

## Oxidative Reactions of Polyarylpyrroles. Part 3.<sup>1</sup> Oxidative Trimerization of 2,5-Diphenylpyrrole

By Salvatore Petruso, Liliana Lamartina, Onofrio Migliara, and Vincenzo Sprio,\* Istituto di Chimica Farmaceutica e Tossicologica, Università di Palermo, via Archirafi 32, 90132 Palermo, Italy

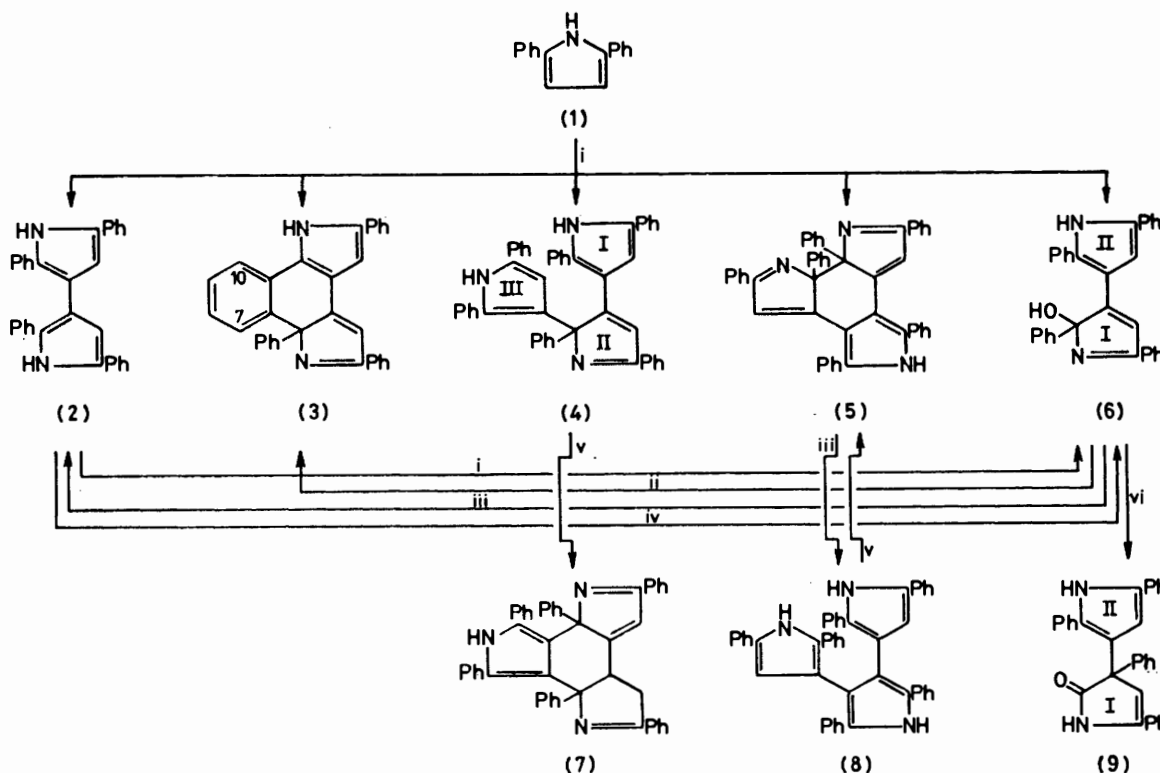
As in the oxidative reaction of 2,3,5-triphenylpyrrole previously studied, the oxidation of 2,5-diphenylpyrrole with potassium dichromate gave the dimer 2,2',5,5'-tetraphenyl-3,3'-bipyrrole (2) and the related hydroxy-derivative 3-(2,5-diphenylpyrrol-3-yl)-2,5-diphenyl-2*H*-pyrrol-2-ol (6), together with the tetracyclic compound 1,6a-dihydro-2,5,6a-triphenylbenzo[*g*]pyrrolo[3,2-*e*]indole (3), whose formation involves the  $\alpha$ -position of the pyrrole nucleus and the  $\alpha'$ -phenyl group of the other pyrrole ring. In addition, large amounts of both the trimer 2,3-bis-(2,5-diphenylpyrrol-3-yl)-2,5-diphenyl-2*H*-pyrrole (4) and the tetracyclic compound 6,6b-dihydro-1,3,5,6a,6b,8-hexaphenyl-2*H*-benzo[1,2-*c*:4,3-*b'*:5,6-*b''*]tripyrrole (5) were obtained. The formation of the various products of the oxidation is demonstrated in terms of the intermediate (2).

In preceding papers<sup>1,2</sup> we reported that oxidation of 2,3,5-triphenylpyrrole with potassium dichromate produced both the 3,3'-pyrrolyl dimer and, by migration of a phenyl group from the  $\alpha$ - to the  $\beta$ -position of a pyrrole ring, the 2,3'-pyrrolyl dimer, as well as related epoxy- and hydroxy-derivatives. Oxidation also gave a benzo-pyrroloindole, by involvement of the  $\alpha$ -position of a pyrrole nucleus and the  $\alpha'$ -phenyl group of the other

products which were separated by column chromatography [Scheme 1; the compounds were eluted in the order (1) to (5)].

### RESULTS AND DISCUSSION

Compound (2) ( $M^+$ , 436) has been characterized as 2,2',5,5'-tetraphenyl-3,3'-bipyrrole on the basis of its <sup>1</sup>H n.m.r. spectrum, which indicates a symmetric structure.



SCHEME 1 Reagents: i,  $K_2Cr_2O_7$ ; ii, aqueous  $H_2SO_4$ ; iii, Zn-AcOH; iv,  $H_2O_2$ ; v,  $KMnO_4$ ; vi, 210 °C

pyrrole ring. The purpose of the study reported herein was to examine the oxidative reaction of 2,5-diphenylpyrrole, in order to verify whether arylpyrroles with free  $\beta$ -positions follow a similar pathway. Oxidation of compound (1) with potassium dichromate in benzene solution at room temperature gave a mixture of

In fact, it shows only one band for two equivalent pyrrole NH protons and only one doublet coupled with NH for the two equivalent CH protons.†

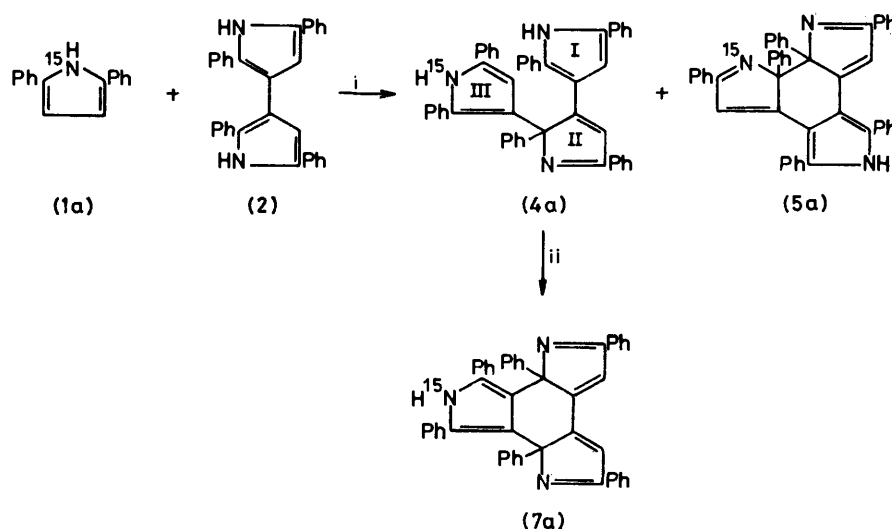
Compound (3) ( $M^+$ , 434) has been isolated in small

† The proton signals of the phenyl groups of all the compounds discussed are given in the Experimental section.

amounts. It was also obtained from the isolated bipyrrrole (2), either by oxidation with potassium dichromate under the same experimental conditions as above or by aerial oxidation. The  $^1\text{H}$  n.m.r. spectrum of compound (3) shows a pyrrole NH band, a CH singlet, a CH doublet coupled with NH, and two double doublets at  $\delta$  8.15 and 8.20 ( $J_o$  6.5 and  $J_m$  1.5 Hz) corresponding to the 7- and 10-H protons, as for the analogous product obtained from the oxidative reaction of the triphenylpyrrole.<sup>2</sup> Hence, compound (3) was identified as 1,6a-dihydro-2,5,6a-triphenylbenzo[*g*]pyrrolo[3,2-*e*]indole.

Other products chromatographically separated in good yields were compounds (4) and (5) ( $M^+$ , 653 and 651,

pyrroles (1) or (1a) links to an  $\alpha$ -position of the bipyrrrole (2); thus, the trimers (4) and (4a) must have either of the structures (A) or (B). To distinguish between these, we examined both compounds (7) ( $M^+$ , 651) and (7a) ( $M^+$ , 652) which were obtained quantitatively from the trimers (4) and (4a), respectively, by oxidation with potassium permanganate at room temperature. In the  $^1\text{H}$  n.m.r. spectrum of compound (7), the presence of only one NH band, which corresponds to one proton, and only one singlet, which corresponds to two equivalent CH protons, indicates a symmetric structure and the compound was identified as 3b,9a-dihydro-1,3,3b,5,8,9a-hexaphenyl-2*H*-benzo[1,2-*c*:3,4-*b'*:6,5-*b''*]tripyrrole. This has been con-

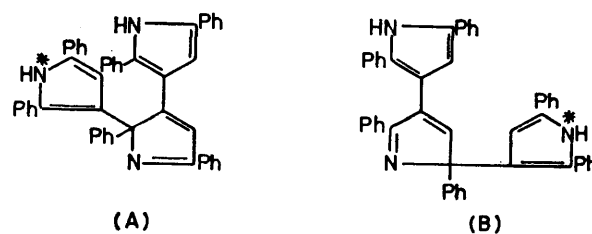


SCHEME 2 Reagents: i,  $\text{K}_2\text{Cr}_2\text{O}_7$ ; ii,  $\text{KMnO}_4$

respectively). Both compounds (4) and (5) were generated *via* the intermediate (2) by further oxidation; in fact, the oxidative reaction of the bipyrrrole (2) with the  $^{15}\text{N}$ -labelled pyrrole (1a) (1 mol equiv.) quantitatively afforded both the  $^{15}\text{N}$ -monolabelled compounds (4a) ( $M^+$ , 654) and (5a) ( $M^+$ , 652) (Scheme 2). In contrast, no trace of compound (5) was found (thin layer chromatography) when the isolated compound (4) was oxidized with potassium dichromate as described above. This indicates that compounds (4) and (5) are not structurally related.

The  $^1\text{H}$  n.m.r. spectrum [ $(\text{CD}_3)_2\text{CO}$ ] of compound (4) shows two pyrrole NH bands at  $\delta$  10.40 and 10.50, a CH singlet at  $\delta$  6.58, and two CH doublets, both coupled with NH, at  $\delta$  6.45 and 6.60. The  $^1\text{H}$  n.m.r. spectrum of compound (4a) in the same solvent shows a pyrrole NH broad band at  $\delta$  10.50, a pyrrole NH double doublet at  $\delta$  10.40 with  $^1J_{\text{HN}}$  95.2 and  $^4J_{\text{HH}}$  2.9 Hz, a CH singlet at  $\delta$  6.57, a CH double doublet at  $\delta$  6.60 with  $^3J_{\text{HN}}$  4.9 and  $^4J_{\text{HH}}$  2.9 Hz, and a CH doublet at  $\delta$  6.44 with  $^4J_{\text{HH}}$  2.7 Hz; addition of  $\text{D}_2\text{O}$  caused both the signals at  $\delta$  10.40 and 10.50 to disappear, that at  $\delta$  6.60 to collapse to a doublet with  $J$  4.9 Hz, and that at  $\delta$  6.44 to collapse to a singlet. These data demonstrate that, when these compounds are formed, a  $\beta$ -position of the diphenyl-

firmed by the  $^1\text{H}$  n.m.r. spectrum of the  $^{15}\text{N}$ -labelled benzotripyrrole (7a), which shows one NH doublet with  $^1J_{\text{HN}}$  95.1 Hz, which corresponds to one proton, and only one singlet, which corresponds to two equivalent CH protons. Consequently, structure (A) was assigned to the parent compounds (4) and (4a).



\* N =  $^{15}\text{N}$  in compound (4a).

Compound (5) also gave a very simplified  $^1\text{H}$  n.m.r. spectrum, characteristic of a symmetric structure: a broad band for one pyrrole NH proton and a singlet for two equivalent CH protons. The reduction of compound (5) with zinc and acetic acid at room temperature afforded compound (8) ( $M^+$ , 653), the  $^1\text{H}$  n.m.r. spectrum of which exhibited two different pyrrole NH bands, one for one pyrrole NH proton and the other for two equivalent pyrrole NH protons, together with only one doublet,

coupled with NH, for two equivalent CH protons. These results were sufficient to identify the compound as 2,2',2'',5,5',5''-hexaphenyl-3,3':4',3''-terpyrrole. This latter compound was reconverted into compound (5) on oxidation with potassium permanganate at room temperature. It follows that, in the oxidative reaction with dichromate, the formation of compound (5) can be understood in terms of rapid bond formation of the 2-2'' junction of the unisolated intermediate (8). Hence, compound (5) was identified as 6a,6b-dihydro-1,3,5,6a,6b,8-hexaphenyl-2*H*-benzo[1,2-*c*:4,3-*b*':5,6-*b*'']tripyrrole. This structural assignment is supported by the ease of cleavage which the  $\alpha$ - $\alpha'$  saturated bond in a symmetrical bis-pyrroline structures is known to undergo with soft reduction agents.<sup>3</sup> Further evidence for this structure is provided by the <sup>1</sup>H n.m.r. spectrum of the <sup>15</sup>N-labelled benzotripyrrole (5a), which shows only a single broad band for one pyrrole NH proton and only one singlet for two equivalent CH protons.

Although we lack specific proof for assignment of stereochemistry to compounds (5) and (7), the former is preferred on the basis that there would be less steric hindrance to the formation of a structure bearing *trans*-angular phenyl groups.

A further product which was chromatographically separated in appreciable yields from the reaction mixture was the oxygenated compound (6) ( $M^+$ , 452). This compound also was obtained by oxidation of the bipyrrrole (2) with both potassium dichromate, as above, and hydrogen peroxide in acetic acid. Also, compound (6) has the 3,3'-pyrrolyl dimer structure; in fact, when reduced with zinc and acetic acid, it was converted back into compound (2); furthermore, it gave compound (3) when treated with aqueous sulphuric acid. The <sup>1</sup>H n.m.r. spectrum of compound (6) shows only one pyrrole NH band, a CH doublet coupled with NH, and a CH singlet. Furthermore, the i.r. spectrum in hexachlorobutadiene exhibits a broad signal at 2 850 cm<sup>-1</sup> (OH). In order to establish the OH position, we examined the isomeric compound (9) ( $M^+$ , 452), obtained by thermal rearrangement of compound (6). The <sup>1</sup>H n.m.r. spectrum of compound (9) exhibits two NH bands and two CH doublets, both coupled with NH. The i.r. spectrum shows two NH bands and carbonyl group band at 1 720 cm<sup>-1</sup>. As for a cyclic amide structure,<sup>4</sup> the mass spectrum shows a significant peak which corresponds to  $[M - \text{NHCO}]^+$  at *m/e* 409 (exact mass measurement). \* These results identified compound (9) as 4-(2,5-diphenylpyrrol-3-yl)-2,4-diphenyl-2-pyrrolin-5-one and, consequently, the parent compound (6) as 3-(2,5-diphenylpyrrol-3-yl)-2,5-diphenyl-2*H*-pyrrol-2-ol. The formation of compound (9) involves the migration of the phenyl group from C-2 to C-3 of the pyrrole ring when heated, as reported for 2,3,4,5-tetraphenyl-2*H*-pyrrol-2-ol which rearranges to give 2,3,4,4-tetraphenyl-2-pyrrolin-5-one.<sup>5</sup>

In summary, the oxidative reaction of 2,5-diphenyl-

\* Found:  $M^+$ , 409.181.  $[\text{C}_{32}\text{H}_{24}\text{N}_2\text{O} - \text{NHCO}]$  requires  $M$ , 409.183.

pyrrole with potassium dichromate initially affords the 3,3'-bipyrrrole (2) which, in turn, undergoes oxidation to give small amounts of the tetracyclic compound (3), along with the hydroxy-dimer (6) and the trimers (4) and (8); the latter was not isolated because it immediately cyclized to the tetracyclic compound (5). It is remarkable that two unsubstituted  $\beta$ -positions in the 2,5-diphenylpyrrole render the trimerizations competitive with the dimerizations.

#### EXPERIMENTAL

M.p.s were determined on a Büchi-Tottoli capillary apparatus. I.r. spectra were recorded on Perkin-Elmer Infracord 137 and Perkin-Elmer 299 spectrophotometers as Nujol mulls (unless otherwise specified), and u.v. spectra on a Hitachi Perkin-Elmer 200 spectrophotometer for ethanolic solutions. <sup>1</sup>H N.m.r. spectra were recorded on Jeol C-60H and Varian FT-80A spectrometers, using tetramethylsilane as internal standard. The mass spectra were measured with a Jeol-01SG-2 double-focusing mass spectrometer at 75 eV (100  $\mu$ A). The samples were directly introduced and heated at *ca.* 200 °C. Exact masses were measured on Ilford O-2 photoplates; perfluorokerosene was used as a reference at a resolving power better than 15 000. Metastable peaks were detected by the acceleration voltage-scanning method. Silica gel for chromatography was Merck (0.05–0.2 mm) in the inactive form.

*Oxidation with Dichromate.*—To a stirred solution of chromatographically pure 2,5-diphenylpyrrole (1) (10 g, 45 mmol) in benzene (200 ml), a solution of potassium dichromate (15 g) in water (100 ml) and acetic acid (20 ml) was added and the mixture was shaken at room temperature for 48 h. Water (200 ml) was added and the aqueous phase, separated from the benzene layer, was extracted with ether (3  $\times$  50 ml). The ethereal extracts, combined with the benzene solution, were neutralized with aqueous sodium hydrogencarbonate, then dried over anhydrous sodium sulphate, filtered, and evaporated under reduced pressure. The residue, after adsorption over neutral alumina, was purified by column (50  $\times$  4 cm) chromatography over silica gel (400 g). Elution with cyclohexane–ethyl acetate (19 : 1) gave 2,5-diphenylpyrrole (1) (2.5 g), m.p. and mixed m.p. [with the initial pyrrole (1)] 146 °C. Further elution in the same solvent system afforded the 2,2',5,5'-tetraphenyl-3,3'-bipyrrrole (2) (0.5 g, 7%) † as white crystals from ethanol, m.p. 175 °C (Found:  $M^+$ , 436.196.  $\text{C}_{32}\text{H}_{24}\text{N}_2$  requires  $M$ , 436.194);  $\nu_{\text{max}}$  3 420 and 3 440 cm<sup>-1</sup> (NH);  $\lambda_{\text{max}}$  332 (log  $\epsilon$  4.57) and 235 nm (4.09);  $\delta$ [(CD<sub>3</sub>)<sub>2</sub>CO] 6.50 (2 H, d, <sup>4</sup> $J_{\text{HH}}$  2.5 Hz, singlet with D<sub>2</sub>O, 4- and 4'-H), 7.00–7.90 (20 H, m, Ph-H), and 10.40 (2 H, br, exchangeable with D<sub>2</sub>O, N- and N'-H). Elution with cyclohexane–ethyl acetate (9 : 1) gave 1,6a-dihydro-2,5,6a-triphenylbenzo[g]pyrrolo[3,2-*e*]indole (3) (0.1 g, 1.5%) as yellow crystals from ethanol, m.p. 180 °C (Found:  $M^+$ , 434.174.  $\text{C}_{32}\text{H}_{22}\text{N}_2$  requires  $M$ , 434.178);  $\nu_{\text{max}}$  (hexachlorobutadiene) 3 350br cm<sup>-1</sup> (NH);  $\lambda_{\text{max}}$  347sh (log  $\epsilon$  4.10), 330sh (4.25), 318 (4.31), 266 (4.31), and 243 nm (4.25);  $\delta$ (CDCl<sub>3</sub>) 6.60 (1 H, d, <sup>4</sup> $J_{\text{HH}}$  2.5 Hz, singlet with D<sub>2</sub>O, 3-H), 6.80 (1 H, s, 4-H), 7.00–7.80 (17 H, m, Ph-H), 8.15 and 8.20 (2  $\times$  1 H, dd,  $J_o$  6.5 and  $J_m$  1.5 Hz, 7- and 10-H), and 8.90 (1 H, br, exchangeable with D<sub>2</sub>O, N-H). Elution with cyclohexane–ethyl acetate (85 : 15)

† All the quoted yields reported in this paper are corrected for recovered starting material.

gave 2,3-bis-(2,5-diphenylpyrrol-3-yl)-2,5-diphenyl-2H-pyrrole (4) (2 g, 27%) as yellow crystals from ethanol, m.p. 170 °C (Found:  $M^+$ , 653.286.  $C_{48}H_{35}N_3$  requires  $M$ , 653.282);  $\nu_{\max}$ . 3 610 and 3 420  $\text{cm}^{-1}$  (NH);  $\lambda_{\max}$ . 308 (log  $\epsilon$  4.47) and 235sh nm (4.33);  $\delta[(\text{CD}_3)_2\text{CO}]$  6.45 (1 H, d,  $J_{\text{HH}}$  2.7 Hz, singlet with  $\text{D}_2\text{O}$ , 4-H of I-ring), 6.58 (1 H, s, 4-H of II-ring), 6.60 (1 H, d,  $^4J_{\text{HH}}$  2.7 Hz, singlet with  $\text{D}_2\text{O}$ , 4-H of III-ring), 6.90–7.90 (30 H, m, Ph-H), and 10.40 and 10.50 (2  $\times$  1 H, s, exchangeable with  $\text{D}_2\text{O}$ , N-H of I- and III-rings). Continued elution with cyclohexane-ethyl acetate (85:15) gave 6a,6b-dihydro-1,3,5,6a,6b,8-hexaphenyl-2H-benzo[1,2-c:4,3-b':5,6-b'']tripyrrole (5) (1.5 g, 20%) as yellow crystals from acetone, m.p. 230 °C (Found:  $M^+$ , 651.262.  $C_{48}H_{33}N_3$  requires  $M$ , 651.267);  $\nu_{\max}$ . 3 300  $\text{cm}^{-1}$  (NH);  $\lambda_{\max}$ . 313 (log  $\epsilon$  4.10), 270sh (4.15), and 248 nm (4.35);  $\delta[(\text{CDCl}_3)]$  6.75 (2 H, s, 3- and 7-H), 6.85–8.10 (30 H, m, Ph-H), and 8.90 (1 H, s, exchangeable with  $\text{D}_2\text{O}$ , N-H). Elution with cyclohexane-ethyl acetate (7:3) gave 3-(2,5-diphenylpyrrol-3-yl)-2,5-diphenyl-2H-pyrrol-2-ol (6) (2.5 g, 33%) as yellow prisms from acetone, m.p. 178 °C (Found:  $M^+$ , 452.192.  $C_{32}H_{24}N_2O$  requires  $M$ , 452.189);  $\nu_{\max}$ . 3 350  $\text{cm}^{-1}$  (NH);  $\nu_{\max}$ . (hexachlorobutadiene) 2 850  $\text{cm}^{-1}$  (OH);  $\lambda_{\max}$ . 314 (log  $\epsilon$  4.13), 278 (4.19), and 240 nm (4.01);  $\delta[(\text{CDCl}_3)]$  6.40 (1 H, s, 4-H of I-ring), 6.70 (1 H, d,  $^4J_{\text{HH}}$  2.7 Hz, singlet with  $\text{D}_2\text{O}$ , 4-H of II-ring), 6.90–7.90 (20 H, m, Ph-H), and 8.60 (1 H, br, exchangeable with  $\text{D}_2\text{O}$ , N-H).

The bipyrrrole (2) (0.2 g, 0.45 mmol) was oxidized by the same method, to give a mixture of the products (3) and (6), which were separated by preparative t.l.c. (cyclohexane-ethyl acetate, 7:3). The compounds were identical (m.p. and i.r., u.v., n.m.r., and mass spectra) with compounds (3) and (6) described above.

*Synthesis of 2,5-Diphenyl[ $^{15}\text{N}$ ]pyrrole (1a).*—To a solution of 1,4-diphenylbutane-1,4-dione (2.38 g, 10 mmol) in acetic acid (15 ml), ammonium acetate (0.8 g, 10 mmol) was added and the mixture was heated under reflux for 1 h at 120 °C (oil-bath). Water (100 ml) was added and the solution, neutralized with aqueous sodium hydrogen-carbonate, was extracted with ether (3  $\times$  100 ml). The ethereal extracts were washed with water, then dried over anhydrous sodium sulphate, and evaporated under reduced pressure. The residue was purified by column (60  $\times$  2 cm) chromatography over silica gel (100 g). Elution with cyclohexane-ethyl acetate (19:1) gave a white solid (1.9 g, 85%), which was recrystallized from ethanol, m.p. 145 °C (Found:  $M^+$ , 220.101.  $C_{16}H_{13}^{15}\text{N}$  requires  $M$ , 220.102);  $\nu_{\max}$ . 3 450  $\text{cm}^{-1}$  (NH);  $\lambda_{\max}$ . 328 (log  $\epsilon$  4.18) and 230 nm (3.58);  $\delta[(\text{CD}_3)_2\text{CO}]$  6.60 (2 H, dd,  $^3J_{\text{HN}}$  4.4 and  $^4J_{\text{HH}}$  2.6 Hz, doublet with  $\text{D}_2\text{O}$ ,  $J$  4.4 Hz, 3- and 4-H), 6.95–8.30 (10 H, m, Ph-H), and 10.50 (1 H, dt,  $^1J_{\text{HN}}$  95.1 and  $^3J_{\text{HH}}$  2.6 Hz, exchangeable with  $\text{D}_2\text{O}$ ,  $^{15}\text{N}$ -H).

*Preparation of 6a,6b-Dihydro-1,3,5,6a,6b,8-hexaphenyl-[6- $^{15}\text{N}$ ]-2H-benzo[1,2-c:4,3-b':5,6-b'']tripyrrole (5a) and 2-(2,5-Diphenyl[ $^{15}\text{N}$ ]pyrrol-3-yl)-3-(2,5-diphenylpyrrol-3-yl)-2,5-diphenyl-2H-pyrrole (4a).*—To a mixture of compounds (1a) (0.4 g, 1.8 mmol) and (2) (0.8 g, 1.8 mmol) in acetic acid (30 ml), 4 ml of a solution of potassium dichromate (1.5 g of dichromate in 10 ml of water and 2 ml of acetic acid) were added as drops with stirring at room temperature. After a few minutes, water (200 ml) was added and the solution was neutralized with aqueous sodium hydrogen carbonate and then extracted with ether. The ethereal extracts were washed with water, dried over anhydrous sodium sulphate, filtered, and evaporated under reduced pressure. A suspension of this residue in acetone (20 ml) gave, after 24 h,

the benzotripyrrrole (5a) (0.2 g, 17%) as yellow crystals from acetone, m.p. 215 °C (decomp.) (Found:  $M^+$ , 652.267.  $C_{48}H_{33}N_3^{15}\text{N}$  requires  $M$ , 652.264);  $\nu_{\max}$ . 3 300  $\text{cm}^{-1}$  (NH);  $\lambda_{\max}$ . 313 (log  $\epsilon$  4.10), 270sh (4.17), and 246 nm (4.36);  $\delta[(\text{CDCl}_3)]$  6.76 (2 H, s, 3- and 7-H), 6.90–8.00 (30 H, m, Ph-H), and 9.11 (1 H, s, exchangeable with  $\text{D}_2\text{O}$ , N-H). The acetic mother liquors were evaporated under reduced pressure and the residue was purified by column (60  $\times$  2 cm) chromatography over silica gel (100 g). Elution with cyclohexane-ethyl acetate (19:1) gave very small amounts of compounds (1a) and (2). Elution with cyclohexane-ethyl acetate (9:1) gave the product (4a) (0.4 g, 33%) as yellow crystals from ethanol, m.p. 160 °C (Found:  $M^+$ , 654.278.  $C_{48}H_{35}N_2^{15}\text{N}$  requires  $M$ , 654.279);  $\nu_{\max}$ . 3 610 and 3 420  $\text{cm}^{-1}$  (NH);  $\lambda_{\max}$ . 308 (log  $\epsilon$  4.50) and 234 nm (4.35);  $\delta[(\text{CD}_3)_2\text{CO}]$  6.44 (1 H, d,  $^4J_{\text{HH}}$  2.7 Hz, singlet with  $\text{D}_2\text{O}$ , 4-H of I-ring), 6.57 (1 H, s, 4-H of II-ring), 6.60 (1 H, dd,  $^3J_{\text{HN}}$  4.9 and  $^4J_{\text{HH}}$  2.9 Hz, doublet with  $\text{D}_2\text{O}$ ,  $J$  4.9 Hz, 4-H of III-ring), 6.75–7.95 (30 H, m, Ph-H), 10.40 (1 H, dd,  $^2J_{\text{HN}}$  95.2 and  $^4J_{\text{HH}}$  2.9 Hz, exchangeable with  $\text{D}_2\text{O}$ ,  $^{15}\text{N}$ -H), and 10.50 (1 H, br, exchangeable with  $\text{D}_2\text{O}$ , N-H). Subsequent elution in the same solvent system furnished a further quantity (0.1 g, 8%) of the pure tripyrrrole (5a), m.p. 215 °C (decomp.).

*Reduction of Compound (5) with Zinc and Acetic Acid.*—To a solution of compound (5) (0.3 g, 0.5 mmol) in acetic acid (30 ml), zinc powder (0.5 g) was added slowly. When the addition was complete, the mixture was stirred for a few minutes at room temperature, and then filtered. Water (100 ml) was added to the solution which was then basified with ammonia and extracted with ether. The ethereal extracts were dried over anhydrous sodium sulphate and then filtered and evaporated under reduced pressure to give 2,2',2'',5,5',5''-hexaphenyl-3,3':4',3''-terpyrrrole (8) (0.28 g, 90%) as a solid which was recrystallized from ethanol, m.p. 148 °C (Found:  $M^+$ , 653.285.  $C_{48}H_{35}N_3$  requires  $M$ , 653.282);  $\nu_{\max}$ . 3 410br  $\text{cm}^{-1}$  (NH);  $\lambda_{\max}$ . 330 (log  $\epsilon$  4.73) and 227 nm (4.45);  $\delta[(\text{CDCl}_3)]$  6.12 (2 H, d,  $^4J_{\text{HH}}$  2.7 Hz, singlet with  $\text{D}_2\text{O}$ , 4- and 4''-H), 6.95–7.50 (30 H, m, Ph-H), 8.23 (2 H, s, exchangeable with  $\text{D}_2\text{O}$ , N- and N''-H), and 8.45 (1 H, s, exchangeable with  $\text{D}_2\text{O}$ , N'-H).

Compound (6) (0.2 g, 0.5 mmol) was reduced by the same method to give the bipyrrrole (2) as white crystals from ethanol, m.p. and mixed m.p. [with a sample of compound (2) obtained in the above experiment] 175 °C.

*Oxidation of Compound (4) with Permanganate.*—A solution of potassium permanganate (0.25 g) in water (10 ml) was added to a solution of compound (4) (0.65 g, 1 mmol) in benzene (30 ml) and the mixture was shaken at room temperature. After 2 h, the reaction was complete and the aqueous phase, separated from the benzene layer, was extracted with benzene (2  $\times$  50 ml). The combined benzene solutions were evaporated under reduced pressure and the residue was purified by column (40  $\times$  2 cm) chromatography over silica gel (70 g). Elution with benzene gave 3b,9a-dihydro-1,3,3b,5,8,9a-hexaphenyl-2H-benzo[1,2-c:3,4-b':6,5-b'']tripyrrole (7) (0.5 g, 80%) as white needles from ethanol, m.p. 263 °C (Found:  $M^+$ , 651.269.  $C_{48}H_{33}N_3$  requires  $M$ , 651.267);  $\nu_{\max}$ . 3 460  $\text{cm}^{-1}$  (NH);  $\lambda_{\max}$ . 310sh (log  $\epsilon$  4.22), 255 (4.34), and 220 nm (4.46);  $\delta[(\text{CD}_3)_2\text{CO}]$  6.42 (2 H, s, 3- and 4-H), 6.70–8.30 (30 H, m, Ph-H), and 10.70 (1 H, s, exchangeable with  $\text{D}_2\text{O}$ , N-H).

Analogously, oxidation of compound (4a) under the same conditions gave 3b,9a-dihydro-1,3,3b,5,8,9a-hexaphenyl-[2- $^{15}\text{N}$ ]-2H-benzo[1,2-c:3,4-b':6,5-b'']tripyrrole (7a) as pale

yellow needles from ethanol, m.p. 263 °C (Found:  $M^+$ , 652.268.  $C_{48}H_{33}N_2^{15}N$  requires  $M$ , 652.264);  $\nu_{\max}$  3 460  $cm^{-1}$  (NH);  $\lambda_{\max}$  310sh (log  $\epsilon$  4.25), 255 (4.38), and 220 nm (4.43);  $\delta[(CD_3)_2CO]$  6.43 (2 H, s, 3- and 4-H), 6.85—8.20 (30 H, m, Ph-H), and 10.67 (1 H, d,  $^1J_{HN}$  95.1 Hz, exchangeable with  $D_2O$ ,  $^{15}N-H$ ).

The terpyrrole (8) (0.65 g, 1 mmol) was oxidized by the same method to give the *benzotripyrrole* (5) as yellow crystals from acetone, m.p. and mixed m.p. [with a sample of compound (5) described above] 230 °C.

*Oxidation of Compound (2) with Hydrogen Peroxide.*—To a solution of compound (2) (0.2 g, 0.5 mmol) in acetic acid (20 ml), 36% hydrogen peroxide (0.5 ml) was added. After 24 h, the solution was evaporated under reduced pressure. The residue was dissolved in water (50 ml) and the resultant solution, basified with ammonia, was extracted with ether (3  $\times$  50 ml). The ethereal extracts were dried over anhydrous sodium sulphate and evaporated to give the product (6) as yellow prisms from acetone, m.p. and mixed m.p. [with a sample of (6) described above] 178 °C.

*Action of Aqueous Sulphuric Acid on Compound (6).*—To a suspension of compound (6) (0.2 g, 0.5 mmol) in ethanol (10 ml), aqueous 10% sulphuric acid (10 ml) was added. The mixture was refluxed for 1 h, water (100 ml) was added, and the solution was basified with aqueous (17 Bé \*) ammonia. Extraction with ether (3  $\times$  50 ml) (after drying over anhydrous sodium sulphate) and evaporation of the

\* Bé = Baumé, a unit of specific gravity ('Handbook of Chemistry and Physics,' 35th edn., eds. C. D. Hogman, R. C. Weast, and C. W. Wallace, 1953, p. 1951).

ether under reduced pressure, gave the *benzopyrroloindole* (3) as yellow crystals from ethanol, m.p. and mixed m.p. [with a sample of compound (3) described above] 180 °C.

*Melting of Compound (6).*—Melting of compound (6) (0.5 g, 1 mmol) *in vacuo* at 210 °C for 30 min gave a solid, which was recrystallized from ethanol. Pale yellow crystals of 4-(2,5-diphenylpyrrol-3-yl)-2,4-diphenyl-2-pyrrolin-5-one (9) were obtained, m.p. 158 °C (Found:  $M^+$ , 452.191.  $C_{32}H_{24}N_2O$  requires  $M$ , 452.189);  $\nu_{\max}$  3 420 and 3 280 (NH), and 1 720  $cm^{-1}$  (CO);  $\lambda_{\max}$  312 (log  $\epsilon$  4.37), 223sh nm (4.32);  $\delta(CDCl_3)$  5.75 (1 H, d,  $^4J_{HH}$  2.0 Hz, singlet with  $D_2O$ , 3-H of I-ring), (1 H, d,  $^4J_{HH}$  3.0 Hz, singlet with  $D_2O$ , 4-H of II-ring), 7.00—7.50 (20 H, m, Ph-H), and 8.40 and 8.90 (2  $\times$  1 H, br, exchangeable with  $D_2O$ , pyrrole and pyrroline N-H).

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