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The behaviour of 2,4,5-triphenylpyrrole and 2-(*p*-tolyl)-4,5-diphenylpyrrole under oxidation conditions with dichromate has been investigated. The several reaction products obtained were separated by column chromatography. In addition to products previously obtained using other oxidizing agents (2), additional products were isolated, namely, the 2,3'-dimers IIIa,b and related oxygenated products Va,b and VIa,b. Their structures were assigned by means of elemental analyses, chemical behaviour and spectroscopic data (ir, uv, nmr and ms).

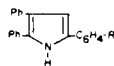
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In the course of investigating oxidation of polyphenylpyrrole (1,2) we wished to explore the oxidation of 2,4,5-triphenylpyrrole (Ia) with dichromate.

Oxidation of Ia with potassium dichromate in benzene solution at room temperature gave several reaction products which were separated by column chromatography. The compounds which were obtained with the yields are listed in Table I, the progressive number indicating the elution order.

In part, the same compounds obtained with other oxidizing agents (2) were isolated. These are 3,3'-pyrrol dimer (IIa) and the condensation product IVa. Other products obtained in appreciable yields (Table I) were

Table I



Pale yellow crystals, m.p. 249-250°, yield 20%; C ₄₄ H ₃₂ N ₂ (M ⁺ 588).	Pale yellow crystals, m.p. 183-184°, yield 20%; C ₄₆ H ₃₆ N ₂ (M ⁺ 616).
Pale yellow crystals, m.p. 242°, yield 16%; C ₄₄ H ₃₂ N ₂ (M ⁺ 588).	Pale yellow crystals, m.p. 220-221°, yield 13%; C ₄₆ H ₃₆ N ₂ (M ⁺ 616).
Yellow crystals, m.p. 269-270°, yield 3%; C ₄₄ H ₃₀ N ₂ (M ⁺ 586).	Yellow crystals, m.p. 200°, yield 3%; C ₄₆ H ₃₄ N ₂ (M ⁺ 614).
Yellow crystals, m.p. 185°, yield 5%; C ₄₄ H ₃₂ N ₂ O (M ⁺ 604).	Yellow crystals, m.p. 190°, yield 10%; C ₄₆ H ₃₆ N ₂ O (M ⁺ 632).
Yellow crystals, m.p. 160°, yield 4%; C ₄₄ H ₃₂ N ₂ O (M ⁺ 604).	Yellow crystals, m.p. 164°, yield 6%; C ₄₆ H ₃₆ N ₂ O (M ⁺ 632).

also dimers with the common skeleton, namely, IIIa (C₄₄H₃₂N₂, M⁺ 588), Va (C₄₄H₃₂N₂O, M⁺ 604) and VIa (C₄₄H₃₂N₂O, M⁺ 604). In fact both Va and VIa gave IIIa by reduction (Scheme I).

The presence of two non equivalent pyrrole NH bands in the ir spectrum (3440 and 3420 cm⁻¹) and in the nmr

spectrum (12.08 and 12.24 δ, exchangeable with deuterium oxide) of IIIa, contrary to the symmetric pyrrol dimer IIa, allows us to assign it the structure of the 2,3'-pyrrol dimer, obtained by migration of a phenyl group from the 2 to the 3 position of the pyrrole ring.

By further oxidation (heating with dichromate in acetic acid) of Va and VIa it follows that these compounds are oxygenated on the B nucleus: in fact both Va and VIa gave the 1-(3,4,5-triphenylpyrrol-2-yl)-2-phenyl-1,2-ethanedione (VIIa) which gave the known 2,3,4-triphenylpyrrole (VIIIa) (3) by alkaline hydrolysis (Scheme I).

The ease of reduction of Va and VIa to IIIa shows a lower oxidation of the B nucleus and it is reasonable to suppose that Va and VIa have epoxy and hydroxy structures, respectively (4).

Compound Va is an epoxide because the ir and the nmr spectra show two pyrrole NH bands. Furthermore, the mass spectrum shows one peak with a relative intensity of 6% at m/e 588 [M-O]⁺⁺ (5) and significant peaks at m/e 499 [M-C₆H₅CO]⁺ and m/e 105 [C₆H₅CO]⁺ (Table II). Although this behaviour agrees with an epoxide structure (5,6), it does not give evidence about the epoxide bridge position, unless the substituents of the B nucleus are differentiated.

Therefore, the 2-(*p*-tolyl)-4,5-diphenylpyrrole (Ib) was oxidized under identical experimental conditions and the related compounds b were obtained (Table I); the correlation was fixed by comparison of the elution time and analytical and spectroscopic data. Also the chemical behaviour was identical: in fact IVb, by oxidation with dichromate in acetic acid, gave IIIb and, by oxidation and following alkaline hydrolysis, VIIIb, through VIIb.

The mass spectrum of Vb allows us to localize, without any doubt, the epoxide bridge between the 2'- and the 3'-positions: in fact this shows the fragments [M-CH₃C₆H₄CO]⁺ and [CH₃C₆H₄CO]⁺ in place of the corresponding [M-C₆H₅CO]⁺ and [C₆H₅CO]⁺ (Table II, Scheme II). Besides fragment [M-C₆H₅]⁺, this spectrum shows one peak at m/e 541 [M-C₆H₄CH₃]⁺, which agrees

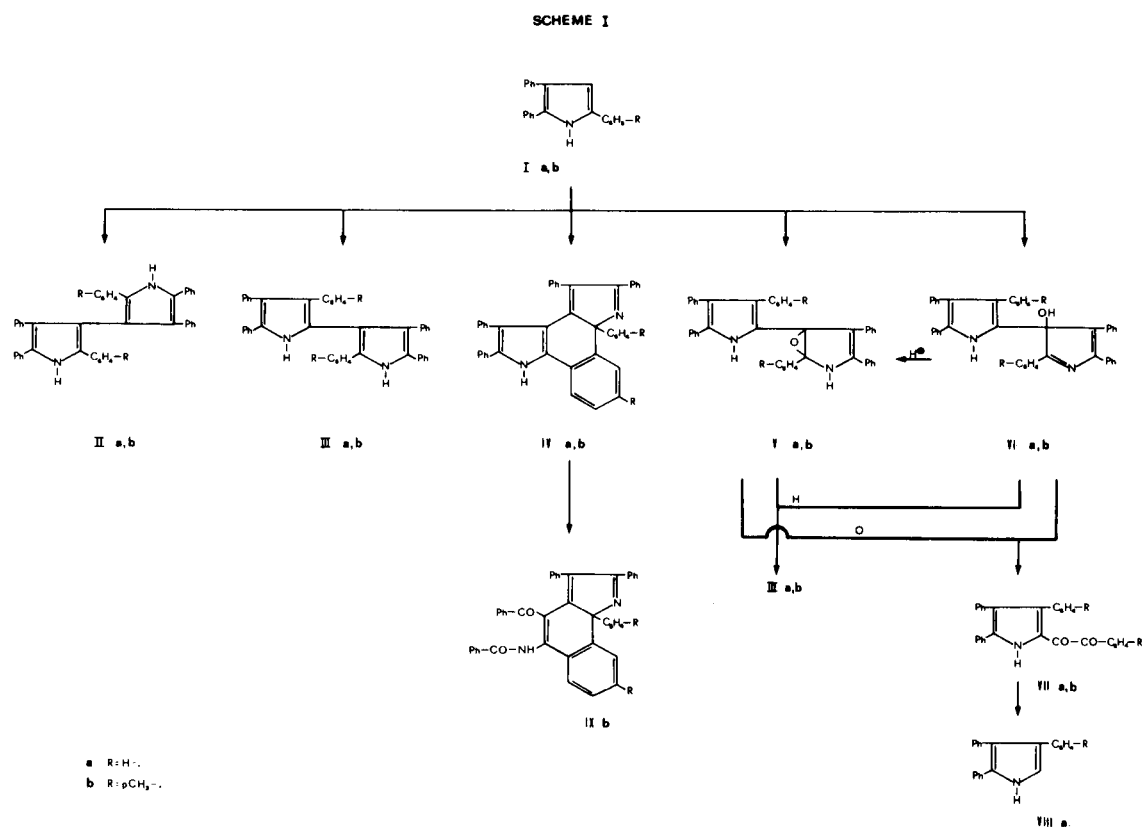


Table II

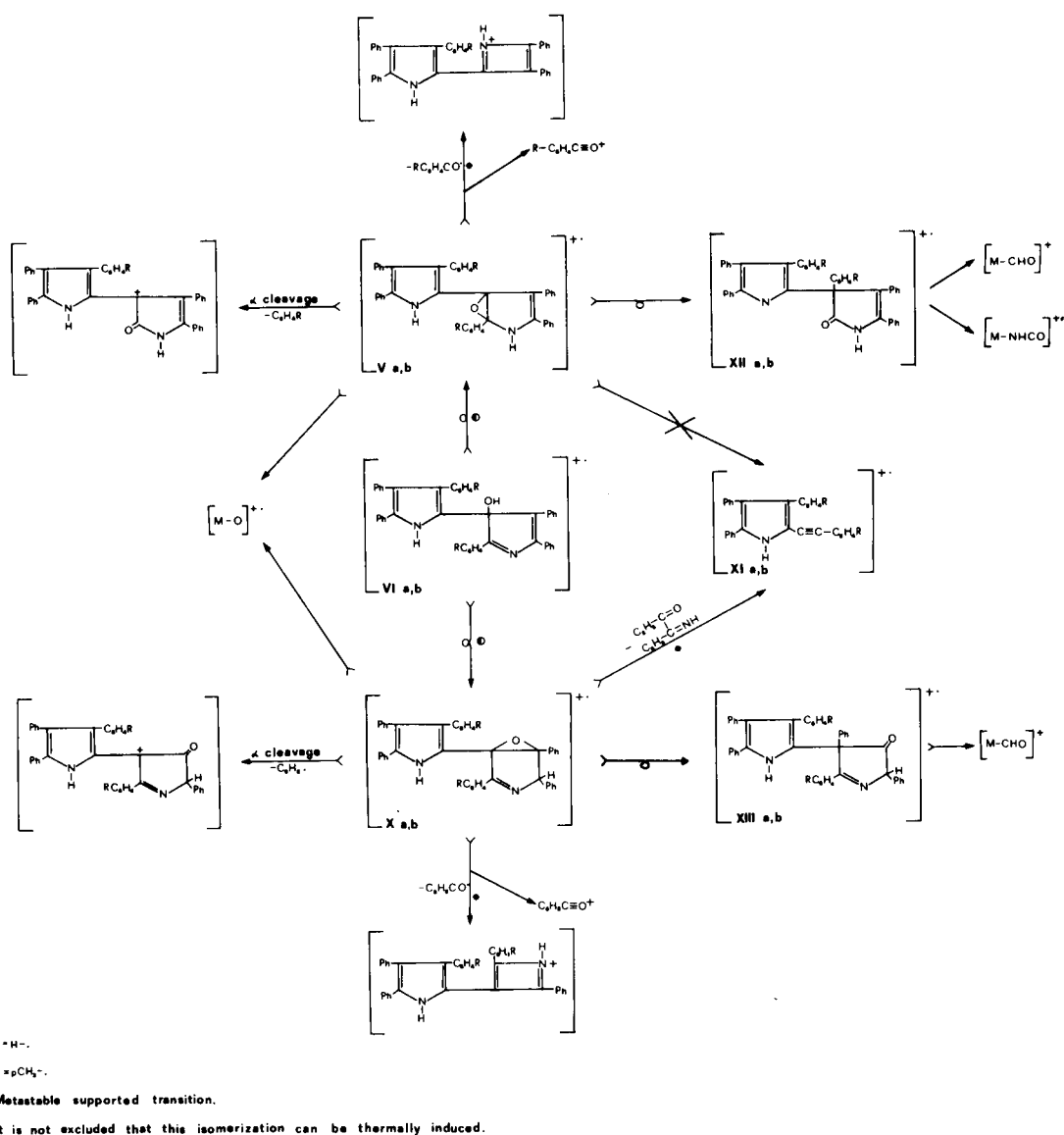
Mass Spectra of V and VI Derivatives

Ion	Va m/e (I%)	Vb m/e (I%)	VIa m/e (I%)	VIb m/e (I%)
[M] ⁺⁺	604 (100)	632 (100)	604 (100)	632 (100)
[M-O] ⁺⁺	588 (5)	616 (15)	588 (2)	616 (5)
[M-CHO] ⁺⁺	575 (5)	603 (5)	575 (5)	603 (16)
[M-NHCO] ⁺⁺	561 (10)	589 (10)	561 (1)	589 (3)
[M-C ₆ H ₅] ⁺	527 (85)	555 (70)	527 (7)	555 (9)
[M-C ₇ H ₇] ⁺	(a)	541 (27)	(a)	541 (18)
[M-C ₆ H ₅ CO] ⁺	499 (32)		499 (5)	527 (8)
[M-CH ₃ C ₆ H ₄ CO] ⁺	(a)	513 (31)	(a)	513 (7)
[M-209] ⁺⁺			395 (7)	423 (13)
[M] ⁺⁺	302 (22)	316 (22)	302 (10)	316 (32)
CH ₃ C ₆ H ₄ C=O ⁺	(a)	119 (7)	(a)	119 (14)
CH ₃ C ₆ H ₄ C≡NH ⁺	(a)		(a)	118 (9)
C ₆ H ₅ C=O ⁺	105 (4)		105 (10)	105 (22)
C ₆ H ₅ C≡NH ⁺	104 (12)	104 (10)	104 (8)	104 (3)
[C ₇ H ₇] ⁺	(a)	91 (5)	(a)	91 (7)
[C ₆ H ₅] ⁺	77 (12)	77 (7)	77 (8)	77 (6)

(a) Impossible to obtain.

SCHEME II

Fragmentation pathways of V and VI derivatives.



with the loss of the substituent in the α -position at the epoxide oxygen (6).

Compound VIa is an hydroxy compound. In fact, the nmr spectrum shows only one pyrrole NH band and the ir spectrum (hexachlorobutadiene) exhibits a signal at 3380 cm^{-1} (NH) and a broad signal at 2800 cm^{-1} (OH). As VIa,b gave Va,b with a catalytic amount of hydrochloric acid, the hydroxyl group can only be on the 2'- or the 3'-position.

Once again the mass spectrum of "labeled" compound VIb allows the structure determination. In fact it shows significant peaks, though with small intensity, for loss of both $\text{CH}_3\text{-C}_6\text{H}_4\text{CO}$ and $\text{C}_6\text{H}_5\text{CO}$. The logical explanation

of this behaviour is that the hydroxyl group is at the 3 position and the above cited peaks are generated through partial isomerization in V and X epoxides (Scheme II); the formation of this latter structure is supported by a peak at $m/e\ 616\ [\text{M-O}]^{++}$. In the spectra of VIa and VIb, the presence of intermediate Xa,b is surrounded by fragment ion XIa,b generated from the molecular ion by one step loss of benzoylmonoisimide (Scheme II, Table II).

Finally, the other significant fragments agree with proposed structures: $[\text{M-NHCO}]^{++}$ ions from intermediate XIIa,b and $[\text{M-HCO}]^+$ ions from XIIa,b and XIIIa,b. The formation of XII and XIII is in agreement with the well known 1,2 transposition reactions of epoxide compounds,

frequently found in either electron-impact-induced (6) and acid catalysis reactions (7,8).

In summary, the oxidation of triphenylpyrrole with dichromate showed, in addition to the more general oxidation pathway beginning with the 3,3'-pyrrol dimer, an interesting formation of the 2,3'-pyrrol dimer. For a better understanding of arylpyrrole chemistry, further studies on the oxidation of triphenylpyrrole under different experimental conditions and on other polyarylpyrroles are in progress.

EXPERIMENTAL

All melting points were taken on a Buchi-Tottoli capillary melting point apparatus and are uncorrected.

Ultraviolet absorption spectra were determined in ethanol solution with a Beckmann DB recording spectrophotometer and infrared absorption spectra with a Perkin Elmer Infracord 137 using nujol mulls (unless otherwise specified).

Nmr spectra (deuteriochloroform; unless otherwise specified) were measured using tetramethylsilane as the internal standard, with a Jeol C-60H and Varian XL-100-15 spectrometers.

The mass spectra were measured with a Jeol JMS-01SG-2 double focusing spectrometer at 75 eV (100 μ A). The samples were directly introduced and heated at about 200°. Exact masses were measured on Ilford Q-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 of 2,4,5-Triphenylpyrrole (Ia) with Dichromate.

To a stirred solution of Ia (15 g.) in benzene (300 ml.), 15 g. of potassium dichromate in water (50 ml.) and acetic acid (5 ml.) were added. After stirring at room temperature for 24 hours, the reaction mixture was washed with aqueous sodium bicarbonate. The benzene solution was dried (sodium sulfate) and evaporated to give a residue which was purified by column (60 x 5 cm) chromatography over silica gel (400 g.). Elution with cyclohexane-benzene (1:1): F₁₋₃ (each 100 ml.) gave 4 g. of 2,3,5-triphenylpyrrole (Ia), m.p. 140-141°. Elution with cyclohexane-benzene (3:7): F₄₋₂₀ (each 100 ml.) gave 3 g. (yield 20%) of 2,4,5,2',4',5'-hexaphenyl-3,3'-bipyrrrole (IIa), m.p. and mixed m.p. 249-250° (2); F₂₇₋₄₀ (each 100 ml.) gave 2.5 g. (yield 16%) of IIIa. Further elution with benzene: F₅₀₋₅₄ (each 100 ml.) gave 0.5 g. (yield 3%) of 1,6-dihydro-2,3,4,5,6a-pentaphenylbenzo[g]pyrrolo[3,2-e]indole (IVa), m.p. and mixed m.p. 269-270° (2). Elution with benzene-ethyl acetate (9:1): F₆₀₋₆₈ (each 100 ml.) gave 0.8 g. (yield 5%) of Va; F₇₂₋₈₀ (each 100 ml.) gave 0.6 g. (yield 4%) of VIa.

3,4,5,2',4',5'-Hexaphenyl-2,3'-dipyrryl (IIIa).

Pale yellow crystals were obtained from ethanol, m.p. 242°; ir (hexachlorobutadiene): 3440 and 3420 cm^{-1} (2 pyrrole NH); uv: λ max nm log ϵ 312 (4.93) 252 sh (4.91) 232 (4.97); nmr (pyridine-d₅): 6.60-8.00 δ (30H, m, aromatic H), 12.08 and 12.24 δ (2H, broad, 2 pyrrole NH, exchangeable with deuterium oxide); MW: 588 (ms).

Anal. Calcd. for C₄₄H₃₂N₂: C, 89.79; H, 5.44; N, 4.76. Found: C, 89.55; H, 5.57; N, 4.83.

1,3,4-Triphenyl-5-(3,4,5-triphenylpyrrol-2-yl)-6-oxa-2-azabicyclo[3.1.0]hex-3-ene (Va).

Yellow crystals were obtained from ethanol, m.p. 185°; ir 3410 cm^{-1} (pyrrole NH); uv: λ max nm log ϵ 302 (3.96) 253 sh (4.08); nmr: 5.80-7.40 δ (30H, m, aromatic H), 9.40 and 9.90 δ (2H, s, NH, exchangeable with deuterium oxide); ms: 604 (M⁺) (see Table II).

Anal. Calcd. for C₄₄H₃₂N₂O: C, 87.39; H, 5.33; N, 4.63. Found: C, 87.40; H, 5.30; N, 4.61.

2,4,5-Triphenyl-3-(3,4,5-triphenylpyrrol-2-yl)-3H-pyrrol-3-ol (VIa).

Yellow crystals were obtained from ethanol, m.p. 160°; ir (hexachlorobutadiene): 3380 (pyrrole NH), 2800 cm^{-1} (broad, OH); uv: λ max nm log ϵ 286 (4.19) 244 sh (4.33); nmr: 6.50-7.70 δ (30H, m, aromatic H), 8.62 δ (1H, s, pyrrole NH, exchangeable with deuterium oxide); ms: 604 (M⁺) (see Table II).

Anal. Calcd. for C₄₄H₃₂N₂O: C, 87.39; H, 5.33; N, 4.63. Found: C, 87.60; H, 5.31; N, 4.49.

Oxidation of Va and VIa. 1-(3,4,5-Triphenylpyrrol-2-yl)-2-phenyl-1,2-ethanedione (VIIa).

A solution of potassium dichromate (0.1 g.) in 5 ml. of water was added dropwise with stirring to a solution of Va or VIa (0.2 g.) in acetic acid (20 ml.). The reaction was completed on a water bath during 10 minutes and the mixture was added to water (100 ml.) and neutralized with aqueous sodium bicarbonate. Extraction with ether gave, after drying (sodium sulfate) and evaporation of the ether, a yellow solid which was recrystallized from ethanol m.p. 215°; ir: 3330 (pyrrole NH) 1680 cm^{-1} (CO); uv: λ max nm log ϵ 348 (4.12) 236 (4.25); nmr: 6.80-8.00 δ (20H, m, aromatic H) 9.75 δ (1H, s, pyrrole NH; exchangeable with deuterium oxide); ms: m/e (ion type, I%) 427 (M⁺, 9), 322 ([M-C₆H₅CO]⁺, 100), 294 ([M-C₆H₅COCO]⁺, 5), 105 ([C₆H₅CO]⁺, 10), 77 ([C₆H₅]⁺, 15).

Anal. Calcd. for C₃₀H₂₁NO₂: C, 84.28; H, 4.95; N, 3.28. Found: C, 84.65; H, 5.05; N, 3.36.

Hydrolysis of VIIa. 2,3,4-Triphenylpyrrole (VIIIa).

The mixture of VIIa (0.2 g.) and 15% ethanolic potassium hydroxide (20 ml.) was heated under reflux for 12 hours. The reaction solution was concentrated under reduced pressure. Water (40 ml.) was added and the mixture was extracted with ether. The combined organic extracts were washed with water, dried over anhydrous sodium sulfate, filtered and the filtrate was concentrated under vacuum. The residue was readily purified by column (5 x 1 cm) chromatography over silica gel (10 g.). Elution with cyclohexane-benzene (1:1) gave 2,3,4-triphenylpyrrole m.p. and mixed m.p. 168° (3).

Reduction of Va and VIa with Zinc and Acetic Acid. 3,4,5,2',4',5'-Hexaphenyl-2,3'-dipyrryl (IIIa).

To a solution of Va or VIa (1 g.) in acetic acid (50 ml.) zinc powder (5 g.) was added over a period of 1 hour. After the addition was complete, the mixture was stirred for 1 additional hour, then filtered and the resulting solution was evaporated under vacuum. The residue was triturated with water (50 ml.) and the suspension, basified with ammonia, was extracted with ether. The extract was dried (sodium sulfate) and evaporated to give a solid, which was crystallized from ethanol, m.p. and mixed m.p. with IIIa, 242°.

Synthesis of 1,2-Diphenyl-4-p-tolyl-1,4-butanedione.

A mixture of 21.2 g. (0.1 moles) of benzoin, 13.4 g. of *p*-tolylacetophenone, 2.4 g. of potassium cyanide in ethanol (60 ml.) and 8 ml. of water was heated under reflux for 1.5 hours. After standing overnight, the crystals were filtered and washed with two 10 ml. portions of ethanol and water. Crystals from acetic acid m.p. 125°; ir: 1670 and 1675 cm^{-1} (2 x CO).

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.10; H, 6.27.

4,5-Diphenyl-2-*p*-tolylpyrrole (Ib).

A mixture of 3 g. of 1,2-diphenyl-4-*p*-tolyl-1,4-butanedione, 6 g. of ammonium acetate and 20 ml. of acetic acid was refluxed for 3 hours. The solution was poured into crushed ice and a product (Ib) was separated which was crystallized from ethanol, m.p. 134-135°; ir: 3420 cm^{-1} (pyrrole NH).

Anal. Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.31; H, 6.29; N, 4.48.

Oxidation of 4,5-Diphenyl-2-*p*-tolylpyrrole (Ib) with Dichromate.

Compound Ib (15 g.) was oxidized by the method described above. The residue was purified by column (60 x 5 cm) chromatography over silica gel (400 g.). Elution with cyclohexane-benzene (1:1): F_{1-5} (each 100 ml.) gave 3 g. of 4,5-diphenyl-2-*p*-tolylpyrrole (Ib), m.p. 134-135°. Elution with cyclohexane-benzene (4:6): F_{7-20} (each 100 ml.) gave 3 g. (yield 20%) of IIb; F_{23-30} (each 100 ml.) gave 2 g. (yield 13%) of IIIb. Elution with benzene: F_{40-45} (each 100 ml.) gave 0.5 g. (yield 3%) of IVb. Further elution with benzene-ethyl acetate (9:1): F_{50-58} (each 100 ml.) gave 1.5 g. (yield 10%) of Vb; F_{64-67} (each 100 ml.) gave 1 g. (yield 6%) of VIb.

2,2'-Di-*p*-tolyl-4,4',5,5'-tetraphenyl-3,3'-dipyrryl (IIb).

Pale yellow crystals were obtained from ethanol, m.p. 183-184°; ir: 3420 cm^{-1} (pyrrole NH); uv: λ max nm log ϵ 330 (4.32) 312 sh (4.30) 270 sh (4.11) 235 sh (4.17); nmr: 2.20 δ (6H, s, 2 x CH_3), 6.60-7.30 δ (28H, m, H aromatic), 8.24 δ (2H, s, 2 pyrrole NH, exchangeable with deuterium oxide).

Exact mass measurement: Calcd. for $C_{46}H_{36}N_2$: 616.2878. Found: 616.2880.

2',3-Di-*p*-tolyl-4,4',5,5'-tetraphenyl-2,3'-dipyrryl (IIIb).

Pale yellow crystals were obtained from ethanol, m.p. 220-221°; ir: 3400 cm^{-1} (broad, pyrrole NH); uv: λ max nm log ϵ 310 (4.75) 255 sh (4.76) 230 (4.85); nmr (acetone- d_6): 2.10 δ (3H, s, CH_3), 2.25 δ (3H, s, CH_3), 6.60-7.60 δ (28H, m, aromatic H), 10.25 δ (1H, broad, NH, exchangeable with deuterium oxide), 10.50 δ (1H, broad, pyrrole NH, exchangeable with deuterium oxide).

Exact mass measurement: Calcd. for $C_{46}H_{36}N_2$: 616.2878. Found: 616.2852.

1-6a-Dihydro-8-methyl-2,3,4,5-tetraphenyl-6a-*p*-tolylbenzo[*g*]pyrrolo[3,2-*e*]indole (IVb).

Yellow crystals were obtained from ethanol, m.p. 200°; ir: 3380 cm^{-1} (broad, NH); uv: λ max nm log ϵ 320 (4.41) 264 sh (4.40); nmr: 2.27 δ (3H, s, CH_3), 2.36 δ (3H, s, CH_3), 6.60-7.90 δ (27H, m, aromatic H) 8.50 δ (1H, s, NH, exchangeable with deuterium oxide); MW 614 (ms).

Anal. Calcd. for $C_{46}H_{34}N_2$: C, 89.87; H, 5.58; N, 4.56. Found: C, 89.77; H, 5.54; N, 4.54.

1-*p*-Tolyl-3,4-diphenyl-5-(3-*p*-tolyl-4,5-diphenylpyrrol-2-yl)-6-oxa-2-azabicyclo[3.1.0]hex-3-ene (Vb).

Yellow crystals were obtained from ethanol, m.p. 190°; ir: 3390 cm^{-1} (pyrrole NH); uv: λ max nm log ϵ 302 (4.04) 256 sh (4.15); nmr: 2.00 δ (3H, s, CH_3), 2.25 δ (3H, s, CH_3), 5.90-7.40 δ (28H, m, aromatic H), 8.80 δ (1H, broad, pyrrole NH), 9.85 δ (1H, s, pyrrole NH); ms: 632 (M^{+}) (see Table II).

Anal. Calcd. for $C_{46}H_{36}N_2O$: C, 87.31; H, 5.73; N, 4.43. Found: C, 87.35; H, 5.98; N, 4.60.

2-*p*-Tolyl-4,5-diphenyl-3-(3-*p*-tolyl-4,5-diphenylpyrrol-2-yl)-3H-pyrrol-3-ol (VIb).

Yellow crystals were obtained from ethanol, m.p. 164°; ir (hexachlorobutane-diene): 3420 cm^{-1} (pyrrole NH); uv: λ max nm log ϵ 308 (4.39) 264 sh (4.42); nmr: 2.20 δ (3H, s, CH_3), 2.25 δ (3H, s, CH_3), 6.30-7.60 δ (28H, m, aromatic H), 8.80 δ (1H, broad, NH, exchangeable with deuterium oxide); ms: 632 (M^{+}) (see Table II).

Anal. Calcd. for $C_{46}H_{36}N_2O$: C, 87.31; H, 5.73; N, 4.43. Found: C, 87.30; H, 5.77; N, 4.47.

Oxidation of IIIb and IVb. 1-(4,5-Diphenyl-3-*p*-tolyl-2-pyrrol-2-yl)-2-*p*-tolyl-1,2-ethanedione (VIIb).

Either compounds IIIb or IVb were oxidized by the same method above mentioned. Yellow needles from ethanol were obtained, m.p. 214-215°; ir: 3320 (pyrrole NH) 1680 cm^{-1} (CO); uv: λ max nm log ϵ 348 (3.89) 263 (3.96) 242 (3.99); nmr: 2.10 δ (3H, s, CH_3), 2.32 δ (3H, s, CH_3), 6.50-7.70 δ (18H, m, aromatic H), 10.10 δ (1H, broad, NH); ms: m/e (ion type, I%) 455 (M^{+} , 10), 336 ($[M-CH_3C_6H_4CO]^+$, 100) 308 ($[M-CH_3C_6H_4COCO]^+$, 4), 119 ($[CH_3C_6H_4CO]^+$, 8), 91 ($[CH_3C_6H_4]^+$, 8).

Anal. Calcd. for $C_{32}H_{25}NO_2$: C, 84.37; H, 5.53; N, 3.08. Found: C, 84.17; H, 5.39; N, 3.24.

Oxidation of IVb. *N*-(4-Benzoyl-8-methyl-2,3-diphenyl-9b-*p*-tolyl-9bH-benz[*g*]indole-5-yl)benzamide (IXb).

A solution of potassium dichromate (0.1 g., 0.001 g.-atom of oxygen) in 5 ml. of water was added dropwise with stirring to a solution of IVb (0.6 g., 0.001 mole) in acetic acid. The temperature was not allowed to exceed 15°. After a short period of time the mixture was added to water (100 ml.) and was neutralized with aqueous sodium bicarbonate. Extraction with ether gave, after drying (sodium sulfate) and evaporation of the ether, a yellow solid which was recrystallized from ethanol, m.p. 246-247°; ir: 3330 (broad, NH) 1680 and 1640 cm^{-1} (CO); uv: λ max nm log ϵ 288 sh (4.21) 256 (4.48); nmr: 2.53 δ (6H, s, 2 x CH_3), 6.20-8.20 δ (27H, m, aromatic H), 11.37 δ (1H, s, NH, exchangeable with deuterium oxide); ms: m/e (ion type, I%) 646 (M^{+} , 100), 541 ($[M-C_6H_5CO]^+$, 56), 105 ($[C_6H_5CO]^+$, 4.4), 77 ($[C_6H_5]^+$, 17).

Anal. Calcd. for $C_{46}H_{34}N_2O_2$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.51; H, 5.29; N, 4.55.

Reduction with Zinc and Acetic Acid of Vb and VIb. 2',3-Di-*p*-tolyl-4,4',5,5'-tetraphenyl-2,3'-dipyrryl (IIIb).

Compounds Vb and VIb were reduced by the same method mentioned above. The reaction quantitatively gave a solid, which was crystallized from ethanol, m.p. and mixed m.p. with IIIb 220-221°.

REFERENCES AND NOTES

- (1) V. Sprio, *Cazz. Chim. Ital.*, **85**, 569 (1955).
- (2) V. Sprio, S. Petruso and L. Lamartina, *J. Heterocyclic Chem.*, **11**, 307 (1974).
- (3) A. Pollak, M. Tisler, *Tetrahedron Letters*, 253 (1964).
- (4) R. Kuhn, H. Kainer, *Ann. Chem.*, **578**, 227 (1952).
- (5) J. Baldas and Q. N. Porter, *Aust. J. Chem.*, **20**, 2655 (1967).
- (6) J. Baldas and Q. N. Porter, "Mass Spectrometry of Heterocyclic Compounds", New York, N. Y., (1971).
- (7) J. Kagan, D. A. Agdeppa, Jr., S. P. Singh, D. A. Mayers, C. Boyajian, C. Poorker and B. E. Firth, *J. Am. Chem. Soc.*, **98**, 4582 (1976) and references therein.
- (8) R. A. Gorski, D. J. Dagli and J. Wemple, *ibid.*, **98**, 4588 (1976) and references therein.