

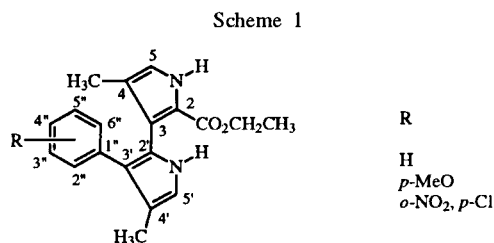
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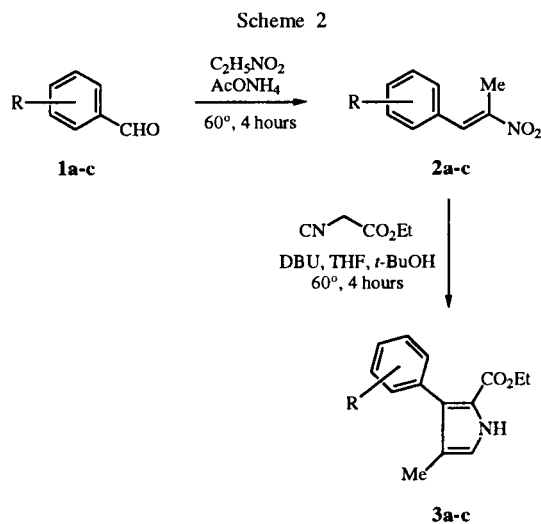
Several ethyl 3-[(3-aryl-4-methyl)-2(1*H*)-pyrrolyl]-4-methyl-1*H*-pyrrole-2-carboxylates have been synthesized using two successive ethyl isocyanide addition-cyclizations to the appropriate nitropropene derivatives.

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As a result of our long-standing interest in the chemical properties of alkyl isocyanides, we have recently described several phenylpyrrolylpyrroles [1]. Subsequently, the synthesis of a series of ethyl 3-[(3-aryl-4-methyl)-2(1*H*)-pyrrolyl]-4-methyl-1*H*-pyrrole-2-carboxylates was accomplished by two successive ethyl isocyanide condensations with the appropriate nitropropene intermediates.

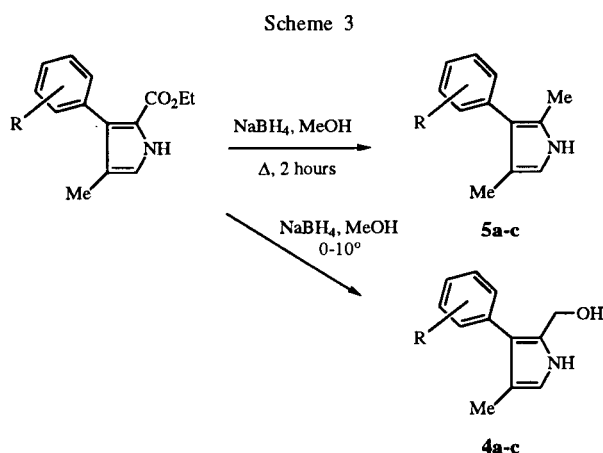


A base-catalyzed condensation of nitroethane to the corresponding benzaldehydes affords the first nitropropene derivatives **2a-c** [2]. These react with one equivalent of ethyl isocyanide previously anionized with one equivalent of DBU in a mixture of tetrahydrofuran and *tert*-butyl alcohol. After four hours of heating (60°), the 3-phenylpyrrole-2-carboxylates **3a-c** are isolated in good yield [3].

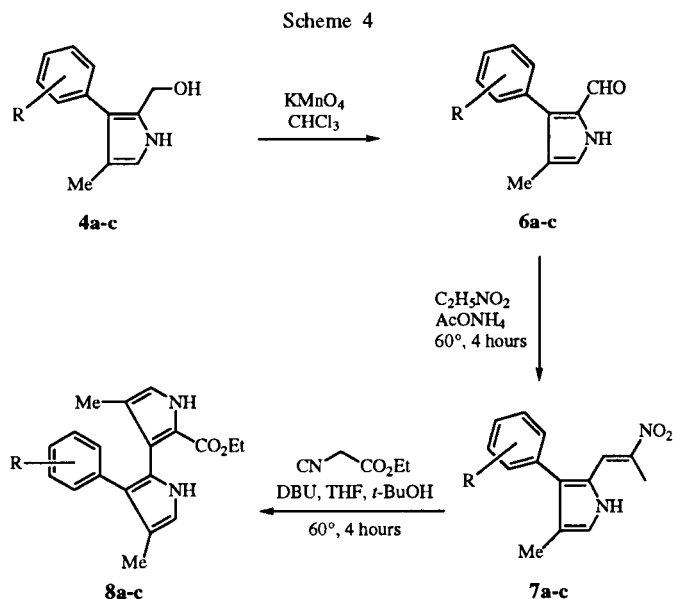


The pyrrole ester groups were subsequently modified to give alcohol derivatives. Attempts to prepare **4a-c** by

heating the esters with sodium borohydride in methanol failed and led to the synthesis of 3-aryl-2,4-dimethyl-1*H*-pyrroles **5a-c**. The desired alcohols are in fact obtained when using a cooled reaction mixture (<10°).



Oxidation of **4a-c** with manganese dioxide provides **6a-c** which reacts with nitroethane using the standard and the described above conditions to afford the second nitropropene



intermediates **7a-c**. The title compounds **8a-c** are finally prepared through a similar cycloaddition of ethyl isocyanide, as previously described.

EXPERIMENTAL

General Methods.

Infrared Spectra were recorded on a Philips PU 9716 apparatus and only noteworthy absorptions (reciprocal centimeters) are listed. The nmr spectra were recorded on a Jeol Lambda 400 using TMS as an internal standard. Chemical shifts are reported in ppm downfield (δ) from TMS.

(E)-1-Aryl-2-nitroprop-1-enes **2a-c**. General Procedure.

To a suspension of ammonium acetate (2.5 equivalents) in nitroethane (50 ml) was added a solution of the appropriate benzaldehyde readily soluble in nitroethane (100 ml). The mixture was heated for 4 hours at 60° after which the solvent was evaporated. The oily residue was washed with water and taken up in diethyl ether. The organics were dried over magnesium sulfate then removed under reduced pressure to give analytically pure **2a-c**.

(E)-1-phenyl-2-nitroprop-1-enes (**2a**).

This compound was obtained as an oil (88%); ¹H nmr (DMSO-d₆): δ 8.39 (s, 1H, CH), 7.29-7.55 (m, 5H, phenyl protons), 2.43 (s, 3H, Me).

Anal. Calcd. for C₉H₉NO₂: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.18; H, 5.57; N, 8.59.

(E)-1-(4-methoxyphenyl)-2-nitroprop-1-ene (**2b**).

This compound was obtained as an oil (76%); ¹H nmr (deuteriochloroform): δ 7.94 (s, 1H, CH), 6.83-7.32 (m, 4H, phenyl protons), 3.79 (s, 3H, OMe), 2.45 (s, 3H, Me).

Anal. Calcd. for C₁₀H₁₁NO₃: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.10; H, 5.73; N, 7.26.

(E)-1-(4-Chloro-2-nitrophenyl)-2-nitroprop-1-ene (**2c**).

This compound was obtained as an oil (84%); ¹H nmr (deuteriochloroform): δ 7.96 (s, 1H, CH), 7.32-7.63 (m, 3H, phenyl protons), 2.46 (s, 3H, Me).

Anal. Calcd. for C₉H₇N₂O₄Cl: C, 44.57; H, 2.88; N, 11.54. Found: C, 44.32; H, 2.76; N, 11.69.

Ethyl 3-Aryl-4-methyl-1H-pyrrole-2-carboxylates **3a-c**. General Procedure.

To a solution of the appropriate nitrovinyl derivatives **2a-c** in tetrahydrofuran (50 ml) and *tert*-butyl alcohol were added DBU (1.1 equivalents) and ethyl isocyanide (1 equivalent). The mixture was stirred for 20 minutes at room temperature then heated for 4 hours at 60°. Concentration of the solvents gave an oil which was washed with water then taken up in diethyl ether. The organic layer was dried over magnesium sulfate and removed under reduced pressure.

Ethyl 4-Methyl-3-phenyl-1H-pyrrole-2-carboxylate (**3a**).

This compound was obtained as an oil (78%); ir (potassium bromide): ν 3300 (NH), 1680 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.82 (s, 1H, NH), 7.20-7.35 (m, 5H, phenyl protons), 6.65 (s, 1H, H₅), 4.13 (m, 2H, OCH₂ ester), 1.98 (s, 3H, Me), 1.13 (m, 3H, CH₃ ester); ¹³C nmr (deuteriochloroform): δ

158.7 (CO), 135.4 (C₁ⁿ), 134.2 (C₃), 127.4 (C₃ⁿ and C₅ⁿ), 126.6 (C₄ⁿ), 125.8 (C₂ⁿ and C₆ⁿ), 121.4 (C₂), 119.1 (C₄), 117.9 (C₅), 58.8 (OCH₂ ester), 15.2 (CH₃ ester), 12.6 (CH₃).

Anal. Calcd. for C₁₄H₁₅NO₂: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.28; H, 6.58; N, 6.10.

Ethyl 4-Methyl-3-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (**3b**).

This compound was obtained as an oil (81%); ir (potassium bromide): ν 3400 (NH), 1680 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.80 (s, 1H, NH), 6.83-7.20 (m, 4H, phenyl protons), 6.68 (s, 1H, H₅), 4.14 (m, 2H, OCH₂ ester), 3.80 (s, 3H, OMe), 1.99 (s, 3H, Me), 1.17 (m, 3H, CH₃ ester); ¹³C nmr (deuteriochloroform): δ 159.8 (C₄ⁿ), 158.0 (CO), 133.4 (C₃), 128.4 (C₁ⁿ), 125.1 (C₂ⁿ and C₆ⁿ), 123.9 (C₅), 120.4 (C₂), 118.1 (C₄), 112.1 (C₃ⁿ and C₅ⁿ), 58.1 (OCH₂ ester), 54.2 (OCH₃), 13.9 (CH₃ ester), 11.8 (CH₃).

Anal. Calcd. for C₁₅H₁₇NO₃: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.41; H, 6.60; N, 5.41.

Ethyl 4-Methyl-3-(4-chloro-2-nitrophenyl)-1H-pyrrole-2-carboxylate (**3c**).

This compound was obtained as an oil (67%); ir (potassium bromide): ν 3300 (NH), 1690 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.82 (s, 1H, NH), 7.30-7.63 (m, 3H, phenyl protons), 6.70 (s, 1H, H₅), 4.15 (m, 2H, OCH₂ ester), 1.98 (s, 3H, Me), 1.16 (m, 3H, CH₃ ester); ¹³C nmr (deuteriochloroform): δ 157.1 (CO), 148.3 (C₂ⁿ), 135.2 (C₃), 134.9 (C₅ⁿ), 133.6 (C₄ⁿ), 130.0 (C₁ⁿ), 127.6 (C₆ⁿ), 125.1 (C₃ⁿ), 122.2 (C₅), 117.8 (C₂), 116.2 (C₄), 59.2 (OCH₂ ester), 14.1 (CH₃ ester), 11.4 (CH₃).

Anal. Calcd. for C₁₄H₁₃N₂O₂Cl: C, 60.77; H, 4.74; N, 10.12. Found: C, 60.67; H, 4.74; N, 10.11.

3-Aryl-2,4-dimethyl-1H-pyrroles **4a-c**. General Procedure.

To a solution of the appropriate pyrrole-2-carboxylate in methanol was added sodium borohydride (1.1 equivalents). The mixture was stirred at room temperature then refluxed 1 hour. Water was slowly added and the reaction mixture was evaporated to dryness under reduced pressure. The residue was taken up with diethyl ether, dried over magnesium sulfate and evaporated to give **4a-c**.

2,4-Dimethyl-3-phenyl-1H-pyrrole (**4a**).

This compound was obtained as an oil (51%); ir (potassium bromide): ν 3200 (NH) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.78 (s, 1H, NH), 7.25-7.38 (m, 5H, phenyl protons), 6.63 (s, 1H, H₅), 2.26 (s, 3H, C₄-CH₃), 2.09 (s, 3H, C₂-CH₃); ¹³C nmr (deuteriochloroform): δ 137.2 (C₁ⁿ), 129.1 (C₃), 128.6 (C₃ⁿ and C₅ⁿ), 127.4 (C₂), 126.9 (C₄ⁿ), 124.9 (C₂ⁿ and C₆ⁿ), 118.2 (C₅), 115.5 (C₄), 12.2 (C₄-CH₃), 11.6 (C₂-CH₃); ms: (m/z, %) 171 (M⁺, 100), 91 (78), 77 (45).

Anal. Calcd. for C₁₂H₁₃N: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.08; H, 7.64; N, 8.19.

2,4-Dimethyl-3-(4-methoxyphenyl)-1H-pyrrole (**4b**).

This compound was obtained as an oil (43%); ir (potassium bromide): ν 3300 (NH) cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.79 (s, 1H, NH), 6.87-7.16 (m, 4H, phenyl protons), 6.13 (s, 1H, H₅), 3.82 (s, 3H, OMe), 2.23 (s, 3H, C₄-CH₃), 2.05 (s, 3H, C₂-CH₃); ¹³C nmr (deuteriochloroform): δ 160.9 (C₄ⁿ), 129.7 (C₁ⁿ), 128.2 (C₃), 127.5 (C₂), 126.4 (C₂ⁿ and C₆ⁿ), 115.2 (C₅), 113.1 (C₄), 111.4 (C₃ⁿ and C₅ⁿ), 54 (OCH₃), 12.1 (C₄-CH₃), 11.7 (C₂-CH₃); ms: (m/z, %) 201 (M⁺, 93), 121 (62), 107 (58).

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.46; H, 7.50; N, 6.95.

2,4-Dimethyl-3-(4-chloro-2-nitrophenyl)-1H-pyrrole (4c).

This compound was obtained as an oil (51%); ir (potassium bromide): ν 3200 (NH) cm^{-1} ; 1H nmr (deuteriochloroform): δ 8.79 (s, 1H, NH), 7.27-7.41 (m, 3H, phenyl protons), 6.59 (s, 1H, H₅), 2.28 (s, 3H, C₄-CH₃), 2.11 (s, 3H, C₂-CH₃); ^{13}C nmr (deuteriochloroform): δ 147.3 (C_{2'}), 134.1 (C_{5'}), 133.7 (C_{4'}), 131.2 (C_{1'}), 128.7 (C_{3'}), 128.6 (C_{6'}), 125.8 (C₂), 122.9 (C_{3'}), 116.1 (C_{5'}), 114.2 (C_{4'}), 11.9 (C₄-CH₃), 10.8 (C₂-CH₃); ms: (*m/z*, %) 171 (M⁺, 100), 91 (78), 77 (45).

Anal. Calcd. for $C_{12}H_{11}NO_2Cl$: C, 60.90; H, 4.68; N, 5.92. Found: C, 60.79; H, 4.68; N, 5.91.

3-Aryl-2-hydroxymethyl-4-methyl-1H-pyrroles 5a-c. General Procedure.

To a cooled solution (<10°C, ice bath) of the appropriate pyrrole-2-carboxylate in methanol was added 1.1 equivalents of sodium borohydride. The reaction mixture was stirred 1 hour at this temperature and water was slowly added. The solvent was removed under reduced pressure and the residue taken up with diethyl ether, dried over magnesium sulfate and evaporated to dryness to give 5a-c as yellow oils.

2-Hydroxymethyl-4-methyl-3-phenyl-1H-pyrrole (5a).

This compound was obtained as an oil (60%); ir (potassium bromide): ν 3500 (OH), 3200 (NH) cm^{-1} ; 1H nmr (deuteriochloroform): δ 8.34 (s, 1H, NH), 7.04 (s, 1H, H₅), 6.60-6.93 (m, 5H, phenyl protons), 4.68 (s, 1H, OH), 4.47 (m, 2H, CH₂), 2.01 (s, 3H, Me); ^{13}C nmr (deuteriochloroform): δ 136.4 (C_{1'}), 130.3 (C_{2'}), 127.9 (C_{4'}), 127.6 (C_{3'} and C_{5'}), 126.1 (C_{3'}), 125.7 (C_{2'} and C_{6'}), 115.3 (C_{5'}), 112.4 (C_{4'}), 58.6 (CH₂), 12.7 (CH₃).

Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.86; H, 6.99; N, 7.47.

2-Hydroxymethyl-3-(4-methoxyphenyl)-4-methyl-1H-pyrrole (5b).

This compound was obtained as an oil (64%); ir (potassium bromide): ν 3400 (OH), 3200 (NH) cm^{-1} ; 1H nmr (deuteriochloroform): δ 7.80 (s, 1H, NH), 7.12 (s, 1H, H₅), 6.73-6.87 (m, 4H, phenyl protons), 4.67 (s, 1H, OH), 4.41 (m, 2H, CH₂), 3.85 (s, 3H, OMe), 1.98 (s, 3H, Me); ^{13}C nmr (deuteriochloroform): δ 158.2 (C_{4'}), 129.3 (C_{2'}), 128.7 (C_{1'}), 127.1 (C_{2'} and C_{6'}), 125.8 (C_{3'}), 115.2 (C_{3'} and C_{5'}), 114.6 (C_{5'}), 111.9 (C_{4'}), 60.1 (CH₂), 54.0 (OCH₃), 10.9 (Me).

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.81; H, 6.95; N, 6.45.

3-(4-Chloro-2-nitrophenyl)-2-hydroxymethyl-4-methyl-1H-pyrrole (5c).

This compound was obtained as an oil (48%); ir (potassium bromide): ν 3500 (OH), 3300 (NH) cm^{-1} ; 1H nmr (deuteriochloroform): δ 8.61 (s, 1H, NH), 7.31-7.44 (m, 4H, phenyl protons and H₅), 4.71 (s, 1H, OH), 4.37 (m, 2H, CH₂), 2.19 (s, 3H, Me); ^{13}C nmr (deuteriochloroform): δ 145.7 (C_{2'}), 135.9 (C_{5'}), 132.9 (C_{6'}), 131.8 (C_{4'}), 129.2 (C_{1'}), 128.1 (C_{2'}), 124.8 (C_{3'}), 121.9 (C_{3'}), 116.5 (C_{5'}), 115.2 (C_{4'}), 58.5 (CH₂), 12.4 (Me).

Anal. Calcd. for $C_{12}H_{11}N_2O_2Cl$: C, 57.50; H, 4.42; N, 11.17. Found: C, 57.46; H, 4.41; N, 11.18.

3-Aryl-4-methyl-1H-pyrrole-2-carboxaldehydes 6a-c. General Procedure.

To a solution of the appropriate 3-aryl-2-hydroxymethyl-4-methyl-1H-pyrrole in chloroform was added manganese dioxide in excess (3 equivalents). The reaction mixture was refluxed for 2 hours and, after cooling down to room temperature, filtrated. The organic layer was washed with water, dried over calcium chloride and evaporated under reduced pressure to give 6a-c as red oils.

4-Methyl-3-phenyl-1H-pyrrole-2-carboxaldehyde (6a).

This compound was obtained as an oil (78%); ir (potassium bromide): ν 3200 (NH), 1650 (CO) cm^{-1} ; 1H nmr (deuteriochloroform): δ 9.93 (s, 1H, CHO), 8.30 (s, 1H, NH), 7.54 (s, 1H, H₅), 7.01-7.34 (m, 5H, phenyl protons), 2.51 (s, 3H, Me); ^{13}C nmr (deuteriochloroform): δ 178.3 (CHO), 139.8 (C_{3'}), 137.2 (C_{1'}), 130.3 (C_{2'}), 127.6 (C_{4'}), 126.4 (C_{2'} and C_{6'}), 126.0 (C_{3'} and C_{5'}), 123.3 (C_{4'}), 118.2 (C_{5'}), 11.8 (CH₃).

Anal. Calcd. for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.78; H, 5.98; N, 7.55.

3-(4-Methoxyphenyl)-4-methyl-1H-pyrrole-2-carboxaldehyde (6b).

This compound was obtained as an oil (72%); ir (potassium bromide): ν 3200 (NH), 1670 (CO) cm^{-1} ; 1H nmr (deuteriochloroform): δ 9.88 (s, 1H, CHO), 8.01 (s, 1H, NH), 7.40 (s, 1H, H₅), 6.91-6.97 (m, 4H, phenyl protons), 3.91 (s, 3H, OMe), 2.34 (s, 3H, Me); ^{13}C nmr (deuteriochloroform): δ 178.4 (CHO), 160.0 (C_{4'}), 138.9 (C_{3'}), 130.7 (C_{2'}), 128.2 (C_{1'}), 127.5 (C_{5'}), 126.4 (C_{2'} and C_{6'}), 117.3 (C_{4'}), 113.1 (C_{3'} and C_{5'}), 55.2 (OCH₃), 11.1 (Me).

Anal. Calcd. for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.27; H, 6.56; N, 7.01.

3-(4-Chloro-2-nitrophenyl)-4-methyl-1H-pyrrole-2-carboxaldehyde (6c).

This compound was obtained as an oil (68%); ir (potassium bromide): ν 3300 (NH), 1670 (CO) cm^{-1} ; 1H nmr (deuteriochloroform): δ 9.95 (s, 1H, CHO), 8.64 (s, 1H, NH), 7.48 (s, 1H, H₅), 7.39-7.45 (m, 3H, phenyl protons), 2.48 (s, 3H, Me); ^{13}C nmr (deuteriochloroform): δ 179.1 (CHO), 146.4 (C_{2'}), 139.2 (C_{3'}), 134.3 (C_{5'}), 132.9 (C_{4'}), 129.1 (C_{2'}), 128.6 (C_{1'}), 126.7 (C_{6'}), 124.7 (C_{5'}), 121.7 (C_{3'}), 117.1 (C_{4'}), 11.7 (Me).

Anal. Calcd. for $C_{12}H_9N_2O_3Cl$: C, 54.46; H, 3.43; N, 10.58. Found: C, 54.32; H, 3.44; N, 10.56.

(E)-1-[(3-Aryl-4-methyl-1H-pyrrolyl)-2-nitroprop-1-enes 7a-c. General Procedure.

To a suspension of ammonium acetate (2.5 equivalents) in nitroethane (50 ml) was added a solution of the appropriate pyrrole-2-carboxaldehyde readily soluble in nitroethane (100 ml). The mixture is heated for 4 hours at 60° after which the solvent was evaporated. The oily residue was washed with water and taken up in diethyl ether. The organics are dried over magnesium sulfate then removed under reduced pressure to give analytically pure 7a-c.

(E)-1-(4-Methyl-3-phenyl-1H-pyrrol-2-yl)-2-nitroprop-1-ene (7a).

This compound was obtained as an oil (67%); ir (potassium bromide): ν 3200 (NH) cm^{-1} ; 1H nmr (deuteriochloroform): δ 8.31 (s, 1H, NH), 7.84 (s, 1H, CH), 6.85-7.32 (m, 5H, phenyl protons), 6.79 (s, 1H, H₅), 2.44 (s, 3H, Me), 2.23 (s, 3H, C₄-CH₃); ^{13}C nmr (deuteriochloroform): δ 143.1 (C-NO₂), 135.8 (C_{1'}), 127.8 (CH), 127.4 (C_{3'} and C_{5'}), 127.0 (C_{3'}), 126.5

(C₄⁺), 124.4 (C₂⁻ and C₆⁺), 116.7 (C₂⁻), 116.1 (C₄⁻), 115.6 (C₅⁻), 13.1 (C₄⁻-CH₃), 12.7 (CH₃).

Anal. Calcd. for C₁₅H₁₆N₂O₂: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.28; H, 5.81; N, 11.54.

(E)-1-[4-Methyl-3-(4-methoxyphenyl)-1H-pyrrol-2-yl]-2-nitroprop-1-ene (7b).

This compound was obtained as an oil (70%); *ir* (potassium bromide): ν 3200 (NH) cm⁻¹; ¹H nmr (deuteriochloroform): δ 7.92 (s, 1H, NH), 7.60 (s, 1H, CH), 7.32-7.44 (m, 4H, phenyl protons), 6.81 (s, 1H, H₅), 3.79 (s, 3H, OMe), 2.51 (s, 3H, Me), 2.36 (s, 3H, C₄⁻-CH₃); ¹³C nmr (deuteriochloroform): δ 160.3 (C₄⁺), 144.3 (C-NO₂), 129.1 (C₁⁺), 128.1 (C₂⁻ and C₆⁺), 127.9 (CH), 126.4 (C₃⁻), 118.2 (C₅⁻), 115.1 (C₄⁻), 114.6 (C₂⁻), 112.1 (C₃⁻ and C₅⁻), 54.2 (OCH₃), 12.9 (C₄⁻-CH₃), 12.6 (CH₃).

Anal. Calcd. for C₁₅H₁₆N₂O₃: C, 66.16; H, 5.92; N, 10.29. Found: C, 66.01; H, 5.93; N, 10.28.

(E)-1-[4-Methyl-3-(4-chloro-2-nitrophenyl)-1H-pyrrol-2-yl]-2-nitroprop-1-ene (7c).

This compound was obtained as an oil (69%); *ir* (potassium bromide): ν 3300 (NH) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.58 (s, 1H, NH), 7.71 (s, 1H, CH), 6.84-7.41 (m, 3H, phenyl protons), 6.76 (s, 1H, H₅), 2.52 (s, 3H, Me), 2.37 (s, 3H, C₄⁻-CH₃); ¹³C nmr (deuteriochloroform): δ 146.8 (C₂⁻), 145.2 (C-NO₂), 135.3 (C₅⁻), 134.6 (C₄⁺), 130.5 (C₁⁺), 128.6 (CH), 128.4 (C₆⁺), 126.7 (C₃⁻), 124.2 (C₃⁻), 118.1 (C₅⁻), 115.1 (C₄⁻), 114.8 (C₂⁻), 12.7 (C₄⁻-CH₃), 12.3 (CH₃).

Anal. Calcd. for C₁₄H₁₂N₃O₄Cl: C, 52.27; H, 3.76; N, 13.06. Found: C, 52.18; H, 3.76; N, 13.03.

Ethyl 4-Methyl-3-[2-(3-aryl-4-methyl)-1H-pyrrolyl]-1H-pyrrole-2-carboxylates 8a-c. General Procedure.

To a solution of the appropriate nitrovinyl pyrrole derivatives 7a-c in tetrahydrofuran (50 ml) and *tert*-butyl alcohol were added DBU (1.1 equivalents) and ethyl isocyanide (1 equivalent). The mixture was stirred for 20 minutes at room temperature then heated for 4 hours at 60°. Concentration of the solvents gave an oil which was washed with water then taken up in diethyl ether. The organic layer was passed through a silica gel pad and removed *in vacuo*.

Ethyl 4-Methyl-3-[2-(4-methyl-3-phenyl)-1H-pyrrolyl]-1H-pyrrole-2-carboxylate (8a).

This compound was obtained as an oil (62%); *ir* (potassium bromide): ν 3200-3400 (2 x NH), 1690 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.78 (s, 1H, NH), 8.28 (s, 1H, NH), 6.93-7.21 (m, 5H, phenyl protons), 7.01 (s, 1H, H₅), 6.76 (s, 1H, H₅), 4.21 (m, 2H, OCH₂ ester), 2.31 (s, 3H, C₄⁻-CH₃), 2.23 (s, 3H, C₄⁻-CH₃), 1.15 (m, 3H, CH₃ ester); ¹³C nmr (deuteriochloroform): δ 158.2 (CO), 136.7 (C₁⁺), 126.9 (C₃⁻ and C₅⁻), 127.2 (C₃⁻), 126.6 (C₄⁺), 125.3 (C₂⁻ and C₆⁺), 121.8 (C₅⁻), 119.7

(C₂⁻), 117.2 (C₄⁻), 116.5 (C₃⁻), 115.1 (C₂⁻), 114.5 (C₄⁻), 116.7 (C₅⁻), 56.2 (OCH₂ ester), 13.4 (CH₃ ester), 12.1 (C₄⁻-CH₃), 11.6 (C₄⁻-CH₃).

Anal. Calcd. for C₁₉H₂₀N₂O₂: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.88; H, 6.52; N, 9.07.

Ethyl 4-Methyl-3-[2-(3-(4-methoxyphenyl)-4-methyl-1H-pyrrolyl)-1H-pyrrole-2-carboxylate (8b).

This compound was obtained as an oil (70%); *ir* (potassium bromide): ν 3300-3500 (NH), 1680 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.56 (s, 1H, NH), 8.09 (s, 1H, NH), 6.78-7.23 (m, 4H, phenyl protons), 6.95 (s, 1H, H₅), 6.72 (s, 1H, H₅), 4.17 (s, 3H, OCH₂ ester), 3.78 (s, 3H, OMe), 2.34 (s, 3H, C₄⁻-CH₃), 2.28 (s, 3H, C₄⁻-CH₃), 1.18 (s, 3H, CH₃ ester); ¹³C nmr (deuteriochloroform): δ 159.4 (C₄⁺), 158.8 (CO), 128.3 (C₁⁺), 126.7 (C₂⁻ and C₆⁺), 126.6 (C₃⁻), 122.1 (C₅⁻), 119.6 (C₂⁻), 118.8 (C₄⁻), 118.1 (C₃⁻), 115.8 (C₅⁻), 113.7 (C₄⁻), 112.8 (C₂⁻), 112.0 (C₃⁻ and C₅⁻), 58.1 (OCH₂ ester), 54.5 (OCH₃), 13.1 (C₄⁻-CH₃), 13.6 (C₄⁻-CH₃), 15.2 (CH₃ ester).

Anal. Calcd. for C₂₀H₂₂N₂O₃: C, 70.99; H, 6.55; N, 8.28. Found: C, 70.81; H, 6.56; N, 8.28.

Ethyl 4-Methyl-3-[2-(3-(4-chloro-2-nitrophenyl)-4-methyl-1H-pyrrolyl)-1H-pyrrole-2-carboxylate (8c).

This compound was obtained as an oil (48%); *ir* (potassium bromide): ν 3200-3400 (NH), 1680 (CO) cm⁻¹; ¹H nmr (deuteriochloroform): δ 8.69 (s, 1H, NH), 8.58 (s, 1H, NH), 7.28-7.37 (m, 3H, phenyl protons), 7.09 (s, 1H, H₅), 6.72 (s, 1H, H₅), 4.21 (s, 3H, OCH₂ ester), 2.35 (s, 3H, C₄⁻-CH₃), 2.31 (s, 3H, C₄⁻-CH₃), 1.22 (s, 3H, CH₃ ester); ¹³C nmr (deuteriochloroform): δ 157.8 (CO), 147.1 (C₂⁻), 134.4 (C₅⁻), 131.7 (C₄⁺), 128.6 (C₁⁺), 128.3 (C₆⁺), 127.1 (C₃⁻), 123.9 (C₃⁻), 122.8 (C₅⁻), 120.9 (C₂⁻), 119.2 (C₄⁻), 118.6 (C₃⁻), 117.4 (C₅⁻), 115.0 (C₄⁻), 114.8 (C₂⁻), 58.7 (OCH₂ ester), 12.4 (C₄⁻-CH₃), 12.8 (C₄⁻-CH₃), 13.3 (CH₃ ester).

Anal. Calcd. for C₁₉H₁₈N₃O₄Cl: C, 58.84; H, 4.68; N, 10.83. Found: C, 58.78; H, 4.66; N, 10.81.

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