471. *Some Reactions of 2-2′-Pyrrolyl-1-pyrrolines*

By J. H. Atkinson and A. W. Johnson

Whereas basification of the methiodide of 2-2′-pyrrolyl-1-pyrroline produces a dimeric product, the corresponding reaction with 2-(4-ethyl-3,5-dimethyl-2-pyrrolyl)-1-pyrroline gives a pyrrolenine derivative. The use of a dipyrromethane derivative in the Vilsmeier reaction with 2-pyrrolidone gives rise to a reduced tripyrrolic compound which can be de-esterified and converted into a reduced tetrapyrrolic product by further condensation with a pyrrole. Formylation of 1-methyl-2-2′-pyrrolylpyrrolidine gives the 5′-formyl derivative which also has been converted into reduced tri- and tetra-pyrrolic compounds. The Vilsmeier reaction with 2,5-dimethylpyrrole and 2-pyrrolidone involves attack at the 3-position of the pyrrole ring and yields a tricyclic compound, formulated as (XVII).

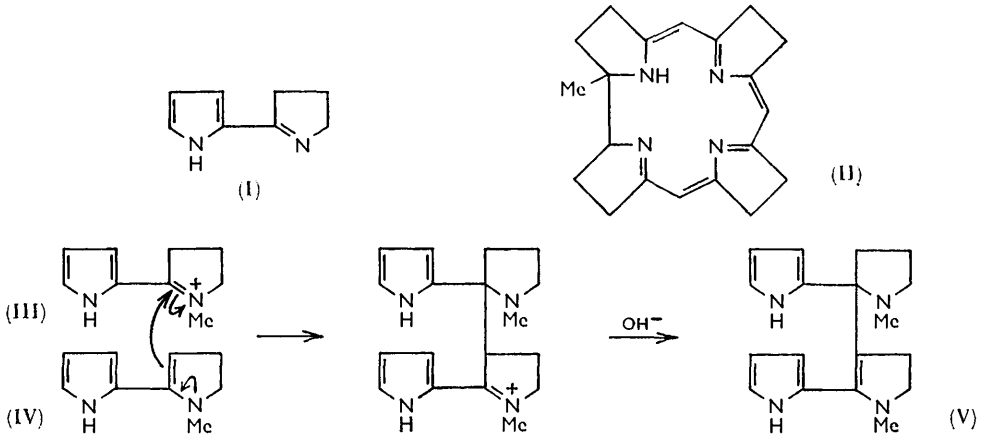
Although several methods are available for the preparation of 2-2′-pyrrolyl-1-pyrrolines [1] (I), they are most conveniently obtained by the method of Rapoport and Castagnoli [2] whereby a pyrrole is condensed with a 2-pyrrolidone in a modified Vilsmeier synthesis.

[1] H. Booth, A. W. Johnson, F. Johnson, and R. A. Langdale-Smith, *J.*, 1963, 650.
[2] H. Rapoport and N. Castagnoli, *J. Amer. Chem. Soc.*, 1962, **84**, 2178.

We have described [3] a preliminary study of the properties of the 2-2'-pyrrolyl-1-pyrrolines, with the object of utilising them as intermediates in syntheses of macrocyclic systems related to 1-methylcorrin (II), and some further reactions are described in the present Paper.

When the methiodide of unsubstituted 2-2'-pyrrolyl-1-pyrroline (III) was treated with base, a dimeric product, $C_{18}H_{24}N_4$, was obtained which was also formed by condensation of pyrrole with 1-methyl-2-pyrrolidone in presence of phosphorus oxychloride, followed by treatment of the intermediate salt with base. The ultraviolet spectrum of the product was similar to that of a 2-2'-pyrrolyl-1-pyrroline but also suggested the presence of an isolated pyrole ring. The infrared spectrum contained an absorption band corresponding to a pyrrolic NH group but no band associated with C=N was present. The main features of the nuclear magnetic resonance (n.m.r.) spectrum were consistent with the presence of six nuclear pyrrolic protons, ten methylenic protons, and two *N*-methyl groups.

This evidence is consistent with a formulation such as (V) for the dimer. Its formation



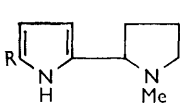
is visualised as an enamine-iminium interaction of the expected 2-pyrroline (IV) with the original salt and the reaction is paralleled by the dimerisation of simple tertiary 2-pyrrolines reported by other workers.[4]

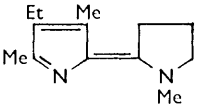
Reaction of the dimer with picric, styphnic, or perchloric acid resulted in the formation of the salts of the original monomer, a reversal of the above scheme, and the perchlorate was also synthesised unambiguously for comparison, from the methiodide (III) and silver perchlorate. Even hydrogenation in presence of platinum caused fission of the dimer and formation of 1-methyl-2-2'-pyrrolylpyrrolidine (VI; R = H). Other reagents which bring about the fission of similar dimers are cited by Leonard and Cook.[4]

However, when the methiodide of 2-(4-ethyl-3,5-dimethyl-2-pyrrolyl)-1-pyrroline was treated with base, the crystalline basic product was not the analogue of (V). It was also formed by condensation of 3-ethyl-2,4-dimethylpyrrole with 1-methylpyrrolidone under Vilsmeier conditions, followed by basification. The product formed a picrate and exhibited strong C=N absorption in the infrared spectrum at 1601 cm.$^{-1}$. The ultraviolet absorption was similar to that of the parent 2-(4-ethyl-3,5-dimethylpyrrolyl)-1-pyrroline. The n.m.r. signal at τ 6·11 (singlet) associated with the *N*-methyl group was appreciably to low field of the usual *N*-methyl absorptions and suggested that the *N*-methyl group might be associated with an extended conjugated system. Structure (VII), which can be derived from the expected 2-pyrroline [cf. (IV)] by a prototropic shift, is suggested for this

[3] J. H. Atkinson, R. Grigg, and A. W. Johnson, *J.*, 1964, 893.
[4] N. J. Leonard and A. G. Cook, *J. Amer. Chem. Soc.*, 1959, **81**, 5627; R. Lukeš, J. Plešek, and J. Trojánek, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1987.

product. The formation of either (V) or (VII) by the basification of different 2-2′-pyrrolyl-1-pyrroline methiodides is evidently governed by the diminution of resistance of the aromatic pyrrole ring towards rearrangement to the non-aromatic pyrrolenine caused by the presence of the three alkyl substituents. Hydrogenation of (VII) gave the corresponding


(VI)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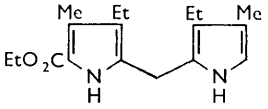
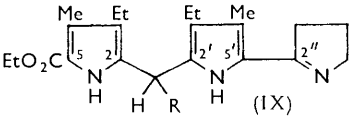
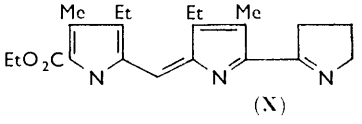
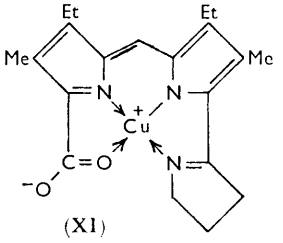

(VIII)

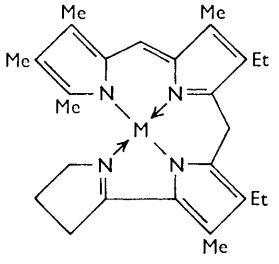
2-2′-pyrrolylpyrrolidine but we have been unable to achieve a 1,6-addition of methyl-lithium to the unsaturated system of (VII). This should have produced an angular methyl substituent at the direct linkage between the rings, a feature of the corrin (II). Examples of 1,6-additions of methylmagnesium iodide and methyl-lithium to dipyrromethenes are known [1] and a further example is cited below.

We have been able to utilise the 2-2′-pyrrolyl-1-pyrrolines as intermediates for the preparation of partially reduced tri- and tetra-pyrrolic systems. By substitution of the


(IX)


(X)


(XI)

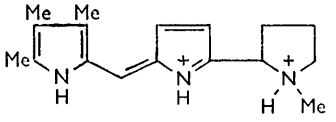

(XII)

5′-unsubsituted dipyrromethane-5-carboxylic ester [5] (VIII) for pyrrole in the Rapoport synthesis we obtained the 5′-(1″-pyrrolin-2″-yl)dipyrromethane ester (IX; R = H), which could be oxidised with manganese dioxide to the corresponding dipyrromethene (X). This ester (X) formed a beautiful green nickel complex which has been formulated as a tetrahedral complex involving two mol. of the substituted dipyrromethene. When oxidation of the dipyrromethane (IX; R = H) was attempted using cupric acetate,[6,7] the dipyrromethene (X) was again obtained, this time as a deep blue copper derivative in which there was a 1 : 1 metal–ligand ratio allowing for a hydrolysis of the ester group. This derivative has been provisionally formulated as the zwitterion (XI).

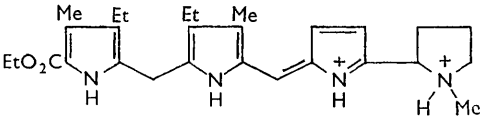
It was hoped that the electron-withdrawing properties of the dipyrromethene system or the corresponding salt in (X) would polarise the pyrroline ring to such an extent that methyl-lithium or methylmagnesium iodide would add to the azamethine linkage to produce an angular methyl substituent at the direct linkage but again this was not realised, for the central carbon–carbon double bond of the dipyrromethene portion of the molecule proved to be more reactive and the only product identified from the additions was the α-methyldipyrromethane ester (IX; R = Me). In another series the acid corresponding to (IX; R = H) was decarboxylated and the product condensed with 2-formyl-3,4,5-trimethylpyrrole,[8] in presence of hydrogen bromide, to give the reduced tetrapyrrolic derivative (XII; M = H_2) as deep red prisms of the dihydrobromide. The base was also characterised as its zinc complex (XII; M = Zn).

[5] A. H. Corwin and E. C. Coolidge, *J. Amer. Chem. Soc.*, 1952, **74**, 5196.
[6] A. W. Johnson and I. T. Kay, *J.*, 1961, 2418.
[7] E. Bullock, R. Grigg, A. W. Johnson, and J. W. F. Wasley, *J.*, 1963, 2326.
[8] A. W. Johnson, N. Shaw, and J. W. F. Wasley, *J.*, 1962, 2556.

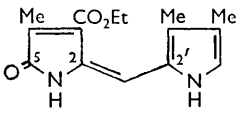
We have also prepared another series of compounds related to (X) and (XII) but containing 1-methylpyrrolidine in place of the 1-pyrroline ring. These preparations involved 1-methyl-2-2′-pyrrolylpyrrolidine [3] (VI; R = H) as starting material, which was obtained



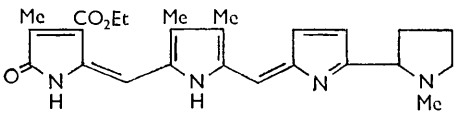
(XIII) 2 Br⁻



(XIV) 2 Br⁻

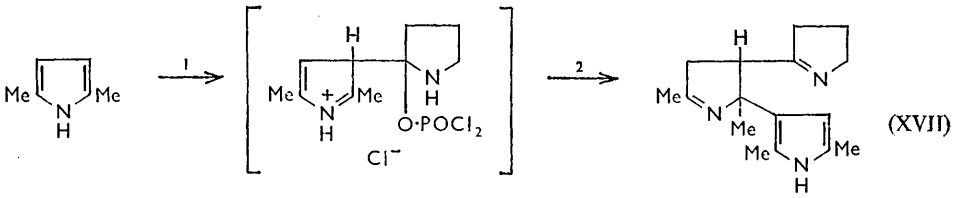


(XV)



(XVI)

from the methiodide of 2-2′-pyrrolyl-1-pyrroline (III) by reduction with sodium borohydride. We had observed previously [3] that (VI; R = H) did not condense with 3,4,5-trialkyl-2-formylpyrroles in presence of acid catalysts, probably because the pyrrolidinium salt deactivates the pyrrole ring towards electrophilic attack (cf. ref. 7). However, reaction of (VI; R = H) with *NN*-dimethylformamide in presence of phosphorus oxychloride gave the 5′-formyl derivative (VI; R = CHO) and this compound could be



(XVII)

Reagents: 1, $POCl_3$, 2-pyrrolidone; 2, 2,5-dimethylpyrrole, base

condensed with 2,3,4-trimethylpyrrole in presence of hydrogen bromide to give the dihydrobromide (XIII), and also with the dipyrromethane-5-carboxylic ester (VIII) under similar conditions to give the reduced tetrapyrrolic salt (XIV). Another variation was the condensation of (VI; R = CHO) with the oxidised dipyrromethene [9] (XV) to give the base (XVI), which was also characterised as its zinc complex. This compound is of interest because it contains the chromophore (apart from the ester substituent) of the bile pigment, mesobiliviolin.[10]

In another attempt to prepare reduced 2,2′-bipyrrolic systems containing angular methyl substituents, we investigated the condensation of 2,5-dimethylpyrrole with 2-pyrrolidone under Vilsmeier conditions. The product, $C_{16}H_{23}N_3$, was not the expected pyrrolinylpyrrolenine but was derived by an initial attack at the 3-position of the pyrrole ring. A second mol. of the 2,5-dimethylpyrrole was then added in a similar manner to the intermediate iminium salt to give the product, formulated as (XVII).

Experimental

Ultraviolet and visible absorption spectra were determined for ethanolic solutions except where otherwise stated. The infrared spectra refer to KBr discs except where otherwise stated. N.m.r. spectra were determined on an A.E.I. RS2 instrument operating at 60 Mc./sec. Light petroleum refers to the fraction, b. p. 60—80°.

1-Methyl-2-2′-pyrrolyl-3-(1-methyl-2-2′-pyrrolyl-2-pyrrolidinyl)-2-pyrroline (V).—(i) 2-2′-Pyrrolyl-1-pyrroline methiodide [3] (2·0 g.) was dissolved in water (20 c.c.) and the solution made strongly alkaline with 40% aqueous sodium hydroxide. The liberated oil was extracted with chloroform (3 × 30 c.c.), the combined extract dried ($MgSO_4$), and the solvent evaporated to give a pale yellow solid (0·55 g.). Crystallisation from benzene gave colourless *needles*, m. p.

[9] J. H. Atkinson, R. S. Atkinson, and A. W. Johnson, *J.*, 1964, 6001.
[10] C. H. Gray, A. Kulezycka, and D. C. Nicholson, *J.*, 1961, 2276.

123—124° (Found: C, 72·8; H, 7·95; N, 18·85%; *M*, 271. $C_{18}H_{24}N_4$ requires: C, 72·9; H, 8·15; N, 18·9%; *M*, 296), $\lambda_{max.}$ 216, 263, and 320·5 mμ (ε 12,860, 1780, and 18,430). Treatment of the foregoing base with ethanolic picric acid gave the *methopicrate* of 2-2′-pyrrolyl-1-pyrroline as yellow laths (from acetone–methanol), m. p. 178—179° (Found: C, 47·8; H, 3·75; N, 19·0. $C_{15}H_{15}N_5O_7$ requires C, 47·75; H, 4·0; N, 18·55%).

Treatment of the base with ethanolic styphnic acid gave the *methostyphnate* of 2,2′-pyrrolyl-1-pyrroline, as yellow micro-needles (from ethanol), m. p. 189—190° (Found: C, 45·7; H, 3·75; N, 17·8. $C_{15}H_{15}N_5O_8$ requires C, 45·8; H, 3·85; N, 17·8%). Treatment of the base with methanolic perchloric acid gave the *methoperchlorate* of 2-2′-pyrrolyl-1-pyrroline as colourless needles (from methanol–ether), m. p. 139—140° (Found: N, 11·2. $C_9H_{13}ClN_2O_4$ requires N, 10·8%). The sample exploded during the combustion analysis. The methoperchlorate of 2-2′-pyrrolyl-1-pyrroline was also prepared from the authentic methiodide, by treatment with silver perchlorate, and found to be identical with the above derivative.

(ii) Phosphorus oxychloride (13·7 c.c.) in dry ether (50 c.c.) was added, with stirring, to a mixture of pyrrole (10·5 c.c.) and 1-methyl-2-pyrrolidone (14·75 g.) in dry ether (100 c.c.) at room temperature. The addition was carried out over 15 min. and the mixture stirred for a further hour. The ether was decanted, the residue washed with more dry ether and dried *in vacuo*. An aqueous solution (250 c.c.) of the residue was made strongly alkaline with 40% aqueous sodium hydroxide, and the liberated base extracted with chloroform (3 × 50 c.c.). The chloroform solution was dried ($MgSO_4$) and the solvent evaporated to give a pale brown crystalline product (17·0 g.). Crystallisation from benzene gave colourless needles identical in every respect with the product from the previous experiment.

The main features of the n.m.r. spectrum (in $CDCl_3$) are as follows (τ values): 8·35 (*N*-methyl; singlet); 7·6 (*N*-methyl; singlet); 4·06 (4′ and 4‴-H; two superimposed multiplets); 3·79 and 3·6 (3′ and 3‴-H; two quartets); 3·17 (5′ and 5‴-H; two superimposed quartets).

1-*Methyl*-2-2′-*pyrrolylpyrrolidine*.—The dimeric base (500 mg.) from the foregoing experiment was dissolved in ethanol (20 c.c.) and hydrogenated at atmospheric pressure and room temperature using Adams catalyst. After the absorption of 2 mol. of hydrogen, the catalyst and solvent were removed leaving a residue which, on distillation, afforded a colourless oil (460 mg.), b. p. 102—104°/16 mm., n_D^{20} 1·5362. This solidified to give needles, m. p. 36—38° (lit.,[3] 36—38°). The *methiodide* formed stout needles (from ethanol–ether), m. p. 171·5—172·5° (Found: C, 41·2; H, 5·7; N, 9·8. $C_{10}H_{17}IN_2$ requires C, 41·1; H, 5·8; N, 9·6%).

4-*Ethyl*-3,5-*dimethyl*-2-(1-*methyl*-2-*pyrrolidinylidene*)*pyrrolenine* (VII).—(i) 2-(4-Ethyl-3,5-dimethyl-2-pyrrolyl)-1-pyrroline methiodide (3 g.) was dissolved in water (50 c.c.) and the solution made strongly alkaline with 40% aqueous sodium hydroxide. The liberated oil, which solidified on cooling, was separated, washed well with water, and dried (1·95 g.). The product was purified by sublimation (115°/0·5 mm.) or by crystallisation from light petroleum when it formed *needles*, m. p. 135—136° (Found: C, 76·2; H, 9·85; $C_{13}H_{20}N_2$ requires C, 76·4; H, 9·85%); $\lambda_{max.}$ 342·5 mμ (ε 24,480), $\lambda_{infl.}$ 277·8 mμ (ε 3720); $\nu_{max.}$ 1603 cm.$^{-1}$ (C=N). The *picrate* formed rhombs (from ethanol), m. p. 124—128° (Found: C, 52·6; H, 5·55; N, 16·6. $C_{19}H_{23}N_5O_7$ requires C, 52·65; H, 5·35; N, 16·2%).

(ii) Phosphorus oxychloride (12·5 g.) in dry ether (25 c.c.) was added, with stirring, to a mixture of 1-methyl-2-pyrrolidone (7·8 g.) and 3-ethyl-2,4-dimethylpyrrole (10·0 g.) in dry ether (50 c.c.) at 0°, during 15 min. After being stirred for a further hour at room temperature the ether was decanted, the residue washed with more ether and dried under vacuum. An aqueous solution (100 c.c.) of the residue was made strongly alkaline with hot 40% aqueous sodium hydroxide and the mixture kept for 1 hr. The aqueous suspension was extracted with chloroform (3 × 50 c.c.), the extract dried, and the solvent removed to give a pale yellow crystalline solid (7·3 g.). The product was crystallised from light petroleum as needles, m. p. 134—136°, identical in every respect with the product from the previous experiment. The n.m.r. spectrum (in $CHCl_3$) showed bands at (τ values): 8·93 (4′-methyl of ethyl group; triplet, J = 7·75 c./sec.); 7·75 (3′-methyl group; singlet); 7·65 (5′-methyl group; singlet); 6·8 (3-methylene group; multiplet); 6·35 (5-methylene group; multiplet); 6·14 (*N*-methyl group; singlet).

2-(4-*Ethyl*-3,5-*dimethyl*-2-*pyrrolyl*)-1-*methylpyrrolidine*.—The product (500 mg.) from the previous experiment was dissolved in methanol (25 c.c.) and hydrogenated at atmospheric pressure and room temperature using Adams catalyst. After the absorption of 1 mol. of

hydrogen, the catalyst and solvent were removed, to give a pale yellow oil (460 mg.), which was converted into the picrate (572 mg.), recrystallisation of which from ethanol gave *prisms*, m. p. 144—146° (Found: C, 52·1; H, 5·85; N, 16·05. $C_{19}H_{25}N_5O_7$ requires C, 52·4; H, 5·8; N, 16·1%). A sample of the base regenerated from the picrate, through the hydrochloride, had $\lambda_{max.}$ 230 mμ (ε 6440).

Ethyl 3,3'-Diethyl-4,4'-dimethyldipyrromethane-5-carboxylate (VIII).—The partial hydrolysis of diethyl 3,3'-diethyl-4,4'-dimethyldipyrromethane-5,5'-dicarboxylate was carried out according to the method of Corwin and Coolidge,[5] but the subsequent decarboxylation was effected by heating the acid (26·0 g.) in ethanolamine (9·0 g.) under reflux for 1 hr. After being poured into water, the aqueous suspension was extracted with ether (2 × 50 c.c.), the ether solution dried, and the solvent evaporated to give a semi-crystalline residue (10·0 g.). Crystallisation from light petroleum gave prisms, m. p. 86—88° (lit.,[5] 88—89°).

Ethyl 3,3'-Diethyl-4,4'-dimethyl-5-(1-pyrrolin-2-yl)dipyrromethane-5'-carboxylate (IX; R = H).—Phosphorus oxychloride (0·6 c.c.; redistilled) in dry ether (5 c.c.) was added, with stirring, to a mixture of 2-pyrrolidone (0·56 g.) and ethyl 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrromethane-5-carboxylate (2·0 g.), in dry ether (50 c.c.), in an atmosphere of nitrogen, at room temperature. After being stirred overnight the ether was decanted, the residue washed with more ether, and dissolved in chloroform (50 c.c.). The chloroform solution was shaken with ammonium hydroxide, followed by water, dried, and the solvent evaporated to give a pale yellow oil. Trituration of the oil with ethanol gave a crystalline solid (1·38 g., 55%), m. p. 133—138° and crystallisation from ethanol gave colourless *needles*, m. p. 145—146° (Found: C, 71·2; H, 8·4; N, 11·8%; *M*, 359. $C_{22}H_{31}N_3O_2$ requires C, 71·5; H, 8·45; N, 11·35%; *M*, 369), $\lambda_{max.}$ 246, 280, 299, and 338·5 mμ (ε 9530, 23,000, 20,100, and 5280) $\lambda_{max.}$ (in ethanolic hydrogen chloride) 277·5 and 339 mμ (ε 21,000 and 30,000), $\nu_{max.}$ (CCl_4) 1609 (C=N), 1680 (bonded ester C=O), and 1702 cm.$^{-1}$ (ester C=O).

The *picrate* formed deep yellow prisms (from ethanol) m. p. 191—192° (Found: C, 56·1; H, 5·5; N, 13·7. $C_{28}H_{34}N_6O_9$ requires C, 56·2; H, 5·7; N, 14·0%).

Ethyl 3,3'-Diethyl-4,4'-dimethyl-5-(1''-pyrrolin-2''-yl)dipyrromethene-5'-carboxylate (X).—Ethyl 3,3'-diethyl-4,4'-dimethyl-5-(1''-pyrrolin-2''-yl)dipyrromethane-5'-carboxylate (100 mg.) was dissolved in chloroform (20 c.c.) and the solution shaken with manganese dioxide at room temperature for 3 hr. The solution was filtered, the solvent evaporated and the residue crystallised from light petroleum, as deep orange *needles* (67 mg., 68%), m. p. 166—167° (Found: C, 71·5; H, 7·75; N, 11·3. $C_{22}H_{29}N_3O_2$ requires C, 71·9; H, 7·95; N, 11·45%), $\lambda_{max.}$ 224, 255, 260·5, and 446 mμ (ε 15,980, 22,850, 27,150, and 26,400), $\lambda_{max.}$ (in ethanolic hydrogen chloride) 275 and 345 mμ (ε 18,230 and 29,750), *i.e.*, indicating the addition of hydrogen chloride to the methene. The *nickel complex* crystallised from light petroleum as green prisms with a red reflex, m. p. 194—196° (Found: N, 10·65. $C_{44}H_{56}N_6NiO_4$ requires N, 10·5%), $\lambda_{max.}$ at 268, 279, 286, 470, 533, and 558 mμ (ε 14,830, 14,320, 13,560, 20,000, 38,400, and 43,500).

Cupric Acetate Oxidation of Ethyl 3,3'-Diethyl-4,4'-dimethyl-5-(1''-pyrrolin-2''-yl)dipyrromethane-5'-carboxylate.—The ester (75 mg.) was dissolved in methanol (10 c.c.) together with copper acetate (100 mg.) and the solution heated under reflux for 6 hr. The solvent was evaporated under reduced pressure, the residue dissolved in chloroform and chromatographed on an alumina column. Elution of a deep blue band with chloroform–methanol (10 : 1) and evaporation of the solvent gave a blue amorphous residue (43 mg.), which was crystallised from chloroform–light petroleum to give deep blue *needles* with a golden reflex, m. p. >300° (Found: C, 58·4; H, 6·2; Cu, 15·65; N, 10·2. $C_{20}H_{23}CuN_3O_2$ requires C, 59·9; H, 5·75; Cu, 15·85; N, 10·5%), $\lambda_{max.}$ 223·5, 300·5, 475, 580, and 625 mμ (ε 18,350, 21,350, 4480, 15,600, and 16,250).

Ethyl 3,3'-Diethyl-4,4',α-trimethyl-5-(1''-pyrrolin-2''-yl)dipyrromethane-5'-carboxylate (IX; R = Me).—A solution of ethyl 3,3'-diethyl-4,4'-dimethyl-5-1''-pyrrolin-2''-yl)dipyrromethene-5'-carboxylate (420 mg.) in dry ether (50 c.c.) was added, dropwise with stirring, to a solution of methylmagnesium iodide (3·1 mol.) in dry ether (100 c.c.) at room temperature. The solution was heated under reflux for 6 hr., cooled, the complex decomposed with water, the ethereal layer separated, and the aqueous layer extracted with ether (2 × 50 c.c.). The combined ether extract was dried and the solvent evaporated to give a pale yellow solid (350 mg.). The product was purified by crystallisation from light petroleum and after sublimation at 160°/0·1 mm. was obtained as colourless *prisms*, m. p. 158—160° (Found: C, 72·0; H, 8·7; N, 10·9. $C_{23}H_{13}N_3O_2$ requires C, 72·0; H, 8·7; N, 10·95%), $\lambda_{max.}$ 284 and 305 mμ (ε 23,000 and 22,850), $\lambda_{max.}$ (in ethanolic hydrogen chloride) 279 and 349 mμ (ε 20,800 and 28,350).

3,3'-Diethyl-4,4'-dimethyl-5-(1''-pyrrolin-2''-yl)dipyrromethane-5'-carboxylic Acid.—The corresponding ethyl ester (above; 1·0 g., 1 mole) was dissolved in ethanol (10 c.c.) and to the solution was added sodium hydroxide (1·1 mole) in water (20 c.c.). After heating the solution under reflux for 4 hr. the ethanol was evaporated, the aqueous solution cooled and just acidified with glacial acetic acid. The precipitate was separated, washed well with water, and dried to give a grey amorphous powder (730 mg.). Crystallisation from chloroform–methanol gave colourless *prisms*, m. p. 220° (decomp.) (Found: N, 12·45. $C_{20}H_{27}N_3O_2$ requires N, 12·3%).

The foregoing acid was decarboxylated by sublimation at 160°/0·1 mm., but the product was not purified and was used immediately in the next stage (below).

Condensation of 3,3'-Diethyl-4,4'-dimethyl-5-(1''-pyrrolin-2''-yl) dipyrromethane with 2-Formyl-3,4,5-trimethylpyrrole.—The foregoing decarboxylation product (90 mg.) was treated with 2-formyl-3,4,5-trimethylpyrrole (42 mg.) in methanol (10 c.c.) in presence of hydrobromic acid (0·1 c.c. of 48% w/v solution in acetic acid). After the solution had been kept for 2 hr. at room temperature, the dihydrobromide was separated, washed with ethanol, and dried (86 mg.). Crystallisation from chloroform–light petroleum gave the *product* (XII; M = H_2) as deep red prisms, m. p. 250° (decomp.) (Found: C, 55·6; H, 6·65; N, 9·3. $C_{27}H_{38}BrN_4$ requires C, 56·0; H, 6·55; N, 9·7%), $\lambda_{max.}$ 229·5, 297, 338·5, and 489 mμ (ε 11,220, 8,920, 26,850, and 73,700).

The zinc complex was obtained by dissolving the above dihydrobromide (60 mg.) in methanol (10 c.c.) and adding a solution of excess of zinc acetate–sodium acetate in water (5 c.c.). The resulting solution was warmed for a few minutes on a water-bath and kept at room temperature for 2 hr. The *complex* was separated, washed with methanol, and crystallised from chloroform–methanol as glittering red needles (48 mg.), m. p. >300° (Found: C, 67·5; H, 7·1; N, 11·85; ZnO, 17·0. $C_{27}H_{34}N_4Zn$ requires C, 67·7; H, 7·1; N, 11·65; ZnO, 17·7%), $\lambda_{max.}$ ($CHCl_3$) 348, 487, and 532 mμ (ε 20,700, 50,200, and 16,550).

2-Formyl-1-(1-methyl-2-pyrrolidinyl)pyrrole.—Phosphorus oxychloride (2·05 g.) in dry ether (10 c.c.) was added, with stirring, to a mixture of 1-methyl-2-2'-pyrrolylpyrrolidine [3] (2·0 g., 1 mole) and *NN*-dimethylformamide (5·0 g., 5 mole.) in dry ether (20 c.c.) at room temperature, and the mixture stirred overnight.

The ether was decanted, the residue washed with more dry ether, and dissolved in chloroform (50 c.c.). The chloroform layer was shaken with aqueous sodium hydroxide, followed by water, dried, and the solvent evaporated to give a dark brown oily residue. Distillation afforded a pale yellow viscous oil (1·1 g.), b. p. 164—165°/17 mm. which crystallised on standing, m. p. 75—82°. Crystallisation from light petroleum followed by sublimation at 75°/0·1 mm., gave colourless *prisms* m. p. 83—84° (Found: C, 67·0; H, 7·6; N, 15·2. $C_{10}H_{14}N_2O$ requires C, 67·4; H, 7·9; N, 15·7%), $\lambda_{max.}$ 250 and 297 mμ (ε 4320 and 20,300), $\nu_{max.}$ 1660 cm.$^{-1}$ (aldehyde C=O) and 1647 cm.$^{-1}$ (aldehyde C=O bonded).

The *picrate* formed deep yellow micro-needles (from acetone), m. p. 215° (decomp.) (Found: C, 47·3; H, 4·5; N, 16·9. $C_{16}H_{17}N_5O_8$ requires C, 47·15; H, 4·2; N, 17·2%).

3,4,5-Trimethyl-5'-(1''-methyl-2''-pyrrolidinyl)dipyrromethene Dihydrobromide.—2-Formyl-1-(1-methyl-2-pyrrolidinyl)pyrrole (100 mg.) and 2,3,4-trimethylpyrrole (60 mg.) were caused to react in methanol (20 c.c.), containing hydrobromic acid (0·1 c.c. of a 48% w/v solution in acetic acid). After several hours at 0°, the crystalline *dihydrobromide* was separated, washed with a little cold methanol, and dried (219 mg., 90%). Crystallisation from methanol containing 1% hydrobromic acid gave deep orange prisms, m. p. 200° (decomp.) (Found: C, 47·1; H, 5·9; N, 9·55. $C_{17}H_{25}Br_2N_3$ requires C, 47·35; H, 5·8; N, 9·75%), $\lambda_{max.}$ 230, 367, and 483 mμ (ε 14,900, 8640, and 123,000).

Condensation of 2-Formyl-1-(1-methyl-2-pyrrolidinyl)pyrrole with Ethyl 3,3'-Diethyl-4,4'-dimethyldipyrromethane-5-carboxylate.—The formyl derivative (80 mg.) and the dipyrromethane ester (135 mg.) in ethanol (10 c.c.) were treated with 48% (w/v) hydrogen bromide in acetic acid (0·1 c.c.). After keeping at 0° for several hours, the crystalline dihydrobomide was separated, washed with a little cold ethanol, and dried (235 mg., 85%). Crystallisation from ethanol containing 1% hydrobromic acid gave the *product* (XIV) as deep orange prisms with a blue-green reflex, m. p. 150° (decomp.) (Found: C, 52·3; H, 6·7; N, 8·8. $C_{28}H_{40}Br_2N_4O_2$ requires C, 52·15; H, 6·2; N, 8·7%), $\lambda_{max.}$ 229, 278, and 840 mμ (ε 8250, 10,000, and 21,900).

Condensation of 2-Formyl-1-(1-methyl-2-pyrrolidinyl)pyrrole with Ethyl 3',4,4'-Trimethyl-5-oxodipyrromethhene-3-carboxylate.—The formyl derivative (150 mg.) and the oxidised dipyrromethene (XV) (230 mg.) were dissolved in ethanol (50 c.c.) together with hydrobromic acid (2·0 c.c. of 48% w/v in acetic acid) and the solution heated under reflux for 15 min. The

deep violet solution was evaporated to dryness under reduced pressure and the residue dissolved in chloroform (50 c.c.). The chloroform solution was washed with ammonium hydroxide solution, followed by water, dried, and the solvent evaporated to give a deep red solid (370 mg.). The residue was dissolved in ether and chromatographed on an alumina column. Elution of the deep wine-red band with ether–chloroform (1 : 1) and crystallisation from ether–light petroleum gave the *product* (XVI) as deep red needles with a green reflex (51·0 mg.), m. p. 153—155° (Found: C, 69·4; H, 6·9; N, 13·0. $C_{25}H_{30}N_4O_3$ requires C, 69·1; H, 6·95; N, 12·9%), $\lambda_{max.}$ 244·5, 259·5, 308·5, 369, 539, and 565 mμ (ε 11,800, 11,200, 13,450, 22,200, 21,700, and 24,200). The zinc complex formed blue solutions with a bright red fluorescence and crystallised from chloroform–light petroleum as glistening purple prisms, m. p. >300°, $\lambda_{max.}$ ($CHCl_3$), 588 and 633 mμ (ε 29,750 and 53,100). Zinc mesobiliviolin [10] has $\lambda_{max.}$ 582·5 and 632·5 mμ.

5-(2,5-*Dimethyl*-3-*pyrrolyl*)-2,5-*dimethyl*-4-(1-*pyrrolin*-2-*yl*)-1-*pyrroline* (XVII).—2,5-Dimethylpyrrole (15·0 g., 1·5 moles) and 2-pyrrolidone (7·5 g., 1 mole.) were dissolved in dry ether (50 c.c.). To the stirred solution at room temperature, phosphorus oxychloride (16·15 g., 1·1 mole.) in dry ether (25 c.c.) was added over 15 min. After stirring for a further hour the ether was decanted and the residual red oil dissolved in water (100 c.c.). The solution was made slightly alkaline with sodium hydroxide solution and extracted with chloroform (3 × 50 c.c.). The combined extract was dried, evaporated to approximately 20 c.c., and chromatographed on an alumina column. Elution with chloroform yielded a fraction (4·45 g.) which crystallised on evaporation of the solvent, and had m. p. 176—182°. Crystallisation from chloroform–light petroleum afforded colourless *needles*, m. p. 181—183° (Found: C, 75·1; H, 8·9; N, 16·5%; *M*, 281. $C_{16}H_{23}N_3$ requires C, 74·65; H, 9·0; N, 16·3%; *M*, 257), $\lambda_{max.}$ 212 mμ (ε 8850), $\nu_{max.}$ 1635 and 1650 cm.$^{-1}$ (non-conjugated C=N). The n.m.r. spectrum (in $CHCl_3$) showed bands at (τ values): 8·85 (5-methyl; singlet); 7·96 (2-methyl; singlet); 7·88 and 7·81 (2′ and 5′-methyls; two singlets); 4·42 (4′-H; doublet, J = 2·3 c./sec.).

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