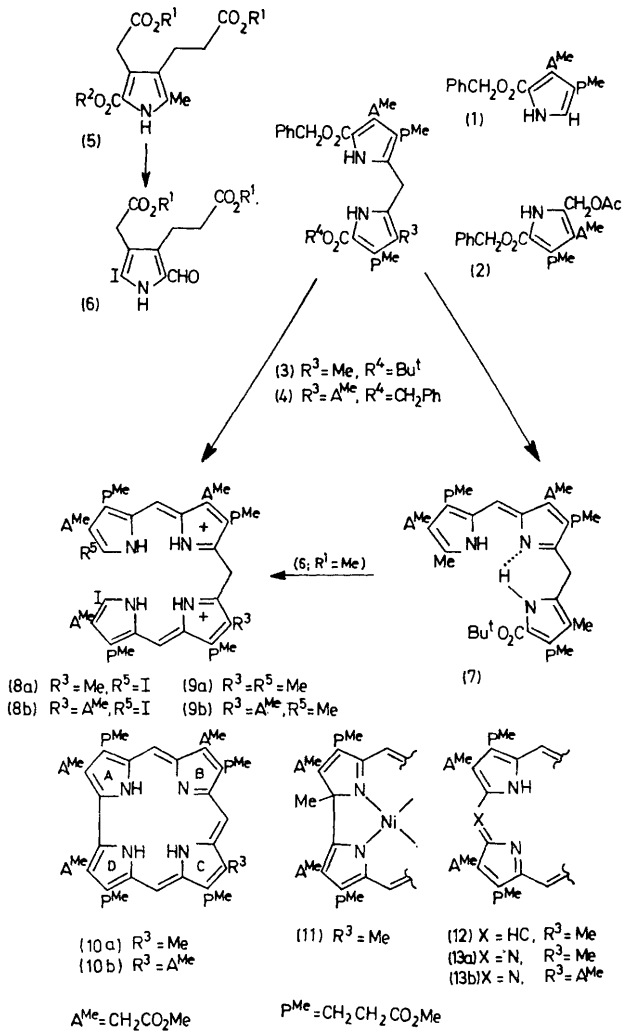
The above-mentioned macrocycles whose synthesis are described here could be involved, in principle, in the biosynthesis of the vitamin B_{12} chromophore.[4]

A key intermediate for the synthesis of both types of macrocycles, *viz.* (**10**) and (**11**), is the 5-iodo-pyrrole aldehyde (**6**)† (R^1 = Me) which was prepared from (**5**; R^1 = Me, R^2 = CH_2Ph) by the usual methods. A similar, but for our purpose less convenient, synthesis of the corresponding dicarboxylic acid (**6**; R^1 = H) starting from (**5**; R^1 = R_2 = Et) had been reported earlier by MacDonald *et al.*[5]

Condensation of (**6**; R^1 = Me) with the pyrrylmethylpyrromethene (**7**) whose synthesis from (**3**) has been reported lately by us,[6] yields (**9a**)† which in the presence of base (piperidine) and nickel ions cyclises, with exclusion of oxygen, to (**11**). Recently[6] we have synthesized the same nickel 1-methyl-tetradehydrocorrin by base-catalysed oxidative cyclisation of the 19*H* analogue of (**9a**).

On heating (**9a**) in dimethylformamide 12-decarboxyuroporphyrin III heptamethyl ester (**12**) is obtained.[7] Alternative syntheses of this porphyrin, which is an isomer of phyriaporphyrin III,[8] have been published recently by Battersby *et al.*[8] and, independently, by us.[6]

For convenience, (**8a**)† was synthesized starting from the same above-mentioned dipyrrylmethane (**3**) which after cleavage of the t-butoxycarbonyl group by CF_3CO_2H, hydrogenolysis (Pd-C) of the benzyl ester and successive decarboxylation of the carboxylic acid obtained, was condensed with 2 mol. of the pyrrole aldehyde (**6**; R^1 = Me) yielding (**8a**) (45% from (**3**).



On the other hand, 1,19-di-iodo-10,24-dihydro-(21*H*)-bilin dihydrobromide (**8b**)† was prepared from the dipyrrylmethane dibenzylic ester (**4**)† which, in turn, was obtained by toluene-*p*-sulphonic acid-catalysed condensation of the

† New compound(s) which gave satisfactory elemental analysis, and mass, electronic, and n.m.r. spectra compatible with the formulation shown.

known pyrroles (**1**)[9] and (**2**),[9] by hydrogenolysis of the benzyl ester groups, decarboxylation of the resulting dicarboxylic acid and, finally, reaction with 2 mol. of the pyrrole aldehyde (**6**; R^1 = Me).

Both 1,19-di-iodo-10,24-dihydro-(21*H*)-bilin dihydrobromides (**8a**) and (**8b**) cyclise when heated in dimethylformamide affording the corroles (**10a**)† and (**10b**] respectively. On the other hand, when treated with sodium azide in boiling methanol (*cf.* ref. 2) (**8a**) and (**8b**) yield the azaporphyrins (**13a**)† and (**13b**)† respectively.

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