The Cyclisation of 1-Bromo-19-methyl- and 1,19-Dimethyl-1,19-dideoxybiladiene-ac Dihydrobromides

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The cyclisation of 1-bromo-1,19-dideoxy-19-methylbiladiene-ac dihydrobromides (I) bearing β-alkyl substituents to porphins in presence of a variety of one-electron oxidising agents has been shown to proceed at room temperature. Cyclisation of 1,19-dideoxy-1,19-dimethylbiladiene-ac dihydrobromides can be effected by cupric salts in boiling *NN*-dimethylformamide for 2 minutes. The alternative cyclisation of a variety of these salts in presence of nickel or cobalt salts yields the corresponding metal 1,19-disubstituted tetradehydrocorrins (VII) which are conveniently isolated as the perchlorates. Cyclisation of the nickel complex of a 1,19-dideoxy-1,19-dimethylbiladiene-ac in presence of ammonium ceric nitrate at room temperature also gave the corresponding nickel 1,19-dimethyltetradehydrocorrin salt (VIII).

In earlier papers,[1-3] we have described a stepwise synthesis of unsymmetrical porphins, involving the cyclisation of 1-bromo-1,19-dideoxy-19-methylbiladiene-ac dihydrobromides [*e.g.* (1)]. The cyclisation can be effected by heating a solution of the 1,19-dideoxybiladiene salt under reflux in *o*-dichlorobenzene, or, in certain cases, even by keeping a solution of the salt in dimethyl sulphoxide and pyridine at room temperature for 48 hours. Our work on the synthesis of naturally occurring porphins containing labile side-chains,[3] has prompted us to seek other mild and rapid methods for the cyclisation of the 1,19-dideoxybiladiene-ac salts, and we have investigated the action of a number of one-electron oxidising agents on solutions of the salts in dimethyl sulphoxide. Comparable yields of porphin obtained after reaction for 2 hours at room temperature with various oxidising agents are listed in Table 1.

The reactions were monitored spectroscopically and there were clear indications that the first step involved

[1] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 22; *Quart. Rev.*, 1966, **20**, 211.

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

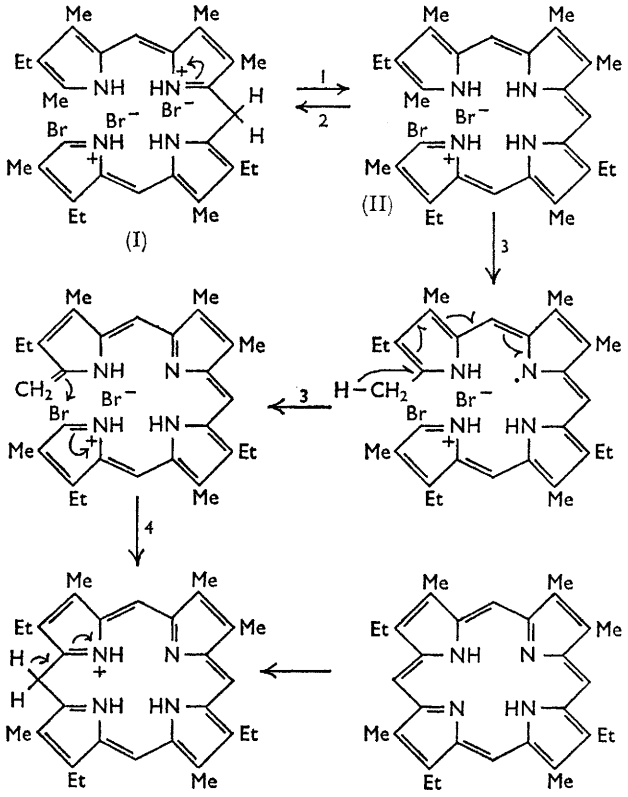
[3] P. Bamfield, R. Grigg, A. W. Johnson, and R. W. Kenyon, *Chem. Chem.*, 1967, 1029; *J. Chem. Soc.* (*C*), 1968, 1259.

TABLE 1

Yields of porphin obtained from oxidations of 1-bromo-1,19-dideoxy-2,12,17-triethyl-3,7,8,13,18-pentamethylbiladiene-ac dihydrobromide (I)

Reagent	Moles oxidant per mole biladiene salt	% Porphin
Benzoyl peroxide	2·9	37·5
Ferric chloride	4·4	25
Lead dioxide	3·0	43·5
Potassium ferricyanide ...	2·25	43
Ammonium ceric nitrate	1·3	46

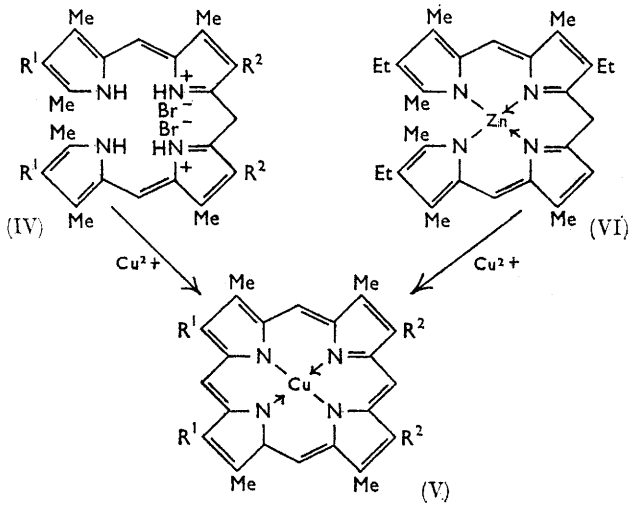
formation of the 1,19-dideoxybilatriene-abc monosalt (II).[4] Furthermore, in the oxidations with ammonium ceric nitrate it was shown that some of the salt (II) remained after 2 hours when only 1 mol. of the oxidant was used, but with 2 or 3 mol. of oxidant, the reaction was faster and all the 1,19-dideoxybilatriene-abc salt was consumed. The results of these experiments lead us to suggest the mechanism shown for the cyclisation reaction.



1, Base; 2, acid; 3, 1 mol. of oxidant; 4, $-Br^-$

The proposed mechanism requires 2 equivalents of the one-electron oxidising agent for complete reaction and this was confirmed by carrying out oxidations with potassium ferricyanide in degassed dimethyl sulphoxide at 10^{-5} mm. for 16 hours using (a) 1 equivalent and (b) 2·2 equivalents of oxidising agent; only in the latter experiment did the reaction go to completion. The first oxidation step, (II) ⟶ (III), will be assisted by the formation of the 1,19-dideoxybilatriene-abc free base, and accordingly, the influence of added pyridine on the cyclisation of (I) was investigated, using potassium ferricyanide (2·25 mol.) in dimethyl sulphoxide as oxidising agent at room temperature. In the absence of pyridine, 43% of porphin was obtained in a standard experiment; this figure was raised to 45% in presence of 1 mol. of pyridine and to 53% in presence of 2 mol. of pyridine. These modified procedures may well prove useful in the synthesis of porphins with labile substituents.

In continuing the general study of porphin syntheses which proceed under mild experimental conditions, we have re-examined the oxidative cyclisation of 1,19-dimethyl-1,19-dideoxybiladiene-ac dihydrobromides which entails loss of one of the methyl substituents, the other providing the porphin meso-carbon. In an earlier paper[5] we have reported that the reaction of the biladiene salt (IV; $R^1 = Me$, $R^2 = Et$) with cupric acetate in methanol gave the corresponding copper porphin (V; $R^1 = Me$, $R^2 = Et$) in 17% yield. Later work[6] in another laboratory showed that, although β-acetyl groups in the terminal rings of the 1,19-dideoxybiladiene-ac salt survived the mild cyclisation conditions, the yield of porphin was reduced to prohibitive levels.



We have now investigated this porphin synthesis in more detail and find that with an excess of cupric salt, the cyclisation of 1,19-dideoxybiladiene-ac salts bearing alkyl substituents can give high yields of porphin after only 2 minutes in boiling *NN*-dimethylformamide. The effects of the nature and concentration of cupric salt are shown in Table 2, the yields of porphin being determined spectrophotometrically.

The ready removal of metal from a copper porphin and the ease of preparation of the intermediates recommend this synthesis of porphins in selected cases. In the present work we have prepared a range of copper

[4] D. Dolphin, A. W. Johnson, J. Leng, and P. van den Broek, *J. Chem. Soc.* (*C*), 1966, 880.
[5] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1961, 2418.
[6] G. M. Badger, R. L. N. Harris, and R. A. Jones, *Austral. J. Chem.*, 1964, **17**, 1013.

TABLE 2

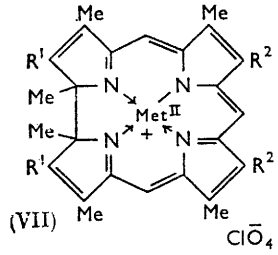
The cyclisation of 1,19-dideoxy-2,18-di-(2-ethoxycarbonylethyl)-8,12-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide by cupric salts in boiling *NN*-dimethylformamide for 2 minutes

Copper(II) salt	Mol.	% Yield of porphin
Chloride,$2H_2O$	1	11·4
,,	2	15·4
,,	3	19·8
,,	4	24·4
,,	5	29·9
,,	10	66·8
,,	20	66·9
,,	30	62·5
Nitrate,$3H_2O$	10	39·1
,,	20	37·5
Sulphate,$5H_2O$	20	49·2
Acetate,H_2O	20	30·3

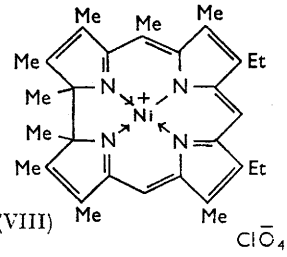
porphins by this method including copper aetioporphyrin II (V; $R^1 = R^2 = Et$),[7] copper mesoporphyrin III diethyl ester (V; $R^1 = CH_2{\cdot}CH_2{\cdot}CO_2Et$, $R^2 = Et$), and copper coproporphyrin II tetraethyl ester (V; $R^1 = R^2 = CH_2{\cdot}CH_2{\cdot}CO_2Et$).

In one experiment an attempt was made to effect oxidative cyclisation of a zinc 1,19-dideoxy-1,19-dimethylbiladiene-ac complex (VI) with cupric chloride. The product was the corresponding copper porphin (V; $R^1 = R^2 = Et$) and since no metal exchange was observed with authentic zinc porphin under the reaction conditions it appears that metal exchange occurred prior to cyclisation.

The 1,19-dideoxy-1,19-dimethylbiladiene-ac dihydrobromides [*e.g.* (IV)] can also be cyclised in presence of base and nickel(II) or cobalt(II) salts with aerial oxidation to give the corresponding metal(II) 1,19-dimethyltetradehydrocorrin salts (VII),[8] usually in high yield. The 1,19-dideoxy-1,19-dimethylbiladiene-ac salts used for the above porphin preparations have been cyclised to the corresponding nickel(II) and cobalt(II) tetradehydrocorrins, which were isolated as the crystalline perchlorates [VII; R^1, R^2 = Et, Et (Ni and Co); $CH_2{\cdot}CH_2{\cdot}CO_2Me$, Et (Ni); $CH_2{\cdot}CH_2{\cdot}CO_2Et$, Et (Ni and Co); $CH_2{\cdot}CH_2{\cdot}CN$, Et (Ni); Me, $CH_2{\cdot}CH_2{\cdot}CO_2Et$ (Ni and Co); Et, $CH_2{\cdot}CH_2{\cdot}CO_2Et$ (Ni); $CH_2{\cdot}CH_2{\cdot}CO_2Et$, $CH_2{\cdot}CH_2{\cdot}CO_2Et$ (Ni and Co)]. In one case, a solution



(VII)



(VIII)

of the nickel complex of 1,19-dideoxy-8,12-diethyl-1,2,3,5,7,13,15,17,18,19-decamethylbiladiene-ac [8] in dimethyl sulphoxide was treated with ammonium ceric nitrate for 16 hours at room temperature, and gave a 39% yield of the corresponding nickel 1,19-dimethyltetradehydrocorrin perchlorate (VIII), suggesting that this type of cyclisation may also proceed by a free radical mechanism.

[7] H. Fischer, P. Halbig, and B. Walach, *Annalen*, 1927, **452**, 8.

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

EXPERIMENTAL

Except where otherwise stated, ultraviolet and visible spectra were determined on chloroform solutions, infrared spectra were determined on KBr discs and n.m.r. spectra on deuteriochloroform solutions using a Perkin-Elmer RS 10 instrument operating at 60 Mc./sec.

Pyrroles

3-(2-Ethoxycarbonylethyl)-5-formyl-2,4-dimethylpyrrole.—Phosphorus oxychloride (8·5 g., 1·1 mol.) was added dropwise with stirring to dry *NN*-dimethylformamide (15 ml.), the temperature being kept below 10° by cooling in ice–water. To this solution was added a solution of 2,4-dimethyl-3-(2-ethoxycarbonylethyl)pyrrole [9] (9·7 g., 1 mol.) in *NN*-dimethylformamide (15 ml.) in 3 equal portions during 5 min. After heating on a steam-bath for 30 min., the mixture was cooled, and poured into water (800 ml.). Sodium acetate (70 g.) was added, the solution heated to 80—85°, and then treated with 10% aqueous sodium hydroxide solution until the solution became yellow. The *product* crystallised in long needles on cooling (1 hr.). It was collected, washed, and dried *in vacuo* (9·5 g., 85·2%), m.p. 95—96°, unchanged after recrystallisation from aqueous ethanol (Found: C, 64·35; H, 7·75; N, 6·15. $C_{12}H_{17}NO_3$ requires C, 64·55; H, 7·7; N, 6·25%), $\nu_{max.}$ ($CHCl_3$) 1620 (CHO) and 1700 (ester carbonyl) $cm.^{-1}$. The n.m.r. spectrum contained signals at τ 0·55 (CHO), 5·85 (q, CH_2 of Et), 7·4 (m, ester CH_2), 7·7 (s, *C*-Me), and 8·75 (t, Me of Et).

t-Butyl 3-(2-Cyanoethyl)-2,4-dimethylpyrrole-5-carboxylate.—Sodium nitrite (22·2 g., 1·1 mol.) in water (75 ml.) was added with stirring to freshly distilled t-butyl acetoacetate (47·4 g., 1 mol.) in glacial acetic acid (120 ml.) at 5—10°. The cooled mixture was stirred for 4 hr. and added, along with zinc dust (66 g.) in small portions, to a well stirred solution of 4,4-diacetylbutyronitrile (45·9 g., 1 mol.; see below) in glacial acetic acid (150 ml.) at 75—80° during 45 min. Stirring was continued at 80—85° for 1 hr. More acetic acid (200 ml.) was added to effect solution, which was filtered through glass wool into cold water (4 l.). The crystalline solid was collected, washed, and crystallised from methanol (250 ml.) to give the *product* as colourless needles (29·1 g., 39%), m.p. 147—148° (Found: C, 67·5; H, 8·15; N, 11·25. $C_{14}H_{20}N_2O_2$ requires C, 67·7; H, 8·1; N, 11·3%), $\lambda_{max.}$ 278 mμ (ε 17,680), $\nu_{max.}$ ($CHCl_3$) 1677 (ester CO) and 2252 (CN) $cm.^{-1}$. The n.m.r. spectrum contained signals at τ 1·28 (broad s, imino proton), 7·45 (q, CH_2), 7·7 (s, 2 *C*-Me), and 8·49 (s, Bu^t).

1,19-Dideoxybiladiene-ac Dihydrobromides

1,19-Dideoxy-2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethylbiladiene-ac Dihydrobromide.—Ammonium hydroxide (3 ml.; *d* 0·88) was added to a mixture of 3-ethyl-5-formyl-

[9] G. M. Badger, R. L. N. Harris, and R. A. Jones, *Austral. J. Chem.*, 1964, **17**, 1002.

2,4-dimethylpyrrole [10] (6·4 g., 2 mol.) and 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (6·4 g., 1 mol.) in methanol (150 ml.), the resulting solution treated with aqueous hydrobromic acid (20 ml.; 48%) and kept at room temperature for 2 hr. The crystalline brick-red product was collected (11·5 g., 87·5%), washed with methanol containing hydrobromic acid and then dry ether. A small amount was crystallised from chloroform–light petroleum in orange-red prisms, m.p. ⩽300°, and was identical with the product prepared earlier [10] by a modified procedure. The zinc complex [10] formed orange-green plates, m.p. 258—260° (not sharp) (Found: C, 70·7; H, 7·2; N, 9·9. Calc. for $C_{33}H_{42}N_4Zn$: C, 70·85; H, 7·5; N, 10·0%). The n.m.r. spectrum contained signals at τ 3·25 (s, C-5 and C-15 meso-protons), 6·18 (s, C-10 CH_2), 7·9 (q, CH_2 of Et groups), 7·82, 8·0, 8·4 (all s, Me), and 9·08 (t, Me of Et groups).

1,19-*Dideoxy*-8,12-*diethyl*-2,18-*di*-(2-*methoxycarbonylethyl*)-1,3,7,13,17,19-*hexamethylbiladiene-ac Dihydrobromide*.—Prepared as above from 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyldipyrromethane [10] (286 mg., 1 mol.) and t-butyl 3-(2-methoxycarbonylethyl)-2,4-dimethylpyrrole-5-carboxylate [11] (562 mg., 2 mol.) in methanol (5 ml.) and aqueous hydrobromic acid (1 ml.; 48%) except that the reaction mixture was heated for 3 min. on the steam-bath. The product (651 mg., 87%) was separated, washed, and crystallised from chloroform–light petroleum when it formed red crystals, m.p. ⩽300° (Found: C, 56·9; H, 6·35; N, 7·15. $C_{37}H_{50}Br_2N_4O_4$ requires C, 57·2; H, 6·4; N, 7·2%), $\lambda_{max.}$ 372, 457, and 529 mμ (ε 13,900, 45,800, and 149,200), λ_{infl} 433 and 498 mμ (ε 14,650 and 37,800), $\nu_{max.}$ 1740 (ester carbonyl). The n.m.r. spectrum (CF_3CO_2H) contained signals at τ −1·7 (broad s, imino), 2·3 (s, C-5 and C-15 methines), 5·3 (s, C-10 CH_2), 6·0 (s, ester Me), 7·1 (m, ester CH_2 and CH_2 of Et groups), 7·2 and 7·5 (both s, *C*-Me), and 8·8 (t, Me of Et groups).

1,19-*Dideoxy*-2,18-*di*-(2-*ethoxycarbonylethyl*)-8,12-*diethyl*-1,3,7,13,17,19-*hexamethylbiladiene-ac Dihydrobromide*.—Prepared as above from 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (3·2 g., 1 mol.) and 3-(2-ethoxycarbonylethyl)-5-formyl-2,4-dimethylpyrrole (above; 4·42 g., 2 mol.) in ethanol (15 ml.) and aqueous hydrobromic acid (7 ml.; 48%). The crystalline product (7·2 g., 90%) was collected, washed, and was recrystallised from chloroform–light petroleum when it formed red needles, m.p. ⩽300° (Found: C, 57·95; H, 6·9; N, 6·9. $C_{39}H_{54}Br_2N_4O_4$ requires C, 58·35; H, 6·8; N, 7·0%), $\lambda_{max.}$ 375, 436, 458, and 532 mμ (ε 16,200, 11,400, 25,700, and 224,500), $\nu_{max.}$ 1615, 1734, 2825, and 2979 cm.$^{-1}$. The n.m.r. spectrum contained signals at τ 2·8 (s, C-5 and C-15 methines), 4·8 (br s, C-10 CH_2), 5·85 (q, ester Et CH_2), 7·3 (s, *C*-Me), 7·65—7·75 (m, Et ester Me and ester CH_2), 8·75 and 9·35 (both t, Me of *C*-Et groups).

1,19-*Dideoxy*-2,18-*di*-(2-*cyanoethyl*)-8,12-*diethyl*-1,3,7,13,17,19-*hexamethylbiladiene-ac Dihydrobromide*.—Prepared as above from 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyldipyrromethane [10] (1·43 g., 1 mol.) and t-butyl 3-(2-cyanoethyl)-2,4-dimethylpyrrole-5-carboxylate (2·48 g., 2 mol.; above) in methanol (30 ml.) with aqueous hydrobromic acid (5 ml.; 48%) by heating under reflux for 10 min. The crystalline *product* (3·1 g., 88%) was separated, washed with methanol (20 ml.) containing hydrobromic acid (1 ml.) and then ether. It formed brick-red prisms, m.p. ⩽300°, after recrystallisation from chloroform (Found: C, 59·35; H, 6·4; N, 11·7. $C_{35}H_{44}Br_2N_6$ requires C, 59·5; H, 6·25; N, 11·45%), $\lambda_{max.}$ 374, 454, and 529 mμ (ε 14,700, 35,600, and 158,800), λ_{infl} 435 and 500 mμ (ε 14,100 and 38,400), $\nu_{max.}$ 2249 (C≡N) cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$–CF_3CO_2H) contained signals at τ −1·95 (br s, iminium), 2·5 (s, C-5 and C-15 meso-protons), 5·42 (s, C-10 CH_2), 7·2—7·6 (complex m, side-chain CH_2 and Me), and 8·82 (t, Me of Et groups).

1,19-*Dideoxy*-8,12-*di*-(2-*ethoxycarbonylethyl*)-1,2,3,7,13,17,18,19-*octamethylbiladiene-ac Dihydrobromide*.—Prepared as above from 2-formyl-3,4,5-trimethylpyrrole (680 mg., 2 mol.) and 3,3′-di-(2-ethoxycarbonylethyl)-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid [11] (1·51 g., 1 mol.) in ethanol (7 ml.) and aqueous hydrobromic acid (1 ml.; 48%), except that the reaction mixture was heated for 10 min. on the steam-bath. The product (1·38 g., 71·5%) was collected, washed and crystallised from chloroform–light petroleum when it formed red-brown crystals, m.p. ⩽300° (Found: C, 57·5; H, 6·25; N, 7·4. $C_{37}H_{50}Br_2N_4O_4$ requires C, 57·2; H, 6·4; N, 7·2%), $\lambda_{max.}$ 369, 434, 456, 490, and 524 mμ (ε 14,600, 20,100, 64,000, 62,400, and 111,000), $\nu_{max.}$ 1737 cm.$^{-1}$ (ester carbonyl). The n.m.r. spectrum (CF_3CO_2H) showed signals at τ −1·8 (s, imino), 2·4 (s, C-5 and C-15 methines), 5·28 (s, C-10 CH_2), 5·55 (q, CH_2 of Et ester groups), 7·2 (m, CH_2 of propionic ester side-chains), 7·22, 7·58, and 7·88 (all s, β-Me substituents), and 8·6 (t, Me of ester Et).

1,19-*Dideoxy*-8,12-*di*-(2-*ethoxycarbonylethyl*)-2,18-*diethyl*-1,3,7,13,17,19-*hexamethylbiladiene-ac Dihydrobromide*.—Prepared as above from 3-ethyl-5-formyl-2,4-dimethylpyrrole [10] (1·51 g., 2 mol.) and 3,3′-di-(2-ethoxycarbonylethyl)-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (2·31 g., 1 mol.) in ethanol (15 ml.) containing hydrobromic acid (5 ml.; 48%) with heating on the steam-bath for 30 sec. The *product* (2·38 g., 59·3%) was separated, washed and crystallised from chloroform–light petroleum when it formed orange-red micro-needles, m.p. ⩽310° (Found: C, 55·2; H, 6·45; N, 6·4. $C_{39}H_{54}Br_2N_4O_4,\frac{1}{2}CHCl_3$ requires C, 55·0; H, 6·4; N, 6·5%), $\lambda_{max.}$ 373, 458, and 526 mμ (ε 13,300, 28,200, and 185,000), $\nu_{max.}$ 1736 cm.$^{-1}$ (ester CO). The n.m.r. spectrum contained signals at τ 2·9 (s, C-5 and C-15 methines), 4·78 (s, C-10 CH_2), 6·08 (q, CH_2 of Et), 7·3—7·75 (m, superimposed protons of *C*-Me groups and CH_2 of ester side-chains), and 8·9 (t, Me of Et).

1,19-*Dideoxy*-2,8,12,18-*tetra*-(2-*ethoxycarbonylethyl*)-1,3,7,13,17,19-*hexamethylbiladiene-ac Dihydrobromide*.—Prepared in the normal manner from a suspension of 3-(2-ethoxycarbonylethyl)-5-formyl-2,4-dimethylpyrrole (2·23 g.; above; 2 mol.) and 3,3′-di-(2-ethoxycarbonylethyl)-4,4′-dimethylpyrrole-5,5′-dicarboxylic acid (2·31 g., 1 mol.) in ethanol (10 ml.) and hydrobromic acid (2 ml.; 48%) by heating on the steam-bath for 5 min. The *product* was separated, washed, and crystallised from chloroform–light petroleum (b.p. 80—100°) when it formed red prisms (2·4 g., 48%), m.p. ⩽300° (Found: C, 54·45; H, 6·05; N, 5·7. $C_{45}H_{62}Br_2N_4O_8,\frac{1}{2}CHCl_3$ requires C, 54·25; H, 6·25; N, 5·6%), $\lambda_{max.}$ 373, 454, and 525 mμ (ε 14,300, 41,300, and 195,500), $\nu_{max.}$ 1737 cm.$^{-1}$ (ester CO). The n.m.r. spectrum (CF_3CO_2H) showed signals at τ 2·5 (s, methines at C-5 and C-15), 5·3 (br s, CH_2 at C-10), 5·65 (q, CH_2 of Et), 7·3—7·6 (m, *C*-Me and CH_2 of ester side-chains), and 8·68 (t, Me of Et).

[10] E. Bullock, R. Grigg, A. W. Johnson, and J. W. F. Wasley, *J. Chem. Soc.*, 1963, 2326.

[11] A. W. Johnson, I. T. Kay, E. Markham, R. Price, and K. B. Shaw, *J. Chem. Soc.*, 1959, 3416.

Porphins

Copper Aetioporphyrin II.—(*i*) A solution of cupric chloride dihydrate (6·2 g., 20 mol.) in *NN*-dimethylformamide (62 ml.) was added to 1,19-dideoxy-2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (1·2 g., 1 mol.) and the mixture heated under gentle reflux for 2 min. After cooling, the crystalline *product* was collected on diatomite, washed with water and methanol (20 ml.), and extracted with chloroform (400 ml.; Soxhlet). The extract was reduced in volume (to *ca.* 10 ml.) and hot methanol was added. Copper aetioporphyrin II [7] crystallised in shining red plates with copper bronze lustre (0·598 g., 60·7%), m.p. $\lt 300°$, $\lambda_{max.}$ 328, 398·5, 525, and 562 mμ ($\varepsilon_{max.}$ 16,500, 322,000, 12,300, and 23,800).

After removal of the copper by acid treatment the resulting porphin was crystallised, $\lambda_{max.}$ 400, 499, 534, 567, and 621 mμ (ε 199,400, 15,960, 11,700, 7640, and 5620). The n.m.r. spectrum (CF_3CO_2H) showed signals at τ −1 (s, 4 *meso*-protons), 5·75 (q, 8 CH_2 protons of Et groups), 6·25 (s, 12 protons of β-Me substituents), 8·22 (t, 12 protons of Me of Et groups), and 14·9 (s, 2 imino-protons) (*cf.* ref. 12).

(*ii*) 1,19-Dideoxy-2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethylbiladiene-ac zinc complex (160 mg., 1 mol.) was added to a solution of cupric chloride dihydrate (1·25 g., 25·6 mol.) in *NN*-dimethylformamide (25 ml.) and the mixture heated on a steam-bath for 10 min. during which time the product partially crystallised. The mixture was then cooled and the crystalline product (48 mg., 31%) separated. The product was identical with that obtained above and the mass spectrum showed an intense molecular ion at *m/e* 539 and 541 (Cu isotopes); $C_{32}H_{36}N_4Cu$ requires *m/e* 539 and 541.

In another experiment using 5 mol. of cupric chloride dihydrate the copper porphin was obtained in 30% yield.

Copper Mesoporphyrin III Diethyl Ester.—(*i*) A mixture of 1,19-dideoxy-8,12-di-(2-ethoxycarbonylethyl)-2,18-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (189 mg.) and cupric acetate (200 mg.) in distilled *NN*-dimethylformamide (4 ml.) was heated under reflux for 2 min. After cooling, the mixture was diluted with water (150 ml.) and extracted with chloroform (3 × 20 ml.). The chloroform extract was washed with a liberal quantity of water, dilute ammonium hydroxide (2N), then water, and dried (Na_2SO_4). It was concentrated and chromatographed on alumina (2 × 20 cm.; Spence H) using chloroform as eluent. The red band was eluted, evaporated, and the *product* crystallised from chloroform–light petroleum (b.p. 80—100°) as shining copper-bronze crystals (78 mg., 47%), m.p. 276—277° [Found: C, 66·3; H, 6·2; N, 7·9%; *M* (mass spectrum), 683. $C_{38}H_{44}CuN_4O_4$ requires C, 66·5; H, 6·6; N, 8·1%; *M*, 683], $\lambda_{max.}$ 328, 398, 526, and 563 mμ (ε 16,100, 349,000, 12,300, and 23,600), λ_{infl} 380 mμ (ε 43,300), $\nu_{max.}$ 1735 cm.$^{-1}$ (ester CO).

(*ii*) A solution of cupric chloride dihydrate (220 mg., 10 mol.) in distilled *NN*-dimethylformamide (10 ml.) was added to 1,19-dideoxy-2,18-di-(2-ethoxycarbonylethyl)-8,12-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (100 mg., 1 mol.), and the mixture heated under reflux for 2 min. After cooling, chloroform (20 ml.) was added to the mixture which was then filtered through a column (2 × 10 cm.) of dry alumina and washed with chloroform till the washings were colourless. The combined chloroform solutions were washed with water, dilute ammonium hydroxide, water, and then dried (Na_2SO_4). After concentration to *ca.* 5 ml., the chloroform solution was chromatographed on an alumina column (2 × 25 cm.) using more chloroform as eluent. The red band was collected and evaporation of the filtered solution yielded the product (47 mg., 55%) as bright red microneedles, m.p. and mixed m.p. with the previous sample 277—278°.

In another experiment, the same reagents were heated under reflux for 2 min. in *o*-dichlorobenzene. Isolation of the product in the same way gave the porphin copper complex (40%).

A series of small scale experiments were carried out (Table 2) to establish the optimum conditions for the above experiment. A solution of the cupric salt (1—30 mol.) in *NN*-dimethylformamide (5 ml.) was added to the biladiene salt (2 mg.) and the mixture heated in an oil-bath at 185° for 2 min. The resulting solution was cooled, chloroform (3 ml.) was added and the product adsorbed on an alumina column and then eluted with more chloroform until the washings were colourless. The chloroform eluate was diluted (to 100 ml.) and the concentration of porphin estimated by measurement of the intensity of the Soret band at 400 mμ.

Copper 3,7-Di-(2-cyanoethyl)-13,17-diethyl-2,8,12,18-tetramethylporphin.—A solution of cupric chloride dihydrate (2·5 g., 20 mol.) in *NN*-dimethylformamide (50 ml.) was added to 2,18-di-(2-cyanoethyl)-1,19-dideoxy-8,12-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (500 mg., 1 mol.), and the mixture heated under reflux for 2 min. After cooling, the crystalline product was separated, washed with dilute ammonium hydroxide, then methanol (20 ml.), and then extracted into chloroform (500 ml.; Soxhlet, 3 days). After concentration of the extract, the *product* crystallised as red shining needles with a copper bronze lustre (221 mg., 53·5%), m.p. $\lt 300°$ with darkening at *ca.* 280° (Found: N, 13·9. $C_{34}H_{34}CuN_6$ requires N, 14·25%), $\lambda_{max.}$ 401, 528, and 564 mμ (ε 154,900, 6780, and 11,180 respectively), $\nu_{max.}$ 2249 cm.$^{-1}$ (CN).

Copper Coproporphyrin II Tetraethyl Ester.—A solution of cupric chloride dihydrate (200 mg., 10·9 mol.) in *NN*-dimethylformamide (10 ml.) was added to 1,19-dideoxy-2,8,12,18-tetra-(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (100 mg., 1 mol.) and the mixture heated under reflux for 2 min. On cooling, the product was extracted into chloroform (3 × 40 ml.), and the extract washed with water and dried (Na_2SO_4). The residue left on removal of the solvent was chromatographed on alumina using chloroform for elution. The porphin fraction was collected, evaporated to dryness, and crystallised from chloroform–light petroleum when it formed red silky needles (33 mg. 39%), m.p. 278—279° (Found: C, 63·35; H, 6·5; N, 6·55. $C_{44}H_{52}CuN_4O_8$ requires C, 63·7; H, 6·3; N, 6·75%), $\lambda_{max.}$ 327, 399, 528, and 564 mμ (ε 17,000, 356,000, 12,600, and 23,400), $\nu_{max.}$ 1735 cm.$^{-1}$ (ester carbonyl).

Cyclisations of 1-Bromo-1,19-dideoxy-3,8,18-triethyl-2,7,12,13,17,19-hexamethylbiladiene-ac dihydrobromide (I) *to 2,12,17-Triethyl-3,7,8,13,18-pentamethylporphin with One-electron Oxidising Agents.*—The following is a typical experiment and the yields obtained by variation of the amounts of reagents are summarised in Table 1.

The biladiene salt [1] (25 mg.) was dissolved in dimethyl sulphoxide (125 ml.) and kept for 10 min. when conversion into the corresponding bilatriene salt was complete. The

[12] R. J. Abraham, A. H. Jackson, and G. *N.* Kenner, *J. Chem. Soc.*, 1961, 3468.

oxidising agent (25 mg.) was then added and the solution kept at 25° for 2 hr. It was then poured into water (500 ml.) and kept for 18 hr. before being filtered through diatomite. After drying, the porphin was extracted from the diatomite with chloroform, the solution concentrated, and the chloroform displaced by light petroleum (b.p. 60—80°) at the boil until crystallisation commenced. The solution was then cooled to 0° and the product, 2,12,17-triethyl-3,7,8,13,18-pentamethylporphin,[1] had $\lambda_{max.}$ 269, 399·5, 499, 535, 567·5, 594, and 622 mμ (ε 7770, 144,000, 13,100, 9420, 6120, 1133, and 4470) with an inflection at 332 mμ (ε 16,300). The n.m.r. spectrum (CF_3CO_2H) showed signals at τ −0·95 (s, meso-protons), 5·65 (q, CH_2 of Et), 6·22, 6·25 (both s, β-Me), 8·17 (t, Me of Et), and 14·8 (br s, iminium).

1,19-*Dimethyltetradehydrocorrin Salts*

2,8,12,18-*Tetraethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin Metal*(II) *Perchlorates*.—(i) *Cobalt derivative*. To a suspension of 1,19-dideoxy-2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (above; 10 g.) in ethanol (400 ml.) was added an aqueous solution of cobaltous acetate (10 g. in 50 ml.) and the solution stirred with aeration at room temperature for 6 hr. The solution was filtered through diatomite and treated with an aqueous solution of sodium perchlorate (20 g. in 50 ml.). The product that separated on diluting with water (1 l.) was collected after 1 hr., washed with water, dry ether and light petroleum. It crystallised from methylene chloride–n-hexane in black needles (8·1 g., 82·2%), m.p. ⩽300° (Found: C, 61·25; H, 6·2; Co, 8·85; N, 8·5. $C_{33}H_{41}ClCoN_4O_4$ requires C, 60·9; H, 6·3; Co, 9·05; N, 8·6%), $\lambda_{max.}$ 282, 342, 498, and 566 mμ (ε 27,000, 22,200, 13,000, and 7740), λ_{infl} 537 mμ (ε 8140).

(ii) *Nickel derivative*. A mixture of the biladiene-ac dihydrobromide (1·147 g.), nickel acetate (1·2 g.), and sodium acetate (1·2 g.) in ethanol (25 ml.) was heated on a steam-bath with aeration for 35 min. Aqueous sodium perchlorate (5 g. in 4 ml.) was added dropwise to the resulting pale red solution with stirring, followed by hot water (30 ml.). On cooling, the *product* separated in shining chocolate-brown prisms, which were collected, washed with water, and dried (1·065 g., 93%). Crystallisation from acetone–ethyl acetate gave chocolate brown silky needles (0·974 g., 83·5%) (Found: C, 61·1; H, 6·2; N, 8·8; Ni, 8·9. $C_{33}H_{41}ClN_4NiO_4$ requires C, 60·9; H, 6·3; N, 8·6; Ni, 9·0%), $\lambda_{max.}$ (EtOH) 276, 353, 454, and 559 mμ (ε 34,100, 32,300, 4770, and 13,940), λ_{infl} 401 mμ (ε 6280). The n.m.r. spectrum (CF_3CO_2H) showed signals at τ 2·4 (s, C-5 and C-15 meso-protons), 2·6 (s, C-10 meso-proton), 7·0 (m, 2 superimposed quartets of CH_2 protons of Et groups), 7·35 and 7·4 (both s, protons of β-Me substituents), 8·55 (m, 2 superimposed triplets of Me of Et groups), and 9·38 (s, C-1 and C-19 Me).

8,12-*Diethyl*-1,2,3,5,7,13,15,17,18,19-*decamethyltetradehydrocorrin Nickel*(II) *Perchlorate* (*cf.* ref. 8).—8,12-Diethyl-1,2,3,5,7,13,15,17,18,19-decamethyldideoxybiladiene-ac nickel complex [8] (100 mg.) dissolved in dimethyl sulphoxide (100 ml.) was treated with ammonium ceric nitrate (100 mg.), kept at room temperature for 16 hr., and then evaporated. The residue was chromatographed on alumina with chloroform elution until the eluate was almost colourless, and subsequent elution with chloroform–methanol (9 : 1). The blue-purple fraction was evaporated, the residue dissolved in methanol (5 ml.) and treated with a solution of sodium perchlorate (200 mg.) in water (80 ml.). The product was collected, dried, and then crystallised from acetone–light petroleum when it formed bronze needles (45·8 mg., 38·8%).

2,18-*Di*-(2-*ethoxycarbonylethyl*)-8,12-*diethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin Metal*(II) *Perchlorates*.—(i) *Nickel derivative*. A mixture of 1,19-dideoxy-2,18-di-(2-ethoxycarbonylethyl)-8,12-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (200 mg.), nickel acetate (200 mg.), and sodium acetate (200 mg.) in ethanol (10 ml.) was heated on the steam-bath for 1 min. and then aerated at room temperature for 10 min. An aqueous solution of sodium perchlorate (1 g. in 5 ml.) was added. The solution on dilution with water (to *ca.* 70 ml.) yielded the *product*. It was collected, washed with water, dissolved in chloroform, and dried ($MgSO_4$). After concentration of the chloroform solution, crystallisation was induced by gradual addition of light petroleum (b.p. 40—60°). The product so obtained formed steel blue-black microneedles, (136 mg., 71·6%), m.p. 231—232° (Found: C, 59·05; H, 5·7. $C_{39}H_{49}ClN_4NiO_8$ requires C, 58·85; H, 6·15%), $\lambda_{max.}$ (EtOH) 276, 353, 449, and 561 mμ ($\varepsilon_{max.}$ 31,900, 31,600, 5370, and 13,600), $\nu_{max.}$ 1735 cm.$^{-1}$ (ester carbonyl). The n.m.r. spectrum contained signals at τ 2·2(s, C-10 meso-proton), 2·4 (s, C-5 and C-15 meso-protons), 5·75 (q, CH_2 of Et), 7·0 (m, CH_2 of side-chain esters), 7·4 (12 protons of β-Me), 8·65 (t, Me protons of ethyl groups), and 9·3 (s, protons of C-1 and C-19 Me).

The corresponding dimethyl ester was formed (84%) by a similar cyclisation of 1,19-dideoxy-8,12-diethyl-2,18-di-(2-methoxycarbonylethyl)-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide. It formed scarlet microneedles, m.p. 237—238° [from chloroform–light petroleum (b.p. 80—100°)] (Found: C, 57·95; H, 5·75; N, 7·25. $C_{37}H_{45}ClN_4NiO_8$ requires C, 57·85; H, 5·85; N, 7·3%), $\lambda_{max.}$ (EtOH) 276, 354, 457, and 563 mμ (ε 30,400, 29,700, 4600, and 13,400), $\nu_{max.}$ 1734 cm.$^{-1}$ (ester carbonyl). The n.m.r. spectrum contained signals at τ 2·4 (s, C-5 and C-15 meso-protons), 2·62 (s, C-10 meso-proton), 6·18 (s, Me ester), 6·9 (m, CH_2 of Et groups and ester side-chains), 7·35 (s, β-Me), 8·55 (t, Me of Et), and 9·3 (s, protons of C-1 and C-19 Me).

(ii) *Cobalt derivative*. Prepared (65%) by a similar cyclisation of 1,19-dideoxy-2,18-di-(2-ethoxycarbonylethyl)-8,12-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide in presence of cobaltous acetate. The product was chromatographed on alumina using chloroform–ethanol (19 : 1). The purple-red fraction was collected and evaporated to dryness. The residual product was crystallised from dichloromethane–n-hexane when it formed long shining steel-grey needles (259 mg., 65·2%), m.p. 208—209° (Found: C, 58·85; H, 5·95; N, 7·0. $C_{39}H_{49}ClCoN_4O_8$ requires C, 58·85; H, 6·15; N, 6·5%), $\lambda_{max.}$ 282, 350, and 499 mμ (ε 30,500, 23,100, and 13,500), λ_{infl} 546 and 568 mμ (ε 8020 and 7480), $\nu_{max.}$ 1737 cm.$^{-1}$ (ester carbonyl).

2,18-*Di*-(2-*cyanoethyl*)-8,12-*diethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin Nickel*(II) *Perchlorate*.—Prepared (60%) in the normal manner from 1,19-dideoxy-2,18-di-(2-cyanoethyl)-8,12-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide, and nickel acetate. The product was purified by chromatography on alumina using ethanol for elution. The violet fraction was collected, evaporated to dryness and the product crystallised from chloroform–light petroleum as black rods (Found: C, 60·55; H, 5·75. $C_{35}H_{39}ClN_6NiO_4$ requires C, 60·0; H, 5·55%), $\lambda_{max.}$ (EtOH) 277, 354, 456, and 562 mμ (ε 29,200, 27,800, 5440, and 12,240), λ_{infl} 375 mμ (ε 7540), $\nu_{max.}$ 2249 cm.$^{-1}$

(C≡N). The n.m.r. spectrum (CF_3CO_2H) showed signals at τ 2·0 (s, C-10 meso-proton), 2·2 (s, C-5 and C-15 meso-protons), 7·0 (m, CH_2 of Et δ groups and CH_2 of side-chains), 7·25 (s, protons of β-Me), 8·45 (t, Me of Et ester), and 9·15 (br s; C-1 and C-19 angular Me).

8,12-*Di*-(2-*ethoxycarbonylethyl*)-1,2,3,7,13,17,18,19-*octamethyltetradehydrocorrin Metal*(II) *Perchlorates*.—(i) *Nickel derivative*. A solution of 1,19-dideoxy-8,12-di-(2-ethoxycarbonylethyl)-1,2,3,7,13,17,18,19-octamethylbiladiene-ac dihydrobromide (above; 150 mg.), sodium acetate (150 mg.), and nickel acetate (150 mg.) in ethanol (3 ml.) was kept at room temperature for 30 min. The *product* which separated on addition of an aqueous solution of sodium perchlorate (50 ml. of 2%) was filtered off, washed with water, and crystallised from ethanol–light petroleum (b.p. 80—100°) when it formed steel-blue needles (140 mg., 94·2%), m.p. 243—244° (Found: C, 57·75; H, 5·4; N, 7·3. $C_{37}H_{45}ClN_4NiO_8$ requires C, 57·85; H, 5·85; N, 7·3%), $\lambda_{max.}$ (EtOH) 273, 351, 457, and 562 mμ (ε 32,200, 34,800, 5100, and 14,400), $\nu_{max.}$ 1735 cm.$^{-1}$ (ester carbonyl). The n.m.r. spectrum contained signals at τ 2·22 (s, C-10 meso-proton), 2·48 (s, C-5 and C-15 meso-protons), 5·85 (q, CH_2 of Et), 6·9 (m, CH_2 of side-chain esters), 7·35 (s, 6 protons of 2 Me groups), 7·48 (s, 12 protons of 4 Me groups), 8·88 (t, Me of Et), and 9·38 (s, C-1 and C-19 Me).

(ii) *Cobalt derivative*. The biladiene salt (287 mg.) in ethanol (100 ml.) was mixed with an aqueous solution of cobaltous acetate (300 mg. in 3 ml.) and the solution stirred with aeration at room temperature for 3 hr. The solution was reduced in volume (to *ca.* 10 ml.) *in vacuo*, and treated with an aqueous solution of sodium perchlorate (2 g. in 50 ml.). The solid which formed was separated, washed with water, ether, and n-hexane, and then crystallised from methylene chloride–n-hexane when it formed shining violet-brown plates (202 mg., 70·5%), m.p. 181—183° (Found: C, 58·0; H, 6·3; N, 7·1. $C_{37}H_{45}ClCoN_4O_8$ requires C, 57·85; H, 5·85; N, 7·3%), $\lambda_{max.}$ 280, 352, 499, and 542 mμ (ε 28,600, 22,200, 13,500, and 8000), λ_{infl} 568 mμ (ε 7360), $\nu_{max.}$ 1733 cm.$^{-1}$ (ester carbonyl).

8,12-*Di*-(2-*ethoxycarbonylethyl*)-2,18-*diethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin Nickel*(II) *Perchlorate*.—Prepared (81%) by cyclisation of 1,19-dideoxy-8,12-di(2-ethoxycarbonylethyl)-2,18-diethyl-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (above). The *product* formed chocolate-brown needles, m.p. 228—229° [from ethanol–light petroleum (b.p. 80—100°)] (Found: C, 59·15; H, 5·95; N, 7·05. $C_{39}H_{49}ClN_4NiO_8$ requires C, 58·85; H, 6·15; N, 6·85%), $\lambda_{max.}$ (EtOH) 276, 353, 405, 452, and 561 mμ (ε 31,000, 32,600, 5690, 4750, and 13,100), $\nu_{max.}$ 1736 cm.$^{-1}$ (ester carbonyl). The n.m.r. spectrum contained signals at τ 2·28 (s, C-10 meso-proton), 2·48 (s, C-5 and C-15 meso-protons), 5·88 (q, CH_2 of Et), 6·85 (m, CH_2 of side-chain esters), 7·38, 7·45 (both s, β-Me), 8·6 (t, Me of Et), and 9·4 (s, C-1 and C-19 Me).

2,8,12,18-*Tetra*-(2-*ethoxycarbonylethyl*)-1,3,7,13,17,19-*hexamethyltetradehydrocorrin Metal*(II) *Perchlorates*.—(i) *Cobalt derivative*. A suspension of 1,19-dideoxy-2,8,12,18-tetra-(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (200 mg.) in ethanol (40 ml.) was mixed with an aqueous solution of cobaltous acetate (200 mg. in 2 ml.) and the solution aerated at room temperature for 2 hr. It was reduced in volume to *ca.* 5 ml., and then treated with an aqueous solution of sodium perchlorate (2 g. in 50 ml.). The crystalline product was collected, washed with water, taken up in ethanol, and chromatographed on alumina using ethanol as solvent. The purple-violet fraction was collected, evaporated to dryness, and the residual product crystallised from ethanol–light petroleum (b.p. 80—100°) in steel blue-black microneedles (80 mg., 51%), m.p. 175° (Found: C, 56·25; H, 5·95; N, 5·85. $C_{45}H_{57}ClCoN_4O_{12}H_2O$ requires C, 56·4; H, 6·15; N, 5·85%), $\lambda_{max.}$ 283, 352, 500, 547, and 571 mμ (ε 29,700, 23,100, 12,400, 7930, and 7750).

(ii) *Nickel derivative*. A mixture of 1,19-dideoxy-2,8,12,18-tetra-(2-ethoxycarbonylethyl)-1,3,7,13,17,19-hexamethylbiladiene-ac dihydrobromide (100 mg.), nickel acetate (100 mg.), and sodium acetate (100 mg.) in ethanol (5 ml.) was heated gently on the steam-bath with aeration for 10 min. Aqueous sodium perchlorate (2 g. in 30 ml.) was then added to the hot blood-red solution. On cooling, the product was extracted with chloroform (3 × 20 ml.) and the combined extracts were washed, dried ($CaSO_4$), and evaporated to dryness. The residual *product* crystallised from ethanol–light petroleum as long blue-black needles (65 mg., 65·3%), m.p. 169—170° (Found: C, 56·8; H, 5·85; N, 5·8. $C_{45}H_{57}ClN_4NiO_{12}$ requires C, 57·5; H, 6·05; N, 5·95%), $\lambda_{max.}$ (EtOH) 276, 354, 446, and 566 mμ (ε 33,050, 33,150, 4670, and 13,600), $\nu_{max.}$ 1739 cm.$^{-1}$ (ester carbonyl). The n.m.r. spectrum (CF_3CO_2H) showed signals at 2·2 (s, C-10 meso-proton), 2·4 (s, C-5 and C-15 meso-protons), 5·8 (2 superimposed quartets of CH_2 protons of ethyl ester groups), 6·9 (m, CH_2 of propionic ester side-chains), 7·34, 7·4 (both s, β-Me), 8·7 (2 superimposed triplets of Me protons of Et ester groups), and 9·32 (s, C-1 and C-19 angular Me).

4,4-*Diacetylbutyronitrile*.—To a solution of sodium ethoxide (from 0·2 g. of sodium) in absolute ethanol (200 ml.) was added acetylacetone (55 g., 1·1 mol.) and acrylonitrile (26·5 g., 1 mol.), with stirring, while the temperature was kept below 45°. After keeping at room temperature for 24 hr., the resulting solution was heated under reflux for 3 hr., acidified with acetic acid (0·6 ml.), and the solvent removed under reduced pressure. After separating the solid, 3,3-di-(2-cyanoethyl)pentane-2,4-dione [13] (16 g., 21%), m.p. 180—181°, the residual oil was fractionated, and the fraction b.p. 80—105°/0·5 mm. was refractionated and gave the *product* (47 g., 69%) as a colourless liquid, b.p. 98—100°/0·5 mm., n_D^{25} 1·47 (Found: C, 62·8; H, 7·35; N, 9·4. $C_8H_{11}NO_2$ requires C, 62·7; H, 7·25; N, 9·15%), $\nu_{max.}$ ($CHCl_3$) 1705, 1725 (ketone CO), and 2248 (CN) cm.$^{-1}$.

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