

SYNTHESIS OF PYRROLOQUINOLINE AND PYRROLO-NAPHTHYRIDINE BY AN INTRAMOLECULAR CYCLISATION REACTION

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Abstract- 4-methylthiopyrrolo[1,2-*a*][1,8]naphthyridine and pyrrolo[1,2-*a*]quinoline were prepared by an intramolecular cyclisation in acidic media of 1-methylsulfinyl-1-methylthio-2-[3-(2-(1-pyrrolyl)pyridin or phenyl)]ethylene.

Tricyclic heteroaromatic compounds with a bridgehead nitrogen atom have been widely studied for their biological activities.¹ In this way, M. Robba *et al.*² have recently reported the synthesis of 4-acetoxypyrrolo[1,2-*a*]quinoline by a five step synthesis from 2-aminobenzoic acid. In continuation of our studies on tricyclic nitrogen bridgehead heterocycles³ we were interested in the synthesis of the 9-aza isoster from 2-aminonicotinic acid.

Thus 2-aminonicotinic acid failed to react with 2,5-dimethoxytetrahydrofuran (DTF) according to the Clauson-Kass reaction⁴ in dioxane or in acetic acid. So 2-aminonicotinic acid was esterified by general procedure to give ethyl 2-aminonicotinate (**1**) in 78% yield. In presence of 4-chloropyridinium hydrochloride, in refluxing dioxane, the ester (**1**) reacted with DTF to give the pyrrolyl derivative (**2**) in 86% yield. Proof of the structure was obtained from mass spectral data with a *m/z* at 216 (40%) and by ¹H-nmr with a triplet at δ : 6.30 for H-3',4'. The ester was saponified with potassium hydroxide to give the expected acid (**3**) in 90% yield. The treatment of **3** with phosphorus pentachloride in benzene gave the acid chloride (**4**) which was too unstable to be isolated.

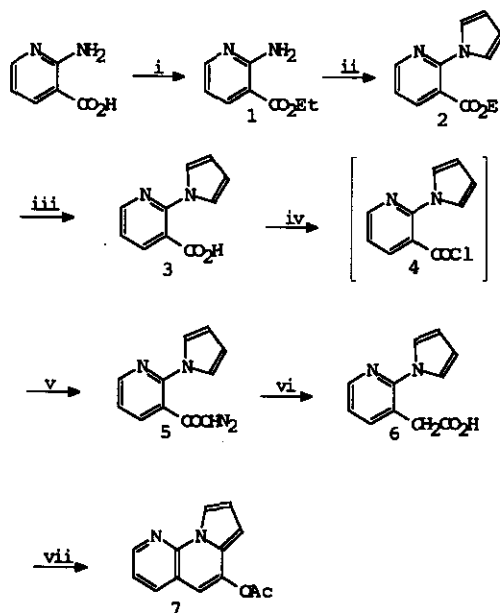
Arndt-Eistert reaction of **4** with diazomethane in dry ether led to the diazoketone (**5**). The structure was

ascertained by ^1H nmr with a singlet at δ : 5.08 for the CHN_2 group and a strong absorption at 2110 cm^{-1} for the $\text{N}=\text{N}$ function in the ir spectrum.

The Wolff rearrangement of **5** in presence of silver oxide, sodium carbonate and sodium thiosulfate led to the expected acetic acid derivative (**6**) in only 5% yield. The reaction in methanol in presence of silver benzoate as catalyst did not improve the yield. These results are in good agreement with the fact that the Wolff rearrangement of the diazoketone prepared from pyridinecarboxylic acid has been reported to be unsuccessful.⁵

The acid (**6**) was then cyclized in refluxing acetic anhydride in good yield. Proof of the structure of **7** was given by mass spectral data with a m/z at 226 with a loss of a CH_2CO moiety to give a fragment at m/z 184. The ^1H -nmr spectrum showed an AMX system for the pyridinic ring, a singlet at δ : 6.85 for H-5, three pyrrolic hydrogen absorptions and the methyl of the acetoxy group at δ 2.43.

Scheme 1

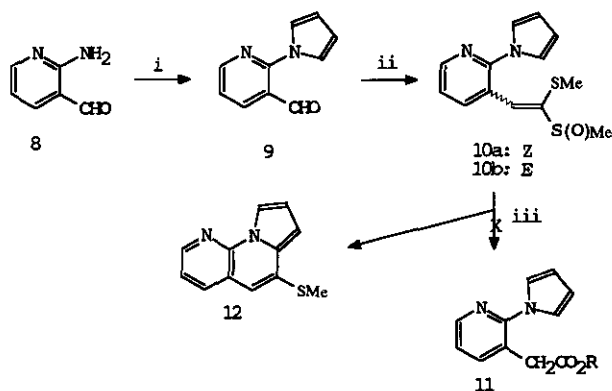


Reagents and conditions: i: SOCl_2 , EtOH ; ii: DTF, 4-chloropyridine hydrochloride, dioxane; iii: KOH , water; iv: PCl_5 , benzene; v: CH_2N_2 , Et_2O ; vi: Ag_2O , Na_2CO_3 , dioxane; vii: Ac_2O , reflux.

In order to improve the poor overall yield of this pyrrolo[1,2-*a*][1,8]naphthyridine, another procedure for one carbon homologation was investigated. A convenient method for ethyl phenylacetate synthesis from benzaldehyde has been reported in a two step procedure.⁶ Thus 2-aminonicotinaldehyde (**8**) reacted with DTF to give 2-(1-pyrrolyl)nicotinaldehyde (**9**) in 66% yield. The Knoevenagel-type condensation of **9** with methyl methylthiomethyl sulfoxide in presence of Triton-B solution afforded a mixture of (*Z*)- and (*E*)-1-methylsulfinyl-1-methylthio-2-[(2-(1-pyrrolyl)pyridin)-3-yl]ethylene (**10a,b**) in 4 and 60% yield respectively. The diastereoisomer (**10a**) was specifically obtained using an excess of reagent. Proof of the structure was obtained by mass spectral data (EI) with a base peak at m/z 215 ($M^+ - SOCH_3$), while in FAB⁺ in a thioglycerol matrix the mass peak appeared at m/z 279 ($M+1$). The ¹H nmr spectra at 400 MHz showed a singlet at δ : 6.46 for the olefinic hydrogen of the *Z* isomer and at 7.66 for the *E* derivative. These values are in good agreement with the data reported by Ogura and Coll.⁶

Dry hydrochloric acid treatment of **10b** in anhydrous ethanol did not lead to the expected ethyl acetate derivative (**11**) but to 4-methylthiopyrrolo[1,2-*a*][1,8]naphthyridine (**12**) in 71% yield as evidence by mass spectral data analysis showing a m/z : 214 (100%). The ¹H nmr spectrum at 400 MHz showed a SCH₃ absorption at δ : 2.61, a singlet at 6.64 ppm for H-5, an AMX pyridinic system and three pyrrolic hydrogens. The ¹³C-nmr spectrum showed a CH₃ absorption at δ : 14.3, 7 CH and 4 quaternary carbons. The complete tertiary carbon determination was carried out by a ¹H-¹³C XHCOR experiment.

Scheme 2



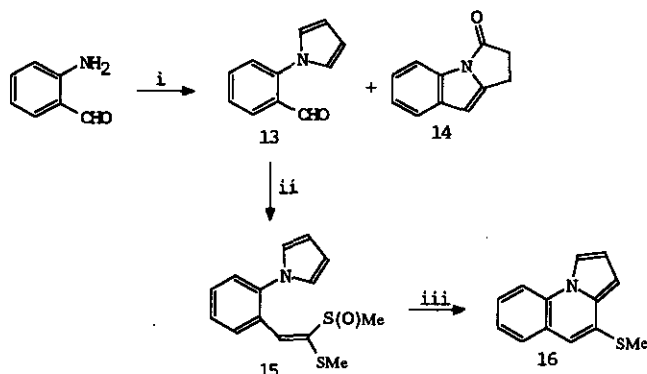
Reagents and conditions: i, DTF, 4-chloropyridine hydrochloride, dioxane; ii, MeS(O)CH₂SMe, Triton-B, THF; iii, HCl, EtOH.

From these results we were interested in studying the generality of this cyclisation process. Thus 2-aminobenzaldehyde using the described procedure, led to the pyrrolyl derivative (**13**) in only poor yield.⁷ The major product was determined to be 1,2-dihydro 1*H*-pyrrolo[1,2-*a*]indol-3-one (**14**).⁸ Structural determination was realized by mass spectrometry with a *m/z*: 171, and confirmed by ¹H and ¹³C-nmr using ¹H-¹H COSY, XHCOR and LRHETCOR experiments.

The aldehyde (**13**) gave the ethylene derivative (**15**) in 50% yield. In an excess of reagents only the *Z* isomer could be isolated. The proof of the structure was derived from ¹H nmr analysis showing an olefinic hydrogen at δ 6.30 and the disappearance of the aldehydic hydrogen absorption.

The acidic ring closure gave the expected tricyclic derivative (**16**) in 97% yield. The structural determination was obtained from mass spectral data with a *m/z* at 213 (27%) and by nmr studies. The ¹H nmr spectra showed both benzene and a pyrrolic systems and a singlet for H-5. The ¹³C nmr spectrum showed a methyl group at δ 14.51, and 8 CH absorptions. The ¹H-¹³C HETCOR led to the attribution of the tertiary carbons.

Scheme 3



Reagents and conditions: i, DTF, 4-chloropyridine hydrochloride, dioxane; ii, MeS(O)CH₂SMe, Triton-B, THF; iii, HCl, EtOH.

EXPERIMENTAL

General. Mp were determined with a Buchi melting point apparatus and are uncorrected. ir spectra were measured on a Beckman Acculab II. Mass spectra were measured with a LKB 2091 mass spectrometer (EI) or JEOL DX300 (FAB⁺). ¹H-Nmr spectra were recorded on a Varian EM 60A, Brüker AC 250 or Brüker AM 400 WB using tetramethylsilane as internal standard. ¹³C-Nmr were recorded on a Brüker AM 400 WB

operating at 100 MHz. *J*-values are given in Hz. Elemental analysis was performed by Microanalytical Center, ENSCM, Montpellier. Solvents were dried and distilled before to use using standard methods. Tlc analysis was carried out on Merck precoated silica gel 60 F₂₅₄ plates.

Ethyl 2-aminonicotinate (1). To a stirred suspension of 2-aminonicotinic acid (7.0 g, 0.05 mol) in dry ethanol (100 ml) cooled to 0°C was added thionyl chloride (3.8 ml, 0.052 mol) without the temperature rose above 0°C. The mixture was refluxed for 4 h. The solution was concentrated in vacuo to ca 20 ml and the hydrochloride was precipitated with ether and filtered. The salt was dissolved in water, basified with 30% ammonia and extracted with dichloromethane. After drying the solution was evaporated to dryness. The residual oil was crystallized from petroleum ether to give 6.5g of 1 (78%) as cream plates; mp 97-99°C [lit.,⁹: 94-96].

Ethyl 2-(1-pyrrolyl)nicotinate (2). A mixture of 1 (2.5 g, 15 mmol), 2,5-DTF (2.8 ml, 19 mmol), and 4-chloropyridinium hydrochloride in dioxane (100 ml) was refluxed for 4 h. After cooling, dioxane was distilled off and the residue extracted with ether. The ethereal layer was dried over sodium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel, eluting with dichloromethane-methanol (98:2 v/v) to give 2.8 g of 2 (86%) as pale yellow oil [lit.,¹⁰: bp 140°C/0.05 mm].

2-(1-Pyrrolyl)nicotinic acid (3). To a solution of potassium hydroxide (1.0 g, 17.8 mmol) in water (10 ml) was added 2 (1.0 g, 4.6 mmol). The mixture was refluxed for 1 h. After cooling a 5 M hydrochloric acid was added until pH 4. The acid which precipitated was filtered, washed with water and dried in an oven. Chromatography on silica gel eluted with dichloromethane-methanol (95:5 v/v) gave 780 mg (90%) of 3 as white plates; mp 153°C; ¹H-nmr (CD₃OD, 60 MHz) 5.43 (s, 1 H, CO₂H), 6.33 (t, 1 H, *J* = 2 Hz, H-3', H-4'), 7.35-7.45 (m, 3 H, H-5, H-2' and H-5'), 8.18 (dd, 1 H, *J* = 7 and 2 Hz, H-4), 8.52 (dd, 1 H, *J* = 5 and 2 Hz, H-6); ms (*m/z*, %) 188 (M⁺, 100), 131 (70); Anal. Calcd for C₁₀H₈N₂O₂: C, 63.83; H, 4.26; N, 14.89. Found: C, 63.98; H, 4.07; N, 15.03.

2-(1-Pyrrolyl)nicotinyl chloride (4). To a solution of 3 (2.0 g, 10.6 mmol) in benzene (400 ml) was added phosphorus pentachloride (2.6 g, 12.5 mmol). The mixture was stirred for 3 h, and benzene was removed *in vacuo* to give 1.6 g (73%) of 4 which was used without purification.

3-Diazoacetyl-2-(1-pyrrolyl)pyridine (5). To a solution of 4 in dry ether (30 ml) cooled to 5°C was added an

excess of diazomethane in ether. The mixture was stirred for 3 h and concentrated *in vacuo* to give 1.5 g of **5** as a yellow oil which became black on standing and was used without purification. Ir (KBr) 2110; $^1\text{H-nmr}$ (CDCl_3 , 60 MHz) 5.08 (s, 1 H, CHN_2), 6.35 (t, 2 H, $\text{J} = 2$ Hz, H-3' and H-4'), 7.15 (t, 2 H, $\text{J} = 2$ Hz, H-2' and H-5'), 7.32 (dd, 1 H, $\text{J} = 7$ and 5 Hz, H-5), 8.05 (dd, 1 H, $\text{J} = 7$ and 2 Hz, H-4), 8.55 (dd, 1 H, $\text{J} = 5$ and 2 Hz, H-6).

3-[2-(1-Pyrrolyl)pyridinyl]acetic acid (6). A solution of **5** (1.10 g, 5 mmol) in dioxane (50 ml) was added a solution of silver oxide (130 mg, 0.56 mmol), sodium carbonate (300 mg, 2.8 mmol) and sodium thiosulfate (300 mg, 1.9 mmol) in water at 60°C. The mixture was stirred at 60°C for 1 h and then 10 min at 90°C. After cooling the solution was acidified at pH 3 with 1 M hydrochloric acid and extracted with ether. The organic layer was dried over sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on silica gel eluted with dichloromethane-methanol (98:2 v/v) to give 800 mg of the starting material. Further elution gave 50 mg of **6** as a pale yellow oil (5%), ms (m/z , %) 202 (M^+ , 55), 201 [(M-H) $^+$, 60], 157 [(M-CO $_2\text{H}$) $^+$, 100]. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$: C, 65.35; H, 4.95; N, 13.86. Found: C, 65.54; H, 4.84; N, 13.72.

4-Acetoxy pyrrolo[1,2-a][1,8]naphthyridine (7). A solution of **6** (20 mg, 0.1 mmol) in acetic anhydride (2 ml, 21.2 mmol) was refluxed for 1 h. The anhydride was distilled off and the residue is treated with a saturated sodium hydrogenocarbonate solution (5 ml) and extracted with methylene chloride. The organic layer was dried over calcium chloride and concentrated *in vacuo*. The residue was chromatographed on silica gel eluted with dichloromethane to give 20 mg of **7** as an orange oil (88%); $^1\text{H-nmr}$ (CDCl_3 , 250 MHz) 2.43 (s, 3 H, CH_3), 6.58 (dd, 1 H, $\text{J} = 3.7$ and 1.4 Hz, H-3), 6.82 (dd, 1 H, $\text{J} = 3.7$ and 2.6 Hz, H-2), 6.85 (s, 1 H, H-5), 7.32 (dd, 1 H, $\text{J} = 7.8$ and 4.7 Hz, H-7), 7.95 (dd, 1 H, $\text{J} = 7.8$ and 1.7 Hz, H-6), 8.35 (dd, 1 H, $\text{J} = 2.6$ and 1.4 Hz, H-1), 8.55 (dd, 1 H, $\text{J} = 4.7$ and 1.7 Hz, H-8); ms (m/z , %) 226 (M^+ , 15), 184 [(M- CH_2CO) $^+$, 100], 155 (45). Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$: C, 69.03; H, 4.42; N, 12.39. Found: C, 68.84; H, 4.63; N, 12.32.

2-Aminonicotinaldehyde (8). The method of Majewicz and Coll.¹¹ was modified as follows. A mixture of nicotinamide (36.5 g, 0.30 mol) and ammonium sulfamate (52 g, 0.45 mol) was melted in an oil bath at 150°C. The temperature was then raised to 200°C at a rate of 5°C per hour and kept at this temperature for 1 h. After cooling at 80°C, water (80 ml) was added and the mixture was made alkaline with 30% ammonia.

The precipitate which was formed was collected, and washed with ether to remove nicotinonitrile. The solid material was refluxed for 4 h in 2*N* HCl (150 ml), made alkaline with sodium hydrogenocarbonate and extracted with ether. The organic layers were dried over sodium sulfate and evaporated to give 9.4 g of **8** as yellow plates (58%) sufficiently pure to be used without purification; mp 99°C [lit.,¹¹ 98-99].

2-(1-Pyrrolyl)nicotinaldehyde (9). A mixture of 2-aminonicotinaldehyde (2.0 g, 9.2 mmol), 4-chloropyridine hydrochloride (2.0 g, 13 mmol) and DTF (1.5 ml, 11 mmol) in dioxane (100 ml) was refluxed for 3 h. The solution was concentrated *in vacuo* and treated with ether. The organic layer was washed with water, dried over sodium sulfate and concentrated *in vacuo*. The residue was chromatographed on silica gel eluted with dichloromethane-methanol (98:2 v/v) to give 570 mg of **9** (66%) as an oil which crystallized on standing; mp <50°C; ¹H-nmr (CDCl₃) 6.48 (t, 2 H, *J* = 2 Hz, H-3' and H-4'), 7.28 (t, 2 H, *J* = 2 Hz, H-2', and H-5'), 7.37 (dd, 1 H, *J* = 7 and 5 Hz, H-5), 8.32 (dd, 1 H, *J* = 7 and 2 Hz, H-4), 8.72 (dd, *J* = 7 and 2 Hz, 1 H, H-6), 10.15 (s, 1 H, CHO). Anal. Calcd for C₁₀H₈N₂O: C, 69.77; H, 4.65; N, 16.28. Found: C, 69.93; H, 4.57; N, 16.04.

(Z)- and (E)-methylsulfinyl-1-methylthio-2-[(2-(pyrrolyl)pyridin)-3-yl]ethylene (10a,b). To a solution of **9** (500 mg, 2.9 mmol) and methyl methylthiomethyl sulfoxide (0.30 ml, 2.9 mmol) in dry THF (5 ml) was added Triton-B 40% solution in methanol (0.30 ml) under nitrogen. The mixture was refluxed for 3 h and concentrated *in vacuo*. The residue was chromatographed on silica gel, eluting with dichloromethane-methanol (98:2 v/v) to give 400 mg of **10b** (60%) as an oil; ir (KBr) 1060; ¹H-nmr (CDCl₃, 400 MHz) 2.24 (s, 3 H, CH₃), 2.77 (s, 3 H, CH₃), 6.31 (t, 2 H, *J* = 2.1 Hz, H-3' and H-4'), 7.14 (t, 2 H, *J* = 2.1 Hz, H-2' and H-5'), 7.26 (dd, 1 H, *J* = 7.7 and 4.6 Hz, H-5), 7.66 (s, 1 H, CH_{ethylene}), 8.14 (dd, 1 H, *J* = 7.8 and 1.5 Hz, H-4), 8.48 (dd, 1 H, *J* = 4.6 and 1.4 Hz, H-6); ms (*m/z*, %) (EI), 215 [(M-SOCH₃)⁺, 100]; (FAB⁺) (thioglycerol), 279 [M+H, 20]; Anal. Calcd for C₁₃H₁₄N₂OS₂: C, 56.11; H, 5.03; N, 10.07. Found: C, 55.93; H, 4.97; N, 10.21. Further elution gave 30 mg (4%) of **10a** as an oil; ¹H-nmr (CDCl₃, 400 MHz) 2.34 (s, 3 H, CH₃), 2.36 (s, 3 H, CH₃), 6.32 (t, 2 H, *J* = 2 Hz, H-3' and H-4'), 6.46 (s, 1 H, CH_{ethylene}), 7.21 (dd, 1 H, *J* = 8 and 4.5 Hz, H-5), 7.23 (t, 2 H, *J* = 2 Hz, H-2' and H-5'), 8.02 (dd, 1 H, *J* = 4.5 and 2 Hz, H-4), 8.38 (dd, 1 H, *J* = 8 and 2 Hz, H-6); ms (*m/z*, %) (EI), 215 [(M-SOCH₃)⁺, 100]. Anal. Calcd for C₁₃H₁₄N₂OS₂: C, 56.11; H, 5.03; N, 10.07; S, 23.02. Found: C, 55.89; H, 4.89; N, 10.32.

4-Methylthiopyrrolo[1,2-a][1,8]naphthyridine (12). Dry hydrogen chloride acid was bubbled for 2 h in a solution of **10b** (220 mg, 0.79 mmol) in dry ethanol (20 ml) at 0°C. The salt which precipitated was filtered, washed with ether and suspended in dichloromethane. Diluted ammonium hydroxide was added and organic layer was collected, dried over calcium chloride and concentrated *in vacuo*. The residue was chromatographed on silica gel eluted with dichloromethane to give 120 mg (71%) of **12** as cream plates; mp 68-70°C; ¹H-nmr (CDCl₃, 400 MHz) 2.61 (s, 3 H, SCH₃), 6.64 (s, 1 H, 5-H), 6.73 (dd, 1 H, $J = 3.7$ and 1.5 Hz, H-3), 6.80 (dd, 1 H, $J = 3.7$ and 2.9 Hz, H-2), 7.26 (dd, 1 H, $J = 7.8$ and 4.7 Hz, H-7), 7.84 (dd, 1 H, $J = 7.8$ and 1.7 Hz, H-6), 8.33 (dd, 1 H, $J = 2.9$ and 1.5 Hz, H-1), 8.47 (dd, 1 H, $J = 4.7$ and 1.7 Hz, H-8); ¹³C-nmr (CDCl₃, 100 MHz) 14.3 (CH₃), 103.4 (C-3), 110.6 (C-5), 112.8 (C-2), 114.1 (C-1), 118.7 (C-5a), 119.9 (C-7), 129.8, 131.2, 134.4 (C-6), 143.1 (C-9a), 145.9 (C-8); ms (*m/z*, %) 214 (M⁺, 100), 181 (70), 155 (80). Anal. Calcd for C₁₂H₁₀N₂S: C, 75.79; H, 5.26; N, 14.74. Found: C, 75.97; H, 5.06; N, 14.60.

2-(1-Pyrrolyl)benzaldehyde (13) and 1,2-dihydro-1H-pyrrolo[1,2-a]indol-3-one (14). A mixture of 2-aminobenzaldehyde (2.0 g, 16.5 mmol), DTF (3.5 ml, 27 mmol) and 4-chloropyridine hydrochloride (3.0 g, 20 mmol) in dioxane (40 ml) was refluxed for 1 h. After cooling dioxane was removed under reduced pressure, the residue was treated with water and extracted with ether. The organic layers were dried over sodium sulfate and evaporated to dryness. The residue was chromatographed on silica gel by elution with petroleum ether:dichloromethane:methanol (50:49:1 v/v) to give 300 mg of **13** (10%) as a brown oil; ¹H-nmr (CDCl₃, 60 MHz), 6.40 (t, 2 H, $J = 2$ Hz, H-3',4'), 6.93 (t, 2 H, $J = 2$ Hz, H-2',5'), 7.50 (m, 3 H, H_{arom.}), 8.00 (m, 1 H, H_{arom.}), 9.83 (s, 1H, CHO); ms (*m/z*, %) 171 (M⁺,100), 143 (76), 130 (37), 115 (31). Further elution gave 800 mg (29%) of **14** as cream plates; mp 149-151°C [lit.,⁸ 149°C]; ¹³C-nmr (CDCl₃, 100 MHz), 19.94 (C-1), 35.14 (C-2), 100.64 (C-9), 113.93 (C-5), 120.82 (C-6), 123.55(C-6), 124.32 (C-7), 130.87 (C-8), 135.67 (C-8a), 143.85 (C-9a), 171.76 (C=O).

1-Methylsulfinyl-1-methylthio-2-[2-(pyrrol-1-yl)phenyl]ethylene (15). The aldehyde (**13**) (25 mg, 0.146 mmol), methyl methylthiomethyl sulfoxide (0.1 ml, 0.119 mg, 0.9 mmol), Triton-B (0.1 ml) in THF (1ml) was refluxed for 30 min. After usual work up the residue was chromatographed on silica gel eluting with cyclohexane:dichloromethane:methanol (80:19:1 v/v) gave 20 mg of **15** (50%) as an orange oil, ¹H-nmr (CDCl₃, 60 MHz), 2.23 (s, 3 H, CH₃), 2.30 (s, 3 H, CH₃), 6.30 (s, 1 H, CH_{ethyleneic}), 6.61 (t, 2 H, $J = 2$ Hz, H-3',4'), 6.88 (t, 2 H, $J = 2$ Hz, H-2',5'), 7.30 (m, 3 H, H_{arom.}), 7.82 (m, 1 H, H_{arom.}). Anal. Calcd

for $C_{14}H_{15}NOS_2$: C, 60.65; H, 5.41; N, 5.05. Found: C, 60.42; H, 5.30; N, 4.89.

4-Methylthiopyrrolo[1,2-a]quinoline (16). Dry hydrogen chloride was bubbled for 40 min in a solution of 15 (20 mg, 0.072 mmol) in anhydrous ethanol (20 ml) at 0°C. The solvent was removed *in vacuo*, the residue was treated with ammonia and extracted with dichloromethane. The organic layers were combined, dried over calcium chloride and concentrated *in vacuo*. The residue was chromatographed on silica gel eluted with dichloromethane to give 15 mg (97%) of 16; 1H -nmr ($CDCl_3$, 400 MHz), 2.62 (s, 3 H, CH_3), 6.69 (dd, 1 H, $J = 3.8$ Hz and 1.4 Hz, H-3), 6.80 (m, 2 H, H-2 and H-5), 7.31 (ddd, 1 H, $J = 8.8$, 7.5 and 1.25 Hz, H-8), 7.45 (ddd, 1 H, $J = 7.8$, 7.5 and 1.4 Hz, H-7), 7.59 (dd, 1 H, $J = 7.8$ and 1.25 Hz, H-6), 7.84 (dd, 1 H, $J = 8.8$ and 1.4 Hz, H-9), 7.86 (dd, 1 H, $J = 3.8$ and 2.9 Hz, H-1); ^{13}C -nmr ($CDCl_3$, 100 MHz), 14.51 (CH_3), 101.91 (C-3), 112.58 (C-1 and C-5), 113.31 (C-2), 114.00 (C-9), 123.71 (C-7), 126.84 (C-8) and 127.40 (C-6); ms (m/z , %) (EI) 213 (M^+ , 27), 180 (36), 154 (30) and 83 (26). Anal. Calcd for $C_{13}H_{11}NS$: C, 73.24; H, 5.16; N, 6.57. Found: C, 73.50; H, 4.99; N, 6.45.

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