Synthesis of Bilenes-*b*. Some Side Reactions

By **J. Michael Conlon, John A. Elix, Geoffrey I. Feutrill, Alan W. Johnson, Md W. Roomi,** and **John Whelan,** School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ

Condensation of a 5-ethoxycarbonyl-5'-formyl-2,2'-dipyrromethane with a fully alkyl-substituted 5-carboxy-2,2'-dipyrromethane in the presence of hydrogen bromide yielded a tripyrrene salt rather than a bilene-*b* salt. In the presence of trifluoroacetic acid with subsequent addition of hydrogen bromide, the bilene-*b* salt obtained from the foregoing components was derived from the self-condensation of two molecules of the formyl component with elimination of one formyl group. The expected bilene-*b* salts were obtained from the above dipyrromethanes when the carboxy-component contained an electronegative substituent, such as acetyl or ethoxycarbonyl, on the non-carboxy-substituted ring.

In extending the scope of our tetradehydrocorrin synthesis,[1,2] we required a method for the preparation of cobalt(II) 19-alkoxycarbonyl-1-methyltetradehydrocorrin salts (I) containing an unsymmetrical arrangement of β-substituents. Previously we had used mainly the cyclisation of biladienes-*ac* (II) for this type of synthesis, but as there were often symmetry restrictions imposed on these intermediates by the methods necessary for

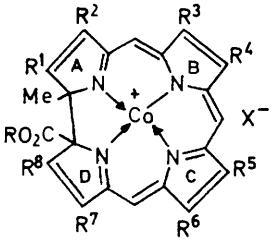
[1] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 30.

[2] R. Grigg, A. W. Johnson, R. Kenyon, V. B. Math, and K. Richardson, *J. Chem. Soc.* (*C*), 1969, 176.

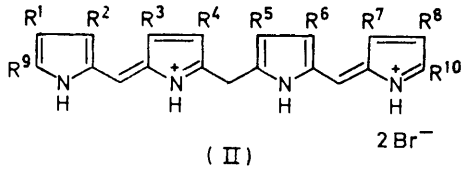
their preparation, we decided to investigate the use of the alternative bilenes-*b* (III), which seemed to offer certain advantages. Like the biladienes-*ac*, the bilenes-*b* have also been used as intermediates in porphin syntheses and much of the information on the synthesis and properties of the bilenes-*b* has been derived from recent studies in this area.

Two main syntheses of bilenes-*b* have been reported. The first, due to Hans Fischer,[3] has also been used by ourselves [4,5] and others,[6] but it is unsatisfactory for the preparation of an unsymmetrically substituted derivative such as (I) as it involves the condensation of two molecules of a 2,3,4-trialkylpyrrole with a 5,5′-bismethoxymethyldipyrromethene. The method was particularly suited for the preparation of deca-alkyl-substituted bilenes-*b*, but gave low yields of those bilenes containing electronegative substituents.

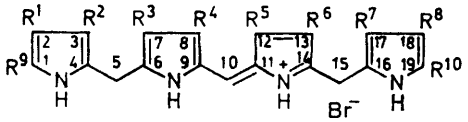
The alternative bilene-*b* synthesis involves the condensation of a 5-formyldipyrromethane with a 5-unsubstituted or 5-carboxydipyrromethane in the presence of hydrogen bromide or trifluoroacetic acid, and it has been used for the preparation of bilenes-*b* containing 1- and 19-methyl substituents [7] or 1- and 19-alkoxycarbonyl groups.[8] The latter class included octa-β-alkyl derivatives and others containing one or two electronegative



(I)

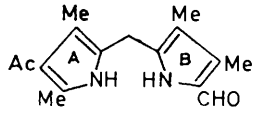


(II)

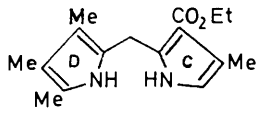


(III)

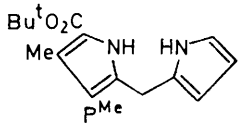
β-substituents. The 1,19-dimethylbilenes-*b* prepared by Clezy [7] all contained an electronegative substituent in ring A or electronegative substituents in rings A and D (positions 2 or 2 and 18) and the formyl group substituted the AB dipyrromethane component. Clezy also



(IV)

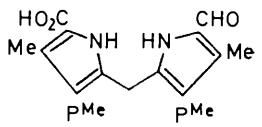


(VI)

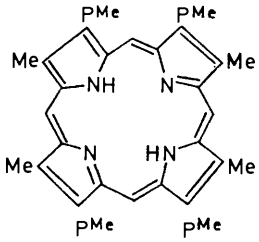


P^{Me} = $CH_2 \cdot CH_2 \cdot CO_2Me$

(V)



(VII)



(VIII)

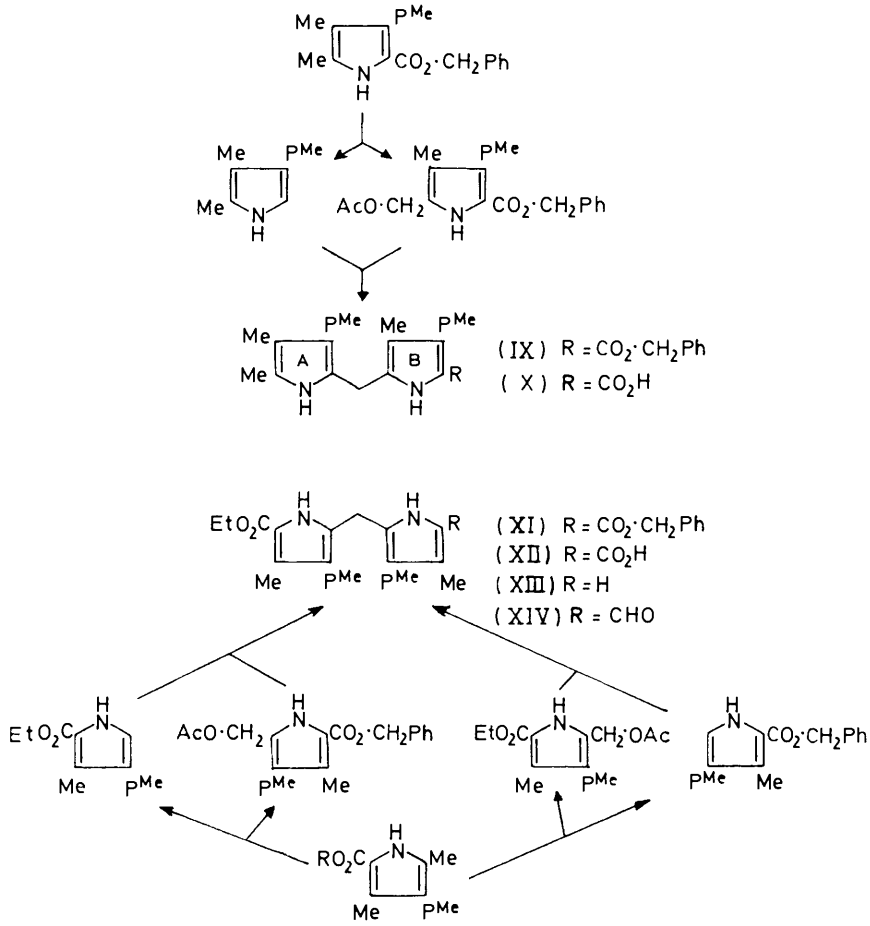
described the synthesis of a 1-methyl-19-t-butoxycarbonylbilene-*b* from the dipyrromethanes (IV) and (V). However, an attempted condensation of the formyldipyrromethane (IV) with the ester (VI) was unsuccessful because of the deactivation of the pyrrolic ring C by the ethoxycarbonyl substituent.

Thus in the examples cited, the 5-formyldipyrromethane AB component for the bilene-*b* synthesis contained an electronegative α- or β-substituent in ring A, but such a substituent in ring C of the C/D component had to be avoided. Porphins, *e.g.* coproporphyrin II (VIII) (ref. 9; see also ref. 10), have also been obtained by self-condensation of 5-formyldipyrromethane-5′-carboxylic acids [*e.g.* (VII)], but this method imposes obvious symmetry restrictions.

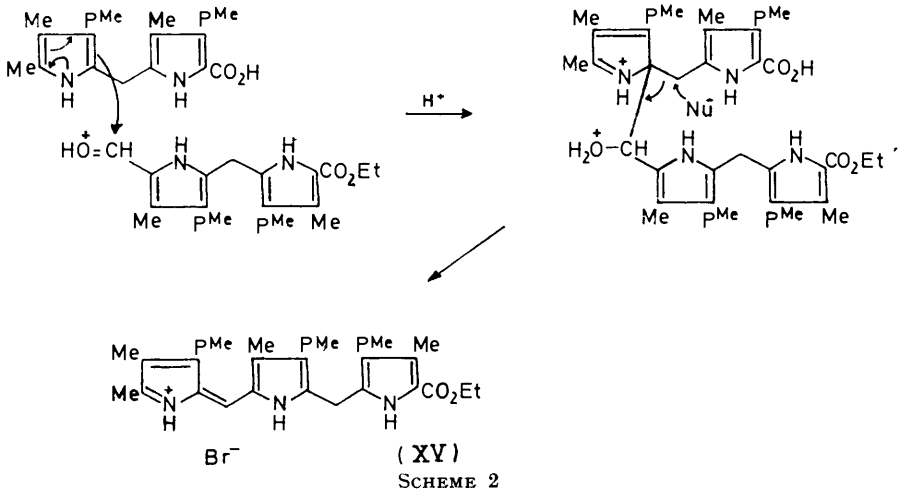
In the first instance we attempted to prepare a cobalt tetradehydrocorrin salt containing the copro III ester arrangement of β-substituents [*i.e.* (I; $R^1 = R^3 = R^5 = R^8 = Me$, $R^2 = R^4 = R^6 = R^7 = P^{Et}$)] which required the intermediacy of the bilene-*b* (III; $R^1 = R^3 = R^5 = R^8 = R^9 = Me$, $R^2 = R^4 = R^6 = R^7 = P^{Et}$, $R^{10} = CO_2Et$). Although α-formylation of dipyrromethane itself [11,12] and alkyldipyrromethanes,[11] especially those containing β-alkoxycarbonylethyl substituents,[13,14] is

[3] H. Fischer and A. Kurzinger, *Z. physiol. Chem.*, 1931, **196**, 213.
[4] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1961, 2418.
[5] I. D. Dicker, R. Grigg, A. W. Johnson, H. Pinnock, K. Richardson, and P. van der Broek, *J. Chem. Soc.* (*C*), 1971, 536.
[6] G. M. Badjer, R. L. N. Harris, and R. A. Jones, *Austral. J. Chem.*, 1964, **17**, 1013.
[7] P. S. Clezy and A. J. Liepa, *Austral. J. Chem.*, 1971, **24**, 1027.
[8] A. H. Jackson, G. W. Kenner, and K. M. Smith, *J. Chem. Soc.* (*C*), 1971, 502.
[9] A. H. Jackson, G. W. Kenner, and J. Wass, *J.C.S. Perkin I*, 1972, 1475.
[10] J. L. Davies, *J. Chem. Soc.* (*C*), 1968, 1392.
[11] R. Chang, P. S. Clezy, A. J. Liepa, and A. W. Nichol, *Austral. J. Chem.*, 1969, **22**, 229.
[12] A. W. Johnson and W. R. Overend, *J.C.S. Perkin I*, 1972, 2681.
[13] G. P. Arsenault, E. Bullock, and S. F. MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 4384.
[14] R. P. Evstigneeva and N. A. Preobrezhenskii, *Zhur obshchei Khim.*, 1966, **36**, 806.

well established, we recognised that in many cases decarboxylation of the corresponding α-carboxylic acids is involved as a preliminary step, the experimental CD component, we decided to attempt the preparation of the required bilene-*b* by condensation of the dipyrromethanes (X) and (XIV), *i.e.* the formyl group was to be



SCHEME 1



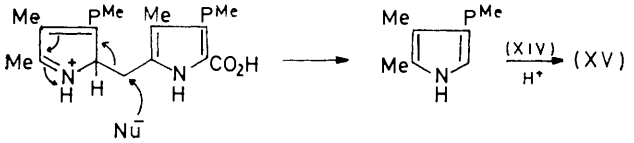
SCHEME 2

conditions for which are often critical, and also that the yields of the formyl derivatives may be variable. Since, in our contemplated synthesis, the preparation of the AB dipyrromethane was more lengthy than that of the placed on the ring intended to become ring C of the product. The route adopted for the preparation of (X) and (XIV) is summarised in Scheme 1 and details of the preparation of the individual pyrroles, mostly by

standard methods, are given in the Experimental section. We draw attention to the use of the valuable method for *C*-methylation in the pyrrole series as exploited by Roomi and MacDonald,[15] and also to the use of toluene-*p*-sulphonic acid in methanol as condensing agent for dipyrromethane formation,[16] which in this series gave yields similar to those obtained using acetic acid.[17]

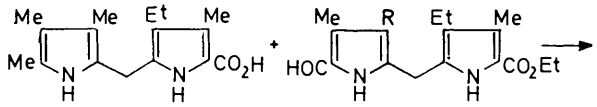
Condensation of the acid (X) [from (IX) by hydrogenolysis] and the aldehyde (XIV) [from (XI) by hydrogenolysis, decarboxylation, and formylation] was effected in the presence of methanolic hydrogen bromide. The product, although having the visible spectrum expected for a bilene-*b* hydrobromide, proved to be the tripyrrene salt (XV), identified by its analytical data and spectral properties. Its formation can be attributed to attack of the formyl group at the site of the α-methylene group of ring A with subsequent fission of ring B (Scheme 2).

Alternatively,* acid-induced cleavage of the AB dipyrromethane may result in production of the α-free pyrrole, which can then condense with the dipyrromethane aldehyde to yield the tripyrrene (XV).

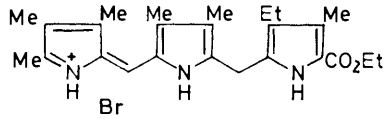


In a related series the dipyrromethanes (XVI) and (XVII; R = Me), containing only alkyl β-substituents and prepared by similar sequences, were condensed in the presence of methanolic hydrogen bromide. Again the product was identified as a tripyrrene (XVIII), formed by decarboxylation, condensation, and fission of (XVI) as before.

The routes leading to the tripyrrenes (XV) and (XVIII) contain certain of the essential features of the mechanism postulated by Mathewson and Corwin [18] for the biogenetic formation of III-type porphyrinogens,

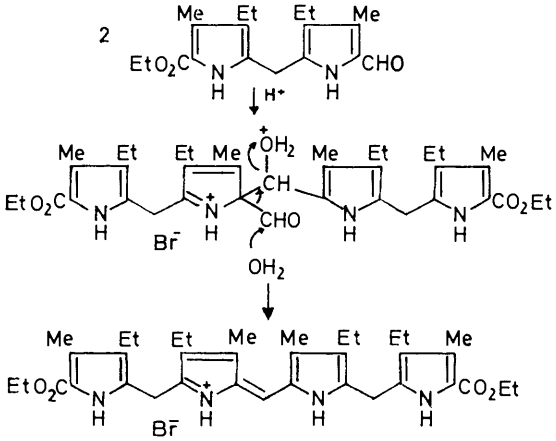


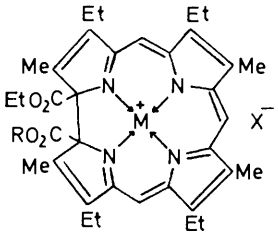
(XVI) (XVII)



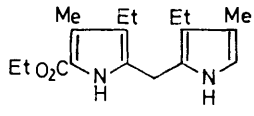
(XVIII)

although the subsequent intramolecular condensation leading to the macrocycle is not possible in the present examples. In order to avoid undue exposure of the free 5-unsubstituted dipyrromethanes to strong acids we have examined the conditions recommended by Clezy [7] in which the dipyrromethane-5-carboxylic acid is mixed with the 5-formyldipyrromethane and then

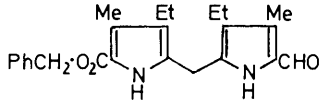




(XIX)



(XX)



(XXI)

treated with trifluoroacetic acid in methanol at room temperature to effect decarboxylation. Condensation is then completed by addition of hydrogen bromide in acetic acid. We have applied this method to the reaction of the acid (XVI) with the aldehyde (XVII; R = Et), and although this reaction gave a bilene-*b* salt, this proved to be (III; $R^1 = R^2 = R^5 = R^8 = Me$, $R^2 = R^3 = R^6 = R^7 = Et$, $R^9 = R^{10} = CO_2Et$), derived from the self-condensation of (XVII). The structure of the product was established by its cyclisation in the presence of nickel(II) or cobalt(II) salts to the corresponding metal tetradehydrocorrin salts (XIX; R = Et). A similar sequence was carried out with (XVI) and the benzyl ester corresponding to (XVII; R = Et); the products were the 1,19-dibenzyl esters (XIX; R = $PhCH_2$, M = Ni or Co). The self-condensation of the 5-formyldipyrromethanes with elimination of one formyl group (probably as formate) is a reaction of a type similar to that already described leading to the tripyrromethene salts.

The alkyldipyrromethane derived from decarboxylation of (XVI) is clearly very sensitive to acids, and under the experimental conditions it appears to be

* This alternative mechanism was suggested by a referee.

[15] M. W. Roomi and S. F. MacDonald, *Canad. J. Chem.*, 1970, **48**, 139, 1689.

[16] A. M. d'Al. Rocha Gonsalves, G. W. Kenner, and K. M. Smith, *Tetrahedron Letters*, 1972, 2203.

[17] P. S. Clezy and A. J. Liepa, *Austral. J. Chem.*, 1970, **23**, 2443.

[18] J. H. Mathewson and A. H. Corwin, *J. Amer. Chem. Soc.*, 1961, **73**, 135; A. R. Battersby, E. Hunt, and E. McDonald, *J.C.S. Chem. Comm.*, 1973, 442.

decomposed completely. However, experience of both Clezy [7] and Kenner [8] indicates that the presence of even one electronegative group on the dipyrromethane will suffice to permit normal condensation with the formyldipyrromethane. In agreement with this we found that condensation of the dipyrromethanes (XX) and (XXI) gave the expected bilene-*b*, the structure of which was supported by its cyclisation to the nickel(II) and cobalt(II) tetrahydrocorrin salts, which were shown to contain both ethyl and benzyl ester groups by mass spectrometry. Comparison of the behaviour of the nickel and cobalt salts in the mass spectrometer showed the cobalt salts to be more stable, *i.e.* they exhibited a diminished tendency to fragmentation, although they were converted more easily into neutral species by loss of HX.

Thus, in the [2 + 2] type syntheses of bilenes-*b*, certain limitations on the structure of each component are apparent. Both the dipyrromethanes should contain an electronegative group as a ring substituent in order to avoid decomposition of the dipyrromethane by the acid catalyst, but the electronegative substituent must not be located on the pyrrole ring which undergoes condensation with the formyl group. Further examples to support this general thesis will be presented in a later paper.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in deuteriochloroform, i.r. spectra for Nujol mulls, and u.v.–visible spectra for solutions in chloroform (except where otherwise stated) with instruments listed in earlier papers in this series. Mass spectra were determined by direct sample insertion into the ion source of an A.E.I. MS9 instrument. M.p.s were determined on a Kofler hot-stage apparatus.

Tripyrrene Formation. (A) *Copro Series*

2-Benzyl 4-t-Butyl 3-(β-Methoxycarbonylethyl)-5-methylpyrrole-2,4-dicarboxylate.—Sodium nitrite (9·4 g) in water (30 ml) was added to an ice-cold solution of methyl benzyl β-oxoadipate [19] (26·4 g) in glacial acetic acid (40 ml) with stirring, at such a rate that the temperature remained below 5°. The mixture was then kept at room temperature overnight. t-Butyl acetoacetate (15·8 g) in acetic acid (40 ml) was then added, followed by zinc dust (26 g) so that the temperature of the mixture remained at 60—70°. The mixture was then heated at 60—70° for 2 h, cooled, poured onto ice, and left overnight. The crude product was separated and dissolved in hot ethanol; the solution was filtered and then cooled at 0°, and the *product* (11·25 g, 45%), m.p. 99—101°, was obtained as needles (Found: C, 66·15; H, 6·65; N, 3·4. $C_{22}H_{27}NO_6$ requires C, 65·8; H, 6·8; N, 3·5%), τ 0·52br (NH), 2·6 (s, aromatic H), 4·7 (s, PhCH_2), 6·4 (s, CO_2Me), 7·05 (m, $[CH_2]_2$), 7·55 (s, 5-CH_3), and 8·45 (s, Bu^t).

2-Benzyloxycarbonyl-3-(β-methoxycarbonylethyl)-5-methylpyrrole-4-carboxylic Acid.—The foregoing ester (16 g) was dissolved in acetic acid (20 ml) at 25°, a 10% w/w solution of hydrogen chloride in acetic acid (80 ml) was added, and the ester was brought into solution by swirling. The mixture was kept at room temperature until precipitation of the free acid occurred. The product was filtered off, washed with water, dried, and crystallised from ethyl acetate to give the *acid* (11·28 g, 82%), m.p. 236—238°, as prisms [Found: C, 62·7; H, 5·6; N, 3·95 (decomp.). $C_{18}H_{19}NO_6$ requires C, 62·6; H, 5·55; N, 4·05%], insufficiently soluble in deuteriochloroform for an n.m.r. determination.

Benzyl 3-(β-Methoxycarbonylethyl)-5-methylpyrrole-2-carboxylate.—The foregoing acid (13·8 g), 2,2′-bipyridyl (0·82 g), and copper(I) oxide (0·28 g) were heated under reflux under nitrogen in diethylene glycol dimethyl ether (50 ml) for 3 h. The mixture was cooled, filtered, and poured onto ice. The separated solid was filtered off, washed with water, dried, and crystallised from ether–petroleum (b.p. 40—60°) to give the *product* (8·75 g, 75·5%) as needles, m.p. 72—74° (Found: C, 67·8; H, 6·4; N, 4·9. $C_{17}H_{19}NO_4$ requires C, 67·75; H, 6·35; N, 4·65%), τ 1·82br (NH), 2·62 (s, aromatic H), 4·15 (d, 4-H), 4·7 (s, PhCH_2), 6·35 (s, CO_2Me), 7·2 (m, $[CH_2]_2$), and 7·8 (s, 5-CH_3).

Benzyl 3-(β-Methoxycarbonylethyl)-4,5-dimethylpyrrole-2-carboxylate.—The foregoing pyrrole (5 g), paraformaldehyde (2·5 g) in acetic acid (40 ml) together with hydriodic acid (40 ml; *d* 1·95), and hypophosphorous acid (8 ml; 50%) (*cf.* ref. 15) were stirred for 3 h under nitrogen at 25°. The mixture was poured into water and extracted with ether (3 × 25 ml). The extract was dried ($MgSO_4$), filtered, treated with a slight excess of ethereal diazomethane, and evaporated. The residue was sublimed at 170° and 0·1 mmHg and crystallised from ether–n-hexane to give the *product* (2·6 g, 50%) as long needles, m.p. 93—95° (Found: C, 68·45; H, 6·75; N, 4·45. $C_{18}H_{21}NO_4$ requires C, 68·55; H, 6·7; N, 4·45%), τ 0·82br (NH), 2·65 (s, aromatic H), 4·7 (s, PhCH_2), 6·4 (s, CO_2Me), 7·25 (m, $[CH_2]_2$), and 7·95 and 8·1 (both s, 4- and 5-CH_3).

Methyl β-(4,5-Dimethylpyrrol-3-yl)propionate.—The foregoing benzyl ester (3·15 g) in ethanol (50 ml) was hydrogenated at room temperature and atmospheric pressure over 10% palladium–carbon (315 mg). Filtration through Celite and evaporation *in vacuo* gave the carboxylic acid, which was decarboxylated by heating at 150° under nitrogen in an oil-bath until evolution of carbon dioxide had ceased (*ca.* 10 min). The residual oil was distilled to give the product (1·58 g), b.p. 120° at 0·05 mmHg (87%), m.p. 55—57° (lit.,[20] 57°; lit.,[19] 50—53°) as needles, which were air-sensitive and preferably used immediately for further condensation (Found: C, 66·0; H, 8·3; N, 7·95. Calc. for $C_{10}H_{15}NO_2$: C, 66·25; H, 8·35; N, 7·75%), τ 2·35br (NH), 3·6 (d, 2-H), 6·3 (s, CO_2Me), 7·35 (m, $[CH_2]_2$), and 7·85 and 8·05 (both s, 4- and 5-CH_3).

Benzyl 5-Acetoxymethyl-3-(β-methoxycarbonylethyl)-4-methylpyrrole-2-carboxylate.—Lead tetra-acetate (4·4 g) was added in portions during 15 min to a solution of the 4,5-dimethylpyrrole benzyl ester (3·15 g) in glacial acetic acid (30 ml). The solution was stirred for 3 h then poured into water (300 ml), and the precipitated product was filtered off, washed with water, dried, and crystallised from ether–n-hexane to give the *acetoxymethylpyrrole* (3·05 g) as white needles, m.p. 91—93° (81·5%) (Found: C, 64·25; H, 6·2; N, 3·75. $C_{20}H_{23}NO_6$ requires C, 64·35; H, 6·2; N, 3·75%), τ 0·7br (NH), 2·65 (s, aromatic H), 4·72 (s, PhCH_2), 5·0 (s, AcO·CH_2), 6·4 (s, CO_2Me), 7·25 (m, $[CH_2]_2$), and 7·98 (s, 4-CH_3 and Ac).

Benzyl 3,4′-Bis-(β-methoxycarbonylethyl)-3′,4,5-trimethyl-2,2′-dipyrromethane-5′-carboxylate (IX).—(i) Methyl β-(4,5-dimethylpyrrol-2-yl)propionate (0·9 g) and the foregoing

[19] S. F. MacDonald and R. J. Stedman, *Canad. J. Chem.*, 1955, **33**, 458.

[20] H. Fischer and H. Orth, ' Die Chemie des Pyrrols,' vol. I, Thieme Verlag, Liepzig, 1934, p. 284.

acetoxymethylpyrrole benzyl ester (1·87 g) in methanol (15 ml) were treated with toluene-*p*-sulphonic acid hydrate (50 mg) and heated under nitrogen at 40° for 4 h. The solvent was removed *in vacuo* and the residue extracted with ether (100 ml); the extracts were washed with water, dried ($MgSO_4$), and evaporated. The product crystallised from ether–n-hexane at 0° to give the *dipyrromethane* (1·88 g, 76%) as needles, m.p. 83—85° (Found: C, 68·2; H, 6·7; N, 5·6. $C_{28}H_{34}N_2O_6$ requires C, 68·0; H, 6·95; N, 5·65%), τ 0·82br and 2·0br (2 × NH), 2·6 (s, aromatic H), 4·7 (s, PhCH_2), 6·12 (s, bridge CH_2), 6·3 and 6·32 (both s, CO_2Me), 6·95 and 7·35 (m, 2 × $[CH_2]_2$), and 7·88, 7·9, and 8·0 (all s, 3'-, 4-, and 5-Me).

(ii) The same quantities of the two pyrroles were dissolved in glacial acetic acid (15 ml) and heated on a steam-bath for 1 h under nitrogen. The mixture was poured onto ice and extracted with ether (3 × 50 ml); the extracts were washed with water, dried ($MgSO_4$), and evaporated and the product was crystallised from ether–n-hexane at 0° to give the dipyrromethane (1·76 g, 71%) as needles, m.p. 83—85°, identical with the previous product.

3,4'-Bis-(β-methoxycarbonylethyl)-3',4,5-trimethyl-2,2'-dipyrromethane-5'-carboxylic Acid (X).—The foregoing benzyl ester (2·48 g) in ethanol (25 ml) was hydrogenated over 10% palladium–charcoal (248 mg) at room temperature and pressure. The catalyst was filtered off through Celite and the solution evaporated *in vacuo* to give an oil which soon crystallised on addition of light petroleum. The product was crystallised from ethyl acetate–n-hexane to give the *acid* (1·68 g, 83%) as prisms, m.p. 134—136° (decomp.), which darkened rapidly in air (Found: C, 61·6; H, 6·4; N, 6·55. $C_{21}H_{28}N_2O_6$ requires C, 62·35; H, 7·0; N, 6·95%), τ 0·72 (s, CO_2H), 2·45br (2 × NH), 6·15 (s, bridge CH_2), 6·3 (s, 2 × CO_2Me), 7·0 and 7·4 (m, 2 × $[CH_2]_2$), and 7·9, 7·95, and 8·1 (3'-, 4-, and 5-Me).

Benzyl Ethyl 3,3'-Bis-(β-methoxycarbonylethyl)-4,4'-dimethyl-2,2'-dipyrromethane-5,5'-dicarboxylate (XI).—(i) Ethyl 3-(β-methoxycarbonylethyl)-4-methylpyrrole-5-carboxylate [21] (2·39 g) and benzyl 2-acetoxymethyl-3-(β-methoxycarbonylethyl)-4-methylpyrrole-5-carboxylate [22] (3·72 g) in methanol (50 ml) were treated with toluene-*p*-sulphonic acid (50 mg) and heated under nitrogen at 40° for 4 h. The solvent was removed *in vacuo*, and the residue extracted with ether (150 ml). The extracts were washed, dried ($MgSO_4$), and evaporated and the product was crystallised from methanol at 0° to give the *dipyrromethane* (4·55 g, 82%) as needles, m.p. 83—85° (Found: C, 65·55; H, 6·6; N, 5·15. $C_{30}H_{36}N_2O_8$ requires C, 65·2; H, 6·55; N, 5·05%), τ 0·65br and 0·72br (2 × NH), 2·65 (s, aromatic H), 5·72 (q, CO_2·CH_2·CH_3), 6·0 (s, bridge CH_2), 6·3 and 6·4 (both s, CO_2Me), 7·35 (m, 2 × $[CH_2]_2$), 7·68 and 7·72 (both s, 4- and 4'-CH_3), and 8·7 (t, CO_2·CH_2·CH_3).

(ii) The same reagents (1/10 scale) in glacial acetic acid (5 ml) were heated on a steam-bath for 1 h under nitrogen. The mixture was poured onto ice and extracted with ether (2 × 25 ml), and the extract was washed, dried, and evaporated. The residue was crystallised from methanol to give the same product (0·42 g, 76%) as needles.

(iii) Benzyl 3-(β-methoxycarbonylethyl)-4-methylpyrrole-5-carboxylate (3·11 g) [23] and ethyl 2-acetoxymethyl-3-(β-methoxycarbonylethyl)-4-methylpyrrole-5-carboxylate (3·01 g) [24] in methanol (50 ml) were treated with toluene-*p*-sulphonic acid (150 mg) and heated under nitrogen at 40° for 4 h. The mixture was worked up as in (i) to yield the dipyrromethane (4·48 g, 81%) identical with the previous products.

(iv) The same reagents (1/10 scale) in acetic acid (5 ml) were heated on a steam-bath for 1 h under nitrogen and the mixture was treated as in (ii) to yield the product (0·45 g, 82%), identical with those obtained in the previous preparations.

5-Ethoxycarbonyl-3,3'-bis-(β-methoxycarbonylethyl)-4,4'-dimethyl-2,2'-dipyrromethane-5-carboxylic Acid (XII).—The benzyl ester (XI) (2·76 g) was hydrogenated at room temperature and pressure in ethanol (50 ml) containing palladium–charcoal (276 mg) until uptake was complete. Filtration through Celite, evaporation, and crystallisation of the residue from ethyl acetate and n-hexane gave the *acid* (1·88 g, 81·5%) as pale pink prisms, m.p. 172—174° (with decarboxylation) (Found: C, 59·85; H, 6·85; N, 6·95. $C_{23}H_{30}N_2O_8$ requires C, 59·75; H, 6·55; N, 6·05%).

Ethyl 3,3'-Bis-(β-methoxycarbonylethyl)-4,4'-dimethyl-2,2'-dipyrromethane-5-carboxylate (XIII).—The acid (XII) (2·09 g) was decarboxylated by heating at 150° and 0·05 mmHg in an oil-bath until evolution of carbon dioxide had ceased (*ca.* 20 min), and the residue was distilled at 180—190° and 0·01 mmHg to give the *product* as a light yellow oil (1·8 g, 86%) (Found: C, 63·1; H, 7·55; N, 6·6. $C_{22}H_{30}N_2O_6$ requires C, 63·15; H, 7·25; N, 6·7%), τ 1·0br and 1·89br (2 × NH), 3·6 (d, 2-H), 5·75 (q, CO_2·CH_2·CH_3), 6·1 (s, bridge CH_2), 6·3 and 6·35 (both s, CO_2Me), 7·38 (m, 2 × $[CH_2]_2$), 7·7 and 7·95 (both s, 4- and 4'-CH_3), and 8·7 (t, CO_2·CH_2·CH_3).

Ethyl 5'-Formyl-3,3'-bis-(β-methoxycarbonylethyl)-4,4'-dimethyl-2,2'-dipyrromethane-5-carboxylate (XIV).—The dipyrromethane (XIII) (2·09 g) in methylene chloride (30 ml) was added during 10 min to a solution of *NN*-dimethylformamide (3·5 ml) and phosphoryl chloride (1·6 ml) in methylene chloride (45 ml) with stirring at 0°. The addition was carried out under nitrogen and stirring was continued for a further 1 h at 25°. Sodium acetate (15 g) in water (25 ml) was then added and the two layers were stirred for 30 min. The organic layer was separated, washed with 5% sodium hydrogen carbonate and again with water, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue crystallised from aqueous ethanol to give the *formylpyrromethane* (1·75 g, 78·5%) as needles, m.p. 123—125° (Found: C, 61·6; H, 6·8; N, 6·05. $C_{23}H_{30}N_2O_7$ requires C, 61·85; H, 6·75; N, 6·25%), τ −0·75 (s, CHO), 0·3br and 0·5br (2 × NH), 5·75 (q, CO_2·CH_2·CH_3), 6·0 (s, bridge CH_2), 6·3 (s, 2 × CO_2Me), 7·35 (m, 2 × $[CH_2]_2$), 7·7 and 7·72 (s, 4- and 4'-CH_3), and 8·72 (q, CO_2·CH_2·CH_3).

Ethyl 3,4',4''-Tris-(β-methoxycarbonylethyl)-3',3'',4,5-tetramethyltripyrrene-2'-carboxylate Hydrobromide (XV).—The carboxylic acid (X) (0·808 g) and the aldehyde (XIV) (0·892 g) in methanol (5 ml) containing aqueous hydrobromic acid (2 ml; 48%) were heated on a water-bath for 5 min and then cooled at 0°. The crystalline brick-red *hydrobromide* (1·216 g, 70%) was collected and washed with n-hexane (Found: C, 57·5; H, 6·8; N, 6·05. $C_{33}H_{44}BrN_3O_8$ requires C, 57·4; H, 6·4; N, 6·1%), τ 2·62 (s, bridge

[21] E. I. Filippovich, R. P. Evstigneeva, and N. A. Preobrezhenskii, *Zhur. obshchei Khim.*, 1961, **31**, 2968.
[22] A. W. Johnson, I. T. Kay, E. Markham, R. Price, and K. B. Shaw, *J. Chem. Soc.*, 1959, 3416.
[23] R. P. Carr, A. H. Jackson, G. W. Kenner, and G. S. Sach, *J. Chem. Soc.* (*C*), 1971, 487.
[24] A. F. Mironov, R. P. Evstigneeva, and N. A. Preobrezhenskii, *Zhur. obschei Khim.*, 1965, **35**, 1945.

=CH–), 5·52 (s, bridge CH_2), 5·70 (q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 6·25 and 6·32 (both s, CO_2Me), 7·32 (m, $[CH_2]_2$), 7·65, 7·7, and 7·95 (all s, nuclear CH_3), and 8·62 (t, $CO_2{\cdot}CH_2{\cdot}CH_3$), $\lambda_{max.}$ 496 and 536 nm (ε 38,800 and 7500).

Tripyrrene Formation. (B) *β-Alkyl Series*

Ethyl 4-Ethyl-3-methylpyrrole-2-carboxylate.—5-Ethoxycarbonyl-3-ethyl-4-methylpyrrole-2-carboxylic acid [25] (5·0 g) was suspended in 1,2-dimethoxyethane (50 ml; distilled over NaH), and 2,2′-bipyridyl (0·5 g) and copper(I) oxide (0·5 g) were added. The mixture was stirred under reflux for 3 h under nitrogen and then cooled, poured into water (300 ml), and extracted with chloroform. The extracts were washed with aqueous sodium hydrogen carbonate and then water, filtered, and dried. The solvent was evaporated off and the residue chromatographed on silica (150 g) with 30% ether–light petroleum for elution. After removal of solvent the product (4·5 g) was obtained as a pale yellow oil which solidified to almost colourless crystals, m.p. 73° (lit.,[26] 75°) (ethanol), τ 3·42 (m, nuclear H), 5·69 (q, ester CH_2), 7·70 (s, nuclear CH_3), 8·63 (t, nuclear $CH_2{\cdot}CH_3$), and 8·33 (t, ester $CH_2{\cdot}CH_3$).

Benzyl Ethyl 3,3′-Diethyl-4,4′-dimethyl-2,2′-dipyrromethane-5,5′-dicarboxylate.—Benzyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate [22] was prepared *in situ* from benzyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate [27] (8·5 g) in acetic acid (95 ml) by treatment with lead tetra-acetate (14·5 g) in portions (1 g) during 30 min. After a further 1 h, the foregoing ester (5·9 g) was added and the mixture was heated on a steam-bath for 1·5 h. After cooling, the product was precipitated by dropwise addition of water to the vigorously stirred mixture. Crystallisation from ethanol gave needles (10·0 g, 70%), m.p. 94° (lit.,[28] 93—95°) (Found: C, 71·6; H, 7·2; N, 6·5%; M^+, 436. Calc. for $C_{26}H_{32}N_2O_4$: C, 71·5; H, 7·4; N, 6·4%; *M*, 436), τ 0·7br (s, NH), 2·67 (s, 5 aromatic H), 4·74 (s, $PhCH_2$), 5·76 (q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 6·13 (s, bridge CH_2), 7·56 (q, 2 × $CH_2{\cdot}CH_3$), 7·67 and 7·68 (both s, 2 × CH_3), 8·70 (t, 2 × $CH_2{\cdot}CH_3$), and 8·96 (t, $CO_2{\cdot}CH_2{\cdot}CH_3$).

Ethyl 3,3′-Diethyl-5′-formyl-4,4′-dimethyl-2,2′-dipyrromethane-5-carboxylate.—(i) A solution of the foregoing dipyrromethane ester (3·25 g) in tetrahydrofuran (50 ml) was hydrogenated at atmospheric pressure over 10% palladium–charcoal (300 mg). When uptake had ceased (*ca.* 1·5 h), the catalyst was separated and the solvent evaporated off under reduced pressure. The residual acid (2·55 g, 97%) was a pale pink amorphous solid which darkened in air. It was decarboxylated by heating at 170° and 3 mmHg for 15 min to yield a brown viscous oil [29] which darkened further on exposure to air, τ 3·63 (s, nuclear H), 5·78 (q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 6·16 (s, bridge CH_2), 7·6 (overlapping q, 2 × $CH_2{\cdot}CH_3$), 7·70 and 7·95 (both s, 2 × CH_3), 8·69 (t, 2 × $CH_2{\cdot}CH_3$), and 8·96 (t, $CO_2{\cdot}CH_2{\cdot}CH_3$).

(ii) The oily monoester, without further purification, was formylated (Vilsmeier method; see later) to yield the 5′-methyleneimine methochloride (2·4 g), which was dissolved in hot water (30 ml). Addition of potassium hydroxide solution (5 ml; 20%) precipitated the *product*, which crystallised from ethanol as pale yellow needles (1·95 g, 80%), m.p. 171—172° (Found: C, 69·4; H, 7·9; N, 8·4. $C_{19}H_{26}N_2O_3$ requires C, 69·1; H, 7·9; N, 8·5%), τ 0·50 (s, CHO), 5·77 (q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 6·07 (s, bridge CH_2), 7·54 (q, 2 × $CH_2{\cdot}CH_3$), 7·70 (s, 2 × CH_3), 8·75 (t, 2 × $CH_2{\cdot}CH_3$), and 8·95 (t, $CO_2{\cdot}CH_2{\cdot}CH_3$).

Ethyl 3-Ethyl-5′-formyl-3′,4,4′-trimethyl-2,2′-dipyrromethane-5-carboxylate (XVII).—This was obtained by a sequence similar to that for the foregoing formyldipyrromethane. Ethyl 4-ethyl-3-methylpyrrole-2-carboxylate (4 g) and benzyl 5-acetoxymethylpyrrole-2-carboxylate [30] (6·6 g) were dissolved in methanol (100 ml) containing toluene-*p*-sulphonic acid (0·5 g) and warmed at 37°. The product began to separate after 0·5 h but the mixture was kept overnight and then diluted with water to yield the ethyl benzyl diester (6 g). This was hydrogenolysed directly as before and the acid was decarboxylated by heating at 200° and 0·01 mmHg until no further carbon dioxide was evolved. The α-unsubstituted dipyrromethane solidified on cooling (yield 1·5 g) and was then dissolved in dichloromethane (20 ml) and added dropwise to a solution of *NN*-dimethylformamide (3 ml) and phosphoryl chloride (1·7 ml) in dichloromethane (50 ml) at 0°. The mixture was then stirred at room temperature for 1 h and heated under reflux for 10 min. The complex was hydrolysed with aqueous sodium hydrogen carbonate and after the usual work-up, gave a dark brown oil which solidified. This was chromatographed on silica gel (30 g) and eluted with 30% ether–light petroleum. The *product* was crystallised from ethanol and yielded off-white needles, m.p. 173—174° (Found: C, 68·15; H, 7·5; N, 8·75. $C_{18}H_{24}N_2O_3$ requires C, 68·35; H, 7·65; N, 8·85%), τ −1·05br and −0·25br (2 × NH), 0·67 (s, CHO), 5·78 (q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 6·07 (s, bridge CH_2), 7·52 (q, nuclear $CH_2{\cdot}CH_3$), 7·72, 7·74, and 7·98 (all s, 3 × CH_3), 8·74 (t, $CO_2{\cdot}CH_2{\cdot}CH_3$), and 8·95 (t, nuclear $CH_2{\cdot}CH_3$).

Benzyl 3-Ethyl-3′,4,4′,5′-tetramethyl-2,2′-dipyrromethane-5-carboxylate.— 2-Benzyloxycarbonyl-4-ethyl-3,5-dimethylpyrrole [27] (24·9 g) was dissolved in acetic acid (200 ml) and lead tetra-acetate (42·2 g) was added in portions (2 g) over 30 min with stirring. After a further 1 h, 2,3,4-trimethylpyrrole (10·9 g) was added and the mixture was heated on a steam-bath for 1 h, diluted with water (100 ml), and cooled with stirring. The *product* was separated after 30 min, washed with aqueous acetic acid, and crystallised from ethanol to give pale yellow needles (21·0 g, 58%), m.p. 134—135° (Found: C, 76·1; H, 7·6; N, 7·5%; M^+, 364. $C_{23}H_{28}N_2O_2$ requires C, 75·8; H, 7·7; N, 7·7%; *M*, 364), τ 2·71 (s, 5 aromatic H), 4·78 (s, $PhCH_2$), 6·23 (s, bridge CH_2), 7·60 (q, $CH_2{\cdot}CH_3$), 7·72, 7·94, 8·07, and 8·10 (all s, 4 × CH_3), and 8·95 (t, $CH_2{\cdot}CH_3$).

Ethyl 4″-Ethyl-3,3′,3″,4,4′,5-hexamethyltripyrrene-2″-carboxylate Hydrobromide (XVIII).—The aldehyde (XVII) (106 mg) and the carboxylic acid (XVI) (obtained by hydrogenolysis of the corresponding benzyl ester) (90 mg) were dissolved in a mixture of methanol (2 ml) and dichloromethane (1 ml). A solution of hydrobromic acid (0·5 ml; 49%) in methanol (1 ml) was added and the mixture was kept overnight. The brick-red *hydrobromide* (85 mg, 51%) was collected and washed with methanol containing a little hydrobromic acid (Found: C, 61·6; H, 7·0; N, 8·4. $C_{25}H_{34}BrN_3O_2$ requires C, 61·47; H, 7·0; N, 8·6%), $\lambda_{max.}$ 279, 370, 495, and 537 nm (ε 11,900, 5100, 40,400, and 6800), τ 2·93 (s, bridge =CH–), 5·71 (s, bridge CH_2), 5·72 (q,

[25] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 22.
[26] Ref. 20, p. 241.
[27] E. Bullock, A. W. Johnson, E. Markham, and K. B. Shaw, *J. Chem. Soc.*, 1958, 1430.
[28] A. H. Jackson, G. W. Kenner, and D. Warburton, *J. Chem. Soc.*, 1965, 1328.
[29] A. H. Corwin and E. C. Coolidge, *J. Amer. Chem. Soc.*, 1952, **74**, 5196.
[30] A. W. Johnson and R. Price, *J. Chem. Soc.*, 1960, 1649.

CO_2·CH_2·CH_3), 7·51 (q, nuclear CH_2·CH_3), 7·32, 7·72, 7·74, 7·78, 7·99, and 8·01 (all s, 6 × CH_3), 8·69 (t, nuclear CH_2·CH_3), and 8·96 (t, CO_2·CH_2·CH_3).

Symmetrical Bilene Formation. β-Alkyl Series

Benzyl 3,3′-Diethyl-5′-formyl-4,4′-dimethyl-2,2′-dipyrromethane-5-carboxylate (XXI).—5-Benzyloxycarbonyl-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrromethane [31] (obtained by decarboxylation of the corresponding 5-carboxylic acid) (2·0 g) in dichloromethane (25 ml) was added over 10 min to a solution of dimethylformamide (1·5 ml) and phosphoryl chloride (3·0 ml) stirred in an atmosphere of nitrogen. After 1 h, sodium acetate (15 g) in water (100 ml) was added and the two layers were stirred vigorously for 30 min. The organic layer was separated, washed with water, 5% sodium hydrogen carbonate solution, and water again, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from ethanol gave the *product* (1·65 g, 80%) as needles, m.p. 179—180° (Found: C, 73·4; H, 7·1; N, 7·1. $C_{24}H_{28}N_2O_3$ requires C, 73·4; H, 7·2; N, 7·2%), τ −0·76br and −0·16br (2 × NH), 2·76 (s, 5 aromatic H), 4·80 (s, PhCH_2), 6·14 (s, bridge CH_2), 7·58 (overlapping q, 2 × CH_2·CH_3), 7·75 and 7·81 (both s, 2 × CH_3), and 8·99 (t, 2 × CH_2·CH_3).

1,19-*Bisethoxycarbonyl*-1,19-*dideoxy*-3,7,13,17-*tetraethyl*-2,8,12,18-*tetramethylbilene*-b *Hydrobromide*.—5-Benzyloxycarbonyl-3-ethyl-3′,4,4′,5′-tetramethyl-2,2′-dipyrromethane (1·82 g) was hydrogenolysed to the carboxylic acid in the usual manner and then dissolved in trifluoroacetic acid (5 ml), and the solution was kept for 2 min before addition to a solution of 5-ethoxycarbonyl-3,3′-diethyl-5′-formyl-4,4′-dimethyl-2,2′-dipyrromethane (1·70 g) in methanol (75 ml). The mixture was stirred for 15 min, a solution of hydrogen bromide in acetic acid (10 ml; 50%) was added dropwise, and the resulting mixture was heated on a steam-bath for 5 min. The product (1·8 g) was collected after 12 h at 0°, and washed with a little methanol containing a few drops of hydrobromic acid and with ether. The *bilene*-b *hydrobromide* was obtained as red microprisms which darkened at *ca.* 180° (Found: C, 64·0; H, 7·6; N, 7·6. $C_{37}H_{51}BrN_4O_4$ requires C, 63·9; H, 7·4; N, 8·05%), $\lambda_{max.}$ 506 nm, $\nu_{max.}$ 1690 cm^{-1} (ester CO), τ 2·88 (s, =CH−), 5·64 (s, 2 × bridge CH_2), 5·73 (q, 2 × CO_2·CH_2·CH_3), 7·53 and 7·60 (overlapping q, 4 × CH_2·CH_3), 7·71—7·73 (superimposed s, 4 × CH_3), 8·66 and 8·96 (overlapping t, 4 × CH_2·CH_3), and 9·06 (t, 2 × CO_2·CH_2·CH_3).

Nickel(II) 1,19-*Bisethoxycarbonyl*-3,7,13,17-*tetraethyl*-2,8,12,18-*tetramethyltetradehydrocorrin Perchlorate*.—A suspension of the foregoing salt (440 mg) in ethanol (50 ml) containing nickel acetate (500 mg) and sodium acetate (1 g) was heated under reflux with aeration for 1 h. The volume of solvent was reduced to *ca.* 25 ml and a hot aqueous solution of potassium nitrate was added slowly and with swirling. On cooling, the *nitrate* was separated and washed with water, and crystallised from ethyl acetate–light petroleum as purple needles (340 mg, 70%), m.p. ∢300° (Found: C, 60·4; H, 6·8; N, 9·2. $C_{37}H_{45}N_5NiO_7$ requires C, 60·8; H, 6·2; N, 9·6%), *m/e* 667 (42%, M^+), 594 (91%, $M^+ - CO_2Et$), 565 (35%, $M^+ - CO_2Et - Et$), 521 (100%, $M^+ - 2CO_2Et$), 297 [6%, $(M^+ - CO_2Et)/2$], and 261·5 [6%, $(M^+ - 2CO_2Et)/2$]. The product was converted into the *perchlorate* by shaking a solution in dichloromethane with aqueous sodium perchlorate. It crystallised from acetone–benzene as purple needles with a bronze lustre, m.p. ∢300° (Found: C, 57·8; H, 5·8; N, 7·1. $C_{37}H_{45}ClN_4NiO_8$ requires C, 57·9; H, 5·9; N, 7·3%), $\lambda_{max.}$ 273, 357, and 572 nm (ε 26,400, 31,700, and 12,800), τ 2·46 and 2·61 (1 *meso*-H and 2 *meso*-H), 6·28 (q, 2 × ester CH_2·CH_3), 7·05 (overlapping q, 4 × CH_2·CH_3), 7·32 and 7·34 (both s, 4 × CH_3), 8·38—8·74 (overlapping t, 4 × CH_2·CH_3), and 9·23 (t, 2 × ester CH_2·CH_3), *m/e* 594 (53%, $M^+ - CO_2Et$), 565 (95%, $M^+ - CO_2Et - Et$), and 521 (100%, $M^+ - 2CO_2Et$).

Cobalt(II) 1,19-*Bismethoxycarbonyl*-3,7,13,17-*tetraethyl*-2,8,12,18-*tetramethyltetradehydrocorrin Perchlorate*.—A suspension of 1,19-dideoxy-1,19-bisethoxycarbonyl-3,7,13,17-tetraethyl-2,8,12,18-tetramethylbilene-*b* hydrobromide (500 mg) in *NN*-dimethylformamide (20 ml), containing cobalt acetate (500 mg), was heated at 70°, with aeration, for 4 h. The product was isolated as in the previous experiment; crystallisation of the *perchlorate* from ethyl acetate–light petroleum gave purple prisms (308 mg, 55%), m.p. ∢300° (Found: C, 58·1; H, 6·4; N, 7·4. $C_{37}H_{45}ClCoN_4O_8$ requires C, 57·9; H, 5·9; H, 7·3%), $\lambda_{max.}$ 284, 355, 507, and 574 nm (ε 26,700, 22,800, 13,000, and 7050), $\nu_{max.}$ 1735 cm^{-1} (ester CO), *m/e* 667 (100%, $M^+ - 1$), 595 (62%, $M^+ - CO_2Et$), 566 (19%, $M^+ - CO_2Et - Et$), and 522 (15%, $M^+ - 2CO_2Et$). The n.m.r. spectrum of the corresponding dicyanocobalt(III) complex [1] showed τ 2·96 (s, 2 *meso*-H), 3·03 (s, 1 *meso*-H), 6·33 (m, ABX system, 2 × ester CH_2·CH_3), 7·07 and 7·19 (overlapping q, 4 × CH_2·CH_3), 7·45 and 7·56 (both s, 4 × CH_3), 8·42—8·79 (overlapping t, 4 × CH_2·CH_3), and 9·16 (t, 2 × CH_2·CH_3).

Nickel(II) *and Cobalt*(II) 1,19-*Bisbenzyloxycarbonyl*-3,7,13,17-*tetraethyl*-2,8,12,18-*tetramethyltetradehydrocorrin Perchlorates*.—(i) 1,19-Bisbenzyloxycarbonyl-3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-1,19-dideoxybilene-*b* hydrobromide was obtained from the attempted condensation of 3-ethyl-3′,4,4′,5-tetramethyl-2,2′-dipyrromethane-5-carboxylic acid (hydrogenolysis of 5-benzyl ester) and 5-benzyloxycarbonyl-3,3′-diethyl-5′-formyl-4,4′-dimethyl-2,2′-dipyrromethane as already described for the corresponding diethyl ester. The *bilene*-b *hydrobromide* was obtained as red microprisms, m.p. 104—106°, $\lambda_{max.}$ 505 nm, $\nu_{max.}$ 1700 cm^{-1} (ester CO), τ 2·79 (m, 2 × Ph), 2·99 (s, =CH−), 4·72 (s, 2 × PhCH_2), 5·69 (s, 2 × bridge CH_2), 7·5 (overlapping q, 4 × CH_2·CH_3), 7·75—7·78 (superimposed s, 4 × CH_3), and 8·90, 8·95, and 9·01 (overlapping t, 4 × CH_2·CH_3).

(ii) The bilene-*b* salt was cyclised in the presence of nickel acetate as already described to yield the *nickel*(II) *tetradehydrocorrin perchloride* (58%) as purple needles with a bronze lustre, m.p. 189° (from acetone–benzene) (Found: C, 63·4; H, 5·9; N, 6·0. $C_{47}H_{49}ClN_4NiO_8$ requires C, 63·3; H, 5·5; N, 6·3%), $\lambda_{max.}$ 275, 361, and 574 nm (ε 29,000, 31,200, and 13,300), τ 2·31 (s, 1 *meso*-H), 2·80 (s, 2 *meso*-H), 2·89—3·16 and 3·36—3·47 (both m, aromatic H), 5·23, 5·37, 5·49, and 5·62 (AB systems for 2 × PhCH_2), 6·96 and 7·24 (overlapping q, 4 × CH_2·CH_3), 7·30 and 7·50 (both s, 4 × CH_3), and 8·40—8·92 (overlapping t, 4 × CH_2·CH_3), *m/e* 656 (38%, $M^+ - CO_2CH_2Ph$), and 521 (100%, $M^+ - 2CO_2CH_2Ph$).

(iii) The bilene-*b* hydrobromide (500 mg) was suspended in *NN*-dimethylformamide (20 ml) containing cobalt(II) acetate (500 mg) and heated at 100° with aeration for 1 h. The *perchlorate*, isolated in the usual manner, formed purple prisms, m.p. 205—206° (from ethyl acetate–light petroleum) (Found: C, 62·6; H, 5·5; N, 6·3. $C_{47}H_{41}$-

[31] M. Broadhurst, R. Grigg, and A. W. Johnson, *J. Chem. Soc.* (*C*), 1971, 3681.

$ClCoN_4O_8$ requires C, 63·3; H, 5·5; N, 6·3%), $\lambda_{max.}$ 278, 359, 513, and 575 nm (ε 46,500, 47,400, 12,400, and 18,500), $\nu_{max.}$ 1740 cm^{-1} (ester CO), *m/e* 656 (75%, $M^+ - CO_2CH_2Ph - 1$) and 521 (100%, $M^+ - 2CO_2CH_2Ph - 1$).

Nickel(II) *and Cobalt*(II) 1-*Benzyloxycarbonyl*-19-*ethoxycarbonyl*-3,7,13,17-*tetraethyl*-2,8,12,18-*tetramethyltetradehydrocorrin Perchlorates*.—(i) 5-Benzyloxycarbonyl-3,3′-diethyl-5′-formyl-4,4′-dimethyl-2,2′-dipyrromethane (XXI) (650 mg) and 5-ethoxycarbonyl-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrromethane (obtained by decarboxylation of the corresponding 5-carboxylic acid) (570 mg) were dissolved in methanol (100 ml) and hydrogen bromide in acetic acid (5 ml; 50%) was added. The mixture was warmed on a steam-bath for 5 min and after 12 h at 0° the red, amorphous product (801 mg, 65%) was separated, washed with a little methanol containing a few drops of hydrobromic acid, and dried. The product, 1-benzyloxycarbonyl-19-ethoxycarbonyl-3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-1,19-dideoxybilene-*b* hydrobromide, decomposed on attempted crystallisation; $\lambda_{max.}$ 507 nm, τ 2·70br (m, 5 aromatic H), 2·84 (s, =CH–), 4·69 (s, 2 × $PhCH_2$), 5·64 (s, 2 × bridge CH_2), 5·74 (q, 2 × $CO_2{\cdot}CH_2{\cdot}CH_3$), 7·6 (overlapping q, 4 × $CH_2{\cdot}CH_3$), 7·70 and 7·72 (both s, 4 × CH_3), and 8·96 and 9·01 (overlapping t, 5 × $CH_2{\cdot}CH_3$ including ester).

(ii) The bilene-*b* salt was cyclised in the presence of nickel acetate as already described to yield the *nickel*(II) *tetradehydrocorrin perchlorate* (55%) as purple plates with a bronze reflex, m.p. 206—208° (from ethyl acetate–light petroleum) (Found: C, 61·0; H, 6·0; N, 6·4. $C_{42}H_{47}ClN_4NiO_8$ requires C, 60·8; H, 5·7; N, 6·75%), $\lambda_{max.}$ 276, 357, and 573 nm (ε 18,500, 21,400, and 8800), τ 2·33, 2·60, and 2·80 (all s, 3 *meso*-H), 2·87—3·13, and 3·36—3·44 (m, 5 aromatic H), 5·22, 5·34, 5·48, and 5·60 (AB system of $PhCH_2$), 6·31 (q, $CO_2{\cdot}CH_2{\cdot}CH_3$), 7·05 (overlapping q, 4 × $CH_2{\cdot}CH_3$), 7·30, 7·40, and 7·50 (all s, 4 × CH_3), 8·68—8·90 (m, 4 × $CH_2{\cdot}CH_3$), and 9·26 (t, $CO_2{\cdot}CH_2{\cdot}CH_3$), *m/e* 729 (<1%, M^+), 656 (11%, $M^+ - CO_2Et$), 594 (55%, $M^+ - CO_2CH_2Ph$), and 521 (100%, $M^+ - CO_2Et - CO_2CH_2Ph$).

(iii) Cyclisation of the bilene-*b* in the presence of cobalt(II) acetate gave the corresponding *cobalt*(II) *tetradehydrocorrin perchlorate* as purple prisms, m.p. 196—197° (from ethyl acetate–light petroleum) (Found: C, 61·0; H, 6·05; N, 6·4. $C_{42}H_{47}ClCoN_4O_8$ requires C, 60·8; H, 5·7; N, 6·75%), $\lambda_{max.}$ 275, 348, 533, and 574 nm (ε 27,700, 30,000, 8050, and 11,800). The salt decomposed extensively in the mass spectrometer but peaks were observed at *m/e* 522 and 521 ($M^+ - CO_2CH_2Ph - CO_2Et$ and $M^+ - CO_2CH_2Ph - CO_2Et - 1$).

We thank the Royal Society for a Commonwealth Bursary (to J. A. E.), the National Research Council of Canada for a Fellowship (to J. W.), and the S.R.C., for a Studentship (to M. C.) and grants (to G. F. and M. W. R.)

[3/1966 *Received*, 25*th September*, 1973]