Air Oxidation of Tetrasubstituted 3-Pyrrolines to their Corresponding Pyrroles in the Solid State

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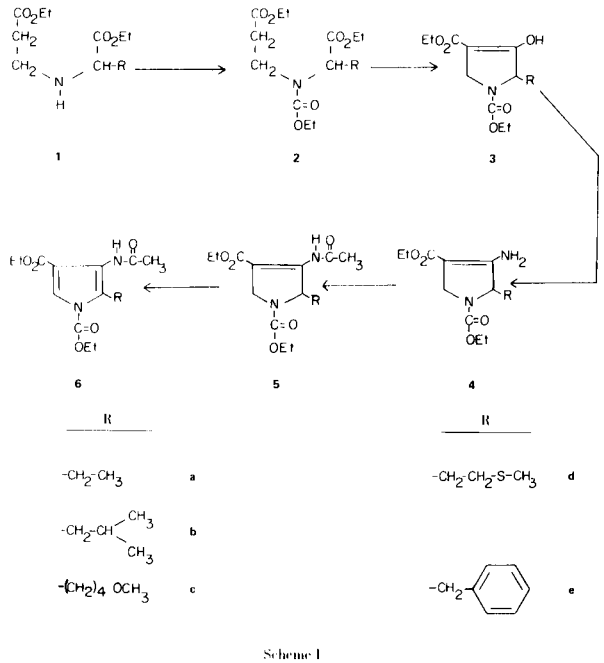
During the course of a synthesis leading to substituted pyrrolo[3,4-*d*]imidazolones, prepared as potential agonists or antagonists of biotin, we encountered a rather unusual air oxidation of 3-pyrrolines to the corresponding pyrroles (1).

Pyrrolidines and pyrrolines have been dehydrogenated to pyrroles by various oxidizing agents such as manganese tetroxide (2), silver oxide (3), hydrogen peroxide (4), and 2,3,5,6-tetrachloro-1,4-benzoquinone (5). Unfortunately, many of these cited reactions have limited usefulness due to either poor yields or to the relative inaccessibility of starting materials. In this publication we are reporting the syntheses of certain tetrasubstituted pyrroles by air oxidation of the corresponding 3-pyrrolines in the solid or neat state. Scheme I is illustrative of the sequence of steps leading to pyrroles **6** (a through e).



Scheme I

Starting diester **1** was prepared by ethanolysis of the corresponding cyanoethylated amino acid according to the method of McKinney (6). Treatment of **1** with ethyl chloroformate followed by Dieckmann cyclization (7-9) in either dry benzene, toluene, or xylene gave the highly enolized β-ketoester **3** as evidenced by infrared spectroscopy. Enamine **4** was obtained in good yield by refluxing **3** with ammonium formate in ethanol (10). Acetylation of **4** was effected by heating in acetic anhydride with or without pyridine. Exposure of **5** to air at room temperature in either daylight or complete darkness for several weeks or heating in the presence of a stream of oxygen afforded pyrrole **6**. Heating in an inert atmosphere or under vacuum failed to produce the corresponding pyrrole. It is interesting to note that the 2-unsubstituted pyrroline (**5**, R = H) and compound **4** (**a** through **e**) do not undergo dehydrogenation to the pyrrole under conditions identical to those used for **5** (**a** through **e**) and remain unchanged. However, it should be noted that the Dieckmann product **3** does undergo extensive decomposition to a complex mixture upon standing in the air. Preliminary attempts to resolve this mixture failed in all cases involving decomposition of **3** (**a-e**).

Although the mechanism of the oxidation of **5** to pyrrole **6** has not yet been resolved, the structural confirmation of the latter was achieved by elemental analysis and examination of spectral data. The hypsochromic shift of 58-63 nm observed in the transformation of **5** to **6** is in accord with the postulated oxidation to a pyrrole (11). The pmr spectra provide further support for the assignment of **6**. The C_5 methylene protons of the pyrroline enamine acetate **5** were found in the range δ 4.20-4.30 and the C_2 methine proton in these same compounds was found at δ 4.40-4.67. Both of these resonances were absent in **6** and were replaced by a sharp singlet at δ 7.86, which can reasonably be assigned to a pyrrole α proton.

EXPERIMENTAL (12)

Ethyl 2-(2-Carbethoxyethylamino)butanoate (**1a**).

A suspension of 2-(2-cyanoethylamino)butyric acid (13) (87.1 g., 0.55 mole) in absolute ethanol (1 l.) was cooled in an ice bath and, while stirring, dry hydrogen chloride was introduced *via* a gas inlet tube. After stirring for 8 hours, a total of 230 g. of hydrogen chloride had been added to the reaction mixture. The

suspension was then allowed to reach room temperature and following an interval of 12 hours it was refluxed for one hour. The ethanol was distilled, the residue dissolved in water (350 ml.), and the resultant clear solution treated with 10% ammonium hydroxide to *p*H 9. The oily product was extracted with chloroform and the extract washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. A colorless liquid was obtained (112 g.). Distillation at 20 mm. gave pure aminoester **1a** (102 g. 80%), b.p. 152-155°; ir (chloroform): 1721 cm^{-1}; pmr (deuteriochloroform): δ 0.94 (t, 3H, J = 7 Hz), 1.25 (t, 3H, J = 7 Hz), 1.26 (t, 3H, J = 7 Hz), 1.59 (m, 2H), 1.90 (s, 1H), 2.33-3.00 (m, 4H), 3.18 (t, 1H, J = 7 Hz), 4.17 (q, 2H, J = 7 Hz), 4.22 (q, 2H, J = 7 Hz).

Anal. Calcd. for $C_{11}H_{21}NO_4$: C, 57.12; H, 9.15; N, 6.06. Found: C, 57.24; H, 9.07; N, 5.98.

Ethyl 2-(2-Carbethoxyethylamino)-3-phenylpropionate (**1e**).

This compound was prepared from 2-(2-cyanoethylamino)-3-phenylpropionic acid (6) by the same procedure as described above for the preparation of **1a**; b.p. 140-141° (0.15 mm.); ir (chloroform): 1724 cm^{-1}; pmr (deuteriochloroform): δ 1.15 (t, 3H, J = 7 Hz), 1.21 (t, 3H, J = 7 Hz), 2.25-2.86 (m, 5H), 2.95 (d, 2H, J = 7 Hz), 3.54 (t, 1H, J = 7 Hz), 4.13 (q, 4H, J = 7 Hz), 7.23 (s, 5H).

Anal. Calcd. for $C_{16}H_{23}NO_4$: C, 65.51; H, 7.90; N, 4.78. Found: C, 65.70; H, 7.93; N, 4.77.

Ethyl 2-[*N*-(2-Carbethoxyethyl)-N-carbethoxy]aminobutanoate (**2a**).

Ethyl chloroformate (28.0 g., 0.26 mole) was added dropwise to previously cooled **1a** (50.0 g., 0.216 mole). Near the end of the addition, the reaction mixture turned solid and a solution of sodium carbonate (13.8 g.) in water (100 ml.) was added. The mixture was warmed at 50° for 2 hours, cooled, and allowed to stand at room temperature overnight. The product was extracted with methylene chloride. The organic layer was washed with water, dried over magnesium sulfate, and concentrated to give a clear liquid (68.8 g.). Distillation at 0.25 mm. gave a colorless fraction (59.9 g., 91%), b.p. 122-124°. The analytical sample was obtained by one additional distillation, b.p. 119-119.5° (0.15 mm.). Tlc on silica gel G (10% methanol in chloroform) showed one spot; ir (chloroform): 1724-1667 cm^{-1}; pmr (deuteriochloroform): δ 0.97 (t, 3H, J = 7 Hz), 1.26 (t, 9H, J = 7 Hz), 1.49-2.30 (m, 2H), 2.70 (t, 2H, J = 7 Hz), 3.52 (t, 2H, J = 7 Hz), 3.87 (t, 1H, J = 8 Hz), 4.17 (q, 6H, J = 7 Hz).

Anal. Calcd. for $C_{14}H_{25}NO_6$: C, 55.42; H, 8.31; N, 4.62. Found: C, 55.50; H, 8.27; N, 4.71.

The following were prepared in a similar manner:

Ethyl 2-[*N*-(2-Carbethoxyethyl)-N-carbethoxy]amino-4-methylpentanoate (**2b**).

This compound was obtained from **1b** (14); b.p. 154-155° (0.30 mm.); ir (chloroform): 1718, 1695 cm^{-1}; pmr (deuteriochloroform): δ 0.97 (d, 6H, J = 6 Hz), 1.25 (t, 9H, J = 7 Hz), 1.42-1.90 (m, 3H), 2.68 (t, 2H, J = 7 Hz), 3.48 (t, 2H, J = 7 Hz), 4.00 (t, 1H, J = 7 Hz), 4.17 (q, 6H, J = 7 Hz).

Anal. Calcd. for $C_{16}H_{29}NO_6$: C, 57.99; H, 8.82; N, 4.23. Found: C, 58.08; H, 8.92; N, 4.22.

Ethyl 2-[*N*-(2-Carbethoxyethyl)-N-carbethoxy]amino-4-methylthiobutanoate (**2d**).

This compound was obtained from **1d** (14) as a viscous oil which decomposed upon attempted distillation; ir (chloroform): 1730, 1698 cm^{-1}; pmr (deuteriochloroform): δ 1.26 (t, 9H, J = 7 Hz), 2.10 (s, 3H), 2.15-2.60 (m, 4H), 2.70 (t, 2H, J = 7 Hz), 3.55 (t, 2H, J = 7 Hz), 4.00 (t, 1H, J = 7 Hz), 4.16 (q, 6H, J = 7 Hz).

Ethyl 2-[*N*-(2-Carbethoxyethyl)-*N*-carbethoxy]amino-3-phenylpropionate (**2e**).

This compound was synthesized from **1e**; b.p. 168-169° (0.35 mm.); ir (chloroform): 1725-1670 cm^{-1}; pmr (deuteriochloroform): δ 1.24 (t, 6H, J = 7 Hz), 1.25 (t, 3H, J = 7 Hz), 2.42 (t, 2H, J = 7 Hz), 3.00-3.70 (m, 4H), 3.80-4.50 (m, 7H), 7.25 (s, 5H).

Anal. Calcd. for $C_{19}H_{27}NO_6$: C, 62.45; H, 7.45; N, 3.83. Found: C, 62.42; H, 7.41; N, 3.83.

1,4-Dicarbethoxy-2-ethyl-3-hydroxy-3-pyrroline (**3a**).

A suspension of sodium (2.3 g., 0.10 mole) in xylene (100 ml.) was heated to reflux and treated dropwise with a solution of **2a** (30.3 g., 0.10 mole) in xylene (50 ml.). A glassy solid product separated from the mixture during the course of the addition. After the addition, reflux was continued for an additional 2 hours and the mixture allowed to stand at room temperature overnight. The cooled reaction mixture was then treated with a solution of glacial acetic acid (13 ml.) in water (50 ml.). The product was extracted into chloroform, the organic layer washed with water, dried, and concentrated yielding a yellow oil (21.2 g., 82%). This compound gave a deep purple color reaction with ferric chloride solution. An analytical sample was obtained by distillation, b.p. 120-121° (0.15 mm.); ir (chloroform): 1695-1618 cm^{-1}; uv (95% ethanol): 278 nm (ε = 5440); pmr (deuteriochloroform): δ 0.83 and 0.90 (2t, 3H, J = 7 Hz), 1.30 and 1.33 (2t, 6H, J = 7 Hz), 1.67-1.93 (m, 2H), 3.33-3.85 (m, 1H), 4.00-4.55 (m, 6H), 4.64 (s, 1H).

Anal. Calcd. for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44; N, 5.44. Found: C, 56.06; H, 7.47; N, 5.51.

In a similar manner the following were prepared:

1,4-Dicarbethoxy-2-isobutyl-3-hydroxy-3-pyrroline (**3b**).

This compound was obtained from **2b**; b.p. 138-140° (0.25 mm.); ir (chloroform): 1757, 1698, 1639 cm^{-1}; uv (95% ethanol): 250 nm (ε = 6250); pmr (deuteriochloroform): δ 0.94 and 0.96 (2d, 6H, J = 6 Hz), 1.26 and 1.28 (2t, 6H, J = 7 Hz), 1.45-1.90 (m, 3H), 2.56 (t, 1H, J = 7 Hz), 3.40-4.00 (m, 2H), 4.23 and 4.26 (2q, 4H, J = 7 Hz), 7.80 (broad s, 1H).

Anal. Calcd. for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.12; N, 4.91. Found: C, 59.05; H, 8.02; N, 4.88.

The semicarbazone of **3b** had m.p. 140-142° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{15}H_{26}N_4O_5$: C, 52.62; H, 7.65; N, 16.36. Found: C, 52.65; H, 7.65; N, 16.31.

1,4-Dicarbethoxy-2-(2-methylthioethyl)-3-hydroxy-3-pyrroline (**3d**).

This compound was prepared from **2d** as a viscous oil; ir (chloroform): 1764, 1727, 1700, 1639 cm^{-1}; uv (95% ethanol): 247 nm (ε = 6,600); pmr (deuteriochloroform): δ 1.29 (t, 6H, J = 7 Hz), 1.98 (s, 3H), 2.05-2.84 (m, 4H), 3.45-3.90 (m, 1H), 3.90-4.50 (m, 6H), 4.65 (s, 1H).

Compound **3d** was further characterized as its copper chelate which was recrystallized from ethanol, m.p. 137-139.5°; uv (95% ethanol): 275 nm (ε = 28,000).

Anal. Calcd. for $C_{26}H_{40}N_2O_{10}S_2Cu$: C, 46.72; H, 6.03; N, 4.19. Found: C, 46.53; H, 6.18; N, 4.35.

1,4-Dicarbethoxy-2-benzyl-3-hydroxy-3-pyrroline (**3e**).

This compound was obtained from **2e** as a viscous oil; ir (chloroform): 1770, 1675-1645 cm^{-1}; uv (95% ethanol): 247 nm (ε = 4220); pmr (deuteriochloroform): δ 1.24 (t, 3H, J = 7 Hz), 1.35 (t, 3H, J = 7 Hz), 2.10 (s, 1H), 2.80-3.74 (m, 3H), 3.88-5.00 (m, 6H), 6.95-7.48 (m, 5H).

1,4-Dicarbethoxy-2-ethyl-3-amino-3-pyrroline (**4a**).

A solution of **3a** (5.35 g., 0.02 mole) and ammonium formate (2.52 g., 0.04 mole) in 20 ml. of absolute ethanol was refluxed for 4 hours. The solvent was removed *in vacuo* and the semi-solid residue partitioned between water and chloroform. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated to yield a light brown oil (5.06 g., 94%). All attempts to crystallize the product failed. Tlc on silica gel G (10% methanol in chloroform) showed the product to be homogeneous; ir (chloroform): 3571, 3425, 1683, 1642 cm^{-1}; uv (95% ethanol): 274 nm (ϵ = 17,000); pmr (deuteriochloroform): δ 0.80 (t, 3H, J = 7 Hz), 1.27 (t, 6H, J = 7 Hz), 2.70 (t, 1H, J = 7 Hz), 4.20 (q, 4H, J = 7 Hz), 4.24 (s, 2H), 4.68 (m, 1H), 5.83 (s, 2H).

Similarly prepared were the following:

1,4-Dicarbethoxy-2-isobutyl-3-amino-3-pyrroline (**4b**).

This compound was synthesized from **3b** and isolated as a viscous oil; ir (chloroform): 3448, 3333, 1667-1613 cm^{-1}; uv (95% ethanol): 276 nm (ϵ = 15,200); pmr (deuteriochloroform): δ 0.95 (d, 6H, J = 6 Hz), 1.30 (t, 6H, J = 7 Hz), 1.50-1.97 (m, 3H), 4.23 (q, 2H, J = 7 Hz), 4.27 (s, 2H), 4.70 (m, 1H), 5.74 (s, 2H).

1,4-Dicarbethoxy-2-(2-methylthioethyl)-3-amino-3-pyrroline (**4d**).

This compound was prepared as a viscous oil from **3d**; ir (chloroform): 3460, 3344, 1680, 1639 cm^{-1}; uv (95% ethanol): 275.5 nm (ϵ = 14,150); pmr (deuteriochloroform): δ 1.28 (t, 6H, J = 7 Hz), 2.10 (s, 3H), 2.15-2.87 (m, 4H), 4.20 (q, 4H, J = 7 Hz), 4.25 (s, 2H), 4.71 (m, 1H), 5.90 (s, 1H), 6.17 (s, 1H).

1,4-Dicarbethoxy-2-benzyl-3-amino-3-pyrroline (**4e**).

This compound was obtained from **3e** as a solid which was recrystallized from isopropyl ether-ethanol mixture, m.p. 121-121.5°; ir (chloroform): 3546, 3413, 1678, 1628 cm^{-1}; uv (95% ethanol): 276.5 nm (ϵ = 11,900); pmr (deuteriochloroform): δ 1.23 (t, 3H, J = 7 Hz), 1.30 (t, 3H, J = 7 Hz), 3.21 (m, 2H), 4.15 (q, 4H, J = 7 Hz), 4.30 (s, 2H), 4.80 (m, 1H), 5.54 (s, 2H), 7.30 (s, 5H).

Anal. Calcd. for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 64.08; H, 6.91; N, 8.76.

1,4-Dicarbethoxy-2-ethyl-3-acetamido-3-pyrroline (**5a**).

A solution of **4a** (2.56 g., 0.01 mole) in acetic anhydride (15 ml.) was heated on an oil bath at 90-100° for 12 hours. The excess acetic anhydride was removed under vacuum to give a light yellow oil (2.90 g., 97%). All attempts to purify and crystallize the product failed. Tlc on silica gel G (10% methanol in chloroform) showed the product to be homogeneous; ir (chloroform): 3322, 1680, 1639 cm^{-1}; uv (95% ethanol): 276 nm (ϵ = 14,300); pmr (deuteriochloroform): δ 0.79 (t, 3H, J = 7 Hz), 1.28 (t, 3H, J = 7 Hz), 1.33 (t, 3H, J = 7 Hz), 1.90 (m, 2H), 2.18 (s, 3H), 4.24 (q, 2H, J = 7 Hz), 4.35 (q, 2H, J = 7 Hz), 4.60 (m, 1H), 10.18 (s, 1H).

Similarly prepared were the following:

1,4-Dicarbethoxy-2-isobutyl-3-acetamido-3-pyrroline (**5b**).

This compound was obtained from **4b** as a crystalline solid, m.p. 72-75° after recrystallization from petroleum ether (b.p. 30-60°); ir (chloroform): 3322, 1679, 1639 cm^{-1}; uv (95% ethanol): 275 nm (ϵ = 15,650); pmr (deuteriochloroform): δ 0.88 (d, 3H, J = 6 Hz), 1.03 (d, 3H, J = 6 Hz), 1.30 (t, 3H, J = 7 Hz), 1.33 (t, 3H, J = 7 Hz), 1.55-1.95 (m, 3H), 2.18 (s, 3H), 4.20 (s, 2H), 4.23 (q, 2H, J = 7 Hz), 4.28 (q, 2H, J = 7 Hz), 4.67 (m, 1H), 10.18 (s, 1H).

Anal. Calcd. for $C_{16}H_{26}N_2O_5$: C, 58.88; H, 8.03; N, 8.58. Found: C, 58.91; H, 8.04; N, 8.48.

1,4-Dicarbethoxy-2-(2-methylthioethyl)-3-acetamido-3-pyrroline (**5d**).

This compound was obtained from **4d** as an oil; ir (chloroform): 3311, 1709-1681, 1639 cm^{-1}; uv (95% ethanol): 275 nm (ϵ = 14,250); pmr (deuteriochloroform): δ 1.29 (t, 3H, J = 7 Hz), 1.32 (t, 3H, J = 7 Hz), 2.10 (s, 3H), 2.19 (s, 3H), 2.20-2.70 (m, 4H), 4.25 (s, 2H), 4.25 (q, 2H, J = 7 Hz), 4.34 (q, 2H, J = 7 Hz), 4.55 (m, 1H), 10.18 (s, 1H).

1,4-Dicarbethoxy-2-benzyl-3-acetamido-3-pyrroline (**5e**).

This compound was obtained from **4e** as a viscous oil; ir (chloroform): 3322, 1681, 1639 cm^{-1}; uv (95% ethanol): 275 nm (ϵ = 16,500); pmr (deuteriochloroform): δ 1.18 (t, 3H, J = 7 Hz), 1.27 (t, 3H, J = 7 Hz), 2.23 (s, 3H), 2.70-3.57 (m, 2H), 4.13 (q, 2H, J = 7 Hz), 4.18 (q, 2H, J = 7 Hz), 4.30 (s, 2H), 4.40 (m, 1H), 7.16 (m, 5H), 10.18 (s, 1H).

1,4-Dicarbethoxy-2-ethyl-3-acetamidopyrrole (**6a**).

A solution of **5a** (0.30 g., 1.0 mmole) in ether (4 ml.) was spread on a large watch glass in such a way as to form a uniform thin film. This film was then allowed to remain in the laboratory for 3 weeks during which time crystals formed on the watch glass. The product was collected and recrystallized from diethyl ether yielding colorless needles (0.21 g., 70%), m.p. 107-108°. An additional recrystallization gave the analytical sample, m.p. 108-108.5°. ir (chloroform): 3247, 1748, 1715 cm^{-1}; uv (95% ethanol): 215 nm (ϵ = 28,700); pmr (deuteriochloroform): δ 1.13 (t, 3H, J = 7 Hz), 1.33 (t, 3H, J = 7 Hz), 1.43 (t, 3H, J = 7 Hz), 2.15 (s, 3H), 2.84 (9, 2H, J = 7 Hz), 4.25 (q, 2H, J = 7 Hz), 4.45 (q, 2H, J = 7 Hz), 7.53 (s, 1H), 7.80 (s, 1H).

Anal. Calcd. for $C_{14}H_{20}N_2O_5$: C, 56.75; H, 6.80; N, 9.45. Found: C, 56.66; H, 6.71; N, 9.38.

The following were prepared in essentially the same manner as described above.

1,4-Dicarbethoxy-2-isobutyl-3-acetamidopyrrole (**6b**).

This compound was obtained in 73% yield from **5b**, m.p. 112-113° after recrystallization from diethyl ether; ir (chloroform): 3436, 1757, 1695 cm^{-1}; uv (95% ethanol): 217 nm (ϵ = 48,780); pmr (deuteriochloroform): δ 0.87 (d, 6H, J = 6 Hz), 1.35 (t, 3H, J = 7 Hz), 1.45 (t, 3H, J = 7 Hz), 1.88 (m, 1H), 2.18 (s, 3H), 2.80 (d, 2H, J = 7 Hz), 4.32 (q, 2H, J = 7 Hz), 4.48 (q, 2H, J = 7 Hz), 7.66 (s, 1H), 7.86 (s, 1H).

Anal. Calcd. for $C_{16}H_{24}N_2O_5$: C, 59.24; H, 7.46; N, 8.64. Found: C, 59.41; H, 7.52; N, 8.61.

1,4-Dicarbethoxy-2-(4-methoxybutyl)-3-acetamidopyrrole (**6c**).

This compound was obtained from **5c** (15) in 68% yield, m.p. 127-128° after recrystallization from chloroform; ir (chloroform): 3425, 1751, 1692 cm^{-1}; uv (95% ethanol): 216 nm (ϵ = 34,700); pmr (deuteriochloroform): δ 1.12-1.30 (m, 2H), 1.33 (t, 3H, J = 7 Hz), 1.45 (t, 3H, J = 7 Hz), 1.80-2.10 (m, 2H), 2.17 (s, 3H), 2.67-3.10 (m, 2H), 3.36 (s, 3H), 3.38 (m, 2H), 4.39 (q, 2H, J = 7 Hz), 4.46 (q, 2H, J = 7 Hz), 7.76 (s, 1H), 7.86 (s, 1H).

Anal. Calcd. for $C_{17}H_{26}N_2O_6$: C, 57.61; H, 7.40; N, 7.91. Found: C, 57.59; H, 7.38; N, 7.99.

1,4-Dicarbethoxy-2-(2-methylthioethyl)-3-acetamidopyrrole (**6d**).

This compound was obtained from **5d** in 78% yield as a viscous oil; ir (chloroform): 3401, 1754, 1692 cm^{-1}; uv (95% ethanol): 214.5 nm (ϵ = 29,750); pmr (deuteriochloroform): δ 1.34 (t, 3H, J = 7 Hz), 1.45 (t, 3H, J = 7 Hz), 2.18 (s, 3H), 2.62 (s, 3H), 3.22 (m, 4H), 4.30 (q, 2H, J = 7 Hz), 4.49 (q, 2H, J = 7 Hz), 7.86 (s, 1H), 8.20 (s, 1H).

1,4-Dicarbethoxy-2-benzyl-3-acetamidopyrrole (**6e**).

This compound was prepared from **5e** in 64% yield as a crystalline solid, m.p. 111-112° after recrystallization from diethyl ether; ir (chloroform): 3436, 1757, 1695 cm^{-1}; uv (95% ethanol): 212 nm (ϵ = 37,860); pmr (deuteriochloroform): δ 1.22 (t, 3H, J = 7 Hz), 1.35 (t, 3H, J = 7 Hz), 2.12 (s, 3H), 4.30 (q, 2H, J = 7 Hz), 4.33 (q, 2H, J = 7 Hz), 4.33 (s, 2H), 7.17 (m, 5H), 7.70 (s, 1H), 7.86 (s, 1H).

Anal. Calcd. for $C_{19}H_{22}N_2O_3$: C, 63.68; H, 6.19; N, 7.82. Found: C, 63.74; H, 6.27; N, 7.85.

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