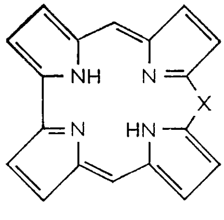
306. *Corroles. Part I. Synthesis*

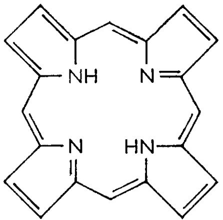
By A. W. JOHNSON and I. T. KAY

Corroles (tetradehydrocorrins) can be prepared by the photocyclisation of 1′,8′-dideoxybiladienes-ac. The products form monohydrobromides and metallic derivatives and the latter, like the parent corroles, form stable anions. The meso-hydrogen atoms of the corroles can be exchanged rapidly for deuterium. Methylation of one of the corroles has given two isomeric *N*-methyl derivatives.

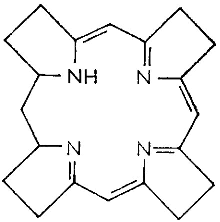
IN one of its tautomeric forms (I; X = CH_2), corrole bears the same relation to porphin (II) as does cyclopentadiene to benzene. A study of the properties of corrole will therefore provide the means of testing the possibility of extending the concepts of the structural requirements necessary to confer aromatic character on a given molecule, to these ring systems which comprise smaller aromatic rings embedded within the 18 π-electron macrocyclic system. Corrole also bears an obvious relation to corrin (III), the chromophore (as its cobaltic complex) of vitamin B_{12}.



(I)

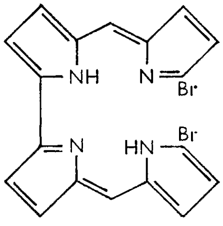


(II)

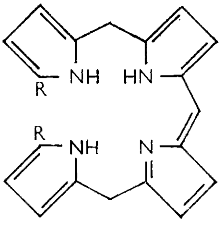


(III)

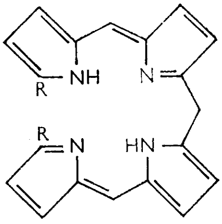
Our attempts to synthesise corroles have involved two general reactions, first the cyclisation of 5,5″-bi-(5′-bromodipyrromethenes) (IV) with the introduction of an extra meso-carbon atom, and secondly the cyclisation of 1′,8′-dideoxybilenes-b (V) and 1′,8′-dideoxybiladienes-ac (VI) with the introduction of a bond to link the terminal α-positions. The first approach using palladium derivatives of 5,5″-bi-(5′-bromodipyrromethenes) gave the oxa-, imino-, methylimino-, and thia-analogues (I; X = O, NH, NMe, and S) of corrole,[1] substances which may also be regarded as the furan, pyrrole, *N*-methylpyrrole, and thiophen analogues in the porphin series. In an earlier Paper [2] we claimed, incorrectly, a synthesis of corrole which was then defined as the macrocyclic system containing eleven double bonds and therefore a " pentadehydrocorrin." This claim was later withdrawn and we now suggest that the term corrole should be used to designate the macrocycle (I; X = CH_2), or more correctly the tautomer (XII), containing only ten double bonds and therefore a " tetradehydrocorrin." In a preliminary Note [3] we inadvertently described (I; X = CH_2) as a pentadehydrocorrin; this was in error.



(IV)



(V)



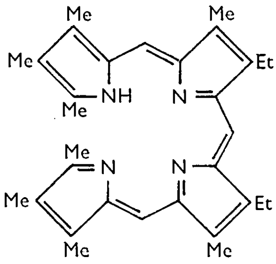
(VI)

---

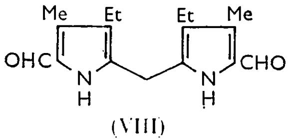
[1] A. W. Johnson, I. T. Kay, and R. Rodrigo, *J.*, 1963, 2336.
[2] A. W. Johnson and R. Price, *J.*, 1960, 1649.
[3] A. W. Johnson and I. T. Kay, *Proc. Chem. Soc.*, 1964, 89.

We have already described[4,5] a method for the preparation of 1′,8′-dideoxy-1′,8′-dimethylbiladienes-ac comprising the condensation of a dipyrromethane-5,5′-dicarboxylic acid with two equivalents of a 2-formyl-5-methylpyrrole. When the resulting 1′,8′-dideoxybiladienes-ac (VI; R = Me) or the 1′,8′-dideoxybilenes-b (V; R = Me)[4,6] in methanolic solution were heated in presence of cupric acetate, cyclisation to the corresponding porphyrin (with loss of one carbon atom) took place. On the other hand, irradiation of methanolic solutions of the 1′,8′-dideoxybiladienes-ac (VI; R = Me) with ultraviolet light caused some cyclisation to the porphyrin but the main product was the 1′,8′-dideoxy-1′,8′-dimethylbilatriene-abc (*e.g.*, VII).[5] We have now examined the irradiation of the 1′,8′-dideoxybiladienes-ac (VI; R = H), and this has resulted in a ready synthesis of corroles.

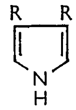
The requisite 1′,8′-dideoxybiladienes-ac were prepared either by condensation of 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyldipyrromethane[5] (VIII) and 3,4-dialkylpyrroles (IX; R = Me or Et) or of dipyrromethane-5,5′-dicarboxylic acids with 3,4-dialkyl-2-formylpyrroles. The 1′,8′-dideoxybiladienes-ac were isolated in yields of over 80% as the crystalline hydrobromides, and in one case, 1′,8′-dideoxy-4,5-diethyl-1,2,3,6,7,8-hexamethylbiladiene-ac [*i.e.*, from (VIII) and (IX; R = Me)], a crystalline zinc complex (X) was obtained. Treatment of this 1′,8′-dideoxybiladiene-ac with formaldehyde gave 3,17-diethyl-2,7,8,12,13,18-hexamethylporphyrin (XI; numbering of porphyrin nucleus[7]) in 57% yield, a method which could form the basis of a generalised porphyrin synthesis.



(VII)

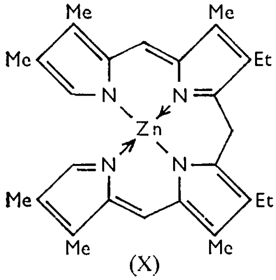


(VIII)

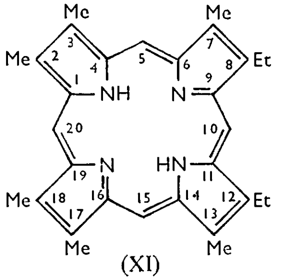


(IX)

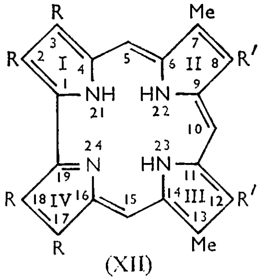
The 1′,8′-dideoxybiladiene-ac hydrobromides were usually suspended in methanol and treated with a slight excess of ammonium hydroxide or aqueous sodium acetate and then the solutions, as shallow layers, were illuminated with light from a 200w bulb at a distance of 5 cm. The colour of the solutions rapidly changed from yellow to green and finally after about 10 minutes to red and on cooling, the crystalline corroles (XII; R = Me; R′ = Et or $CH_2\cdot CH_2\cdot CO_2Me$) were obtained in yields of 20—60%. They readily formed purple crystalline monohydrobromides (porphyrins give dihydrobromides). Corroles contain an aromatic (18 π-electron) chromophore and solutions in chloroform show an absorption spectrum which contains an intense Soret band. A comparison of the spectra



(X)



(XI)



(XII)

---

[4] A. W. Johnson and I. T. Kay, *J.*, 1961, 2418.

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

[6] H. Fischer and A. Kürzinger, *Z. physiol. Chem.*, 1931, **196**, 213.

[7] I.U.P.A.C. rules for nomenclature of vitamins, *J. Amer. Chem. Soc.*, 1960, **82**, 5582.

of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole [the corrole ring is numbered in the same manner as porphyrin (II) and corrin (III) [7]] and the corresponding porphyrin is shown in Fig. 1.

A solution of the corrole in strong sulphuric acid, or to a lesser extent in trifluoroacetic acid, showed a spectrum (Fig. 2) which contained a new band at 670 mμ but no Soret band and it is suggested that under these conditions the corrole is present as a dication (XIII) of the tautomeric non-aromatic form. This salt reverted to the original corrole on basification. Addition of dilute alkali to solutions of the corrole also causes large spectral changes, although with retention of the Soret band (Fig. 2), because of the formation of the stable aromatic anion (XIV). The structure of this anion bears the same relation to porphyrin as does the cyclopentadienyl anion to benzene. The ready formation of corrole anions is in marked contrast to the behaviour of porphyrins [8] and the contrast is emphasised further by the rapid exchange of all three *meso*-protons of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole for deuterium when solutions in deuterated trifluoroacetic acid are examined by n.m.r. spectroscopy.[9]

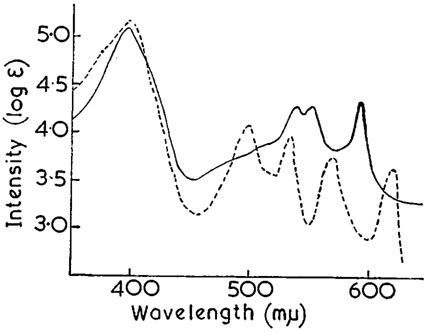


FIG. 1. Visible absorption spectra of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (———) and the corresponding porphyrin (- - - -) in chloroform

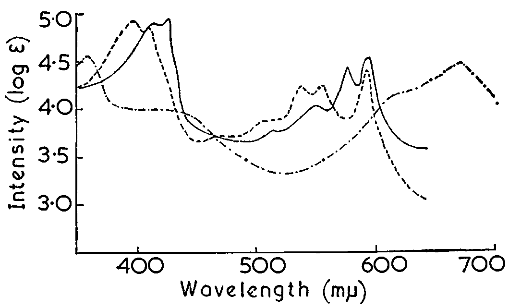
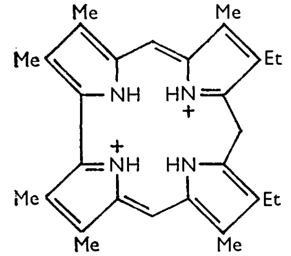
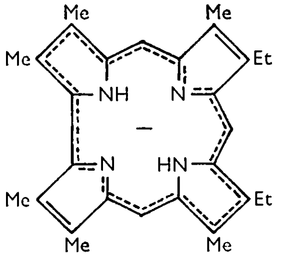


FIG. 2. Visible absorption spectra of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole in *NN*-dimethylformamide (- - - - -), *NN*-dimethylformamide containing one drop of 1% aqueous sodium hydroxide (———), and in concentrated sulphuric acid (— · — · —)

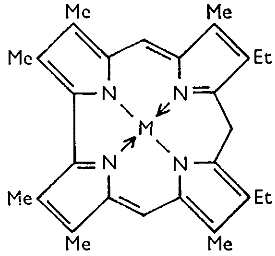
Moderately stable crystalline nickel and copper derivatives of corroles have been prepared either by the addition of nickel or copper cations to solutions of the corrole or by the inclusion of these metallic ions before the irradiation of the 1′,8′-dideoxybiladiene-ac.



(XIII)



(XIV)



(XV)

The zinc derivative was markedly less stable. Absence of the Soret band in the spectrum of these corrole metal complexes (Fig. 3) suggests that they are derived from the tautomeric

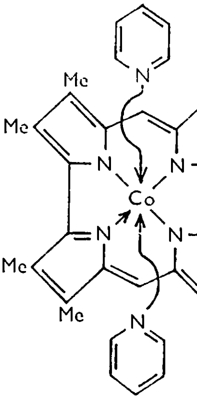
---

[8] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 1963, **85**, 818.

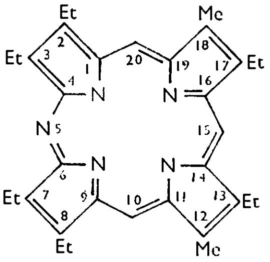
[9] R. B. Woodward and V. Škarić, *J. Amer. Chem. Soc.*, 1961, **83**, 4676; R. J. Abraham, A. H. Jackson, and G. W. Kenner, *J.*, 1961, 3468; R. Bonnett and G. F. Stephenson, *Proc. Chem. Soc.*, 1964, 291.

non-aromatic base (XV; M = Ni, Cu) corresponding to the dication (XIII), and in agreement with this view, it is observed that addition of alkali to the green solutions of the nickel complex (XV; M = Ni) causes the reappearance of the Soret band in the spectrum (Fig. 3) corresponding to the formation of the nickel complex of the anion (XIV), which forms red solutions. This striking colour change is very sharp, and is reversed by acidification. Treatment of the corrole with cobaltous acetate in presence of pyridine gave purple prisms of the cobaltic dipyridyl complex (XVI), but this was readily converted to the planar cobaltous complex (XV; M = Co) with loss of pyridine by the action of hot methanol.

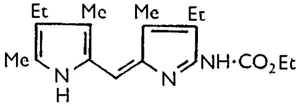
In the case of 1′,8′-dideoxy-3,6-dimethyl-1,2,4,5,7,8-hexaethylbiladiene-ac, a second product in addition to the corresponding corrole (XII; R = R′ = Et) was obtained from the photocyclisation when it was carried out on an ammoniacal solution. The new compound, formed as the minor product, was identified as the corresponding monazaporphyrin (XVII). Such compounds have been described by Fischer,[10] but were obtained usually in low yield, *e.g.*, by the action of bromine in acetic acid on dipyrromethene-5-urethanes (XVIII). The n.m.r. spectrum of the corrole (XII; R = R′ = Et), determined on a deuteriochloroform solution with tetramethylsilane as internal reference, was in accord with the assigned structure. It contained a singlet at τ 0·88 (C_5 and C_{15} meso-protons), a singlet at 1·18 (C_{10} meso-proton), three overlapping quartets centred about 6·18 (12 protons of methylenes of ethyl groups; types 2,18; 3,17; and 8,12), a singlet at 6·72 (6 protons



(XVI)



(XVII)



(XVIII)

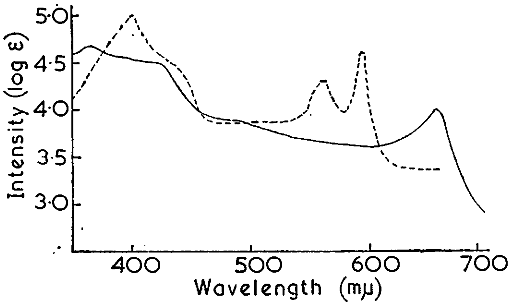


Fig. 3. Visible absorption spectra of nickel 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole in *NN*-dimethylformamide (———) and in *NN*-dimethylformamide containing one drop of 1% aqueous sodium hydroxide (– – – –)

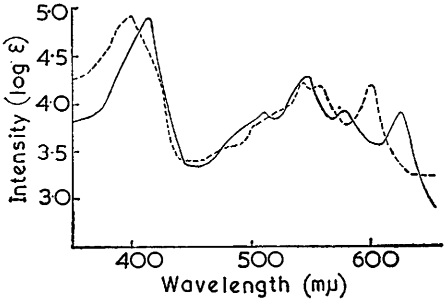
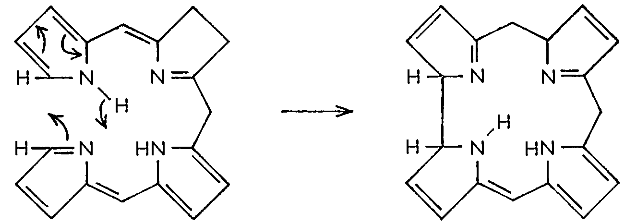


Fig. 4. Visible absorption spectra of 8,12-diethyl-2,3,7,13,17,18,22-heptamethylcorrole (———) (XXIII) and 8,12-di-ethyl-2,3,7,13,17,18,21-heptamethylcorrole (XXII) in chloroform

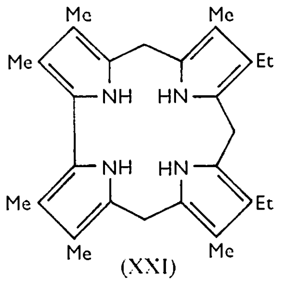
---

[10] H. Fischer and H. Orth, "Die Chemie des Pyrrols," **2**, ii, p. 408 (1943); F. Endermann and H. Fischer, *Annalen*, 1939, **538**, 172.

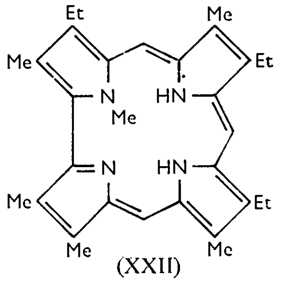
of 7,13 methyl groups), three overlapping triplets centred about 8·30 (18 protons of methyls of ethyl groups; three types as above) and a broad singlet at 13·48 (3 protons of imino groups).



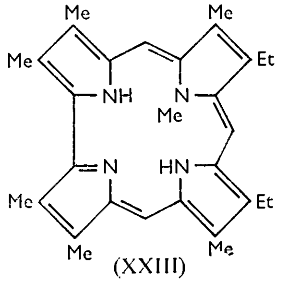
(XIX) (XX)



(XXI)



(XXII)



(XXIII)

The requisite oxidation step in the photoinduced cyclisation of the 1′,8′-dideoxybiladienes-ac is brought about by atmospheric oxidation although in the case of cyclisations conducted in presence of cupric salts, these may act as the oxidising agent. Although the precise mechanism of the photocyclisation step has not been established it is possible that it proceeds by electron shifts such as are depicted in (XIX) and the macrocyclic intermediate (XX) undergoes an irreversible dehydrogenation to the corrole. If the two reactive α-positions are prevented, *e.g.*, by the presence of adjacent bulky groups, from approaching each other sufficiently closely to permit bond formation, then other reactions may occur such as the formation of the azaporphyrin when two ethyl groups (in contrast to methyls) occupy the positions adjacent to the reactive centres. For the same reason the zinc complex of 8,12-diethyl-2,3,7,13,17,18-hexamethylbiladiene-ac did not yield any corrole on irradiation. Complexes of zinc are known to exist in a tetrahedral configuration in most cases, and it is assumed that in the 1′,8′-dideoxybiladiene-ac zinc complex the terminal α-groups will not be able to take up positions suitable for reaction.

Hydrogenation of solutions of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole in presence of platinum gave a colourless solution from which unstable colourless needles, probably the "corrologen" (XXI) could be isolated. Solutions of this product were rapidly oxidised in air or in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [11] to the original corrole but in presence of acid the reduction product gave the corresponding porphyrin on oxidation. This is caused by the acid decomposition of the corrologen, in the same manner as the acid randomisation of porphyrinogens,[12] to pyrrolic intermediates which then recombine and are oxidised to porphyrins.

As the corroles exist as anions in alkaline solution it was expected that methylation would occur readily under these conditions and in fact the reaction of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole yielded two products, both of which proved to be *N*-methyl derivatives. One of these (XXII) showed an absorption spectrum (Fig. 4) similar to that of corrole itself and contained the *N*-methyl group on the bipyrrole side of

---

[11] E. A. Braude, A. G. Brook, and R. P. Linstead, *J.*, 1954, 3569.

[12] D. Mauzerall, *J. Amer. Chem. Soc.*, 1960, **82**, 2601, 2605; I. T. Kay, *Proc. Nat. Acad. Sci. U.S.A.*, 1962, **84**, 2437.

the molecule and the other (XXIII), which showed a different type of absorption, contained the *N*-methyl group on the dipyrromethene side. The isomers were distinguished by n.m.r. spectroscopy on the grounds of the dissimilar absorptions associated with the nuclear ethyl groups caused by the adjacent *N*-methyl group in (XXIII), a phenomenon not shown by the isomer (XXII). The spectra which were determined on deuteriochloroform solutions as before, also revealed the non-equivalence of the I—II and III—IV dipyrromethene portions of the *N*-methyl derivatives. The spectra of (XXII) and (XXIII) are described in the Table.

N.m.r. absorptions (τ-scale) in spectra of the *N*-methyl derivatives (XXII) and (XXIII)

Assignment	Compound (XXII)	Compound (XXIII)
3 *meso*-Hydrogens	0·72s (1)	0·54s (2)
	0·93s (1)	0·64s (1)
	1·03s (1)	
6 β-Methyl groups	6·55s (3)	6·33s (3)
	6·68s (6)	6·42s (6)
	6·72s (3)	6·52s (3)
	7·08s (3)	6·56s (3)
	7·20s (3)	6·70s (3)
2 Methylenic groups	6·23 (2 overlapping quartets)	6·03 (2 overlapping quartets)
2 Methyl groups of ethyl substituents	8·28t (6)	8·15t (3), 8·50t (3)
2 Imino-groups	13·0s (broad; 2)	13·58s (broad; 2)
N-Methyl group	13·12s (3)	14·46s (3)

The overall spread in the n.m.r. absorptions, which is associated with the strength of the ring current,[13] is markedly greater in (XXIII) than (XXII) and is possibly an inverse measure of the distortion of the planar aromatic ring caused by the *N*-methyl group in different environments.

EXPERIMENTAL

Ultraviolet and visible absorption spectra were determined for chloroform solutions except where otherwise stated. Nuclear magnetic resonance spectra were measured on an AEI RS 2 instrument operating at 60 Mc./sec.

3,4-Diethyl-2-formylpyrrole.—3,4-Diethylpyrrole [14] (4·6 g.) in *NN*-dimethylformamide (30 c.c.) was cooled to 0° and phosphorus oxychloride (6·38 g., 3·9 c.c.) added during 15 min. with stirring. Stirring was then continued for a further 1·5 hr. at room temperature, and then the solution was poured into water (100 c.c.) and basified by the addition of 20% aqueous sodium hydroxide. The oily product solidified overnight at 0°, and was separated, washed well with cold water, and dried, giving crude *aldehyde* (4·8 g.), m. p. 44—47°. This was purified by short-path distillation on to a cold finger at 85°/15 mm., and formed colourless prismatic needles, m. p. 46—48° (Found: C, 71·6; H, 8·45; N, 9·3. $C_9H_{13}NO$ requires C, 71·5; H, 8·65; N, 9·25%).

(*A*) 1′,8′-*Dideoxybiladienes-ac.*—(i) 1′,8′-*Dideoxy*-4,5-*diethyl*-1,2,3,6,7,8-*hexamethylbiladiene-ac.* (*a*) 3,3′-Diethyl-5,5′-diformyl-4,4′-dimethyldipyrromethane [5] (200 mg.; m. p. 219—221°; previously [5] incorrectly reported as >300°) and 3,4-dimethylpyrrole (145 mg.) in methanol (20 c.c.) were treated with hydrobromic acid (2 c.c., 50%), the solution heated on the water-bath for 1 min. and then kept at room temperature for 2 hr. The product was separated, washed with methanol containing a little hydrobromic acid, then with ether, and dried. The salt formed red-brown prisms with a green lustre (344 mg., 81%), m. p. >300°, from chloroform–methanol containing a little hydrobromic acid. When crystallised from chloroform solutions in this way, the *salt* contained 0·5 mol. of crystallisation of chloroform (positive carbylamine test) (Found: C, 53·5; H, 5·6; N, 8·5. $C_{29}H_{38}Br_2N_4,\frac{1}{2}CHCl_3$ requires C, 53·5; H, 5·85; N, 8·45%).

(*b*) 3,3′-Diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (2·42 g.) and 3,4-dimethyl-2-formylpyrrole (1·89 g.) were warmed to solution in methanol (200 c.c.) and hydrobromic acid (20 c.c.; 50%) added. The solution was kept for 2 hr. at room temperature, and

---

[13] *E.g.* A. W. Johnson and D. Oldfield, *Tetrahedron Letters*, 1964, 1549.

[14] U. Eisner, A. Lichtarowicz, and R. P. Linstead, *J.*, 1957, 733.

the product (4·1 g., 89%) was isolated as above (Found: C, 53·0; H, 5·7; N, 8·15%). The *dihydrobromide* was crystallised from a large volume of methanol containing a few drops of hydrobromic acid, whereby the chloroform of crystallisation was removed (Found: C, 57·9; H, 6·0; N, 9·35. $C_{29}H_{38}Br_2N_4$ requires C, 57·8; H, 6·35; N, 9·3%); $\lambda_{max.}$ 288, 373, 458, and 522 mμ (ε, 2720, 15,800, 20,000, and 190,000, respectively).

The *zinc complex* (X) was prepared from a boiling methanolic solution of the hydrobromide and zinc acetate. It formed glistening red prisms with a green reflex, slow decomp. >230°, from chloroform–methanol [Found: C, 68·9; H, 6·55; N, 11·1; Ash (ZnO), 16·4. $C_{29}H_{34}N_4Zn$ requires C, 69·1; H, 6·8; N, 11·1; ZnO, 16·15%]; $\lambda_{max.}$ 394, 464, and 513 mμ (ε, 12,700, 53,900, and 52,800, respectively).

(ii) 1′,8′-*Dideoxy*-1,2,4,5,7,8-*hexaethyl*-3,6-*dimethylbiladiene-ac dihydrobromide.* 3,4-Diethyl-2-formylpyrrole (604 mg.; 2 mole.) and 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (636 mg.; 1 mole.) were warmed to solution in methanol (25 c.c.) and then hydrobromic acid (3 c.c.) added. The solution was allowed to cool to room temperature and then kept at 0° for 1 hr. The crystalline product was separated, washed with methanol containing a little hydrobromic acid, then with ether, and dried. The *product* (1·17 g.; 89%) which darkened >160° without melting, formed red-brown prisms from methanol containing a trace of hydrobromic acid (Found: C, 59·8; H, 6·85; N, 8·8. $C_{33}H_{46}Br_2N_4$ requires C, 59·9; H, 7·05; N, 8·55%); $\lambda_{max.}$ 288, 373, 458, and 523 mμ (ε, 2710, 16,600, 20,800, and 170,000, respectively).

(iii) 1′,8′-*Dideoxy*-4,5-*di*-(2′-*methoxycarbonylethyl*)-1,2,3,6,7,8-*hexamethylbiladiene-ac dihydrobromide.* Dibenzyl 4,4′-dimethyl-3,3′-di(2-methoxycarbonylethyl)dipyrromethane-5,5′-dicarboxylate [15] (2·0 g.) in methanol (150 c.c.) was hydrogenated at 1 atm. pressure in the presence of Adams catalyst. When hydrogen uptake had ceased, the solution was reduced to *ca.* 40 c.c. under reduced pressure and the resulting suspension of the dipyrromethane-5,5′-dicarboxylic acid treated with 3,4-dimethyl-5-formylpyrrole (1 g.) and the solution heated to the boiling point. Hydrobromic acid (4 c.c.) was then added, the solution allowed to cool to room temperature and then kept at 0° for 1 hr. The *crystalline salt* was separated, washed with methanol containing a little HBr, and ether, and dried (1·90 g.; 81%). It was crystallised from a large volume of chloroform as red-brown prisms with a green lustre, m. p. (slow decomp.) >215° (Found: C, 55·2; H, 6·0; N, 7·4. $C_{33}H_{42}Br_2N_4O_4$ requires C, 55·15; H, 5·9; N, 7·8%); $\lambda_{max.}$ 291, 373, 457, and 520 mμ (ε, 2810, 15,300, 25,100, and 157,000, respectively).

3,17-*Diethyl*-2,7,8,12,13,18-*hexamethylporphyrin* (XI) (with DR. R. L. N. HARRIS).—1′,8′-Dideoxy-1,2,3,6,7,8-hexamethyl-4,5-diethylbiladiene-ac dihydrobromide (0·2 g.) was suspended in methanol (100 c.c.) containing 30% aqueous formaldehyde (10 c.c.) and 1 drop of 50% hydrogen bromide in acetic acid. The mixture was heated under reflux for 24 hr., and the crystalline precipitate collected and washed with methanol. The porphyrin (86 mg., 57%) was thus obtained as steel-blue micro-prisms, m. p. >300° (Found: C, 80·2; H, 7·4; N, 12·5. Calc. for $C_{30}H_{34}N_4$: C, 79·95; H, 7·6; N, 12·45%); $\lambda_{max.}$ 269, 400, 498, 535, 568, 597, and 624 mμ (ε, 4570, 129,000, 7410, 5620, 3800, 892, and 2820, respectively); $\lambda_{infl.}$ 330 mμ (ε, 14,800).

(*B*) *Corroles.*—(i) 8,12-*Diethyl*-2,3,7,13,17,18-*hexamethylcorrole* (XII; R = Me; R′ = Et). 1′,8′-Dideoxy-4,5-diethyl-1,2,3,6,7,8-hexamethylbiladiene-ac dihydrobromide (100 mg.), suspended in methanol (50 c.c.) contained in a 1 l. conical flask, was treated with ammonium hydroxide (2 c.c., *d* 0·88) and the solution illuminated over a 200w tungsten bulb at a distance of approximately 5 cm. for 10 min. During this time, the colour of the solution rapidly changed from yellow to green and finally to red. The solution was kept at 0° for 1 hr., the crystalline *product* separated, washed with methanol, and crystallised from chloroform–methanol, forming red needles (42 mg.; 58%), m. p. 255—257° (some decomp.) (Found: C, 79·5; H, 7·6; N, 12·6. $C_{29}H_{34}N_4$ requires C, 79·4; H, 7·8; N, 12·75%); (i) $\lambda_{max.}$ 396, 536, 550, and 593 mμ (ε, 123,100, 18,100, 18,100, and 21,450); $\lambda_{infl.}$ 346, 408, 474, 502, and 525 mμ (ε, 16,610, 99,200, 3290, 6750, and 8280, respectively); (ii) $\lambda_{max.}$ in concentrated sulphuric acid 292, 358, and 671 mμ (ε, 19,700, 50,300, and 28,700, respectively).

The corrole base (150 mg.), suspended in acetone (30 c.c.) was treated with hydrobromic acid (3 c.c.; 50%) and while the solution was boiling on the water-bath, water (30 c.c.) was slowly added and after most of the acetone had boiled off the solution was allowed to cool. The *monohydrobromide* was separated, dried, and recrystallised from chloroform–light petroleum as

---

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

glittering purple needles (157 mg., 88%), m. p. ≮300° (Found: C, 66·9; H, 6·7; Br, 14·5; N, 11·1. $C_{29}H_{35}BrN_4$ requires C, 67·04; H, 6·8; Br, 15·4; N, 10·8%); $\lambda_{\text{max.}}$ 406 and 577 mμ (ε, 138,000 and 24,420, respectively); $\lambda_{\text{infl.}}$ 504 and 544 mμ (ε, 2490 and 8720, respectively).

Nickel complex. (*a*) 8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole (47 mg.) in chloroform (30 c.c.)–methanol (15 c.c.) was treated with a solution of nickel chloride (385 mg.) in dilute ammonium hydroxide solution (3 c.c.). Methanol was then added to the boiling solution at such a rate as to keep the volume constant and until all the chloroform had been replaced by methanol. The product was separated, washed with methanol and crystallised from chloroform–methanol, forming glittering steel-blue prisms (44 mg.; 82%) decomp. >210°, [Found: C, 69·8; H, 6·15; N, 10·9; Ash (NiO), 15·1. $C_{29}H_{32}N_4Ni$ requires C, 70·3; H, 6·5; N, 11·3; NiO, 15·0%]; $\lambda_{\text{max.}}$ 349 and 652 mμ (ε, 45,100 and 9200, respectively); $\lambda_{\text{infl.}}$ 419 mμ (ε, 27,800).

(*b*) To 1′,8′-dideoxy-4,5-diethyl-1,2,3,6,7,8-hexamethylbiladiene-ac dihydromide (100 mg.) suspended in methanol (100 c.c.) was added a solution of nickel chloride (300 mg.) in dilute ammonium hydroxide (5 c.c.) and the solution illuminated over a 200w tungsten lamp for 10 min. The solid was separated and crystallised from chloroform–methanol as glittering steel blue prisms (55 mg.; 67%), with light absorption identical to that above. Light absorption in acetone (10 ml.) containing aqueous sodium hydroxide (5 drops of 10%): $\lambda_{\text{max.}}$ 397, 521, 554, and 587 mμ (ε, 54,200, 4930, 10,100, and 22,400, respectively).

Copper complex. (*a*) To 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (105 mg.) in pyridine (5 c.c.) was added a solution of cupric acetate (105 mg.) in pyridine and the solution kept for 5 min. at room temperature with occasional swirling. The *product* was separated, washed with methanol, and crystallised from pyridine as purple needles (104 mg.; 86%), m. p. ≮300° [Found: C, 69·6; H, 6·15; N, 11·15; Ash (CuO), 16·0. $C_{29}H_{32}CuN_4$ requires C, 69·65; H, 6·45; N, 11·2; CuO, 15·9%]; $\lambda_{\text{max.}}$ 396 and 549 mμ (ε, 8200 and 10,000, respectively); $\lambda_{\text{infl.}}$ 502 mμ (ε, 7100).

(*b*) To a suspension of 1′,8′-dideoxy-4,5-diethyl-1,2,3,6,7,8-hexamethylbiladiene-ac dihydrobromide (100 mg.) in methanol (50 c.c.) was added cupric acetate (100 mg.) and the solution kept for 15 min. at room temperature with occasional shaking. The fine precipitate of the copper corrole complex was separated on diatomite, washed with methanol (100 c.c.), and crystallised from pyridine as purple hairs (55 mg.; 66%). The light absorption was similar to that of the previous product.

Cobaltic dipyridino-complex. 8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole (102 mg.) in pyridine (5 c.c.) containing cobalt acetate (100 mg.) was heated on the steam-bath for 15 min., hot methanol (40 c.c.) was added, the solution allowed to cool. The *product* was separated, washed with methanol and crystallised from pyridine–methanol as glittering purple prisms (103 mg.) (Found: C, 71·9; H, 6·2; N, 12·6. $C_{39}H_{41}CoN_6$ requires C, 71·75; H, 6·35; N, 12·85%).

Cobaltous complex. The foregoing dipyridino-complex (90 mg.) was dissolved in hot chloroform (20 c.c.) and hot methanol (10 c.c.) added. On cooling, the *crystalline product* was separated (60 mg.) as black needles and washed with methanol. It tended to decompose on attempted crystallisation from chloroform–methanol (Found: C, 70·7; H, 6·35; N, 10·9. $C_{29}H_{32}CoN_4$ requires C, 70·3; H, 6·5; N, 11·3%).

(ii) 8,12-*Diethyl*-2,3,7,13,17,18,21-*heptamethyl*- (XXII) *and* 8,12-*Diethyl*-2,3,7,13,17,18,22-*heptamethyl-corrole* (XXIII).—8,12-*Diethyl*-2,3,7,13,17,18-hexamethylcorrole (300 mg.) in acetone (70 c.c.) containing anhydrous potassium carbonate (5 g.) was treated with methyl iodide (5 c.c.), and the solution heated under reflux for 30 min. The potassium carbonate was separated, washed with acetone and the combined filtrates evaporated to dryness. The residue was dissolved in benzene (5 c.c.) and chromatographed on a dry-packed column (1·5 × 30 cm.) of Kieselgel " G." The first (red) fraction was eluted with benzene—the elution being checked spectroscopically at intervals.

After removal of the solvent, the *residue* (XXII) formed mauve prisms (116 mg.; m. p. slow decomp. >210°) from acetone–methanol (Found: C, 79·0; H, 8·20; N, 11·95; NMe, 4·1. $C_{30}H_{36}N_4$ requires C, 79·6; H, 8·0; N, 12·35; NMe, 6·4%); $\lambda_{\text{max.}}$ 400, 541, 559, and 600 mμ (ε, 86,200, 15,900, 15,900, and 15,700, respectively); $\lambda_{\text{infl.}}$ at 502 and 521 mμ (ε, 5370 and 8160).

Elution of the chromatogram was continued with benzene until the second (blue-red) fraction became spectroscopically pure and completely separated from the foregoing fraction when the column was then eluted with chloroform-methanol (4 : 1). After removal of the solvent this *fraction* (XXIII) formed steel blue prisms (50 mg.; m. p. 212—213°) from acetone–methanol (Found: C, 80·3; H, 8·25; N, 12·35; NMe, 3·65. $C_{30}H_{36}N_4$ requires C, 79·6; H, 8·0; N, 12·35; NMe, 6·4%); $\lambda_{max.}$ 413, 510, 527, 547, and 625 mμ (ε, 76,500, 7480, 8260, 15,000, and 7660, respectively).

(iii) 2,3,8,12,17,18-*Hexaethyl*-7,13-*dimethylcorrole* (XII; R = R′ = Et). (*a*) 1′,8′-Dideoxy-1,2,4,5,7,8-hexaethyl-3,6-dimethylbiladiene-ac dihydrobromide (500 mg.) in stirred methanol (1800 c.c.) was illuminated by a medium-pressure mercury lamp (Hanovia) and sodium acetate (2 g.) was added. The solution was illuminated for 15 min. without cooling at the end of which time the solution was boiling. This was repeated for a further 500 mg. of biladiene and the combined methanolic solutions evaporated to dryness under reduced pressure. The residue was dissolved in chloroform (*ca.* 15 c.c.) and after filtration through diatomite, chromatographed on a column (1·5 × 40 cm.) of alumina (Spence type H). The corrole was eluted with chloroform and the elution followed by means of a hand spectroscope. The *product* formed sheaves of purple-red needles (157 mg.; 21%; m. p. 211—212°) from chloroform–methanol (Found: C, 79·8; H, 8·7; N, 11·1. $C_{33}H_{42}N_4$ requires C, 80·15; H, 8·55; N, 11·3%); $\lambda_{max.}$ 346, 396, 408, 537, 552, and 592 mμ (ε, 16,220, 115,000, 99,300, 17,400, 18,300, and 23,000); $\lambda_{infl.}$ 503 and 516 mμ (ε, 7060 and 8830, respectively).

Copper complex. 1′,8′-Dideoxy-1,2,4,5,7,8-hexaethyl-3,6-dimethylbiladiene-ac dihydrobromide (260 mg.) in methanol (100 c.c.) was treated with cupric acetate (260 mg.), and the solution kept at room temperature for 10 min. with occasional swirling. The *product* was separated, washed with methanol, and crystallised from chloroform–methanol, forming red-brown needles, m. p. $\nless$300° [Found: C, 71·1; H, 7·1; N, 10·2; Ash (CuO), 14·8. $C_{33}H_{40}CuN_4$ requires C, 71·25; H, 7·25; N, 10·1; CuO, 14·3%]; $\lambda_{max.}$ 397 and 549 mμ (ε, 90,000 and 11,400); $\lambda_{infl.}$ 502 mμ (ε, 7240).

Nickel complex. 1′,8′-Dideoxy-1,2,4,5,7,8-hexaethyl-3,6-dimethylbiladiene-ac dihydrobromide (233 mg.) in methanol (150 c.c.) was treated with a solution of nickel chloride (400 mg.) and sodium acetate (800 mg.) in water (5 c.c.) and the solution illuminated by a 200w tungsten bulb at a distance of 5 cm. for 10 min. On cooling, the *complex* was separated, washed with water and methanol, and crystallised from chloroform–methanol, forming purple-black needles (127 mg.; 65%), m. p. $\nless$300° [Found: C, 71·4; H, 7·0; N, 10·1; Ash (NiO), 14·2. $C_{33}H_{40}N_4Ni$ requires C, 71·9; H, 7·3; N, 10·15; NiO, 13·55%]; $\lambda_{max.}$ 360 and 659 mμ (ε, 51,900 and 11,200, respectively); $\lambda_{infl.}$ 420 mμ (ε, 33,200).

(*b*) 1′,8′-Dideoxy-1,2,4,5,7,8-hexaethyl-3,6-dimethylbiladiene-ac dihydrobromide (500 mg.) in stirred methanol (1750 c.c.) was treated with ammonium hydroxide (20 c.c.; *d* 0·88) and the solution illuminated by a medium-pressure mercury lamp (Hanovia) for 10 min. without cooling so that at the end of this time the heat generated by the lamp had caused the solution to boil. The solvent was removed under reduced pressure, the residue dissolved in chloroform (10 c.c.), the solution filtered and chromatographed on a column (1·5 × 30 cm.) of alumina (Spence " H "); the band which fluoresced red under u.v. light was collected and the solvent removed under reduced pressure. The residue was dissolved in benzene (5 c.c.) and re-chromatographed on a column (2 × 10 cm.) of dry-packed Kieselgel " G." The product, 2,3,7,8,13,17-*hexaethyl*-12,18-*dimethyl*-5-*azaporphyrin* (XVII) was eluted with benzene and after removal of the solvent formed steel-blue prisms (21 mg.), m. p. 304—305°, from chloroform–methanol (Found: C, 77·8; H, 7·9; N, 14·0. $C_{33}H_{41}N_5$ requires C, 78·05; H, 8·15; N, 13·8%); $\lambda_{max.}$ 273, 380, 480, 506, 538, 560, and 613 mμ (ε, 8250, 91,800, 4210, 7520, 23,800, 7880, and 24,350, respectively).

The corrole was eluted as a second fraction from the column by chloroform–methanol (4 : 1) and gave purple-red needles (47 mg.; m. p. and mixed m. p. with the above corrole, 212—213°). The light absorption data and thin layer chromatographic characteristics (silica–benzene) were identical with those of the previous preparation.

(iv) 8,12-*Di*-(2-*methoxycarbonylethyl*)-2,3,7,13,17,18-*hexamethylcorrole* (XII; R = Me; R′ = $CH_2{\cdot}CH_2{\cdot}CO_2Me$).—To a suspension of 1′,8′-dideoxy-4,5-di-(2-methoxycarbonylethyl)-1,2,3,6,7,8-hexamethylbiladiene-ac dihydrobromide (100 mg.) in methanol (50 c.c.) was added sodium acetate (250 mg.), and the solution illuminated over a 200w lamp bath (5 cm.) for 10 min. The solution was then reduced to *ca.* 15 c.c. and kept overnight at 0°. The *corrole* was separated, washed with methanol, and crystallised from chloroform–methanol; it formed purple prismatic needles (17 mg.; 22%), m. p. 206—209° (Found: C, 71·5; H, 7·15; N, 9·65. $C_{33}H_{38}N_4O_4$ requires C, 71·45; H, 6·9; N, 10·1%); $\lambda_{max.}$ 325, 398, 409, 540, 551, and 594 mμ (ε, 17,150, 112,000, 92,000, 14,630, 15,150, and 15,900, respectively); $\lambda_{\text{infl.}}$ 500 and 514 mμ (ε, 7570 and 8300).

Copper complex. 1′,8′-Dideoxy-4,5-di-(2-methoxycarbonylethyl)-1,2,3,6,7,8-hexamethylbiladiene-ac dihydrobromide (200 mg.) suspended in methanol (100 c.c.) was treated with cupric acetate (200 mg.) and the solution set aside for 10 min. with occasional shaking. The *product* was separated, washed with methanol, and crystallised from chloroform–methanol, forming small red-brown needles (102 mg.; 59%) which appeared purple in bulk, m. p. $\nless$300° [Found: C, 64·3; H, 5·7; N, 9·2; Ash (CuO), 13·7. $C_{33}H_{36}CuN_4O_4$ requires C, 64·3; H, 5·9; N, 9·1; CuO, 12·95%]; $\lambda_{\text{max.}}$ 397 and 546 mμ (ε, 91,200 and 9750); $\lambda_{\text{infl.}}$ 504 mμ (ε, 7880).

This work was carried out during the tenure of an I.C.I. Fellowship by one of us (I. T. K.).

THE UNIVERSITY, NOTTINGHAM. [*Received, July* 1*st*, 1964.]