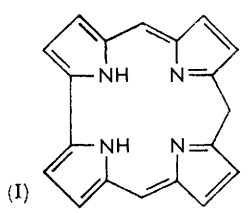
431. *The Condensation of 2,2′-Bipyrroles with 2-Formylpyrroles and 5,5′-Diformyldipyrromethanes.*

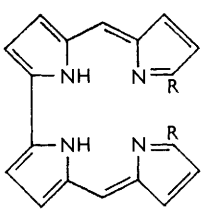
By E. Bullock, R. Grigg, A. W. Johnson, and J. W. F. Wasley.

The acid-catalysed condensations named in the title involve only one of the two free α-positions of the bipyrrole even in the presence of an excess of the formyl compound. From the 2-formylpyrroles, the products are 5-pyrrol-2″-yldipyrromethenes, which can also be prepared by condensation of 5-formyl-2,2′-bipyrroles and α-free pyrroles. The 5-pyrrol-2″-yldipyrromethene group includes the bacterial pigment, prodigiosin. The reaction of 2,2′-bipyrroles with 5,5′-diformyldipyrromethanes yields the hexapyrrolic compounds (XI). Irradiation of a 1′,8′-dideoxy-1′,8′-dimethylbiladiene-ac in air gives some porphyrin but mainly the corresponding 1′,8′-dideoxybilatriene-abc.

Because of its general resemblance to the chromophore of vitamin B_{12}, we have attempted to synthesise derivatives of the ring system (I). One approach was the condensation of 2,2′-bipyrroles with 2-formylpyrroles which, it was hoped, might give the linear tetrapyrroles (II; R = Me) by analogy with the corresponding reaction of dipyrromethanes with 2-formylpyrroles which gives the 1′,8′-dideoxybiladienes-ac [1] (*e.g.*, III); indeed some further examples of this reaction are provided in the present paper (see below). Moreover, the 1′,8′-dideoxy-1′,8′-dimethylbiladienes-ac (III; R = Me) can be oxidatively cyclised to porphyrins with cupric acetate and it was intended to apply a similar method for the cyclisation of compound (II; R = Me). The 2,2′-bipyrroles required for the reaction were prepared by Ullmann condensation of 2-iodopyrroles,[2] and the 2-formylpyrroles were prepared from pyrroles by use of phosphorus oxychloride and *NN*-dimethylformamide.[3] The physical properties, and particularly the ultraviolet and visible absorption spectra, of the products of condensation of 2,2′-bipyrroles and 2-formylpyrroles



(I)



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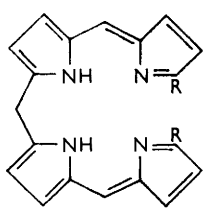


(III)

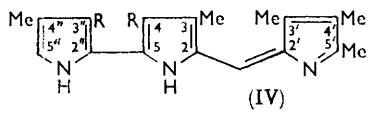
were thus expected to resemble those of the bromo-compounds (II; R = Br) which had been obtained by Ullmann self-condensations of 5,5′-dibromodipyrromethenes,[4] but this was not the case. Analysis and particularly nuclear magnetic resonance spectra of the new series (see below) showed that they were 5-pyrrol-2″-yldipyrromethenes (*e.g.*, IV) and thus, in spite of the excess of 2-formylpyrrole present, condensation had occurred at only one of the two unsubstituted α-positions of the 2,2′-bipyrrole system. The reason for the failure of the bipyrrole to react with two mol. of the 2-formylpyrrole is probably that the monocondensation product is a resonance hybrid with contributing canonical forms such as (V), which deactivate the molecule to further electrophilic attack at the other α-position of the 2,2′-bipyrrole system. In support of this viewpoint, it has been found that formylation of the 2,2′-bipyrroles by the *NN*-dimethylformamide–phosphorus oxychloride

[1] Johnson and Kay, *J.*, 1961, 2418.
[2] Grigg, Johnson, and Wasley, *J.*, 1963, 359.
[3] For a review see Kleinspehn and Briod, *J. Org. Chem.*, 1961, **26**, 1652.
[4] Johnson and Price, *J.*, 1960, 1649; Johnson and Kay, *Proc. Chem. Soc.*, 1961, 168.

method which involves cationic intermediates [5] has yielded mainly monoformyl compounds, *e.g.*, (VI), but in one case a small quantity of a diformyl derivative (VII) was also isolated.

Several examples of the synthesis of 5-pyrrol-2″-yldipyrromethenes have been provided in the present paper, from, on the one hand, 4,4′-dimethyl-, 4,4′-diethyl-, and 3,3′,4,4′-tetramethyl-2,2′-bipyrroles, and, on the other, 2-formyl-3,4,5-trimethyl- and 3-ethyl-5-formyl-2,4-dimethyl-pyrrole and ethyl 5-formyl-2,4-dimethylpyrrole-3-carboxylate in various permutations. In one case, the condensation of 3,3′,4,4′-tetramethyl-2,2′-bipyrrole with the above-mentioned pyrrole ester, the reaction took another course when methanol was substituted for ethanol as solvent, the sole product being diethyl 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate hydrobromide [6] (VIII), formed by self-condensation of the formylpyrrole ester.

The bacterial pigment, prodigiosin (IX), is a substituted 5-pyrrol-2″-yldipyrromethene [7-9] and it has been synthesised [7,9] by the condensation of 5-formyl-4-methoxy-2,2′-bipyrrole with 2-methyl-3-n-pentylpyrrole. This represents a modification of the present method, but it is clearly preferable when the bipyrrolic fragment is unsymmetrical as in (IX). We have prepared the compound (IV; R = CO_2Et) by condensation of diethyl 5-formyl-4,4′-dimethyl-2,2′-bipyrrole-3,3′-dicarboxylate and 3,4,5-trimethylpyrrole.



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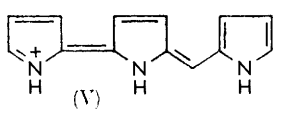

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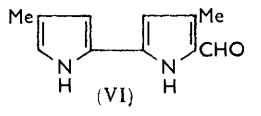
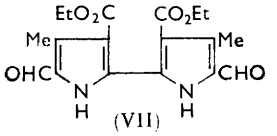


(VI)



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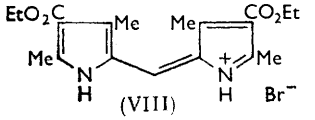

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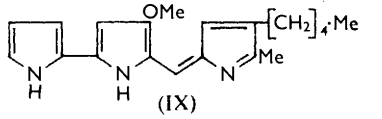


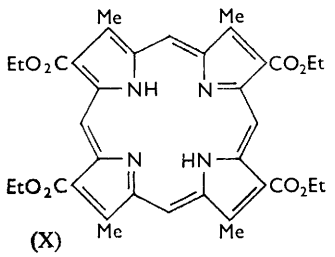
(IX)

The nuclear magnetic resonance spectra of the tripyrrolic compounds are consistent with the structures proposed and in particular the relative intensities of the signals from the nuclear substituents rule out four-ring structures such as (II; R = Me). As an example, the pentamethyl derivative (IV; R = H) in trifluoroacetic acid showed absorption at 2·25 (1), 2·47 (1), 2·76 (1), 4·80 (1), 7·07 (3), 7·44 (9), and 7·76 (3) τ, the figures in parentheses representing relative peak areas. The spectrum is clearly consistent with structure (IV; R = H) in that the fifteen methyl protons and four single protons (at positions 4, 3″, and 5″ and the *meso*-position) are all represented in the spectrum. Pyrrolic nuclear protons on carbon would be expected to absorb at about 2—3 τ and the absorption of a dipyrromethene salt [10] shows a methene-bridge proton at about 2·2 τ. However, one " aromatic " proton in compound (IV; R = H) giving rise to the absorption at 4·80 τ differs markedly from the others and, in an attempt to determine which proton this was, another pyrrolyldipyrromethene (IV; R = CO_2Et) was examined. This showed no absorption near 4·80 τ and it is therefore probable that one of the β-protons is in an unusual environment in the salts. Absorptions due to $^+$NH protons are observed in some examples around −0·5 τ. The ultraviolet and visible spectra of the salts of the 5-pyrrol-2″-yldipyrromethenes showed an intense band between 530 and 590 mμ but the position

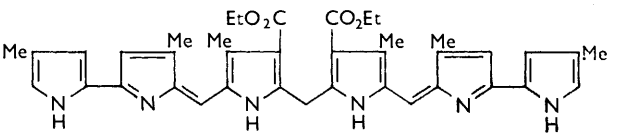
[5] Rapoport and Castagnoli, *J. Amer. Chem. Soc.*, 1962, **84**, 2178; Silverstein, Ryskiewicz, and Willard, *Organic Syntheses*, 1956, **36**, 74.
[6] Corwin and Brunings, *J. Amer. Chem. Soc.*, 1942, **64**, 2106.
[7] Wasserman, McKeon, Smith, and Forgione, *J. Amer. Chem. Soc.*, 1960, **82**, 506.
[8] Narni and Nicholaus, *Rend. Accad. Sci. fis. e mat.* (Soc. natz. sci. Napoli), 1959, **26**, 3; *Chem. Abs.*, 1961, **55**, 9370.
[9] Rapoport and Holden, *J. Amer. Chem. Soc.*, 1960, **82**, 5510; 1962, **84**, 635.
[10] E. Bullock, unpublished observation.

and intensity of the band varied widely according to the number and position of the substituents, *e.g.*, prodigiosin (IX) at pH 2·9, $\varepsilon_{max.}$ 132,000 at 541 mμ,[11] 5-(3″,4″-dimethylpyrrol-2″-yl)-3,3′,4,4′,5′-pentamethyldipyrromethene (IV; R = Me) hydrobromide, $\varepsilon_{max.}$ 69,000 at 587 mμ.

In another attempt to prepare derivatives of system (I) by direct condensation, the 2,2′-bipyrroles were condensed with 5,5′-diformyldipyrromethanes, themselves obtained by direct formylation of the dipyrromethane or the corresponding 5,5′-dicarboxylic acid which readily loses carbon dioxide during the formylation. This method again corresponds to a well-established porphyrin synthesis.[12] Methanolic hydrochloric acid under reflux was first investigated as a condensing agent for the reaction of diethyl 5,5′-diformyl-4,4′-dimethyldipyrromethane-3,3′-dicarboxylate and diethyl 4,4′-dimethyl-2,2′-bipyrrole-3,3′-dicarboxylate, but the product proved to be the porphyrin (X),[13] formed by the self-condensation of the diformyldipyrromethane. The same porphyrin was obtained from the diformyl compound by condensation [13] with diethyl 4,4′-dimethyldipyrromethane-3,3′-dicarboxylate as well as by self-condensation in hot methanolic hydrochloric acid.



(X)



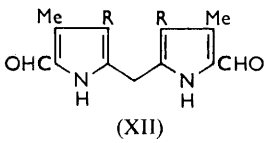
(XI)

However, when the 5,5′-diformyldipyrromethanes were condensed with 2,2′-bipyrroles in the presence of methanol containing a little hydrobromic acid at room temperature or below, crystalline salts were obtained which proved to be dihydrobromides, *e.g.*, of (XI), condensation having again occurred at only one of the unsubstituted α-positions of each of the 2,2′-bipyrrole fragments. The nature of the condensation products (XI) was established by analysis and spectral studies. The ultraviolet and visible spectra closely resembled those of the tripyrrolic compounds (IV), and the nuclear magnetic resonance spectra also had many features in common with those of the pyrrolyldipyrromethanes (IV). The nuclear magnetic resonance spectrum of compound (XI) in trifluoroacetic acid included the following absorptions: resolved triplet near 8·81 τ (methyl groups of ethyl esters); singlets at 7·66, 7·40, and 7·35 τ (nuclear methyl groups); distorted quartet near 5·49 τ (methylene groups of ethyl esters superimposed on nuclear methylene group[10]); singlets at 4·92, 2·82, and 2·58 τ (ring and methane bridge protons); and broad singlets at −0·34 0·51, and −0·88 ($^+$NH absorption). The ratio of the peak areas of the methyl triplet to the total ring methyl absorption was 1 : 3, and not 1 : 2 as would have been expected from a 4-ring macrocycle. The three non-equivalent $^+$NH absorptions were also consistent with structure (XI).

The free bases (XI) were readily obtained from the dihydrobromides, and they were further characterised as zinc complexes which were obtained by reaction with zinc acetate and appeared from analyses to contain two atoms of zinc and two acetate groups for each molecule of hexapyrrolic compound (XI), although the precise structure of the metal complexes was not determined and spectral evidence for the presence of acetoxy-groups

[11] Morgan and Tanner, *J.*, 1955, 3305.
[12] MacDonald, *J. Amer. Chem. Soc.*, 1957, **79**, 2659; Woodward, Ayer, Beaton, Bickelhaupt, Bonnett, Buchschacher, Closs, Dutler, Hannah, Hauck, Ho, Langemann, Le Goff, Leimgruber, Lwowski, Sauer, Valenta, and Volz, *ibid.*, 1960, **82**, 3800; Tarlton, MacDonald, and Baltazzi, *ibid.*, p. 4389.
[13] Arsenault, Bullock, and MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 4384.

was not obtained. Four examples of the hexapyrrolic compounds (XI) were prepared from the dialdehydes (XII; R = Me, Et, and CO_2Et) and the 4,4′-dialkyl-2,2′-bipyrroles, but diethyl 5,5′-diacetyl-4,4′-dimethyldipyrromethane-3,3′-dicarboxylate failed to condense



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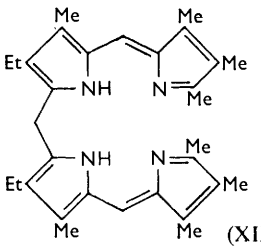

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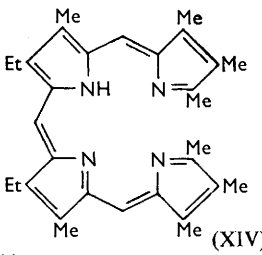

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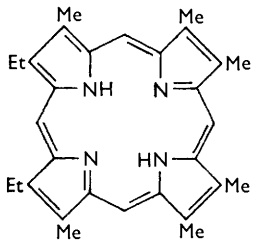

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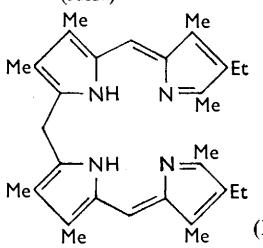

(XVI)

with diethyl 4,4′-dimethyl-2,2′-bipyrrole-3,3′-dicarboxylate. It is thus apparent that many of the methods of easy ring closure which can be used for the synthesis of the porphyrin macrocycle cannot be applied to the preparation of the ring system (I). Other methods are at present under investigation.

Ultraviolet irradiation of the 1′,8′-dideoxy-1′,8′-dimethylbiladienes-ac (II) was attempted with the object of effecting cyclisation to a derivative of the macrocycle (I), but in the case of compound (XIII) the product was mainly the corresponding 1′,8′-dideoxy-1′,8′-dimethylbilatriene-abc (XIV) and a porphyrin, probably 1,8-diethyl-2,3,4,5,6,7-hexamethylporphyrin (XV). The same porphyrin, as its copper complex, was obtained from the biladiene-ac (XIII) as well as from the isomer (XVI) by the action of cupric acetate [1] in chloroform–methanol, and a similar cyclisation of 1′,8′-dideoxy-1,4,5,8-tetraethyl-1′,2,3,6,7,8′-hexamethylbiladiene-ac gave the copper complex of ætioporphyrin II.

Experimental

Ultraviolet absorption spectra were determined for chloroform solutions except where otherwise stated. Molecular weights were determined by the Rast method. Light petroleum refers to the fraction of b. p. 60—80°.

(*A*) *Acyl-pyrroles and -dipyrromethanes.*—(i) 3-*Ethyl*-5-*formyl*-2,4-*dimethylpyrrole*. *NN*-Dimethylformamide (10 c.c.) was added to a solution of cryptopyrrole [14] (12 g.) in dry ether (150 c.c.), and the mixture was added dropwise with stirring to a solution of phosphorus oxychloride (9 c.c.) in dry ether (150 c.c.). The mixture was then stirred for a further 1 hr., the solvent removed under reduced pressure, and the residue of imine hydrochloride dissolved in water (300 c.c.). This solution was filtered to remove the dipyrromethene (500 mg.) formed as a by-product, and treated with aqueous sodium hydroxide until the aldehyde was precipitated. The product was separated, washed with water, and crystallised from aqueous ethanol, forming long colourless needles (6 g., 42%), m. p. 105—106° (lit.,[15] 106°). 2-Formyl-3,4,5-trimethylpyrrole (75%), m. p. 145—146°, was prepared in a similar manner from 2,3,4-trimethylpyrrole.[16]

[14] Johnson, Markham, Price, and Shaw, *J.*, 1958, 4254.
[15] Fischer and Schubert, *Ber.*, 1923, **56**, 1209; 1924, **57**, 612.
[16] Johnson, Shaw, and Wasley, *J.*, 1962, 2556.

(ii) *Ethyl 5-formyl-2,4-dimethylpyrrole-3-carboxylate.* Ethyl 2,4-dimethylpyrrole-3-carboxylate (2 g.) was treated in a manner similar to the above. On completion of the addition, the mixture was heated under reflux for 20 min. The solvent was removed under reduced pressure, the imine hydrochloride dissolved in water, and the aldehyde precipitated with aqueous sodium hydroxide. The product crystallised from aqueous ethanol as colourless needles (2 g., 85%), m. p. 170° (lit.,[17] 165°) (Found: C, 61·8; H, 6·5; N, 7·1. Calc. for $C_{10}H_{13}NO_3$: C, 61·5; H, 6·7; N, 7·2%).

(iii) *3,3'-Diethyl-5,5'-diformyl-4,4'-dimethyldipyrromethane.* Diethyl 3,3'-diethyl-4,4'-dimethyldipyrromethane-5,5'-dicarboxylate [18] (9 g.) was dissolved in ethanol (200 c.c.), and sodium hydroxide (2 g.) in water (50 c.c.) was added. The mixture was heated under reflux for 2 hr., the ethanol then distilled off, water (250 c.c.) added and the mixture filtered from any unchanged dipyrromethane. The solution was made acid to Congo Red with glacial acetic acid, the 5,5'-dicarboxylic acid being precipitated. This was extracted in ether (3 × 150 c.c.). The extract was dried ($MgSO_4$) and solvent removed under reduced pressure, leaving the dicarboxylic acid (7 g., 92%).

The acid (3·2 g.) was suspended in ethylene dichloride (80 c.c.) and *NN*-dimethylformamide (1·8 c.c.), and phosphorus oxychloride (1·9 c.c.) was added. The mixture was warmed gently on a steam-bath until reaction commenced, and then kept at room temperature for 6 hr. The solvent was removed under reduced pressure, and the residue treated with hot water until the filtrate was colourless, and then with aqueous sodium hydroxide until the aldehyde was precipitated. The *product* was separated, washed with water, and crystallised from chloroform–light petroleum as colourless needles (1·6 g., 56%), m. p. >300° (Found: C, 71·0; H, 7·25; N, 9·8%; *M*, 294. $C_{17}H_{22}N_2O_2$ requires C, 71·3; H, 7·75; N, 9·8%; *M*, 286).

(iv) *5,5'-Diformyl-3,3',4,4'-tetramethyldipyrromethane.* Diethyl 3,3',4,4'-tetramethyldipyrromethane-5,5'-dicarboxylate [19] was hydrolysed as above, except that the acid was too insoluble to be extracted in ether. The dicarboxylic acid (1·5 g.) was treated as in the previous experiment. The aldehyde was precipitated with aqueous sodium hydroxide, but did not crystallise (m. p. >300°; 1·2 g., 88%).

(v) *5,5'-Diacetyl-3,3'-diethyl-4,4'-dimethyldipyrromethane.* Freshly prepared 3,3'-diethyl-4,4'-dimethyldipyrromethane-5,5'-dicarboxylic acid (4·5 g.; see above) was dissolved in 1 : 2 acetic anhydride–acetic acid (130 c.c.) and to this was added 60% perchloric acid (1 c.c.). The mixture was kept at room temperature for 20 min., water (600 c.c.) was added, and the whole was kept overnight in the refrigerator. The *product* was separated, washed with aqueous sodium hydrogen carbonate, dried, and crystallised from chloroform–light petroleum (charcoal), forming colourless needles (3·1 g., 70%), m. p. 192—194° (Found: C, 72·6; H, 8·45; N, 8·75%; *M*, 337. $C_{19}H_{26}N_2O_2$ requires C, 72·6; H, 8·35; N, 8·9%; *M*, 314).

(vi) *Diethyl 5,5'-diacetyl-4,4'-dimethyldipyrromethane-3,3'-dicarboxylate.* Diethyl 4,4'-dimethyldipyrromethane-3,3'-dicarboxylate [20] (1 g.) was dissolved in glacial acetic acid (10 c.c.) and acetic anhydride (11·5 c.c.). 60% Perchloric acid (0·15 c.c.) was added to the solution which was kept at room temperature for 30 min., then poured into water (300 c.c.) and stirred for 15 min. The precipitated *diacetyl derivative* was separated and crystallised from ethanol; it (0·75 g., 60%) had m. p. 152—158°, raised to 163—165° (colourless needles) by recrystallisation from ethanol followed by sublimation at 170°/0·1 mm. (Found: C, 63·1; H, 6·45; N, 6·75. $C_{21}H_{26}N_2O_6$ requires C, 62·7; H, 6·5; N, 6·95%). The infrared spectrum ($CHCl_3$ solution) showed strong max. at 3400 (>NH), 1680 (ester C=O), and 1640 (ketonic C=O) $cm.^{-1}$.

(*B*) *5-Formyl-2,2'-bipyrroles.*—(i) *5-Formyl-4,4'-dimethyl-2,2'-bipyrrole.* 4,4'-Dimethyl-2,2'-bipyrrole [2] (30 mg.) was dissolved in ethylene dichloride (20 c.c.) and *NN*-dimethylformamide (28 mg., 2 mol.), and phosphorus oxychloride (58 mg., 2 mol.) was added. The deep green solution was kept for 4 hr. and the solvent was removed under reduced pressure, leaving a pale yellow solid. This solid was dissolved in water (100 c.c.) and hydrolysed with 10% aqueous sodium hydroxide, until the *formyl compound* was precipitated. It was separated, washed with water, and crystallised from chloroform–light petroleum, then sublimed in a vacuum at 150°; it formed pale yellow needles (25 mg., 63%), m. p. 203—205° (decomp.)

[17] Fischer and Zerweck, *Ber.*, 1922, **55**, 1945.
[18] Fischer and Halbig, *Annalen*, 1926, **447**, 123; **448**, 199.
[19] Fischer and Walach, *Annalen*, 1926, **450**, 127.
[20] Andrews, Corwin, and Sharp, *J. Amer. Chem. Soc.*, 1950, **72**, 491.

(Found: C, 69·9; H, 6·5%; *M*, 183. $C_{11}H_{12}N_2O$ requires C, 70·2; H, 6·4%; *M*, 188), $\lambda_{max.}$ (in $CHCl_3$) 249 and 380 mμ (ε 7760 and 18,600, respectively).

(ii) *Diethyl 5-formyl-4,4′-dimethyl- and 5,5′-diformyl-4,4′-dimethyl-2,2′-bipyrrole-3,3′-dicarboxylate.* Diethyl 4,4′-dimethyl-2,2′-bipyrrole-3,3′-dicarboxylate [2] (2·32 g.) was dissolved in warm *NN*-dimethylformamide (50 c.c.) and the solution cooled to room temperature. Phosphorus oxychloride (1·40 c.c., 2 mol.) was added dropwise with stirring during 10 min., and the green solution heated on the steam-bath for 3½ hr., kept at room temperature for a further 3 hr., and then poured into water (450 c.c.). 10% Aqueous sodium hydroxide solution was added until a smell of amine was apparent, and, after a further 30 min., the solid which had been precipitated was separated, washed with water, dissolved in ethanol (150 c.c.), and heated under reflux with charcoal (1 g.) for 20 min. The hot solution was filtered and kept overnight. A small amount of precipitated diformyl compound was treated separately (see below). The filtrate was concentrated to *ca.* 30 c.c. and the crystalline *monoformyl derivative* (0·74 g., 27%), m. p. 193—197°, which was eventually formed was separated. Sublimation at 200°/0·2 mm. gave pale yellow needles, m. p. 202—203° (Found: C, 61·5; H, 6·2; N, 8·5%; *M*, 352. $C_{17}H_{22}N_2O_5$ requires C, 61·1; H, 6·6; N, 8·4%; *M*, 334), $\lambda_{max.}$ 254, 364, and 377 mμ (ε 17,000, 27,900, and 25,350, respectively).

The insoluble material was purified by extraction (Soxhlet) with chloroform (75 c.c.), and sublimation at 210°/0·1 mm. to give yellow plates of the *diformyl compound*, m. p. 295° (decomp.) (Found: C, 59·9; H, 6·2; N, 7·95. $C_{18}H_{22}N_2O_6$ requires C, 59·65; H, 6·1; N, 7·75%), $\lambda_{max.}$ 264 and 393 mμ (ε 40,450 and 14,800) with inflections at 292 and 409 mμ (ε 12,950 and 13,700, respectively).

(*C*) *5-Pyrrol-2″-yldipyrromethanes.*—(i) *3,3′,4′,5′-Tetramethyl-5-(4″-methylpyrrol-2″-yl)dipyrromethene hydrobromide.* 4.4′-Dimethyl-2,2′-bipyrrole [2] (160 mg.), and 2-formyl-3,4,5-trimethylpyrrole [16] (140 mg.) were dissolved in methanol (50 c.c.), and hydrogen bromide (7 drops of 48%) in acetic acid was added. The solution immediately became deep purple, and the *hydrobromide* crystallised after about 10 min. It was separated and crystallised from chloroform–light petroleum as fine blue needles (250 mg., 68%), m. p. >350° (Found: C, 59·6; H, 5·95; N, 11·5; Br, 21·7. $C_{18}H_{22}BrN_3$ requires C, 60·0; H, 6·15; N, 11·65; Br, 22·2%), $\lambda_{max.}$ 302, 376, 396, 545 (shoulder), and 576 mμ (ε 15,400, 7000, 6750, 44,800, and 111,000, respectively).

The hydrobromide (50 mg.) was dissolved in chloroform (40 c.c.), and aqueous ammonia (2 drops; *d* 0·88) was added. The solution changed from violet to orange-red and it was chromatographed on alumina (Spence's type H) and eluted with chloroform. The free base was eluted as an orange-red solution and after removal of the solvent under reduced pressure crystallised from light petroleum as glistening green prisms, m. p. 208° (decomp.), $\lambda_{max.}$ (in EtOH) 228 (shoulder), 286, 339, and 497 mμ (ε 7600, 9450, 4900, and 26,600, respectively).

(ii) *4′-Ethyl-3,3′,5′-trimethyl-5-(4″-methylpyrrol-2″-yl)dipyrromethene hydrobromide.* Prepared similarly from 4,4′-dimethyl-2,2′-bipyrrole [2] (160 mg.) and 3-ethyl-5-formyl-2,4-dimethylpyrrole (150 mg.; above), this *hydrobromide* (185 mg., 51%) crystallised from chloroform–light petroleum as blue needles, m. p. >300° (Found: C, 60·9; H, 6·4; N, 10·8; Br, 20·9. $C_{19}H_{24}BrN_3$ requires C, 60·9; H, 6·45; N, 11·2; Br, 21·35%), $\lambda_{max.}$ 303, 377, 396, 545 (shoulder), and 576 mμ (ε 14,900, 6850, 6700, 46,900, and 115,000, respectively).

The free base formed glistening green prisms (from light petroleum), m. p. 187° (decomp.), $\lambda_{max.}$ (in EtOH) 231 (shoulder), 286, 341, and 502 mμ (ε 9040, 11,300, 6020, and 38,400, respectively).

(iii) *Ethyl 3,3′,5′-trimethyl-5-(4″-methylpyrrol-2″-yl)dipyrromethene-4-carboxylate hydrobromide.* Prepared similarly from 4,4′-dimethyl-2,2′-bipyrrole [2] (160 mg.) and ethyl 5-formyl-2,4-dimethylpyrrole-3-carboxylate (200 mg.; above), the *hydrobromide* (220 mg., 53%) crystallised from chloroform–light petroleum as blue needles, m. p. >300° (Found: C, 57·5; H, 5·65; N, 9·6; Br, 19·0. $C_{20}H_{24}BrN_3O_2$ requires C, 57·4; H, 5·8; N, 10·05; Br, 19·1%), $\lambda_{max.}$ 270, 300, 348, 379, 393, 534, and 566 mμ (ε 7600, 14,300, 5420, 6220, 5620, 38,600, and 99,200, respectively).

(iv) *3-Ethyl-5-(4″-ethylpyrrol-2″-yl)-3′,4′,5′-trimethyldipyrromethene and its hydrobromide.* 2-Formyl-3,4,5-trimethylpyrrole [16] (820 mg., 2 mol.) was dissolved in warm methanol (50 c.c.), and oxygen-free nitrogen was bubbled through the solution for 5 min. 4,4′-Diethyl-2,2′-bipyrrole [2] (559 mg., 1 mol.) was added to the solution which was warmed until the bipyrrole dissolved and then cooled to room temperature while the nitrogen atmosphere was maintained.

Hydrogen bromide (1·1 c.c. of a 50% w/v solution in glacial acetic acid) was added. The solution immediately became red-purple and the *hydrobromide* crystallised. After 20 min. at room temperature, the salt was separated, washed with methanol, and dried at 90° (933 mg., 81%). It crystallised from chloroform–methanol as red-brown feathery needles (Found: C, 62·1; H, 6·75; N, 10·7; Br, 21·1. $C_{20}H_{26}BrN_3$ requires C, 61·85; H, 6·75; N, 10·8; Br, 20·6%), $\lambda_{max.}$ 302, 379, 398, and 580 mμ (ε 13,800, 5980, 5920, and 111,000, respectively), with inflections at 345 and 545 mμ (ε 4800 and 45,300, respectively).

The free *base* was obtained by shaking a chloroform solution of the salt with dilute aqueous ammonia and formed green prisms (light petroleum), m. p. 187—189° (decomp.) (Found: C, 77·7; H, 8·35; N, 14·0. $C_{20}H_{25}N_5$ requires C, 78·1; H, 8·2; N, 13·7%), $\lambda_{max.}$ (in EtOH) 286, 338, 501, and 570 mμ (ε 12,200, 6080, 38,500, and 9350, respectively) with a shoulder at 228 mμ (ε 9600).

(v) *3,4′-Diethyl-5-(4″-ethylpyrrol-2″-yl)-3′,5′-dimethyldipyrromethene hydrobromide.* 4,4′-Diethyl-2,2′-bipyrrole (566 mg., 1 mol.) and 3-ethyl-5-formyl-2,4-dimethylpyrrole (910 mg., 2 mol.) were allowed to react in methanol (50 c.c.) containing hydrobromic acid (1·1 c.c. of 48% w/v solution in acetic acid) in an atmosphere of nitrogen. After 80 min. at room temperature the crystalline *hydrobromide* was separated, washed with methanol, and dried at 100° (985 mg., 81·5%). Recrystallisation from chloroform–methanol gave reddish needles with a blue reflex (Found: C, 62·6; H, 7·3; N, 10·6; Br, 19·7. $C_{21}H_{28}BrN_3$ requires C, 62·65; H, 7·0; N, 10·45; Br, 19·85%), $\lambda_{max.}$ 302, 376, 395, and 575 mμ (ε 15,850, 6770, 6680, and 122,000, respectively) with a shoulder at 540 mμ (ε 46,800).

(vi) *Ethyl 3-ethyl-5-(4″-ethylpyrrol-2″-yl)-3′,5′-dimethyldipyrromethene-4-carboxylate hydrobromide.* This was prepared similarly from ethyl 5-formyl-2,4-dimethylpyrrole-3-carboxylate (1·035 g., 2·58 mol.) and 4,4′-diethyl-2,2′-bipyrrole (385 mg., 1 mol.) in methanol (40 c.c.) with the addition of 50% w/v hydrogen bromide in acetic acid (0·8 c.c.). The mixture was stored in an atmosphere of nitrogen for 19½ hr., then the precipitated *hydrobromide* was separated, washed with methanol, and dried at 90° (840 mg., 91%). It crystallised from chloroform–methanol as red rods with a blue reflex (Found: C, 59·2; H, 6·4; N, 9·35; Br, 17·4. $C_{22}H_{28}BrN_3O_2$ requires C, 59·2; H, 6·3; N, 9·65; Br, 17·9%), $\lambda_{max.}$ 271, 300, 348, 379·5, 395, and 570 mμ (ε 7600, 13,500, 5650, 6600, 8700, and 109,000, respectively) with a shoulder at 539 mμ (ε 60,400).

(vii) *5-(3″,4″-Dimethylpyrrol-2″-yl)-3,3′,4,4′,5′-pentamethyldipyrromethene hydrobromide.* The reaction was carried out as in the previous experiment with 2-formyl-3,4,5-trimethylpyrrole (762 mg., 2 mol.) and 3,3′,4,4′-tetramethyl-2,2′-bipyrrole (520 mg., 1 mol.) in ethanol (50 c.c.) in the presence of hydrogen bromide (0·55 c.c. of a 50% w/v solution in glacial acetic acid). The mixture was stored at room temperature for 55 min., then the crystalline *salt* was separated, washed with ethanol, and dried at 90° (689 mg., 64%). It recrystallised from chloroform–methanol as red-brown feathery needles (Found: C, 61·8; H, 6·6; N, 11·0; Br, 20·6. $C_{20}H_{26}BrN_3$ requires C, 61·85; H, 6·75; N, 10·8; Br, 20·6%), $\lambda_{max.}$ 268, 311, 398, and 587 mμ (ε 8250, 7750, 10,250, and 69,000, respectively).

(viii) *Ethyl 5-(3″,4″-dimethylpyrrol-2″-yl)-3,3′,4,5′-tetramethyldipyrromethene-4′-carboxylate hydrobromide* was prepared similarly from ethyl 5-formyl-2,4-dimethylpyrrole-3-carboxylate (1·11 g., 2·58 mol.) and 3,3′,4,4′-tetramethyl-2,2′-bipyrrole (415 mg., 1 mol.) in ethanol (37·5 c.c.) in an atmosphere of nitrogen in the presence of a 50% solution (0·83 c.c.) of hydrogen bromide in acetic acid. After 6 hr. at room temperature, the *salt* was separated, washed, and dried (650 mg., 68%); it crystallised from chloroform–methanol as olive-green needles (Found: C, 59·1; H, 6·55; N, 9·2; Br, 17·8. $C_{22}H_{28}BrN_3O_2$ requires C, 59·2; H, 6·3; N, 9·6; Br, 17·9%), $\lambda_{max.}$ 269, 304, 404, and 586 mμ (ε 9200, 7700, 10,250, and 66,700, respectively), with shoulders at 491 and 557 mμ (ε 12,600 and 49,500).

When the experiment was repeated but with methanol as solvent and the reaction mixture at room temperature for 19 hr., a different hydrobromide (272 mg.) was obtained which crystallised from chloroform–methanol as red plates with a blue sheen, $\lambda_{max.}$ 248, 348, and 475 mμ (ε 9970, 3700, and 148,000, respectively). This product was identified as diethyl 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate hydrobromide [6] (Found: C, 53·7; H, 5·95; N, 6·5; Br, 18·5. Calc. for $C_{19}H_{25}BrN_2O_4$: C, 53·65; H, 5·9; N, 6·6; Br, 18·8%).

(ix) *Ethyl 5-(3″-ethoxycarbonyl-4″-methylpyrrol-2″-yl)-3,3′,4′,5′-tetramethyldipyrromethene-4-carboxylate hydrobromide.* Diethyl 5-formyl-4,4′-dimethyl-2,2′-bipyrrole-3,3′-dicarboxylate (700 mg.) and 2,3,4-trimethylpyrrole (458 mg.) were dissolved in ethanol (55 c.c.). The solution

was cooled to room temperature and hydrogen bromide (1 c.c of 48% w/v solution in acetic acid) added. The *product* crystallised at once. After 50 min. at room temperature it was separated, washed with ethanol, and dried at 100° (932 mg., 88%). From chloroform–methanol it formed red rods with a blue reflex (Found: C, 57·1; H, 5·9; N, 8·35; Br, 15·7. $C_{24}H_{30}BrN_3O_4$ requires C, 57·1; H, 6·0; N, 8·35; Br, 15·85%), $\lambda_{max.}$ 323 and 560 mμ (ε 20,950 and 68,400, respectively).

(*D*) 1′,8′-*Dideoxy*-1′,8′-*dipyrrol*-2″-*ylbiladienes-ac.*—(i) 1′,8′-*Dideoxy*-4,5-*diethoxycarbonyl*-2,3,6,7-*tetramethyl*-1′,8′-*di*-(4″-*methylpyrrol*-2″-*yl*) *biladiene-ac and its dihydrobromide.* 4,4′-Dimethyl-2,2′-bipyrrole (160 mg., 2·34 mol.) and diethyl 5,5′-diformyl-4,4′-dimethyldipyrromethane-3,3′-dicarboxylate [18] (160 mg., 1 mol.) were dissolved in methanol (50 c.c.), and hydrogen bromide (8 drops of a 48% solution in acetic acid) was added. The mixture was kept for 2 hr., then the precipitated *dihydrobromide* was separated; it crystallised from chloroform as dark green needles (240 mg., 64%), m. p. >300° (Found: C, 57·2; H, 5·15; N, 9·95; Br, 20·1. $C_{39}H_{42}Br_2N_6O_4$ requires C, 57·2; H, 5·15; N, 10·25; Br, 19·55%), $\lambda_{max.}$ 300, 382, 397, 525, 564, and 590 mμ (ε 25,650, 10,250, 12,450, 12,300, 98,600, and 135,000, respectively).

The dihydrobromide (100 mg.) was dissolved in chloroform (150 c.c.) and shaken with a slight excess of dilute aqueous ammonia. The chloroform layer was separated, washed with water (3 × 100 c.c.), dried, and chromatographed on alumina (Spence's type H). The free *base* was eluted as an orange-red solution from which it was isolated and crystallised from chloroform–methanol as orange needles (75 mg.), m. p. >300° (Found: C, 71·2; H, 6·5. $C_{39}H_{40}N_6O_4$ requires C, 71·4; H, 6·15%), $\lambda_{max.}$ 289, 340, 481, and 500 mμ (ε 19,500, 12,900, 67,600 and 66,070, respectively).

The free base (50 mg.) was dissolved in chloroform (50 c.c.), and a solution of zinc acetate (100 mg.) in methanol (10 c.c.) was added. The colour of the solution changed from orange-red to red-violet and the *zinc complex* separated; it crystallised from chloroform–methanol as red-purple needles (50 mg.), m. p. >300° (Found: C, 56·9; H, 5·1; N, 8·9; Zn, 15·1. $C_{43}H_{46}N_6O_8Zn_2$ requires C, 57·0; H, 5·1; N, 9·2; Zn, 14·5%), $\lambda_{max.}$ 276, 294, 353, 478 (shoulder), 505, 553, and 585 mμ (ε 18,140, 19,420, 13,280, 64,900, 203,300, 33,550, and 23,300, respectively).

When the zinc complex (10 mg.) in chloroform (30 c.c.) was mixed with 48% hydrogen bromide (1 c.c. of acetic acid solution) and the mixture was shaken for 30 min. the colour of the solution changed from red-violet to blue-violet and the solid hydrobromide separated. This formed green needles from chloroform and the absorption spectrum was identical with that of the base hydrobromide (above).

(ii) 1′,8′-*Dideoxy*-4,5-*diethoxycarbonyl*-2,7-*diethyl*-1′,8′-*di*-(4″-*ethylpyrrol*-2″-*yl*)-3,6-*dimethylbiladiene-ac and its hydrobromide.* Diethyl 5,5′-diformyl-4,4′-dimethyldipyrromethane-3,3′-dicarboxylate [18] (376 mg., 1 mol.) was dissolved in methanol (37·5 c.c.), and oxygen-free nitrogen bubbled through the solution for 5 min. 4,4′-Diethyl-2,2′-bipyrrole (188 mg., 1 mol.) was then added while the nitrogen atmosphere was maintained. The solution was cooled and hydrogen bromide (0·38 c.c. of a 50% w/v solution in glacial acetic acid) was added. The flask was tightly stoppered and the purple solution kept at room temperature for 2½ hr. The *salt* was separated (148 mg., 34% based on the bipyrrole) and crystallised from chloroform as green prisms (Found: C, 53·4; H, 5·45; N, 8·25; Halogen, calc. as Br, 35·0. $C_{43}H_{52}Br_2N_6O_4,CHCl_3$ requires C, 53·05; H, 5·35; N, 8·45; Halogen as Br, 34·4%), $\lambda_{max.}$ 302, 379, 393, 520, and 587 mμ (ε 29,700, 13,320, 13,650, 117,800, and 144,800, respectively). The purple mother-liquor from the reaction was poured into dilute aqueous ammonia and extracted with chloroform (6 × 50 c.c.). The mixed chloroform extracts were washed with water (2 × 150 c.c.), dried, and concentrated (to 50 c.c.). The solution was chromatographed on Spence's alumina (type H) and eluted with chloroform. The first orange-red fraction contained the free *base* which crystallised from chloroform–methanol as orange needles (54 mg., 15% based on bipyrrole) (Found: C, 72·2; H, 6·8; N, 12·6. $C_{43}H_{50}N_6O_4$ requires C, 72·25; H, 7·05; N, 12·75%), $\lambda_{max.}$ 289, 341, 486, and 503 mμ (ε 19,900, 13,800, 69,600, and 69,300, respectively).

The experiment was repeated with 1·6 mol. of the bipyrrole. The yield of salt was 65% and of the free base 13·7% (based on bipyrrole). When 2 mol. of the bipyrrole were used the yield of salt was 85% and of free base 9·7%. The *zinc derivative* of the base formed purple needles (from chloroform–methanol) [Found: C, 58·8; H, 5·9; N, 8·7; Ash, 18·5. $C_{47}H_{56}N_6O_8Zn_2$ requires C, 58·6; H, 5·85; N, 8·7; Ash (ZnO), 16·5%], $\lambda_{max.}$ 272, 295, 358, 477 (shoulder), 501, 551, and 585 mμ (ε 17,700, 18,000, 13,700, 72,500, 211,500, 33,750, and 22,500, respectively).

(iii) 1′,8′-*Dideoxy*-4,5-*diethyl*-2,3,6,7-*tetramethyl*-1′,8′-*di*-(4″-*methylpyrrol*-2″-*yl*)*biladiene-ac dihydrobromide*. Prepared similarly from 4,4′-dimethyl-2,2′-bipyrrole (160 mg.) and 3,3′-diethyl-5,5′-diformyl-4,4′-dimethyldipyrromethane (170 mg.), this *dihydrobromide* crystallised from chloroform as golden-green needles (260 mg., 68%), m. p. >300° (Found: C, 60·8; H, 5·85; N, 11·0; Br, 22·05. $C_{37}H_{44}Br_2N_6$ requires C, 60·7; H, 6·05; N, 11·45; Br, 21·85%), $\lambda_{max.}$ 306, 382, 403, 441, 540, 583, and 627 mμ (ε 29,300, 14,000, 15,100, 5770, 58,700, 82,700, and 155,600, respectively).

(iv) 1′,8′-*Dideoxy*-2,3,4,5,6,7-*hexamethyl*-1′,8′-*di*-(4″-*methylpyrrol*-2″-*yl*)*biladiene-ac dihydrobromide*. Prepared similarly from 4,4′-dimethyl-2,2′-bipyrrole (3 mg.) and 5,5′-diformyl-3,3′,4,4′-tetramethyldipyrromethane (3 mg.), this *dihydrobromide* (5 mg.) crystallised from chloroform as green needles with a golden sheen, $\lambda_{max.}$ 303, 379, 403, 438, 535, and 623 mμ (ε 29,500, 13,500, 14,450, 5500, 77,600, and 141,300, respectively).

(v) *Tetraethyl* 1,4,5,8-*tetramethylporphyrin*-2,3,6,7-*tetracarboxylate*. (*a*) Diethyl 4,4′-dimethyl-2,2′-bipyrrole-3,3′-dicarboxylate [2] (171 mg.) and diethyl 5,5′-diformyl-4,4′-dimethyldipyrromethane-dicarboxylate [18] (208 mg.) were heated under reflux in methanol (273 c.c.) containing concentrated hydrochloric acid (3·5 ml.) for 4 hr., and the solution was then cooled and kept at room temperature for 13 hr. The crystals were separated, washed with methanol, and dried (50 mg.). From chloroform, the porphyrin [13] formed flat blue needles (Found: C, 66·2; H, 5·7; N, 8·5. Calc. for $C_{36}H_{38}N_4O_8$: C, 66·5; H, 5·85; N, 8·55%), $\lambda_{max.}$ 280, 421, 519, 533, 596, and 652 mμ (ε 22,000, 250,000, 13,000, 7000, 5000, and 4400, respectively).

(*b*) Prepared by a similar method from diethyl 4,4′-dimethyldipyrromethane-3,3′-dicarboxylate [20] (176 mg.) and 5,5′-diformyl-4,4′-dimethyldipyrromethane-3,3′-dicarboxylate [18] (208 mg.) in methanol (273 c.c.) containing concentrated hydrochloric acid (3·5 c.c.) (cf. ref. 13), the porphyrin (106 mg., 29%) crystallised from the cooled reaction mixture and recrystallised from chloroform as flat blue needles which were identical with the above preparation.

(*c*) Diethyl 5,5′-diformyl-4,4′-dimethyldipyrromethane-3,3′-dicarboxylate (50 mg.) was heated under reflux in methanol (50 c.c.) containing concentrated hydrochloric acid (1 c.c.) as above. The product (19 mg.) which crystallised from the reaction mixture had the same ultraviolet and visible light absorption as the previous two preparations.

(*E*) 1′,8′-*Dideoxy*-1′,8′-*dimethylbiladienes-ac and Cyclisation Reactions* (cf. ref. 1).—(i) 1′,8′-*Dideoxy*-1,4,5,8-*tetraethyl*-1′,2,3,6,7,8′-*hexamethylbiladiene-ac dihydrobromide*. 3,3′-Diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (1·5 g.; see above) was suspended in methanol (50 c.c.) and 3-ethyl-5-formyl-2,4-dimethylpyrrole was added followed by hydrogen bromide (1 c.c. of a 48% solution in acetic acid). The mixture was heated under reflux for 5 min., then cooled. The product crystallised as dark green rods of the *dihydrobromide* which recrystallised from chloroform–light petroleum as reddish-green rods (1·5 g., 46%), m. p. >300° (Found: C, 60·2; H, 6·8; N, 8·3; Br, 24·6. $C_{33}H_{46}Br_2N_4$ requires C, 60·2; H, 7·05; N, 8·5; Br, 24·25%), $\lambda_{max.}$ 284, 377, 466, and 533 mμ (ε 4170, 17,000, 28,200, and 214,000, respectively).

The dihydrobromide (300 mg.) was dissolved in methanol (75 c.c.), and an ethanolic solution of zinc acetate (250 mg.) was added. The mixture was heated under reflux for 5 min., then kept for 2 hr. The *zinc complex* separated and crystallised from chloroform–methanol as reddish-green needles (150 mg.), m. p. 258° (decomp.) (Found: N, 9·95. $C_{33}H_{42}N_4Zn$ requires N, 10·0%), $\lambda_{max.}$ 292, 312, 380, 467, and 515 mμ (ε 6600, 6920, 11,200, 75,900, and 74,100, respectively).

(ii) 1′,8′-*Dideoxy*-1,1′,2,3,4,5,6,7,8,8′-*decamethylbiladiene-ac dihydrobromide*. Prepared similarly from 3,3′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid (see above) and 2-formyl-3,4,5-trimethylpyrrole, the *product* (65%) crystallised from chloroform–light petroleum as green rods with a reddish lustre, m. p. >300° (Found: C, 58·0; H, 6·35; N, 8·85; Br, 26·55. $C_{29}H_{38}Br_2N_4$ requires C, 57·8; H, 6·35; N, 9·3; Br, 26·55%), $\lambda_{max.}$ 288, 372, 454, and 527 mμ (ε 3310, 15,800, 25,100, and 190,000, respectively). The *zinc complex* formed reddish-green needles (Found: N, 11·1. $C_{29}H_{34}N_4Zn$ requires N, 11·1%), $\lambda_{max.}$ 290, 313, 380, 471, and 517 mμ (ε 6170, 6460, 10,000, 64,600, and 67,600, respectively).

(iii) 1′,8′-*Dideoxy*-4,5-*diethyl*-1,1′,2,3,6,7,8,8′-*octamethylbiladiene-ac dihydrobromide*. Prepared from 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (1·5 g.) and 2-formyl-3,4,5-trimethylpyrrole (1·4 g.), the *product* (1·4 g., 44%) crystallised from chloroform–light petroleum as reddish-green needles (Found: C, 58·8; H, 6·4; N, 8·8; Br, 25·2. $C_{31}H_{42}Br_2N_4$ requires C, 59·05; H, 6·7; N, 8·9; Br, 25·35%), $\lambda_{max.}$ 284, 374, 464, and 531 mμ (ε 4470, 13,500, 24,000, and 182,000, respectively). The *zinc complex* formed reddish-green

needles (from chloroform–methanol) (Found: N, 10·5. $C_{31}H_{38}N_4Zn$ requires N, 10·5%), $\lambda_{max.}$ 293, 312, 385, 471, and 525 mμ (ε 16,600, 1480, 11,500, 72,500, and 66,100, respectively).

(iv) 1',8'-*Dideoxy*-1,8-*diethyl*-1',2,3,4,5,6,7,8'-*octamethylbiladiene-ac dihydrobromide*. Prepared similarly from 3,3',4,4'-tetramethyldipyrromethane-5,5'-dicarboxylic acid and 3-ethyl-5-formyl-2,4-dimethylpyrrole, the *hydrobromide* (50%) was obtained as reddish-green rods (from chloroform–light petroleum) (Found: C, 58·6; H, 6·4; N, 8·8; Br, 25·0. $C_{31}H_{42}Br_2N_4$ requires C, 59·05; H, 6·7; N, 8·9; Br, 25·35%), $\lambda_{max.}$ 290, 377, 456, 460, and 528 mμ (ε 2950, 15,500, 26,900, 25,100, and 200,000, respectively).

Ultraviolet Irradiation of 1',8'-*Dideoxy*-4,5-*diethyl*-1,1',2,3,6,7,8,8'-*octamethylbiladiene-ac*. The dihydrobromide (500 mg.) of this compound was dissolved in methanol (500 c.c.), and aqueous ammonia (*d* 0·88; 1 c.c.) was added. The solution immediately changed from orange-red to greenish-yellow, and it was irradiated under an ultraviolet lamp for 18 hr. The solvent was removed under reduced pressure and the residue dissolved in chloroform (50 c.c.), dried ($MgSO_4$), chromatographed on alumina, and eluted with more chloroform. The first red band was identified as a porphyrin, probably 1,2-diethyl-3,4,5,6,7,8-hexamethylporphyrin [1] (hand spectroscope). The solvent was removed from this fraction and the residue crystallised from chloroform–methanol as purple needles (17 mg.), m. p. >300° (Found: N, 12·2. Calc. for $C_{30}H_{34}N_4$: N, 12·45%), $\lambda_{max.}$ 401, 502, 535, 570, and 624 mμ (ε 129,000, 10,200, 7950, 5370, and 3890, respectively). A second band, bright green, gave, on removal of the solvent and crystallisation from methanol, 1',8'-*dideoxy*-4,5-*diethyl*-1,1',2,3,6,7,8,8'-*octamethylbilatriene-abc* as blue needles (150 mg.) (Found: C, 79·8; H, 8·05; N, 12·4. $C_{31}H_{38}N_4$ requires C, 79·75; H, 8·2; N, 12·0%), $\lambda_{max.}$ 305, 385, and 705 mμ (ε 19,950, 53,700, and 12,000, respectively) with an inflection at 605 mμ (ε 10,500).

1,2-*Diethyl*-3,4,5,6,7,8-*hexamethylporphyrin*.—(i) 1',8'-Dideoxy-4,5-diethyl-1,1',2,3,6,7,8,8'-octamethylbiladiene-ac dihydrobromide (150 mg.) in chloroform (30 c.c.) was cyclised by means of cupric acetate (150 mg.) in methanol (20 c.c.). The mixture was heated under reflux for 2 min., the chloroform removed by distillation, and the residue cooled. The solid which separated was dissolved in chloroform and chromatographed on alumina, and the porphyrin band (hand spectroscope) was collected. Removal of the solvent and crystallisation of the copper complex [1] from chloroform–methanol gave purple needles (22 mg., 19%) [Found: C, 70·5; H, 6·05; N, 11·1; Ash (CuO), 15·3. Calc. for $C_{30}H_{32}CuN_4$: C, 70·35; H, 6·3; N, 10·95; CuO, 15·1%], $\lambda_{max.}$ 330, 398, 527, and 564 mμ (ε 17,400, 339,000, 12,600, and 25,100, respectively).

The copper complex (50 mg.) was suspended in concentrated sulphuric acid (5 c.c.) and heated on a steam-bath for 10 min. The solution was cooled, diluted, and basified with aqueous ammonia, and extracted with chloroform. The dried extract was purified by chromatography on alumina, and the porphyrin fraction yielded purple needles (35 mg.) (from chloroform–methanol) (Found: C, 79·7; H, 7·5; N, 12·25. Calc. for $C_{30}H_{34}N_4$: C, 79·95; H, 7·6; N, 12·45%), $\lambda_{max.}$ 397, 499, 534, 567, and 620 mμ (ε 126,000, 10,000, 8130, 5500, and 3800, respectively).

(ii) The copper complex (25 mg., 21%) was prepared by a similar method from 1',8'-dideoxy-1,8-diethyl-1',2,3,4,5,6,7,8'-octamethylbiladiene-ac dihydrobromide (150 mg.) [Found: C, 70·2; H, 6·1; N, 11·1; Ash (CuO) 15·3%]. The light absorption was identical with that of the previous preparation.

Ætioporphyrin-II Copper Complex.—Prepared similarly from 1',8'-dideoxy-1,4,5,8-tetraethyl-1',2,3,6,7,8'-hexamethylbiladiene-ac dihydrobromide (150 mg.), this copper complex (26 mg., 22%) formed purple needles (from chloroform–methanol) (Found: C, 71·2; H, 6·95; N, 9·95. Calc. for $C_{32}H_{36}CuN_4$: C, 71·15; H, 6·7; N, 10·35%), $\lambda_{max.}$ 330, 401, 528, and 564 mμ (ε 17,000, 309,000, 12,000, and 24,500, respectively).

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