

A Novel Ring Transformation of 3a,5,6a-Triaryl-3,3a-dihydro-2H-furo[3,2-b]pyrrole-2,6(6aH)-diones into 3-Aroyl-2,5-diarylpyrrole Derivatives

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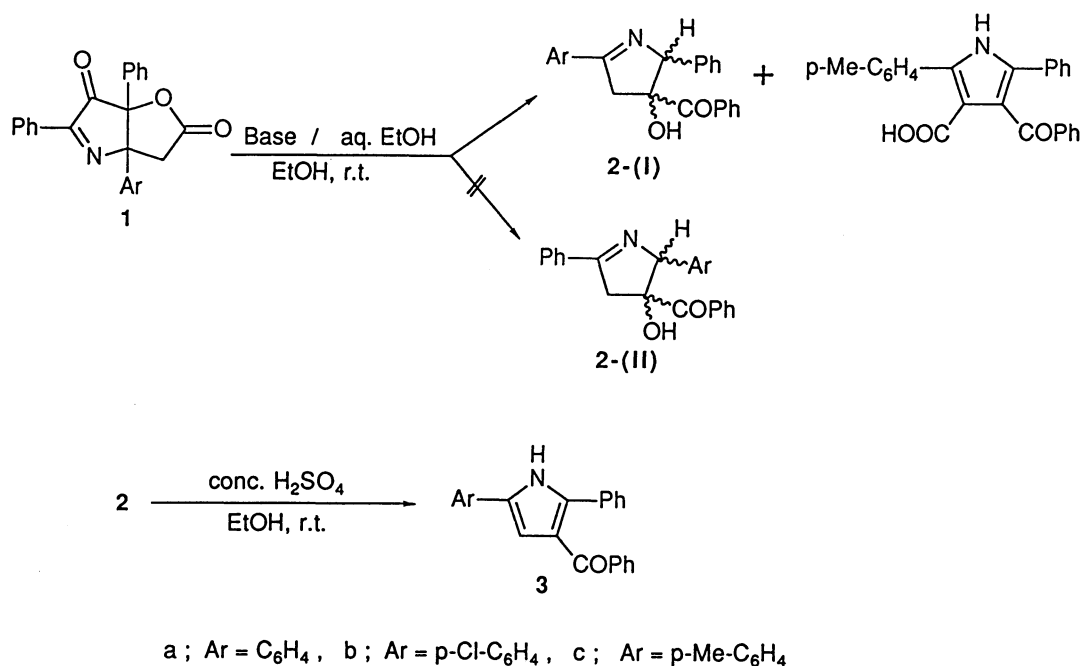
Under aqueous conditions dimethylamine, piperidine, and triethylamine catalyzed the ring-transformation reaction of triaryl-2H-furo[3,2-b]pyrrole-2,6(6aH)-diones (**1**), giving benzoylhydroxy-1-pyrrolines **2**, which afforded benzoylpyrroles **3** upon acid-catalyzed dehydration. The lactone-ring-opened amides **6** were obtained in the reaction of **1** with methylamine, pyrrolidine, piperidine, and perhydroazepine at room temperature in ethanol. Pyrrolidine and piperidine produced pyrrolocarboxamides **7** when the reaction was carried out in aqueous ethanol under reflux. Amides **6** afforded **7** upon treatment with the amines under the above-mentioned conditions.

From synthetic viewpoints heterocycles are important as the masked form of a functional group(s) and as a starting substance used to construct another type of heterocyclic ring via a ring-transformation reaction.

The preparation of 3a,5,6a-triaryl-3,3a-dihydro-2H-furo[3,2-b]pyrrole-2,6(6aH)-diones (**1**)^{1,2} was recently reported. These are of interest since they possess three active sites (imino function, ketonic carbonyl, and ester group) toward nucleophiles in the molecule. We investigated the reactions of **1** with various amines and found a novel ring-transformation reaction of **1** into polysubstituted pyrrole derivatives, which is described in the present paper.

Results and Discussion

In the reaction of **1a** with nitrogen nucleophiles in aqueous ethanol at room temperature, it was found that dimethylamine and piperidine behaved as bases, not as a nucleophile, producing the ring-transformed 1-pyrroline **2a** in 61 and 48% yields, respectively. Pyrrolines **2b** and **2c** were obtained as shown in Scheme 1 and Table 1. A small amount (9% yield) of 3-benzoyl-2-phenyl-5-*p*-tolylpyrrole-4-carboxylic acid was formed in the reaction of **1c**. Diethylamine and triethylamine also catalyzed the transformation of **1a**, giving **2a** in similar yields. On the other hand, an inorganic base, such as sodium



Scheme 1.

Table 1. Ring-Transformation of **1** into 1-Pyrroline **2**

Substrate	Base	Time/h	Products (Yield/%)
1a	Me ₂ NH	28	2a (61)
1a	(CH ₂) ₅ NH	11.5	2a (48)
1a	Et ₃ N	20	2a (53)
1a	aq NaOH	24	A complex mixture ^{a)}
1b	Me ₂ NH	33	2b (29)
1c	Me ₂ NH	7	2c (71) ^{b)}

a) Compound **1a** was recovered in 11% yield after the work-up. b) 3-Benzoyl-5-phenyl-2-*p*-tolylpyrrole-3-carboxylic acid was obtained in 9% yield.

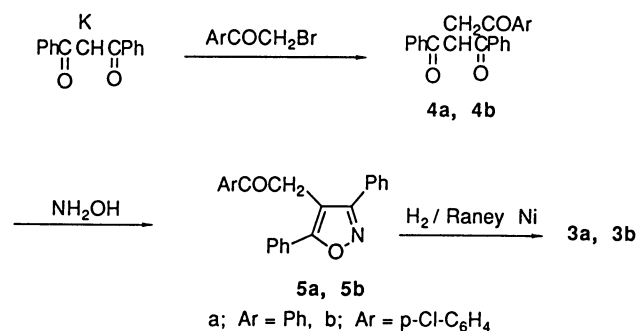
hydroxide in aqueous ethanol, was not effective for the above-mentioned ring-transformation of **1a**, though **1a** in the reaction mixture disappeared rapidly. This was probably due to salt-formation via the hydrolysis of the lactone ring; the starting **1a** was regenerated during the work-up and obtained in 11% yield together with a complex mixture of unidentified products.

On the basis of the acid-catalyzed dehydration of **2** into benzoyldiarylpyrrole **3** and the authentic synthesis of **3a**^{3,4)} and **3b** (Scheme 2), the structure of **3** was established as being **2-(I)**. The regioisomer **2-(II)** was excluded. Trans-configuration between the phenyl group and the benzoyl one may be favorable for **2**.

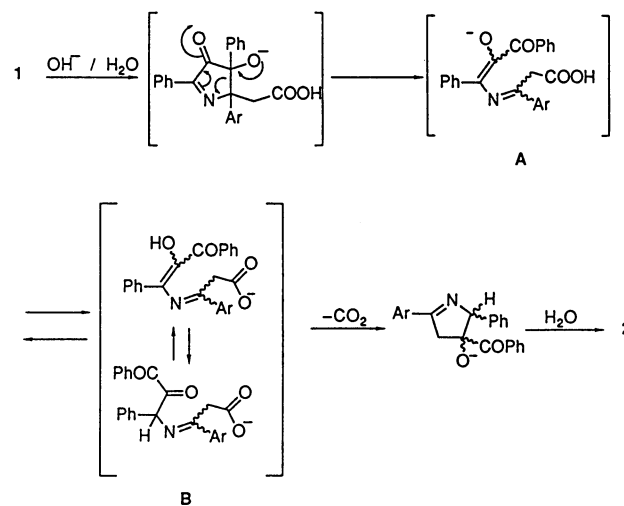
The reaction of **1a** with methylamine, pyrrolidine, piperidine, and perhydroazepine afforded the lactone-ring-opened amides **6a** (84%), **6b** (79%), **6c** (25%), and **6d** (17%) at room temperature in ethanol without any

additional water.⁵⁾ The transformation of **6a** into the corresponding pyrrolecarboxamide employing triethylamine as a base-catalyst resulted in the formation of a complex mixture. On the other hand, **6b** was converted into **7a** when it was treated with triethylamine in ethanol under reflux. Although pyrrolidine also caused the conversion of **6b** into **7a** in 41% yield, a complex mixture of unidentified products was formed upon the treatment of **6b** with potassium acetate in refluxing ethanol. Pyrrolecarboxamides **7a**, **7c**, and **7d** were prepared in one-pot when the reaction of **1** with pyrrolidine was carried out in refluxing ethanol. Piperidino derivative **7b** was also obtained from **1a** in 34% yield, accompanied by decarboxylated benzoylpyrrole **3a** in 19% yield (Scheme 3 and Table 2).

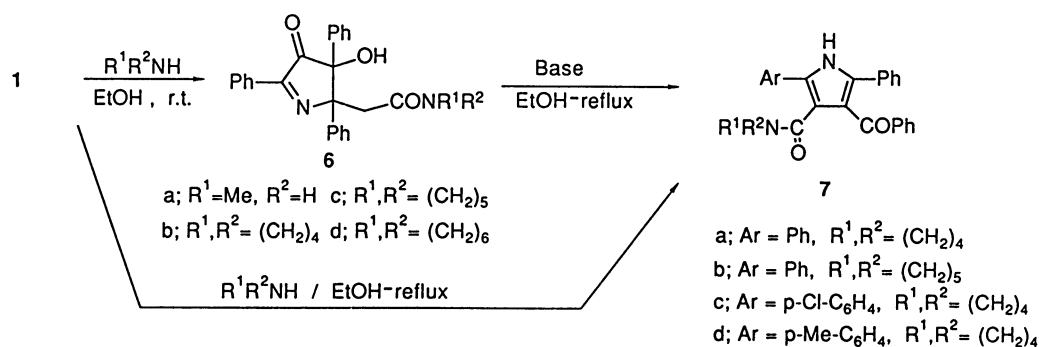
A mechanism for the ring-transformation of **1** into **2** is tentatively proposed (Scheme 4). Lactone ring-opening by an attack of a hydroxide ion and a subsequent cleavage of the central C-C bond of **1** gives anion **A**, which isomerizes into more stable carboxylate ion **B**. The decarboxylation of **B** followed by the ring-closure gives **3**. The formation pathway of pyrrolecarboxamide **7** is considered to be similar. Though lactone-ring-opening and salt-formation were confirmed, as men-



Scheme 2.



Scheme 4.



Scheme 3.

Table 2. Transformation into Pyrrolecarboxamide 7

Substrate	Amine or Base	Time/h	Products (Yield/%)
6a	Triethylamine	5.5	A complex mixture
6b	Triethylamine	20	7a (30)
6b	Pyrrolidine	3	7a (41)
6b	CH ₃ CO ₂ K	7	A complex mixture
1a	Pyrrolidine	20	7a (66)
1a	Piperidine	20	7b (34) ^a
1b	Pyrrolidine	26	7c (41)
1c	Pyrrolidine	22.5	7d (50)

a) Compound **3a** was obtained in 19% yield.

tioned above, inorganic bases were ineffective for transforming **1** into **2**. The reason has not yet been clarified.

Experimental

General. All of the melting points were determined on a Mitamuraiken MELT THERMO and are uncorrected. The IR spectra were measured as KBr pellets on a Nippon-Bunko IR-700. The NMR spectra were recorded at 270 MHz with a JEOL GSX-270 and at 100 MHz with a JEOL FT-100 using TMS as an internal standard in CDCl₃. The mass spectra were obtained on a JEOL JMS-OISG-2 mass spectrometer at 75 eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

3-Benzoyl-2,5-diphenyl-1-pyrrolin-3-ol (2a). After a mixture of **1a** (1.00 g, 2.72 mmol) and 40% aqueous dimethylamine (2.8 ml, 25 mmol) in ethanol (20 ml) was stirred at room temperature for 28 h, it was poured into water. A precipitated solid was filtered and recrystallized from a 1:1-mixture of ethanol and hexane, giving **3a** (0.57 g, 61%): Colorless crystalline powder; mp 162–164 °C; IR 3200, 1675, and 1613 cm⁻¹; ¹H NMR δ=3.12 (1H, d, *J*=20 Hz, D₂O-exchanged), 4.05 (1H, d, *J*=20 Hz, became s with D₂O-treatment), 5.66 (1H, s), and 6.72–7.84 (16H, m); ¹³C NMR δ=49.16, 87.89, 90.13, 127.38, 127.55, 127.92, 128.09, 128.71, 129.83, 131.31, 132.38, 133.59, 134.55, 136.35, 171.92, and 199.42; MS *m/z* 341 (M⁺).

Found: C, 80.81; H, 5.80; N, 4.18%. Calcd for C₂₃H₁₉NO₂: C, 80.91; H, 5.61; N, 4.10%.

3-Benzoyl-2-*p*-chlorophenyl-5-phenyl-1-pyrrolin-3-ol (2b). A mixture of **1b** (500 mg, 1.25 mmol) and 40% aqueous dimethylamine (1.4 ml, 12 mmol) in ethanol (20 ml) was stirred at room temperature for 33 h, and then poured into water. A precipitated solid was filtered, giving **2b** (135 mg, 29%): Colorless crystalline powder (ethanol); mp 188–189 °C; IR 3200, 1677, 1607, and 1600 cm⁻¹; ¹H NMR δ=3.12 (1H, d, *J*=18 Hz), 4.12 (1H, d, *J*=18 Hz), 5.71 (1H, s), and 6.70–7.90 (15H, m); MS *m/z* 377 (M⁺) and 375 (M⁺).

Found: C, 73.06; H, 4.87; N, 3.49%. Calcd for C₂₃H₁₈NO₂Cl: C, 73.50; H, 4.83; N, 3.73%.

3-Benzoyl-5-phenyl-2-*p*-tolyl-1-pyrrolin-3-ol (2c) and 3-Benzoyl-5-phenyl-2-*p*-tolylpyrrole-3-carboxylic Acid. A mixture of **1c** (500 mg, 1.31 mmol) and 40% aqueous dimethylamine (1.5 ml, 13.4 mmol) in ethanol (20 ml) was stirred at room temperature for 7 h. It was worked up as described above, giving **2c** (330 mg, 71%): Colorless crystalline powder (a 1:1-mixture of hexane and ethyl acetate); mp 144–146 °C; IR 3200, 1680, and 1610 cm⁻¹; ¹H NMR δ=2.40 (3H, s), 3.20

(1H, d, *J*=18 Hz), 4.10 (1H, d, *J*=18 Hz), 5.71 (1H, s), and 6.82–7.84 (14H, m); ¹³C NMR δ=21.57, 49.16, 87.82, 90.12, 126.14, 127.35, 127.90, 128.03, 128.06, 128.56, 129.40, 129.83, 130.94, 132.80, 134.54, 136.54, 141.72, 171.73, and 199.52; MS *m/z* 355 (M⁺).

Found: C, 80.81; N, 5.91; N, 3.83%. Calcd for C₂₄H₂₁NO₂: C, 81.10; H, 5.96; N, 3.94%.

The filtrate was adjusted to pH=3 by an addition of concentrated hydrochloric acid, giving [3-Benzoyl-5-phenyl-2-*p*-tolylpyrrole-3-carboxylic Acid-H₂O (1/0.25)] (46 mg, 9%): Colorless needles (a mixture of hexane and ethyl acetate); mp 245–247 °C; IR 3400–2800, 3270, 1676, and 1645 cm⁻¹; MS *m/z* 381 (M⁺).

Found: C, 78.11; H, 5.13; N, 3.59%. Calcd for (C₂₅H₁₉NO₃+0.25·H₂O): C, 77.80; H, 5.09; N, 3.62%.

3-Benzoyl-2,4-diphenylpyrrole (3a). Concentrated sulfuric acid (0.4 ml) was added to a solution of **3a** (120 mg, 0.35 mmol) in ethanol (50 ml) at room temperature. After 1 min, the mixture was poured into water and a precipitated solid was collected by filtration to give **3a** (104 mg, 91%): Mp 162–164 °C (lit.⁴) mp 167 °C).

Similarly **3b** (89 mg, 0.24 mmol) and **3c** (172 mg, 0.48 mmol) gave **5b** (74 mg, 87%) and **5c** (163 mg, 100%), respectively.

3-Benzoyl-5-*p*-chlorophenyl-2-phenylpyrrole (3b): Colorless needles (ethanol); mp 218–220 °C; IR 3200, 1593, and 1571 cm⁻¹; ¹H NMR δ=6.80 (1H, d, *J*=4 Hz, became s with D₂O-treatment), 7.20–7.50 (14H, m), and 8.70 (1H, s, D₂O-exchanged); MS *m/z* 359 (M⁺) and 357 (M⁺).

Found: C, 77.09; H, 4.08; N, 4.11%. Calcd for C₂₃H₁₆NOCl: C, 77.20; H, 4.51; N, 3.91%.

3-Benzoyl-2-phenyl-5-*p*-tolylpyrrole (3c): Pale-yellow needles (ethanol); mp 161–162 °C; IR 3200 and 1590 cm⁻¹; ¹H NMR δ=2.34 (3H, s), 6.76 (1H, d, *J*=3 Hz), 7.00–7.50 (12H, m), 7.60–7.90 (2H, m), and 8.96 (1H, s); MS *m/z* 337 (M⁺).

Found: C, 85.18; H, 5.75; N, 4.25%. Calcd for C₂₄H₁₉NO: C, 85.03; H, 5.68; N, 4.15%.

2-Benzoyl-4-*p*-chlorophenyl-1-phenylbutane-1,4-dione (4b). To a stirred mixture of dibenzoylmethyl potassium⁵ (11.0 g, 42.0 mmol) in anhydrous acetone (60 ml) was added dropwise a solution of *p*-chlorophenacyl bromide (10.2 g, 43.7 mmol) in anhydrous acetone (20 ml) for 10 min. After the mixture was stirred for 12 h at room temperature, a precipitated solid was filtered. The filtrate was evaporated in vacuo, leaving a residue which, upon trituration with ethanol and recrystallization from ethanol, afforded **4b** as colorless prisms; mp 103–104 °C; IR 1700 and 1675 cm⁻¹; ¹H NMR δ=3.70 (2H, d, *J*=6 Hz), 6.08 (1H, t, *J*=6 Hz), and 7.24–8.04 (14H, m); ¹³C NMR δ=37.97, 51.43, 128.68, 128.98, 129.01, 129.73, 133.78, 134.47, 135.47, 140.04, 195.59, and 195.63; MS *m/z* 378 (M⁺) and 376 (M⁺).

Found: C, 73.10; H, 4.63%. Calcd for C₂₃H₁₇O₃Cl: C, 73.31; H, 4.55%.

4-(*p*-Chlorophenylmethyl)-3,5-diphenylisoxazole (5b). A mixture **4b** (6.60 g, 17.5 mmol), hydroxylammonium chloride (2.20 g, 31.7 mmol), water (4 ml), and ethanol (21 ml) was heated under reflux for 12 h. A precipitated solid was filtered and recrystallized from ethanol to afford **5c** (1.71 g, 26%) as colorless needles; mp 128–129 °C; IR 1670 cm⁻¹; ¹H NMR δ=4.22 (2H, s) and 7.24–7.92 (14H, m); ¹³C NMR δ=34.81, 106.74, 127.12, 127.86, 128.32, 128.91, 129.02, 129.11, 129.18, 129.67, 130.15, 134.35, 140.28, 164.13, 168.09, and 195.08; MS *m/z* 375 (M⁺) and 373 (M⁺).

Found: C, 73.83; H, 4.40; N, 3.85%. Calcd for $C_{23}H_{16}NO_2Cl$: C, 73.90; H, 4.31; N, 3.75%.

Authentic Synthesis of 3b. After a mixture of **5b** (213 mg, 0.57 mmol) and Raney nickel (W-4) (7 ml) in ethanol was stirred at room temperature for 12 h under a hydrogen atmosphere, insoluble materials were filtered off. The filtrate was evaporated in vacuo, leaving a residue which, upon recrystallization from ethanol, gave **3b** (19 mg, 9%).

N-Methyl-(4-hydroxy-2,4,5-triphenyl-1-pyrrolin-3-on-5-yl)acetamide (6a). A mixture of **1a** (1.00 g, 2.72 mmol) and 40% aqueous methylamine (1.5 ml, 25 mmol) in ethanol (20 ml) was stirred at room temperature for 1 h; the precipitates were then filtered to give **6a** (0.91 g, 84%): Yellow needles (a mixture of benzene and hexane); mp 177–179 °C; IR 3360, 3200, 1740, and 1630 cm^{-1} ; 1H NMR δ =2.56 (3H, d, J =5 Hz, became s with D_2O -treatment), 2.81 (1H, d, J =14 Hz), 3.55 (1H, d, J =14 Hz), 5.82 (1H, broad s, D_2O -exchanged), 6.69 (1H, s, D_2O -exchanged), 6.80–7.60 (13H, m), and 8.20–8.40 (2H, m); ^{13}C NMR δ =26.65, 48.03, 78.96, 83.78, 125.88, 126.11, 127.75, 127.99, 128.46, 128.81, 130.46, 132.16, 138.09, 142.49, 167.97, 171.49, and 200.90; MS m/z 398 (M^+).

Found: C, 75.49; H, 5.67; N, 7.05%. Calcd for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.03%.

N,N-Tetramethylene-(4-hydroxy-2,4,5-triphenyl-1-pyrrolin-3-on-5-yl)acetamide (6b). A mixture of **1a** (1.00 g, 2.72 mmol) and pyrrolidine (1.5 ml, 25 mmol) in ethanol (20 ml) was treated as described above, giving **6b** (0.94 g, 79%) as yellow crystalline powder: Mp 158–160 °C; IR 3118, 1745, and 1609 cm^{-1} ; 1H NMR δ =2.10–2.92 (4H, m), 2.84–3.80 (6H, m), 6.80–7.20 (9H, m), 7.20–7.60 (5H, m), and 8.30–8.50 (2H, m); ^{13}C NMR δ =24.18, 25.78, 45.70, 46.20, 47.53, 80.07, 84.22, 125.96, 126.61, 126.66, 127.67, 127.96, 128.28, 128.78, 130.55, 132.16, 138.01, 142.83, 167.38, 169.47, and 200.98; MS m/z 438 (M^+).

Found: C, 76.46; N, 6.00; H, 6.15%. Calcd for $C_{28}H_{26}N_2O_3$: C, 76.69; H, 5.98; N, 6.39%.

N,N-Pentamethylene-(4-hydroxy-2,4,5-triphenyl-1-pyrrolin-3-on-5-yl)acetamide (6c). A mixture of **1a** (1.00 g, 2.72 mmol) and piperidine (1.5 ml, 24 mmol) in ethanol (20 ml) was stirred at room temperature for 7 h. The precipitates were filtered and chromatographed. After **1a** (0.20 g, 20%) was eluted with benzene, acetone-eluate gave **6c** (0.31 g, 25%): Yellow plates (hexane); mp 135–138 °C; IR 3150, 1748, and 1597 cm^{-1} ; 1H NMR δ =0.72–1.60 (6H, m), 2.10–2.52 (6H, m), 6.80–7.60 (14H, m), and 8.32–8.48 (2H, m); ^{13}C NMR δ =24.05, 25.21, 26.31, 42.53, 43.22, 48.02, 79.58, 84.06, 125.97, 126.12, 126.56, 127.63, 127.96, 128.22, 128.42, 128.69, 129.04, 130.65, 132.11, 138.11, 143.09, 167.57, 169.17, and 200.97; MS m/z 452 (M^+).

Found: C, 77.44; H, 6.31; N, 6.19%. Calcd for $C_{29}H_{28}N_2O_3$: C, 76.97; H, 6.24; N, 6.19%.

N,N-Hexamethylene-(4-hydroxy-2,4,5-triphenyl-1-pyrrolin-3-on-5-yl)acetamide (6d). A mixture of **1a** (500 mg, 1.36 mmol) and perhydroazepine (0.8 ml, 9.2 mmol) in ethanol (20 ml) was stirred at room temperature for 8 h. It was then poured into water, extracted with dichloromethane, dried (magnesium sulfate), and then evaporated in vacuo to leave a residue which was chromatographed. Dichloromethane eluted **6d** (110 mg, 17%): Yellow prisms (a 1:1-mixture of hexane and ethanol); mp 168–170 °C; IR 3190, 1751, and 1604 cm^{-1} ; 1H NMR δ =0.60–2.00 (8H, m), 3.00–3.69 (6H, m), 6.72–7.60 (14H, m), and 8.20–8.45 (2H, m); ^{13}C NMR δ =26.24, 26.68, 27.23, 28.70, 43.07, 46.02, 48.75, 79.68, 83.93,

125.99, 126.14, 126.53, 126.59, 127.64, 127.94, 128.42, 128.65, 130.64, 132.05, 138.20, 143.21, 167.61, 170.88, and 200.99; MS m/z 466 (M^+).

Found: C, 77.17; H, 6.65; N, 5.87%. Calcd for $C_{30}H_{30}N_2O_3$: C, 77.22; H, 6.48; N, 6.00%.

N,N-Tetramethylene-4-benzoyl-2,5-diphenylpyrrole-3-carboxamide (7a). A mixture of **1a** (200 mg, 0.54 mmol) and pyrrolidine (200 mg, 2.81 mmol) in ethanol (16 ml) was heated under reflux for 20 h. After it was cooled to room temperature, it was poured into water (80 ml). To this mixture, concentrated hydrochloric acid (0.4 ml) was added dropwise. The precipitates were filtered, and then washed with ether (20 ml) to give **7a** (125 mg, 55%). The filtrate was extracted with dichloromethane (20 ml $\times$ 2). The extract was dried (magnesium sulfate) and the solvent was evaporated in vacuo to leave a residue which was chromatographed. The fraction eluted using a 1:1-mixture of ethyl acetate and ether afforded **7a** (25 mg, 11%): Pale-yellow crystalline powder (a 7:3-mixture of hexane and benzene); mp 243–244 °C; IR 3200, 1648, and 1597 cm^{-1} ; 1H NMR δ =1.40–2.00 (4H, m), 2.80–3.40 (4H, m), 6.80–7.60 (15H, m), and 9.42 (1H, s); ^{13}C NMR δ =24.34, 25.69, 45.46, 47.96, 120.46, 120.77, 126.00, 127.24, 127.61, 127.67, 127.91, 128.22, 128.61, 128.94, 129.11, 129.25, 129.61, 130.98, 131.15, 131.83, 136.37, 138.57, 165.94, and 192.56; MS m/z 420 (M^+).

Found: C, 80.14; H, 5.85; N, 6.23%. Calcd for $C_{28}H_{24}N_2O_2$: C, 79.98; H, 5.75; N, 6.66%.

N,N-Pentamethylene-4-benzoyl-2,5-diphenylpyrrole-3-carboxamide (7b). A mixture of **1a** (500 mg, 1.36 mmol) and piperidine (0.75 ml, 7.00 mmol) in ethanol (18 ml) was heated under reflux for 20 h. After being cooled, it was poured into water. The precipitates were filtered and chromatographed, being eluted with a 1:1-mixture of ethyl acetate and dichloromethane **7b** (200 mg, 34%): Pale-yellow crystalline powder (a 7:3-mixture of hexane and benzene); mp 243–244 °C; IR 3190, 1640 (sh), and 1602 cm^{-1} ; 1H NMR δ =0.80–1.60 (6H, m), 3.02–3.60 (4H, m), 7.00–7.80 (15H, m), and 8.99 (1H, s); ^{13}C NMR δ =24.51, 25.13, 25.70, 42.36, 47.99, 119.42, 120.85, 126.32, 127.61, 127.81, 128.17, 128.33, 128.56, 128.81, 129.41, 129.64, 130.88, 131.13, 131.82, 136.31, 138.57, 165.94, and 192.48; MS m/z 434 (M^+).

Found: C, 80.05; H, 6.16; N, 6.50%. Calcd for $C_{29}H_{26}N_2O_2$: C, 80.16; H, 6.03; N, 6.45%.

N,N-Tetramethylene-4-benzoyl-2-p-chlorophenyl-5-phenylpyrrole-3-carboxamide (7c). A solution of **1b** (200 mg, 0.50 mmol) and pyrrolidine (183 mg, 2.58 mmol) in ethanol (16 ml) was heated under reflux for 26 h. After being cooled to room temperature, it was poured into water (80 ml). This mixture was adjusted to pH=3 by adding concentrated hydrochloric acid (0.4 ml). The precipitates were filtered and washed with ether (20 ml), giving **[7c-H₂O (1/0.5)]** (56 mg, 24%). The filtrate was extracted with dichloromethane (20 ml $\times$ 2), dried (magnesium sulfate), and then evaporated in vacuo to leave a residue which was chromatographed. The fraction eluted with ether afforded additional **[7c-H₂O (1/0.5)]** (39 mg, 17%): Pale-yellow crystalline powder (ethanol); mp 200–205 °C (decomp); IR 3200, 1640 (sh), and 1598 cm^{-1} ; 1H NMR δ =1.24–2.00 (4H, m), 2.80–3.60 (4H, m), 6.80–7.90 (14H, m), and 9.42 (1H, s); ^{13}C NMR δ =24.40, 25.48, 45.43, 48.02, 120.37, 125.93, 127.60, 127.96, 128.12, 128.57, 128.61, 128.86, 128.93, 129.18, 129.51, 129.60, 130.87, 131.07, 136.33, 138.47, 165.94, and 192.47; MS m/z 456 (M^+) and 454 (M^+).

Found: C, 72.53; H, 5.21; N, 5.90%. Calcd for $(C_{28}H_{23}-$

N₂O₂Cl+0.5·H₂O): C, 72.49; H, 5.21; N, 6.04%.

***N,N*-Tetramethylene-4-benzoyl-5-phenyl-2-*p*-tolylpyrrole-3-carboxamide (7d).** A mixture of **1c** (200 mg, 0.52 mmol) and pyrrolidine (190 mg, 2.68 mmol) in ethanol (16 ml) was heated under reflux for 22.5 h. After being cooled to room temperature, it was poured into water (80 ml). To this mixture, concentrated hydrochloric acid (0.4 ml) was added dropwise. The precipitates were filtered and washed with ether to give **7d** (115 mg, 50%): Pale-yellow crystalline powder (a mixture of hexane and ethyl acetate); mp 205–206 °C; IR 3214, 1648, and 1600 cm⁻¹; ¹H NMR δ=1.24–1.98 (4H, m), 2.30 (3H, s), 2.88–3.48 (4H, m), 6.80–7.62 (14H, m), and 8.90 (1H, s); ¹³C NMR δ=21.14, 24.37, 25.59, 45.34, 47.82, 120.16, 125.89, 127.46, 127.53, 127.96, 128.12, 128.68, 129.43, 131.14, 131.61, 136.23, 137.20, 138.60, 166.15, and 192.58; MS *m/z* 434 (M⁺).

Found: C, 79.98; H, 6.04; N, 5.95%. Calcd for C₂₉H₂₆-

N₂O₂: C, 80.16; N, 6.03; N, 6.45%.

References

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