# A One-step Conversion of N-Acylaminoketones into 5-Alkylidene-3-pyrrolin-2-ones

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A simple and efficient one-pot synthesis of 5-alkylidene-3-pyrrolin-2-ones **3a,e-g** from *N*-acylaminoketones is described. A mechanism is proposed and it is substantiated by synthethising and converting the proposed intermediates into the pyrrolinones **3a,e-g**.

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Our interest in the synthesis and chemical behaviour of pyrrolinones [1,2], prompted us to investigate a convenient synthesis of 5-alkylidene-3-pyrrolin-2-ones in one step, in view of their use as sun-screening agents. In fact these compounds show uv maxima in the range 290-346 nm, which is the region where sun protecting compounds would have maximum adsorbance of uv radiations [3].

It is known [4] that  $\alpha$ -acylaminoketones of type 1, where the amide moiety possesses a  $\alpha$ -hydrogen atom mobile, undergo the cyclization to 2-pyrrolinones 2 by means of alkali.

We have found that when the reaction was carried out on compounds 1a,e-g with sodium ethoxide at reflux temperature for 8 hours the derivatives 3 was obtained in good yield. In view of the ready accessibility of starting material, which can be prepared from  $\alpha$ -aminoacids through a Dakin-West [5] or a modified Dakin-West reaction [6], this method appears a convenient procedure to prepare compounds of type 3.

Formation of the pyrrolinones 3 can be rationalized by the following reaction scheme:

The pyrrolinone 2 with a hydrogen atom at position 5 can be easily oxidized by atmospheric oxygen to form 4. Ethoxide ion can promote elimination of water to yield compound 3 directly or through the substitution of hydroxy with an ethoxy group followed by ethanol elimination.

The above mechanism is supported by the fact that reducing the reaction time, the intermediates 2, 4, and 5 can be observed (tlc and pmr spectra). These compounds can be prepared under different conditions: thus α-acylamino-ketones 1a-g treated with an aqueous solution of potassium hydroxide for 2 hours at 90° under nitrogen yielded the pyrrolinones 2a-g. Oxidation of compounds 2a-c,e to 4a-c,e was accomplished by bubbling oxygen in alkaline solutions at room temperature. The hydroxypyrrolinone 4b treated with sodium ethoxide yielded the ethoxy derivative 5b. Treatment of 2a,e-g or 4a,e or 5a,e with ethoxide ion at reflux temperature gave the corresponding alkylidenepyrrolinones 3a,e-g.

Of the two possible geometrical forms of compounds 3a,e-g only one isomer was observed. On the basis of comparison of spectroscopy values (mainly the proton resonances of CH and CH<sub>3</sub> groups) to literature data [7], it was concluded that the isomers isolated had the configuration Z. This preferential formation is possibly a consequence of the presence of a methyl group at position 4 which interacts with the bulky group on the exocyclic double bond. The corresponding isomer E can be prepared by photochemical isomerization. Thus irradiation of the methanolic solution of 3e-Z with a medium pressure mercury lamp yielded an equilibrated mixture from which the isomer E can be obtained. It is noteworthy that under these conditions we isolated in low yield three dimers whose structures are currently under investigation.

#### **EXPERIMENTAL**

The ir spectra were recorded on a Perkin-Elmer 283 spectrometer using potassium bromide discs. The pmr spectra were recorded for deuteriochloroform solutions with a Perkin-Elmer R600 instrument; chemical shifts (J in Hz) are reported in ppm downfield from internal tetramethylsilane. The uv spectra were measured for solutions in methanol with a Cary 14 spectrophotometer. Silica gel plates (Merck F254) were used for analytical and preparative tlc. Extracts were dried over sodium sulphate and solvents were evaporated in vacuo.

#### General Procedure for Acylaminoketones la-g.

A solution of sodium acetate trihydrate (62 mmoles) in water (30 ml) was slowly added under vigorous stirring to a mixture of the aminoketone hydrochloride (27 mmoles) in water (30 ml) and phenylacetyl chloride (35 mmoles) in chloroform (100 ml). The chloroform solution was separated, dried, and evaporated to give compounds 1 [8]; 1a (yield 62%), mp 52-55° (from cyclohexane); ir 3280 (NH), 1710 (CO), 1630 (CONH) cm<sup>-1</sup>; pmr:  $\delta$  0.74 (t, 3 CH<sub>3</sub>—CH<sub>2</sub>, J = 7.0), 1.68 (m, 3, CH<sub>3</sub>—CH<sub>2</sub> + NH), 2.15 (s, 3, CH<sub>3</sub>CO), 3.58 (s, 2, CH<sub>2</sub>—CO), 4.61 (m, 1, CH), 7.31 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for  $C_{13}H_{17}NO_2$ : C, 71.21; H, 7.81; N, 6.39. Found: C, 71.61; H, 7.92; N, 6.24.

Compound **1b** (yield 83%) had mp 111-113° (from aqueous acetone); ir: 3340 (NH), 1720 (CO), 1650 (CONH) cm<sup>-1</sup>; pmr:  $\delta$  1.68 (brs, 1, NH), 2.05 (s, 3, CH<sub>3</sub>), 3.56 (s, 2, CH<sub>2</sub>), 5.44 and 5.55 (s, 1, CH), 7.29 (m, 10, 2 × C<sub>6</sub>H<sub>3</sub>).

Anal. Calcd. for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.01; H, 6.52; N, 5.51.

Compound 1c (yield 69%) had mp 113-115° (from cyclohexane); ir: 3360 (NH), 1715 (CO), 1640 (CONH) cm<sup>-1</sup>; pmr:  $\delta$  1.62 (s, 1, NH), 2.07 (s, 3, CH<sub>3</sub>), 3.52 (s, 2, CH<sub>2</sub>), 5.45 and 5.55 (s, 1, CH), 7.25 (m, 9, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>4</sub>).

Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>ClNO<sub>2</sub>: C, 67.66; H, 5.34; Cl, 11.75; N, 4.66. Found: C, 67.23; H, 5.24; Cl, 11.70; N, 4.43.

Compound 1d (yield 81%) had mp 97-99° (from aqueous ethanol); ir: 3350 (NH), 1715 (CO), 1640 (CONH) cm<sup>-1</sup>; pmr:  $\delta$  1.60 (brs, 1, NH), 2.06 (s, 3, CH<sub>3</sub>), 3.50 (s, 2, CH<sub>2</sub>), 3.80 (s, 3, OCH<sub>3</sub>), 5.45 and 5.56 (s, 1, CH), 7.02 (AA'BB', 4, C<sub>6</sub>H<sub>4</sub>), 7.29 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.54; H, 6.44; N, 4.63.

Compound 1e (yield 75%) had mp 94-95° (from cyclohexane); ir: 3320 (NH), 1710 (CO), 1650 (CONH) cm<sup>-1</sup>; pmr:  $\delta$  1.57 (brs, 1, NH), 2.11 (s, 3, CH<sub>3</sub>), 3.00 (m, 2, CH<sub>2</sub>—CH), 3.53 (s, 2, CH<sub>2</sub>CO), 4.79 (m, 1, CH), 7.26 (m, 10, 2 × C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.77; H, 7.04; N, 5.08.

Compound **1f** (yield 71%) had mp 97-99° (from cyclohexane); ir: 3300 (NH), 1720 (CO), 1650 (CONH) cm<sup>-1</sup>; pmr:  $\delta$  1.62 (brs, 1, NH), 2.14 (s, 3, CH<sub>3</sub>), 3.01 (m, 2, CH<sub>2</sub>—CH), 3.48 (s, 2, CH<sub>2</sub>CO), 4.80 (m, 1, CH), 7.20 (m, 9, C<sub>8</sub>H<sub>4</sub> + C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>ClNO<sub>2</sub>: C, 68.46; H, 5.71; Cl, 11.23; N, 4.44. Found: C, 68.50; H, 5.80; Cl, 11.15; N, 4.31.

Compound **1g** (yield 72%) had mp 98-100° (from aqueous ethanol); ir: 3320 (NH), 1720 (CO), 1660 (CONH) cm<sup>-1</sup>; pmr:  $\delta$  1.61 (s, 1, NH), 2.11 (s, 3, CH<sub>3</sub>), 2.99 (m, 2, CH<sub>2</sub>—CH), 3.47 (s, 2, CH<sub>2</sub>CO), 3.82 (s, 3, OCH<sub>3</sub>), 4.79 (m, 1, CH), 7.20 (m, 9,  $C_8H_5 + C_6H_4$ ).

Anal. Calcd. for C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>: C, 73.29; H, 6.80; N, 4.50. Found: C, 72.91; H, 6.66; N, 4.32.

#### General Procedure for Alkylidenepyrrolinones 3a,e-g.

The acylaminoketone 1 (1 mmole) was refluxed with sodium ethoxide (3 mmoles) in ethanol (10 ml) for 8 hours. After cooling, the resulting solid pyrrolinone 3 was filtered off, washed with water and crystallized. The ethanol solution was concentrated and the residue was washed with water and extracted with chloroform. The extracts were evaporated to yield another crop of 3. In some cases it was contaminated with the corresponding ethoxy-derivative 5.

Compound **3a** (yield 51%) was obtained as yellow-orange needles, mp 235-237° (from ethanol); ir: 3180 (NH), 1670 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 228 (3.77) and 292 nm (4.40); pmr:  $\delta$  1.60 (brs, 1, NH), 1.94 (d, 3, CH<sub>3</sub>, J = 7.4), 2.19 (s, 3, CH<sub>3</sub>CO), 5.42 (q, 1, CH, J = 7.4), 7.44 (brs, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>13</sub>NO: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.04; H, 6.58; N, 7.20.

Compound **5a** (yield 6%) was obtained as white crystals, mp 122-124° (from sublimation at 70°/0.04 mm Hg); ir: 3230 (NH), 1705 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 225 nm (4.09); pmr  $\delta$  0.89 (t, 3, CH<sub>3</sub>—CH<sub>2</sub>—C, J = 7.4), 1.17 (t, 3, CH<sub>3</sub>—CH<sub>2</sub>—0, J = 7.1), 1.54 (brs, 1, NH), 1.92 (m, 2, CH<sub>2</sub>—C), 1.99 (s, 3, CH<sub>3</sub>CO), 3.25 (m, 2, CH<sub>2</sub>—O), 7.43 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>15</sub>H<sub>19</sub>NO<sub>2</sub>: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.54; H, 7.83; N, 5.81.

Compound **3e-**Z (yield 87%) was obtained as white crystals, mp 221-222° (from ethanol and sublimation at  $100^{\circ}/0.04$  mm Hg); ir: 3200 (NH), 1685 (CO) cm<sup>-1</sup>; uv  $\lambda$  max (log  $\epsilon$ ): 226 (4.11) and 341 nm (4.54); pmr:  $\delta$  1.62 (brs, 1, NH), 2.32 (s, 3, CH<sub>3</sub>), 6.28 (s, 1, CH), 7.35 (s, 5, C<sub>6</sub>H<sub>5</sub>), 7.42 (s, 5, C<sub>6</sub>H<sub>6</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>15</sub>NO: C, 82.76; H, 5.75; N, 5.36. Found: C, 82.80; H, 5.79; N, 5.02.

Compound 5e (yield 3%) was obtained as white crystals, mp 134-136° (from aqueous methanol); ir: 3200 (NH), 1700 (CO) cm<sup>-1</sup>; pmr:  $\delta$  1.15 (t, 3, CH<sub>3</sub>—CH<sub>2</sub>, J = 7.0), 1.56 (brs, 1, NH), 2.05 (s, 3, CH<sub>3</sub>CO), 3.19 (m, 4, 2 × CH<sub>2</sub>), 7.23 (s, 5, C<sub>6</sub>H<sub>5</sub>), 7.33 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for  $C_{20}H_{21}NQ_2$ : C, 78.15; H, 6.89; N, 4.56. Found: C, 77.99; H, 6.74; N, 4.29.

Compound **3f** (yield 81%) was obtained as white needles, mp 235-237° (from ethanol); ir: 3200 (NH), 1690 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 228 (3.98), 236 (3.96), and 344 nm (4.58); pmr:  $\delta$  1.56 (s, 1, NH), 2.31 (s, 3, CH<sub>3</sub>), 6.28 (s, 1, CH), 7.41 and 7.46 (s, 9, C<sub>6</sub>H<sub>4</sub> + C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>ClNO: C, 73.10; H, 4.74; Cl, 11.99; N, 4.74. Found: C, 72.79; H, 4.65; Cl, 12.18; N, 4.66.

Compound **3g** (yield 81%) was obtained as yellow crystals, mp 194-195° (from ethanol); ir: 3200 (NH), 1690 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 229 (4.15), 245 (3.94) and 346 nm (4.57); pmr:  $\delta$  1.56 (s, 1, NH), 2.31 (s, 3, CH<sub>3</sub>), 3.85 (s, 3, OCH<sub>3</sub>), 6.24 (s, 1, CH), 7.26 (AA'BB', 4, C<sub>6</sub>H<sub>4</sub>), 7.40 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for  $C_{19}H_{17}NO_2$ : C, 78.33; H, 5.88; N, 4.81. Found: C, 78.11; H, 5.97; N, 4.92.

# General Procedure for Pyrrolinones 2a-f.

The aminoacylketone 1 (10 mmoles) was heated at  $90^{\circ}$  with 3N aqueous potassium hydroxide (150 ml) for 2 hours under nitrogen. After cooling the resulting pyrrolinone 2 was filtered off, washed with water and crystallized. The alkaline solution was acidified to precipitate another crop of 2.

Compound 2a (yield 65%) had mp 170-172° (from cyclohexane); ir: 3210 (NH), 1680 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 232 nm (4.10); pmr:  $\delta$  0.93 (t, 3, CH<sub>3</sub>—CH<sub>2</sub>, J = 7.4), 1.67 (m, 3, CH<sub>2</sub> + NH), 2.07 (s, 3, CH<sub>3</sub>), 4.05 (m, 1, CH), 7.42 (s, 5, C<sub>6</sub>H<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>15</sub>NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.93; H, 7.35; N, 6.74.

Compound **2b** (yield 70%) had mp 199-201° (from cyclohexane); ir: 3190 (NH), 1670 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 230 nm (4.17); pmr:  $\delta$  1.62 (s, 1, NH), 1.88 (s, 3, CH<sub>3</sub>), 4.98 (s, 1, CH), 7.32 (s, 5, C<sub>6</sub>H<sub>5</sub>), 7.44 (s, 5, C<sub>6</sub>H<sub>5</sub>). Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>NO: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.84; H, 6.20; N, 5.92.

Compound **2c** (yield 85%) had mp 165-167° (from aqueous methanol); ir: 3220 (NH), 1680 (CO) cm<sup>-1</sup>; pmr:  $\delta$  1.65 (brs, 1, NH), 1.88 (s, 3, CH<sub>3</sub>), 4.96 (s, 1, CH), 7.40 (brs, 9, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>17</sub>H<sub>14</sub>ClNO: C, 71.96; H, 4.97; Cl, 12.49; N, 4.94. Found: C, 71.89; H, 5.06; Cl, 12.62; N, 4.90.

Compound **2d** (yield 64%) had mp 183-185° (from benzene); ir: 3220 (NH), 1680 (CO) cm<sup>-1</sup>; pmr:  $\delta$  1.60 (s, 1, NH), 1.88 (s, 3, CH<sub>3</sub>), 3.83 (s, 3, OCH<sub>3</sub>), 4.96 (s, 1, CH), 7.21 (AA'BB', 4, C<sub>6</sub>H<sub>4</sub>), 7.33 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.11; H, 6.13; N, 4.83.

Compound **2e** (yield 84%) had mp 165-166° (from aqueous methanol); ir: 3220 (NH), 1665 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 235 nm (4.10); pmr:  $\delta$  1.76 (brs, 1, NH), 2.13 (s, 3, CH<sub>3</sub>), 2.96 (m, 2, CH<sub>2</sub>), 4.20 (m, 1, CH), 7.27 (s, 5, C<sub>6</sub>H<sub>3</sub>), 7.39 (s, 5, C<sub>6</sub>H<sub>3</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>NO: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.98; H, 6.52; N, 5.51.

Compound **2f** (yield 87%) had mp 183-186° (from ethanol); ir: 3200 (NH), 1680 (CO) cm<sup>-1</sup>; pmr:  $\delta$  1.56 (s, 1, NH), 2.17 (s, 3, CH<sub>3</sub>), 2.93 (m, 2, CH<sub>2</sub>), 4.21 (m, 1, CH), 7.30 (s, 5, C<sub>6</sub>H<sub>5</sub>), 7.39 (s, 4, C<sub>6</sub>H<sub>4</sub>).

Anal. Calcd. for  $C_{18}H_{16}CINO$ : C, 72.61; H, 5.38; Cl, 11.90; N, 4.71. Found: C, 72.55; H, 5.24; Cl, 12.01; N, 4.58.

# General Procedure for 5-Hydroxypyrrolinones 4a-c.e.

A stream of oxygen was bubbled into a solution of pyrrolinones 2a-c,e (1 mmole) in acetone (30 ml) and 1N potassium hydroxide (1 ml) until the starting material disappeared. The solution was evaporated to yield compounds 4a-c,e.

Compound 4a (yield 62%) had mp 132-134° (from cyclohexane and sublimation at 100°/0.04 mm Hg); ir: 3350 (OH), 3240 (NH), 1690 (CO) cm<sup>-1</sup>; pmr:  $\delta$  0.85 (t, 3, CH<sub>3</sub>—CH<sub>2</sub>, J = 7.1), 1.79 (m, 3, CH<sub>2</sub> + NH), 2.01 (s, 3, CH<sub>3</sub>CO), 3.26 (s, 1, OH), 7.38 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>: C, 71.87; H, 6.96; N, 6.45. Found: C, 72.14; H, 7.05; N, 6.04.

Compound **4b** (yield 78%) had mp 180-181° (from ethanol); ir: 3370 (OH), 3290 (NH), 1700 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 260 nm (3.80); pmr:  $\delta$  1.48 (s, 1, NH), 1.84 (s, 3, CH<sub>3</sub>), 2.74 (brs, 1, OH), 7.36 (brs, 10, 2  $\times$  C<sub>6</sub>H<sub>3</sub>). Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub>: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.82; H, 5.66; N, 5.24.

Compound 4c (yield 75%) had mp 170-172° (from aqueous methanol); ir: 3360 (OH), 3280 (NH), 1700 (CO) cm<sup>-1</sup>; pmr:  $\delta$  1.58 (s, 1, NH), 1.87 (s, 3, CH<sub>3</sub>), 3.27 (s, 1, OH), 7.38 (brs, 9,  $C_6H_5$  +  $C_6H_4$ ).

Anal. Calcd. for C<sub>17</sub>H<sub>14</sub>ClNO<sub>2</sub>: C, 68.11; H, 4.67; Cl, 11.83; N, 4.67. Found: C, 67.96; H, 4.66; Cl, 11.95; N, 4.38.

Compound 4e (yield 80%) had mp 168-171° (from ethanol); ir: 3380 (OH), 3280 (NH), 1690 (CO) cm<sup>-1</sup>; pmr:  $\delta$  1.63 (brs, 1, NH), 2.17 (s, 3, CH<sub>3</sub>), 3.09 (AB, 2, CH<sub>2</sub>, J = 13.7), 6.10 (brs, 1, OH), 7.30 (s, 5, C<sub>4</sub>H<sub>5</sub>), 7.36 (s, 5,

 $C_6H_5$ ).

Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.04; H, 6.07; N, 4.80.

#### 5-Ethoxy-3,5-diphenyl-4-methylpyrrolin-2-one (5b).

Compound 4b (170 mg) was refluxed with sodium ethoxide (obtained from 40 mg of sodium) in ethanol (10 ml) for 3 hours. The solution was evaporated and the residue was extracted with chloroform. Evaporation of the extracts gave the pyrrolinone 5b (140 mg, 75%), mp 129-130° (from petroleum ether and sublimation at 110°0.04 mm Hg); ir: 3220 (NH), 1690 (CO) cm<sup>-1</sup>; pmr: δ 1.31 (t, CH<sub>3</sub>—CH<sub>2</sub>, J = 7.0), 1.68 (brs, 1, NH), 1.82 (s, 3, CH<sub>3</sub>), 3.46 (m, 2, CH<sub>2</sub>), 7.44 (s, 5, C<sub>6</sub>H<sub>5</sub>), 7.47 (s, 5, C<sub>6</sub>H<sub>5</sub>). Anal. Calcd. for C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.48; H, 6.42; N, 4.50.

# 5-Benzylidene-3-phenyl-4-methylpyrrolin-2-one (3e-E).

A solution of the Z-isomer of 3e (0.2 g) in methanol (200 ml) was irradiated for 4 hours with a 365 nm wavelength from a medium pressure mercury lamp filtered with a cupric sulfate solution. The methanolic solution was evaporated and the residue was extracted with ethyl acetate. The extracts were evaporated to yield a mixture of the Z and E isomer of 3e (ratio 42:58 based on pmr analysis) which were separated by layer chromatography with chloroform/methanol (60:1, v/v) as eluent. The faster running band yielded the isomer 3e-Z (ir and pmr spectra identical with starting material). The slower running band yielded the isomer 3e-E, mp 201-203° (from ethyl acetate); ir: 3200 (NH), 1680 (CO) cm<sup>-1</sup>; uv:  $\lambda$  max (log  $\epsilon$ ) 226 (3.93) and 322 nm (4.35); pmr:  $\delta$  1.64 (brs, 1, NH), 1.89 (s, 3, CH<sub>3</sub>), 6.66 (s, 1, CH), 7.35 (s, 5, C<sub>6</sub>H<sub>5</sub>), 7.42 (s, 5, C<sub>6</sub>H<sub>5</sub>).

Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>NO: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.45; H, 5.58; N, 5.44.

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