# Synthesis of Tetradehydrocorrins, Corroles, and Corrologens related to 12-Decarboxyuroporphyrin III and Uroporphyrin III

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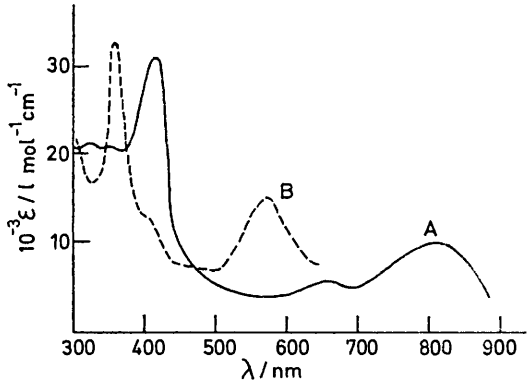
The title compounds have been synthesized, for the first time, from the corresponding 1,19-dimethyl-, 1-methyl-19-iodo-, and 1,19-di-iodo-biladiene-ac derivatives respectively, by means of methods described earlier. The 1,19-di-iodobiladienes-ac could be cyclized, in the presence of sodium azide, to the corresponding 20-aza-porphyrins.

NOT long ago, the possibility of synthesizing tetradehydrocorrin derivatives containing an unsymmetrical arrangement of β-substituents was considered.[1] The route followed involved the use of bilenes-b as intermediates whose synthesis was attempted by means of known methods. However, the occurrence of some side-reactions (mainly fragmentations and self-condensations) imposed severe restrictions to the choice of the substitution pattern of the dipyrrylmethanes which were used as starting materials. Since several 1,19-dideoxybiladienes-ac of the uroporphyrin III and 12-decarboxyuroporphyrin III types became recently available,[2] we have now studied their cyclization to tetradehydrocorrins and corroles under the conditions described earlier [3,4] for the synthesis of alkyl substituted derivatives [5] (Scheme 1). Thus, when methanolic solutions of the biladiene-ac salts (1a and b) were warmed in the presence of nickel acetate, cyclization occurred rapidily to the nickel tetradehydrocorrins, isolated as the bromides (5a and b) (48 and 41%, respectively). Related cyclizations of biladienes-ac containing β-methoxycarbonylmethyl [6] and β-methoxycarbonylethyl [3,6] substituents have been described. Similarly in the presence of cobalt salts the corresponding cobalt complexes (6a and b) were obtained. The latter are, however, unstable compounds in air at room temperature.

On the other hand, cyclizations of the biladienes-ac (2a and b) or (3a and b) (note the use of 1-methyl-19-iodobiladienes-ac rather than the 1-methyl-19-bromo derivative utilised earlier [7]) in the presence of nickel acetate and a small amount of piperidine gave the nickel 1-methyltetradehydrocorrins (7a) [31 and 40% from (2a) and (3a), respectively] and (7b) [21 and 27% from (2b) and (3b), respectively]. In agreement with the properties of other nickel 1-methyltetradehydocorrins,[7,8] the complexes (7a and b) are protonated and deuteriated at C-19, as evidenced by the remarkable change of colour of their solutions, on acidification, from green to violet as well as by the characteristic electronic (Figure) and n.m.r. spectral changes observed on addition of trifluoroacetic acid or deuteriotrifluoroacetic acid, respectively.

In the original synthesis of corroles,[9] alkaline solutions of the 1,19-diunsubstituted biladienes-ac were warmed over a lamp-bath in order to achieve cyclisation. However, corroles bearing more than two functionalized 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 -18 positions thwart photocyclization of 1,19-diunsubstituted biladienes-ac,[9] so that sterically hindered corrole derivatives are not accessible by this procedure. A more promising method seems to be the thermal cyclization of 1,19-dibromobiladienes-ac [10] although no example was known



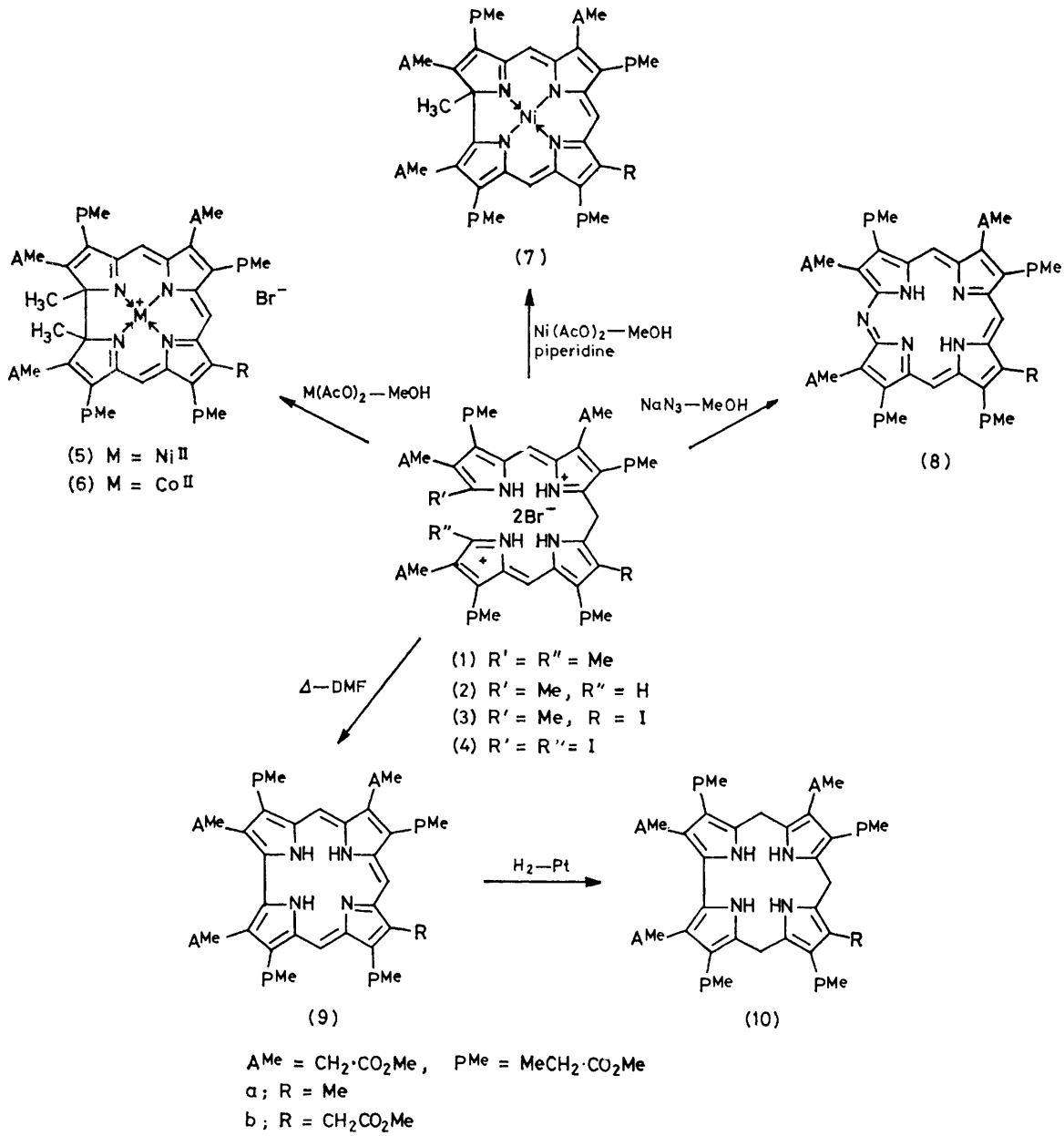

Electronic spectra of the 1-methyltetradehydrocorrin (7a) in A, $CH_2Cl_2$ and B, $CF_3CO_2H$

of its application to the synthesis of compounds bearing substituents other than alkyl groups on rings A and D [*cf.* (9a and b)].

We now report the synthesis (Scheme 2) of the more reactive 1,19-di-iodobiladiene-ac dihydrobromides (4a and b) whose substitution patterns correspond to that of uroporphyrin III and 12-decarboxyuroporphyrin III, respectively, as is also shown by their transformation

[1] J. M. Conlon, J. A. Elix, G. I. Feutrill, A. W. Johnson, Md W. Roomi, and J. Whelan, *J.C.S. Perkin I*, 1974, 713.
[2] J. Engel and A. Gossauer, *Annalen*, 1976, 1637.
[3] R. Grigg, A. W. Johnson, R. Kenyon, V. B. Math, and K. Richardson, *J. Chem. Soc.* (*C*), 1969, 176.
[4] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 30.
[5] Preliminary communications, J. Engel and A. Gossauer, *J.C.S. Chem. Comm.*, 1975, 570, 713.
[6] H. H. Inhoffen, F. Fattinger, and N. Schwarz, *Annalen*, 1974, 412.
[7] D. A. Clarke, R. Grigg, R. L. N. Harris, A. W. Johnson, I. T. Kay, and J. W. Shelton, *J. Chem. Soc.* (*C*), 1967, 1648.
[8] R. Grigg, A. W. Johnson, and K. W. Shelton, *J. Chem. Soc.* (*C*), 1968, 1291.
[9] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.
[10] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 22.

into the corresponding corroles (9a and b). Thus, when warmed in dimethylformamide on the steam-bath for 10 min, the 1,19-di-iodobiladienes-ac (4a and b) cyclize smoothly to the corresponding corroles (9a and b) (27 and 18%, respectively). Hydrogenation of these corroles in the presence of platinum oxide (*cf.* ref. 9) gave the corresponding corrologens (10a and b) which were obtained as pale, easily oxidisable crystalline products which were characterized by their spectral properties. Their relative stability probably arises from the presence of propionic and acetic ester residues at the β-positions of the pyrrole rings which, as is well known, act as stabilizing groups against oxidation (*cf.* ref. 11). It is noteworthy that, as in the case of bilanes of the uroporphyrinogen III and 12-decarboxyuroporphyrinogen III types,[12] *four* broad singlets are observable in the $^1$H n.m.r. spectra of (10a and b) when measured in $CDCl_3$, corresponding to the protons bonded to the nitrogen atoms. The protons of the methylene bridges absorb in the range δ 3.8—3.9.

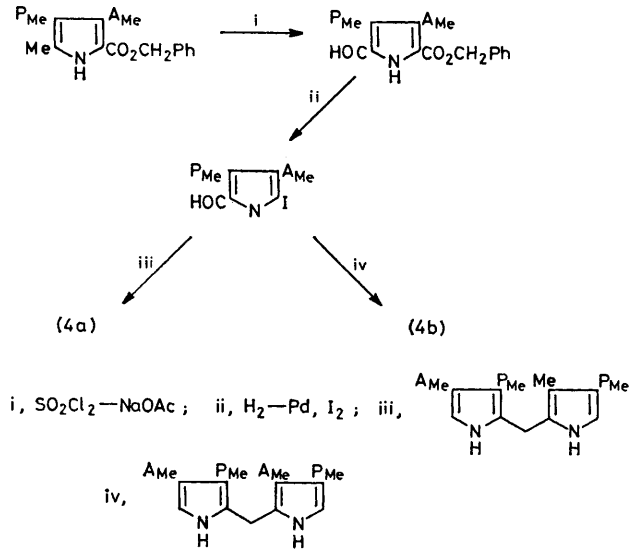



SCHEME 1 Cyclisation of 1,19-dideoxybiladienes-ac

Finally, the above mentioned 1,19-di-iodobiladienes-ac (4a and b) like the 1,19-diunsubstituted biladienes-ac,[9] reacted with methanolic sodium azide to give the corresponding monoazaporphyrins (8a and b) (58 and 48%,

[11] S. F. MacDonald, *J. Amer. Chem. Soc.*, 1957, **79**, 2659.
[12] A. Gossauer and J. Engel, *Annalen*, 1977, 225.

respectively). The latter reaction confirms, in addition to the analytical data, the structure of the 1,19-di-iodobiladienes-ac (4a and b) prepared here for the first time.




SCHEME 2 Preparation of 1,19-di-iodobiladienes

## EXPERIMENTAL

M.p.s are uncorrected and were determined with a Kofler hot stage apparatus (Reichert). U.v. and visible spectra were recorded on a Leitz–Unicam SP 800 B spectrophotometer using methylene chloride solutions unless otherwise specified. I.r. spectra were run on a Perkin-Elmer model 157 G spectrometer for KBr discs. $^1$H N.m.r. spectra were recorded on Varian T-60 and XL-100 instruments as well as on a Brüker-Physik AG model HFX-90 for deuteriochloroform solutions unless otherwise specified. Chemical shifts δ are expressed downfield from internal tetramethylsilane. Mass spectral data were obtained at an ionizing voltage of 70 eV on AEI MS 9 and MS 30 instruments. Elemental analysis were performed by I. Beetz (Kronach/Obfr.) and F. Pascher (Bonn) Microanalytical Laboratories. Preparative layer chromatography of mixtures (50 mg per plate) made use of 2 mm thick plates measuring 100 × 20 cm precoated with silica gel H (E. Merck, Darmstadt).

*Pyrroles.—Benzyl 5-formyl-4-(2-methoxycarbonylethyl)-3-methoxycarbonylmethylpyrrole-2-carboxylate.* Sulphuryl chloride (4.3 ml) was added dropwise to an ice-cooled solution of benzyl 4-(2-methoxycarbonylethyl)-3-methoxycarbonylmethyl-5-methylpyrrole-2-carboxylate [13] (9.3 g) in anhydrous ether (180 ml) with vigorous stirring, over 15 min, and the mixture was stirred at room temperature for a further 45 min. After evaporation of the solvent *in vacuo*, below 20 °C, the remaining sulphuryl chloride was removed by repeated addition of ether and evaporation to dryness on the rotary evaporator. The oily residue obtained was treated with a solution of sodium acetate (25 g) in water (400 ml); the mixture was boiled for 3 min, then quickly cooled at 0 °C, and extracted repeatedly with methylene chloride. The organic phases were combined, dried ($Na_2SO_4$), and the solvent was evaporated *in vacuo*. The remaining residue was crystallized from methanol–water and recrystallized from methylene chloride–n-hexane to give the *product* (8.1 g, 84%), m.p. 117 °C (Found: C, 61.85; H, 5.55; N, 3.55. $C_{20}H_{21}NO_7$ requires C, 62.0; H, 5.45; N, 3.6%), $\tilde{\nu}_{max.}$ 3 200, 1 720, 1 665, 753, and 700 cm$^{-1}$, δ 2.53 (t, $CH_2CH_2CO_2Me$), 3.03 (t, $CH_2CH_2CO_2Me$), 3.60 and 3.62 (both s, $OCH_3$) 3.82 (s, $CH_2CO_2Me$), 5.30 and 7.40 (both s, $PhCH_2$), and 9.83 (s, CHO), *m/e* 387 (10%, $M^+$), 356 (6), 327 (4), 296 (14), 268 (33), 264 (23), and 91 (100, tropylium ion).

*5-Formyl-4-(2-methoxycarbonylethyl)-3-methoxycarbonylmethylpyrrole-2-carboxylic acid.* The foregoing benzylic ester (2.73 g) was dissolved in tetrahydrofuran (30 ml), morpholinomethylpolystyrene (2.73 g) was added, and the mixture was hydrogenated at room temperature over 10% palladized charcoal (273 mg) until the theoretical amount of hydrogen was consumed (*ca.* 30 min). After removal of the catalysts by filtration, the filtrate was diluted with n-hexane, and chilled to −21 °C. A crystalline *product* separated (1.73 g, 83%) which did not require further purification, m.p. 154—155 °C (Found: C, 52.5; H, 4.95; N, 4.7. $C_{13}H_{15}NO_7$ requires C, 52.55; H, 5.1; N, 4.7%), $\tilde{\nu}_{max.}$ 3 183, 2 783, 1 724, 1 668, and 1 631 cm$^{-1}$, δ 2.60 (t, $CH_2CH_2CO_2Me$), 3.04 (t, $CH_2CH_2CO_2Me$), 3.67 and 3.76 (both s, $OCH_3$), 3.94 (s, $CH_2CO_2Me$), 9.17br (s, NH), 9.78 (s, CHO), and 10.52br (s, OH), *m/e* 297 (60%, $M^+$), 265 (52), 237 (73), 178 (81), and 160 (100).

*2-Formyl-5-iodo-3-(2-methoxycarbonylethyl)-4-methoxycarbonylmethylpyrrole.* The foregoing pyrrolecarboxylic acid (400 mg) was dissolved in aqueous methanol (3 ml, 50%), sodium hydrogencarbonate (400 mg) was added, the mixture was warmed to 45 °C, and then treated dropwise, with stirring, with a solution of iodine (250 mg) in methanol (2 ml). The mixture was stirred at 40 °C for a further 90 min, and then poured into ice–water (30 ml). After 3 h the separated solid was filtered off, washed with water, dried, and crystallized from methylene chloride–n-hexane to yield the *product* (239 mg, 47%) as needles, m.p. 122 °C (Found: C, 38.2; H, 3.75; N, 3.5. $C_{12}H_{14}INO_5$ requires C, 38.0; H, 3.7; N, 3.7%), $\tilde{\nu}_{max.}$ 3 183, 1 748, 1 718, and 1 654 cm$^{-1}$, δ 2.58 (t, $CH_2CH_2CO_2Me$), 3.08 (t, $CH_2CH_2CO_2Me$), 3.50 (s, $CH_2CO_2Me$), 3.72 and 3.73 (both s, $OCH_3$), 9.46 (s, CHO), and 9.73br (s, NH), *m/e* 379 (50%, $M^+$), 347 (29), 320 (35), 260 (58), 192 (42), 129 (88), 106 (52), and 32 (100).

*Biladienes-ac.—1,19-Di-iodo-3,8,13,17-tetrakis-(2-methoxycarbonylethyl)-2,7,18-trismethoxycarbonylmethyl-12-methyl-10,23-dihydro-21H-bilin dihydrobromide* (4a). A solution of the foregoing pyrrole carbaldehyde (152 mg) in methylene chloride (3 ml) was treated with a solution of crude 3,4′-bis-(2-methoxycarbonylethyl)-4-methoxycarbonylmethyl-3′-methyl-2,2′-dipyrrylmethane in methylene chloride (obtained from 108 mg of the corresponding benzyl 5-carboxylate according to the indications given in ref. 2). The mixture was warmed on a steam-bath until it began to boil, then hydrobromic acid in acetic acid (7 drops; 40%) was added, and the solution allowed to cool. On standing at room temperature, a part of the formed biladiene-ac dihydrobromide separated. Crystallization was completed by dilution with ether and cooling to −21 °C. The *product* (140 mg, 54%) was separated, washed with ether, and dried *in vacuo*, m.p. 118 °C, $\lambda_{max.}$ 548 (log ε 4.96) and 468 nm (4.41), $\tilde{\nu}_{max.}$ 3 350, 2 900, 1 732, and 1 613 cm$^{-1}$, δ 2.09 (s, $CH_3$), 2.5—3.2 (16 H, m, $CH_2CH_2CO_2Me$), 3.57 (4 H, s, 2- and 18-$CH_2CO_2Me$), 3.53, 3.63, 3.65, 3.73 (each s, $OCH_3$), 3.84

[13] A. R. Battersby, D. A. Evans, K. H. Gibson, E. McDonald, and L. Nixon, *J.C.S. Perkin I*, 1973, 1546.

(s, 7-C$H_2$CO$_2$Me), 5.17br (s, CH$_2$), and 7.69br 2 H, s, =CH), *m/e* 872 ($M^+$ − [2 HBr + 2I]), 829, 814, 800, 757, 742, 698, and 571.

1,19-*Di-iodo*-3,8,13,17-*tetrakis*-(2-*methoxycarbonylethyl*)-2,7,12,18-*tetrakismethoxycarbonylmethyl*-10,23-*dihydro*-21H-*bilin dihydrobromide* (4b). Prepared as above from crude 3,4′-bis-(2-methoxycarbonylethyl)-3′,4-bismethoxycarbonylmethyl-2,2′-dipyrrylmethane (obtained from 65 mg of the corresponding dibenzyl 5,5′-dicarboxylate according to the indications given in ref. 2). The *product* (92 mg, 68%) had m.p. 153 °C (Found: C, 41.95; H, 4.5; N, 4.0. $C_{47}H_{56}Br_2I_2N_4O_{16}$ requires C, 41.9; H, 4.2; N, 4.15%), $\lambda_{max.}$ 547 (log ε 4.97) and 469 nm (4.70), $\tilde{\nu}_{max.}$ 3 360, 2 908, 1 735, and 1 608 cm$^{-1}$, δ 2.3—3.2 (16 H, m, C$H_2$C$H_2$CO$_2$Me), 3.63, 3.68, 3.74 (30 H, each s, OCH$_3$ overlapping 2-, 12-, and 18-C$H_2$CO$_2$Me), 3.84 (s, 7-C$H_2$CO$_2$Me), 5.13br (s, CH$_2$), and 7.8br (2 H, s, =CH).

*Tetradehydrocorrins.*— 3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,18-*trismethoxycarbonylmethyl*-1,12,19-*trimethyltetradehydrocorrinnickel*(II) *bromide* (5a). Biladiene-ac dihydrobromide (1a) [2] (100 mg) was dissolved in methanol (5 ml) containing nickel acetate (100 mg), and the mixture was warmed at 50 °C for 45 min with occasional shaking. The deep violet solution obtained was chromatographed on silica gel eluting with methylene chloride, and the *product* was purified by repeated preparative t.l.c. on silica gel eluting with methylene chloride–acetone (94 : 6). After evaporation of the solvent, the residue was dissolved in methylene chloride and shaken with saturated aqueous KBr solution. The organic phase was dried by filtration through cotton, the solvent evaporated, and the remaining residue (49 mg, 48%) crystallized from acetone–ether, m.p. 69—71 °C (Found: C, 53.3; H, 5.4; Br, 8.0; N, 5.6. $C_{47}H_{55}BrN_4NiO_{14}$ requires C, 54.3; H, 5.3; Br, 7.7; N, 5.4%), $\lambda_{max.}$ 278 (log ε 4.47), 356 (4.41), and 568 nm (4.11), $\tilde{\nu}_{max.}$ 2 885 and 1 723 cm$^{-1}$, δ(CD$_2$Cl$_2$) 0.63 (6 H, s, 1- and 19-CH$_3$), 2.70 (s, 12-CH$_3$), 2.88br (8 H, t, CH$_2$C$H_2$CO$_2$Me), 3.34br (8 H, t, C$H_2$-CH$_2$CO$_2$Me), 3.64, 3.68, 3.79, 3.84 (each s, OCH$_3$), 4.13 (4 H, s, 2- and 18-C$H_2$CO$_2$Me), 4.23 (s, 7-C$H_2$CO$_2$Me), and 7.77br (3 H, s, =CH), *m/e* 956 ($M^+$ − HBr), 940, 897, 882, and 866.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,12,18-*tetrakismethoxycarbonylmethyl*-1,19-*dimethyltetradehydrocorrinnickel*(II) *bromide* (5b). Prepared as above (41%) from the corresponding biladiene-ac dihydrobromide (1b),[2] the *product* melts at 59—61 °C (Found: C, 54.3; H, 5.6; N, 5.2. $C_{49}H_{57}BrN_4NiO_{16}$ requires C, 53.7; H, 5.2; N, 5.2%), $\lambda_{max.}$ 277 (log ε 4.38), 357 (4.34), 423 (3.99), and 569 (4.01) nm, $\tilde{\nu}_{max.}$ 2 890 and 1 723 cm$^{-1}$, δ(CD$_2$Cl$_2$) 0.59 (6 H, s, 1- and 19-CH$_3$), 2.88 (8 H, m, CH$_2$C$H_2$CO$_2$Me), 3.32 (8 H, m, C$H_2$CH$_2$CO$_2$Me), 3.59, 3.61, 3.63, 3.73, 3.76, 3.81 (each s, OCH$_3$), 4.10 (4 H), 4.17 (2 H), 4.20 (2 H) (each s, C$H_2$-CO$_2$Me), and 7.74br and 7.83br (s, =CH), *m/e* 1 015 ($M^+$ − Br), 999, 970, 940, and 462.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,18-*trismethoxycarbonylmethyl*-1,12,19-*trimethyltetradehydrocorrincobalt*(II) *bromide* (6a). This was prepared as above by cyclization of the corresponding biladiene-ac dihydrobromide (1a) (50 mg) in the presence of cobalt(II) acetate (50 mg) and sodium acetate (50 mg). The *product* (20 mg, 40%) is not stable in air at room temperature, m.p. 78—80 °C (Found: C, 54.5; H, 5.1; N, 5.4. $C_{47}H_{55}BrCoN_4O_{14}$ requires C, 54.3; H, 5.3; N, 5.4%), $\lambda_{max.}$ 281 (log ε 4.33, 356 (4.28), 500 (4.13), and 580 nm (3.71), *m/e* 956 ($M^+$ − Br), 941, 928, 897, 883, 239, and 180.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,12,18-*tetrakismethoxycarbonylmethyl*-1,19-*dimethyltetradehydrocorrincobalt*(II) *bromide* (6b). Prepared as above (44%) from the corresponding biladiene-ac dihydrobromide (1b), the product had m.p. 83 °C, $\lambda_{max.}$ 281 (log ε 4.33), 353 (4.30), 500 (4.12), and 583 nm (3.70), *m/e* 1 016 ($M^+$ − Br), 1 001, 941, 883, and 180.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,18-*trismethoxycarbonylmethyl*-1,12-*dimethyltetradehydrocorrin nickel* (7a). (i) A solution of nickel acetate (50 mg) in methanol (3 ml) containing 1 drop of piperidine was heated under reflux for 2 min before biladiene-ac dihydrobromide (2a) [2] (50 mg) was added. The mixture was heated on a steam-bath for 1 min, whereupon it was quickly cooled to 0 °C. The *product* which precipitated was separated, purified by preparative t.l.c. on silica gel eluting with methylene chloride–methanol (98 : 2) and crystallized from methylene chloride–n-hexane yielding crystals (14 mg, 31%), m.p. 52—54 °C (Found: C, 59.2; H, 6.1; N, 5.6. $C_{46}H_{52}N_4NiO_{14}$ requires C, 58.6; H, 5.6; N, 5.9%), $\lambda_{max.}$ 325 (log ε 4.23), 418 (4.50), and 804 nm (3.99), δ(CD$_2$Cl$_2$) 1.46 (s, 1-CH$_3$), 2.38 (s, 12-CH$_3$), 2.72 (8 H, m, CH$_2$C$H_2$-CO$_2$Me), 3.18 (8 H, m, C$H_2$CH$_2$CO$_2$Me), 3.63, 3.66, 3.67, 3.69, 3.72, 3.74 (each s, OCH$_3$), 3.83, 3.87, 3.96 (each s, C$H_2$CO$_2$Me), and 6.18, 6.92, and 7.32 (each s, =CH), δ(F$_3$C-CO$_2$D) 0.82 (s, 1-CH$_3$), 2.77 (s, 12-CH$_3$), 3.06 (8 H, m, CH$_2$C$H_2$CO$_2$Me), 3.49 (8 H, m, C$H_2$CH$_2$CO$_2$Me), 3.87, 3.92, 4.00, 4.10 (each s, OCH$_3$), 4.29, 4.37 (both s, C$H_2$CO$_2$Me), and 7.71, 7.76, and 7.89 (each s, =CH), *m/e* 944/942 ($M^+$), 884, 869, 855, 797, and 723.

(ii) A solution of nickel acetate (50 mg) in methanol (5 ml) containing 1 drop of piperidine was heated under reflux for 5 min before the biladiene-ac dihydrobromide (3a) [2] (50 mg) was added. The mixture was then treated as in (i), whereby a nickel complex was obtained (16 mg, 40%) whose analytical data were identical with those of the foregoing product.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,12,18-*tetrakismethoxycarbonylmethyl*-1-*methyltetradehydrocorrinnickel* (7b). This was prepared as above by cyclization of the corresponding 1-methylbiladiene-ac dihydrobromide (2b) [2] (50 mg) or, alternatively, 1-methyl-19-iodobiladiene-ac dihydrobromide (3b) [2] (50 mg) (yield 21 and 27%, respectively). Crystallized from methylene chloride–n-hexane the *product* had m.p. 56—58 °C (Found: C, 57.8; H, 5.7; N, 5.5. $C_{48}H_{54}N_4NiO_{16}$ requires C, 57.6; H, 5.4; N, 5.6%), $\lambda_{max.}$ (methanol) 320 (log ε 4.52) and 796 nm (3.96), δ 1.48 (s, 1-CH$_3$), 2.70 (8 H, t, CH$_2$C$H_2$CO$_2$Me), 3.18 (8 H, t, C$H_2$CH$_2$CO$_2$Me), 3.65, 3.68, 3.70, 3.72, 3.75 (each s, OCH$_3$), 3.81, 3.83, 3.86, 3.96 (each s, C$H_2$CO$_2$Me), and 6.15, 6.97, and 7.37 (each s, =CH), *m/e* 1 000/1 002 ($M^+$), 942, 884, 699, 461, and 355.

*Azaporphyrins.*— 3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,18-*trismethoxycarbonylmethyl*-12-*methyl*-20-*azaporphin* (12-*decarboxy*-20-*azauroporphyrin III heptamethyl ester*) (8a). A solution of the 1,19-di-iodobiladiene-ac dihydrobromide (4a) (20 mg) and sodium azide (100 mg) in methanol (5 ml) was heated under reflux for 16 h, and then evaporated *in vacuo*. The residue obtained was purified by preparative t.l.c. on silica gel eluting with methylene chloride–methanol (98 : 2) and crystallization from the same solvent (yield 8 mg, 58%), m.p. >230 °C (Found: C, 61.85; H, 5.5; N, 8.15. $C_{45}H_{51}N_5O_{14}$ requires C, 61.0; H, 5.8; N, 7.9%), $\lambda_{max.}$ 613 (log ε 4.21), 563 (4.11), 540 (4.24), 504 (3.81), and 386 nm (5.06), $\tilde{\nu}_{max.}$ 3 360, 2 905,

1 729, 1 438, and 1 170 cm$^{-1}$, δ 3.30br (8 H, t, $CH_2CH_2$-$CO_2Me$), 3.55 (s, $CH_3$), 3.62, 3.68, 3.69, 3.77, 3.81 (each s, $OCH_3$), 4.30br (t, $CH_2CH_2CO_2Me$), 5.00, 5.12, 5.18 (each s, $CH_2CO_2Me$), and 9.96, 9.98, and 10.04 (each s, =CH), *m/e* 885 ($M^+$), 827, 825, 769, 711, and 696.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,12,18-*tetrakismethoxycarbonylmethyl*-20-*azaporphin* (20-*Azauroporphyrin III octamethyl ester*) (8b). Prepared as above (48%) from the corresponding 1,19-di-iodobiladiene-ac dihydrobromide (4b) (20 mg), the *product* had m.p. >230 °C (Found: C, 58.1; H, 6.4; H, 8.4. $C_{47}H_{53}N_5O_{16}$ requires C, 59.8; H, 5.65; N, 7.4%), $\lambda_{max.}$ 614 (log ε 4.27), 564 (3.87), 538 (4.27), 500 (3.87), and 391 nm (4.92), $\tilde{\nu}_{max.}$ 3 360, 2 910, 1 732, 1 436, 1 340, and 1 177 cm$^{-1}$, δ −2.76br (s, NH), 3.27 (8 H, m, $CH_2CH_2CO_2Me$), 3.64, 3.67, 3.69, 3.74, 3.78, 3.83 (each s, $OCH_3$), 4.28 (8 H, t, $CH_2CH_2CO_2Me$), 4.92 (4 H), 4.97 (4 H) (both s, $CH_2CO_2Me$), and 9.86 (2 H) and 9.89 (both s, =CH), *m/e* 943 ($M^+$), 884, 826, and 769.

*Corroles.*— 3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,18-*trismethoxycarbonylmethyl*-12-*methylcorrole* (9a). A solution of 1,19-di-iodobiladiene-ac dihydrobromide (4a) (50 mg) in *NN*-dimethylformamide (1 ml) was heated on a steam-bath for 10 min, whereupon water (30 ml) was added. After saturation of the solution with sodium chloride, the mixture was extracted repeatedly with ether, the organic phases were combined, washed with water, dried ($Na_2SO_4$), and evaporated. The remaining residue was chromatographed on silica gel eluting with methylene chloride–methanol (98 : 2) and the *product* was crystallized from methanol (yield 9 mg, 27%) m.p. 140 °C, $\lambda_{max.}$ 595 (log ε 4.32), 555 (4.32), 544 (4.32), 410 (4.98), and 396 nm (5.08), $\tilde{\nu}_{max.}$ 3 380, 2 900, 1 712, 1 439, and 1 171 cm$^{-1}$, δ 3.14br (8 H, t, $CH_2CH_2CO_2Me$), 3.35 (s, $CH_3$), 3.67, 3.68, 3.73, 3.75, 3.81 (each s, $OCH_3$), 4.11br (8 H, t, $CH_2CH_2CO_2Me$), 4.80, 4.92, 5.00 (each s, $CH_2CO_2Me$), and 8.95, 9.22, and 9.32 (each s, =CH), *m/e* 872 ($M^+$), 814, 799, 311, and 283.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,12,18-*tetrakismethoxycarbonylmethylcorrole* (9b). Prepared as above (18%) by cyclization of the corresponding 1,19-di-iodobiladiene-ac dihydrobromide (4b) (6 mg), the *product* had m.p. 77—80 °C (Found: C, 59.55; H, 6.1; N, 5.4. $C_{47}H_{54}N_4O_{16}$ requires C, 60.35; H, 6.25; N, 6.0%), $\lambda_{max.}$ 595 (log ε 4.20), 556 (4.20), 546 (4.20), 412 (4.88), and 399 nm (4.98), $\tilde{\nu}_{max.}$ 3 360, 2 910, and 1 715 cm$^{-1}$, δ 3.20 (8 H, m, $CH_2CH_2CO_2Me$), 3.67, 3.71, 3.74, 3.81 (each s, $OCH_3$), 4.17 (8 H, m, $CH_2CH_2CO_2Me$), 4.86 (4 H), 4.96 (4 H) (both s, $CH_2CO_2Me$), and 9.11 (1H) and 9.33 (2H) (both s, =CH), *m/e* 930 ($M^+$), 899, 872, and 857.

*Corrologens.*— 3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,18-*trismethoxycarbonylmethyl*-12-*methylcorrologen* (10a). Corrole (9a) (10 mg), dissolved in methylene chloride–methanol (10 ml; 5 : 1), was hydrogenated at room temperature and pressure after addition of $PtO_2$ (3 mg), until a colourless solution was obtained. The catalyst was filtered off under argon, and the solution evaporated *in vacuo* to give a pale yellow residue which was crystallized from n-hexane, under argon, yielding a light oxidisable *product* (8 mg, 81%) of m.p. 153—156 °C (Found: C, 61.4; H, 6.2; N, 6.7. $C_{45}H_{56}N_4O_{14}$ requires C, 61.65; H, 6.45; N, 6.4%), $\lambda_{max.}$ (methanol) 275 nm (log ε 3.92), $\tilde{\nu}_{max.}$ 3 330, 2 910, 1 725, 1 445, and 1 178 cm$^{-1}$, δ 2.01 (s, $CH_3$), 2.3—2.9 (16 H, m, $CH_2CH_2CO_2Me$), 3.39 (4 H), 3.44 (2 H) (both s, $CH_2CO_2Me$), 3.53, 3.54, 3.65, 3.67 (each s, $OCH_3$), 3.81 (2 H), 3.83 (4 H) (both s, $CH_2$), and 6.94br, 7.02br, 7.86br, and 8.68br (each s, NH), *m/e* 876 ($M^+$), 845, 821, and 803.

3,8,13,17-*Tetrakis*-(2-*methoxycarbonylethyl*)-2,7,12,18-*tetrakismethoxycarbonylmethylcorrologen* (10b). Prepared as above (80%) by hydrogenation of the corresponding corrole (9b) (10 mg), the product had m.p. 151 °C (Found: C, 61.2; H, 6.1; N, 6.05. $C_{47}H_{58}N_4O_{16}$ requires C, 60.35; H, 6.25; N, 6.0%), $\lambda_{max.}$ (methanol) 275 nm (log ε 3.93), $\tilde{\nu}_{max.}$ 3 320, 2 900, 1 732, and 1 440 cm$^{-1}$, δ 2.3—2.9 (16 H, m, $CH_2CH_2CO_2Me$), 3.38, 3.43, 3.51, 3.55 (each s, $CH_2CO_2$-Me), 3.50 3.67, 3.70, 3.72 (each s, $OCH_3$), 3.82, 3.84. 3.86 (each s, $CH_2$), and 6.56br, 6.84br, 8.97br, and 9.35br (s, NH), *m/e* 934 ($M^+$), 903, 875, 861, 847, and 467 ($M^{2+}$).

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