Pergamon

Tetrahedron, Vol. 52, No. 26, pp. 8707-8724, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00448-6

Extended Heterocyclic Systems 1. The Synthesis and Characterisation of Pyrrolylpyridines, Alternating Pyrrole:Pyridine Oligomers and Polymers, and Related Systems

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Abstract: The Stetter procedure has been adapted to produce oligomeric and polymeric pyrrolylpyridines, which have been characterised by ^{13}C NMR spectroscopy. The lower activity of 2-(pyrrol-2-yl)pyridines towards quaternisation permits selective N-alkylation of 2-, 3- and 4-(pyrrol-2-yl)pyridines.

Introduction

The synthesis of novel organic systems, which have potential as semi-conducting materials, is of considerable current interest[1] and a large number of the reported systems comprise oligomeric or polymeric heterocyclic systems. However, the effectiveness as semi-conductors of such systems, which generally contain exclusively either electron-excessive[2a] or electron-deficient rings,[2b] relies upon oxidative or reductive doping. Oligomers and polymers possessing alternating π-electron-excessive and π-electron-deficient heteroarenes not only provide a synthetic challenge but could also provide a range of materials which possess semi-conducting properties without recourse to doping. Such systems would also be attractive as potential organic non-linear optical materials, a general requirement of which is the presence of electron-acceptor or electron-donor groups within an extended conjugated system.[3]

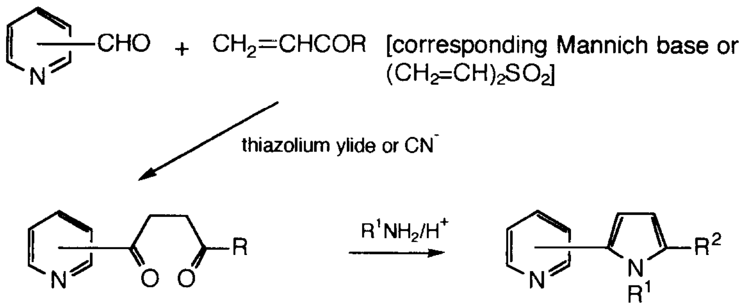
In this communication we report the synthesis and characterisation of simple 2-(pyrrol-2-yl)pyridines and oligomeric alternating pyrrole:pyridine systems, which provide a general procedure for the synthesis and characterisation of the alternating pyrrole:pyridine polymer.

Results and Discussion

Of the various procedures available for the synthesis of pyrrole and pyridine rings[4] suitable for adaptation to the preparation of pyrrolylpyridines,[5] the one offering the most versatility from readily accessible starting compounds involves the Paal-Knorr formation of the pyrrole ring from a 1,4-dicarbonyl system. The pyridyl diketones were obtainable *via* the Stetter protocol[6] from the appropriate formylpyridine and either a pre-formed vinylketone or the Mannich base precursor (Scheme 1). The effectiveness of the procedure depended significantly upon the choice of catalyst and there appeared to be no obvious rationale behind the relative yields obtained with the different catalysts (*cf.* ref. 6). Other routes were available to the simple monopyridyl diketones but, compared with the Stetter synthesis, lower yields were invariably obtained. Symmetrical

1,4-di(2-, 3- or 4-pyridyl)butan-1,4-diones were most effectively prepared by reaction of divinylsulfone with the appropriate formylpyridine in the presence of a thiazolium ylide catalyst.

Compounds **3a** and **b** were prepared from either from 2,6-diformylpyridine and the appropriate vinyl ketone or the Mannich base, or from the bis-Mannich base of 2,6-diacetylpyridine and appropriate formylarene, while **5b** was obtained from the bis-Mannich base of 1,4-diacetylbenzene and 2-formylpyridine.



1

2-pyridyl
a R = Me
b R = Ph
c R = 2-pyridyl
d R = 3-pyridyl

3-pyridyl
e R = Me
f R = Ph
g R = 3-pyridyl

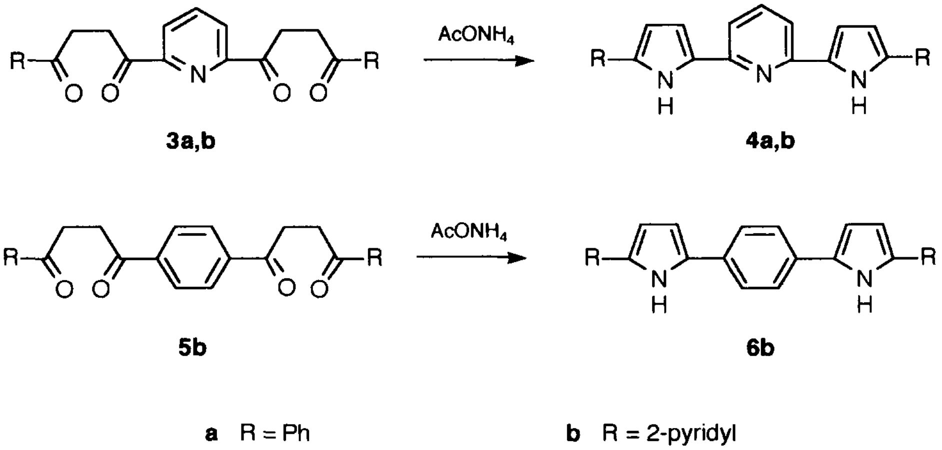
4-pyridyl
h R = Me
i R = Ph
j R = 4-pyridyl

2

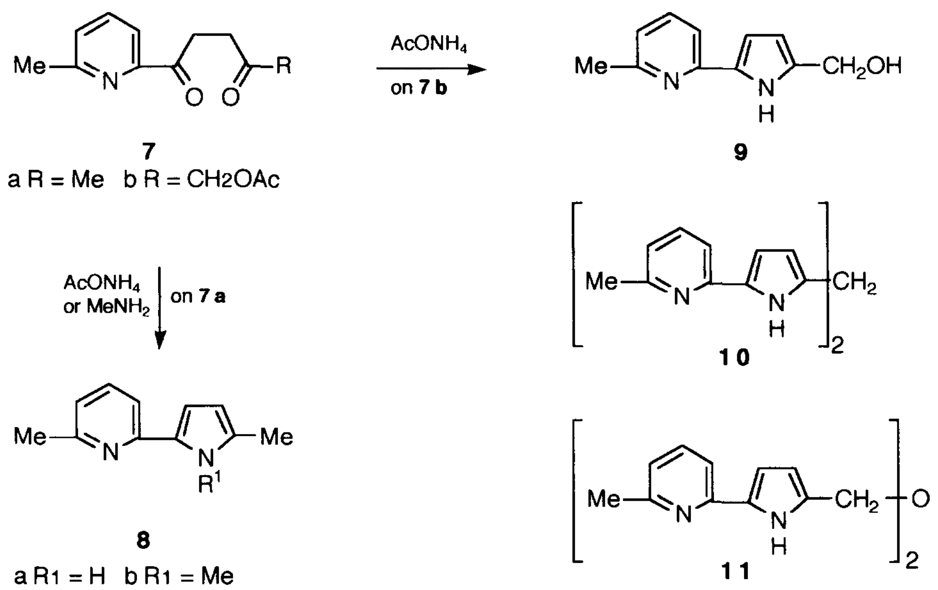
2-pyridyl
a R^1 = H, R^2 = Me
b R^1 = R^2 = Me
c R^1 = Et, R^2 = Me
d R^1 = Ph, R^2 = Me
e R^1 = H, R^2 = Ph
f R^1 = H, R^2 = 2-pyridyl
g R^1 = H, R^2 = 3-pyridyl
3-pyridyl
h R^1 = H, R^2 = Me
i R^1 = R^2 = Me
j R^1 = H, R^2 = Ph
k R^1 = H, R^2 = 3-pyridyl
4-pyridyl
l R^1 = H, R^2 = Me
m R^1 = R^2 = Me
n R^1 = H, R^2 = Ph
o R^1 = H, R^2 = 4-pyridyl
p R^1 = Me, R^2 = 4-pyridyl

Scheme 1

With the exception of 1-(6-methyl-2-pyridyl)-5-acetoxypentan-1,4-dione **7b**, all of the diketones were converted in high yield into the corresponding pyrroles and 1-alkyl- or 1-arylpyrroles using standard Paal-Knorr procedures (Schemes 1 and 2). In contrast, **7b** reacted with ammonium carbonate to produce the hydroxymethylpyrrole **9**, instead of the expected acetoxy derivative, together with the dipyrrolylmethane **10** and di(pyrrolylmethyl)ether **11** (Scheme 3).



Scheme 2



Scheme 3

Examination of the spectroscopic data for the simple pyrrolylpyridines and oligomers indicated that ^{13}C NMR spectroscopy, coupled with IR spectroscopy, was potentially the best analytical technique to provide confirmatory structural evidence for their formation. The technique could be extended to the characterisation of the related pyrrole:pyridine polymers. The ^{13}C NMR data for 2-(pyrrol-2-yl)pyridines and their diketone precursors, presented in detail in the Experimental Section, are summarised and correlated in Tables 1 - 3. The 1,4-dicarbonyl systems also exhibited characteristic triplets in the region 31.7 - 37.0 ppm (with a mean position of 32.0 ppm) assignable to the methylene groups and singlets over the range 197.2 - 206.9 ppm (with a mean position of 200.5 ppm) characteristic of the carbonyl groups. The signals for the phenyl and 1,4-phenylene rings were observed in predictable positions.[7]

The 3- and 4-pyridyl systems were also characterised by their ^{13}C NMR spectra, as recorded in the Experimental Section.

Table 1. ^{13}C NMR Chemical Shifts (ppm) for the 2-Substituted Pyridine Ring of 1-(2-Pyridyl)butan-1,4-diones (1a-d) and 2-(pyrrol-2-yl)pyridines (2a-g)

β'-C	β-C	γ-C	α'-C	α-C
Diketones				
121.8 ± 0.0	127.2 ± 0.2	136.9 ± 0.1	149.2 ± 0.2	153.4 ± 0.2 (s)
Pyrroles				
120.5 ± 0.7	118.7 ± 0.5	136.4 ± 0.5	149.1 ± 0.2	150.7 ± 0.7 (s)

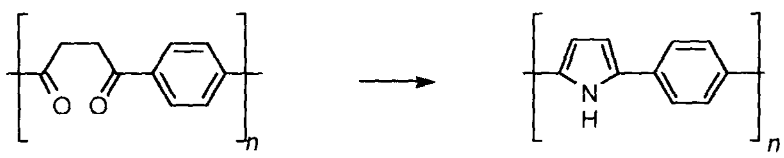
Table 2. ^{13}C NMR Chemical Shifts (ppm) for the Symmetrical 2,6-Disubstituted Pyridine Ring of 2,6-Di(pyrrol-2-yl)pyridines (4a,b) and 2,6-Di(1,4-dioxobutyl)pyridines (3a,b).

β-C	γ-C	α-C
Diketones		
125 ± 0.0	138.0 ± 0.0	152.3 ± 0.1
Pyrroles		
126.7 ± 0.0	132.5 ± 0.2	*ca.* 148.8

Table 3. ^{13}C NMR Chemical Shifts (ppm) for the 2,5-Disubstituted Pyrrole Ring of 2-Alkyl-5-aryl/heteroaryl-, 5-Aryl-2-heteroaryl- and 2,5-Diheteroarylpyrroles (2a-p, 4, 6, 8-11)

α-C	α'-C	β-C	β'-C
Symmetrical 2,5-Disubstituted Pyrroles			
133.1 ± 0.1	133.1 ± 0.1	108.5 ± 0.5	108.5 ± 0.5
Unsymmetrical 2,5-Disubstituted Pyrroles			
130.2 ± 0.9	132.7 ± 1.2	108.8 ± 0.3	109.7 ± 0.3

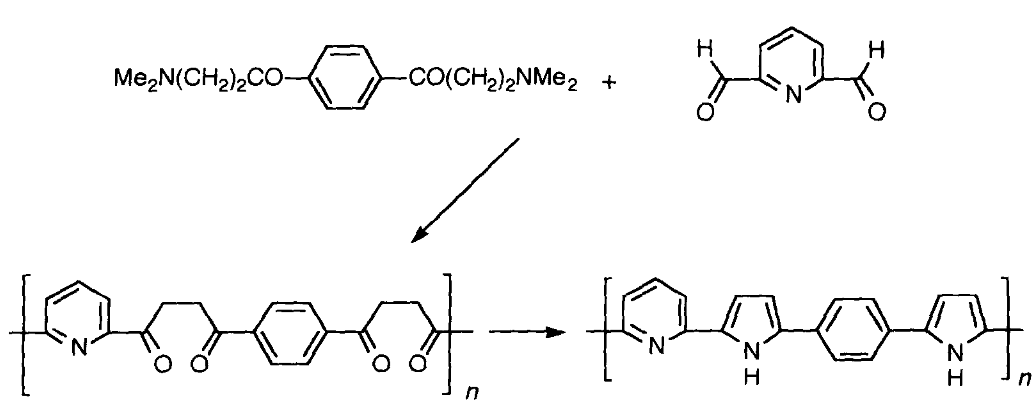
Extension of the Stetter reaction using diformylarenes and the Mannich bases derived from diacetylarenes produced polymeric butan-1,4-diones, which could be converted by prolonged reaction with liquid ammonia into the pyrrole-containing polymer. The model reaction of 1,4-diformylbenzene with the bis-Mannich base derived from 1,4-diacetylbenzene gave the polymer **12**, which was subsequently converted into **13** (*cf.* ref. 8).



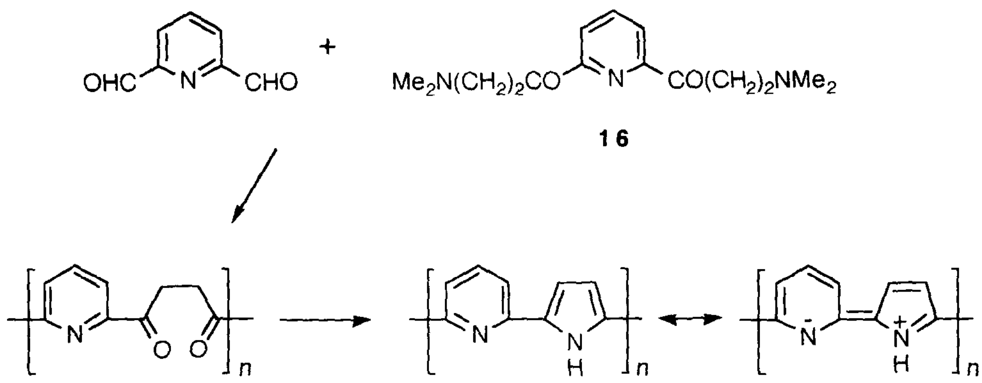
12 **13**

A similar reaction of the bis-Mannich base of 1,4-diacetylbenzene with 2,6-diformylpyridine produced the polymeric diketone **14**, which was converted into the polymer **15**; the analogous reaction of the bis-Mannich base of 2,6-diacetylpyridine with 2,6-diformylpyridine produced the alternating pyrrole:pyridine polymer **18**, *via* the diketone **17**. It is noteworthy that, although the bis-Mannich base derived from 2,6-diacetylpyridine **16**, the original synthesis of which was reported by Kröhnke,[9] has a chemical behaviour expected for such as system, the spectroscopic data are totally incompatible with the structure. Only broad band ^{1}H and ^{13}C NMR spectra were observed and it is conceivable that the product decomposes readily during the spectral measurements and the observed data relates to a mixture of the Mannich base and the vinyl ketone.

The polymers were found to be soluble only in concentrated sulfuric acid and were insoluble in conventional organic solvents. Although elemental analysis for the polymers were not entirely satisfacfory, the structures of the pyrrole:pyridine polymer **18** and its precursor **17** were characterised by comparison of their ^{13}C NMR solid state spectra with the solution phase data presented in Tables 1 and 2 (see Table 4). The slight discrepancies between the solid state and solution phase data can be rationalised in terms of the anisotropic effects of the aromatic rings in the relatively rigidly structured polymer, compared with the conformationally mobile state of the "monomer" systems. The absence of both infrared and NMR spectral evidence for the butan--1,4-dione functions in the spectra for polymer **18** confirms the complete conversion of the dione polymer **17** into **18**, and the lack of spectral evidence for any aliphatic end groups is compatible with molecular weight > 4000 (as determined by mass spectroscopic measurements) indicative of the presence of at least 30 repeating units in **18**.



14 **15**

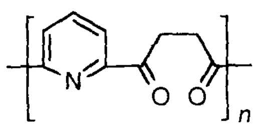
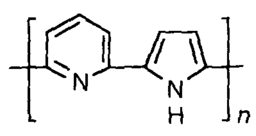


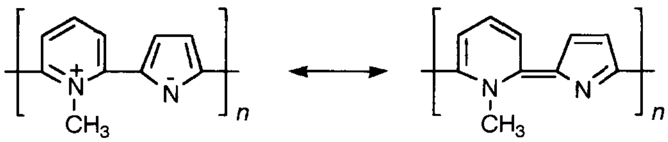
16

17 18

During the course of our work,[10] Wynberg[8] described the preparation of polymer **13** and showed that, when doped with iodine, it had semi-conducting properties. The rationale behind our hypothesis that the alternating heterocyclic polymer **18** should have semi-conducting properties without recourse to dopants lie in the expected electronic interaction between the two rings and that the zwitterionic canonical form would have considerable importance in the resonance hybrid structure of the polymer. It was logical to extend this rationale to the proposition that the polymer **19**, derived from quaternisation of the pyridine rings and deprotonation of the pyrrole ring, would have a higher propensity to transference of electrons along the polymer chain.

Table 4. Correlation of Solid State ^{13}C NMR spectral data (ppm) for the Heteroaryl Polymers (17 and 18) and Mean Chemical Shifts of simple Pyrrolylpyridines, measured in $CDCl_3$.

System	Solid State Spectral Data for Polymer	Solution State Spectral Data for "Monomer"	Assignment
	34.9	32.0	CH_2
	125.6	125.0	β-pyridine
	137.8	138.0	γ-pyridine
	151.4	152.4	α-pyridine
	199.7	199.8	C=O
	109.3	108.5	β-pyrrole
	119.9	126.7	β-pyridine
	130.2	133.2	α-pyrrole
	136.5	132.7	γ-pyridine
	148.7	148.8	α-pyridine



19

Quaternisation of all of the 3-and 4-pyridyl systems with iodomethane proceeded normally under mild conditions, but the corresponding reactions of the simple 2-pyridyl systems, e.g. **2a**, required prolonged reaction at temperatures in excess of 100°C in a sealed tube. 4-(5-(4-pyridyl)pyrrol-2-yl)pyridine **2o** was quaternised under 'normal' conditions to produce the bismethiodide and the mono-N-methylated salts was not isolated while, in contrast, 2-(5-(3-pyridyl)pyrrol-2-yl)pyridine **2g** was quaternised under mild conditions to yield 1-methyl-3-(5-(2-pyridyl)pyrrol-2-yl)pyridinium iodide, but the bismethiodide could not be obtained, even prolonged reaction at high temperature. Not unexpectedly, N-methylation of 2,5-di(5-phenylpyrrol-2-yl)pyridine **4a** could not be effected even under the forcing conditions, but surprisingly, 2-(5-(2-pyridyl)pyrrol-2-yl)pyridine **2f** also failed to react under the more vigorous conditions even after 3 weeks.

The slower rate of quaternisation of the 2-pyridyl systems under mild conditions can be rationalised in terms of the steric shielding of the pyridyl lone pair of electrons by the pyrrole rings. Additionally, for compounds **2a** and **2e**, H-bonding between the pyrrolyl NH and the pyridine nitrogen atom is possible. This would have the two-fold effect of (a) reducing the availability of the lone pair for nucleophilic attack on the alkylating agent and (b) restraining the two rings in a coplanar conformation thereby increasing the steric hindrance to approach by the alkylating agent on the pyridyl lone pair of electrons. There is some evidence for this postulate, as it was observed that the ease of N-alkylation of 2-(1-substituted pyrrol-2-yl)pyridines, e.g. **2b**, **c** and **d**, and also of the analogous 2-furyl and 2-thienyl derivatives[11] was greater than that for **2a**. For these compounds, H-bonding is absent and, in the case of the 1-substituted pyrrolyl derivatives, the greater steric interaction between the two rings is such that the they no longer adopt a coplanar conformation.[12] The acidity of the conjugate acids of the pyrrolylpyridines (Table 5) provides some confirmation of the change in coplanarity, with the consequent decreased in conjugation between the two rings and reduced acidity, as the bulk of the substituent on the pyrrolyl nitrogen atom is increased.

Table 5. Acidity of the Conjugate acids of 2-(Pyrrol-2-yl)pyridines

Compound	pK_a
2-(5-Methylpyrrol-2-yl)pyridine (**2a**)	5.87 ± 0.01
2-(1,5-Dimethylpyrrol-2-yl)pyridine (**2b**)	5.35 ± 0.04
2-(1-Ethyl-5-methylpyrrol-2-yl)pyridine (**2c**)	5.20 ± 0.01
2-(5-Methyl-1-phenylpyrrol-2-yl)pyridine (**2d**)	5.37 ± 0.03

A fuller report of the physical properties of the pyrrolylpyridines systems will be reported elsewhere.

EXPERIMENTAL

Infrared spectra were recorded for mulls in Nujol or as liquid films using a Perkin-Elmer 295 spectrometer and the ^{1}H NMR spectra at 60 or 90 MHz were measured for *ca.* 25 - 30% solutions in $CDCl_3$, unless otherwise indicated, using a JEOL PMX-60SI or EX-90Q spectrometer. ^{13}C NMR spectra were measured at 22.5 MHz using the JEOL EX-90Q spectrometer (in cases where coincidental, or close, signals were not resolved, they are indicated by *). All chemical shifts are expressed relative to Me_4Si. Solid state ^{13}C NMR spectra at 25 MHz were obtained using the UEA200 spectrometer. pKa measurements of the conjugate acids of the pyrrolylpyridines were determined spectrophotometrically using the standard procedures.[13]

General procedure for the preparation of the mono- and dipyridylbutan-1,4-diones

Method A: But-3-en-2-one (35 g, 0.5 mol), 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (16.2 g, 0.06 mol) and dry triethylamine (30.3 g, 0.3 mol) in dry dioxane (40 ml) were heated at 90 - 100°C under nitrogen. The appropriate monoformylpyridine (0.4 mol) or diformylpyridine (0.2 mol) in dry dioxane (80 ml) was added dropwise slowly over a period of 2h, and the mixture was then stirred at 90 - 100°C for further 12h. The mixture was cooled to room temperature and the solvents were removed under vacuum. Water (300 ml) was added and the aqueous layer was extracted with dichloromethane (3 x 50 ml). The combined organic extracts were washed brine (2 x 25 ml) and dried ($MgSO_4$). Filtration and removal of the solvent gave a crude product, as a dark brown oil and the product was purified by recrystallisation, distillation, or chromatography from silica gel column.

Method B: The appropriate bromopyridine (0.042 mol) in diethyl ether (100 ml) was quickly cooled with efficient stirring to -78°C. *n*-Butyl lithium (26 ml of 1.6 M hexane solution, 0.042 mol) was added in one portion and the solution was stirred 5 min. N,N,N',N'-tetramethylsuccinamide[14,15] (3.61 g, 0.021 mol) in tetrahydrofuran (3 ml) was then added dropwise and the mixture was stirred at -78°C for 4h, before being allowed to warm to room temperature. Water (50 ml) was added and the mixture was extracted with dichloromethane (3 x 50 ml). The combined organic extracts were washed brine (10 ml) and dried (Na_2CO_3). Filtration and removal of the solvent gave an orange/yellow liquid. The crude product was purified by chromatography eluting with ethyl acetate:petroleum ether (1:1), followed by recrystallisation from ethanol.

Method C: Sodium acetate (0.33 g, 0.004 mol) and 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (0.54 g, 0.002 mol) were added to the appropriate formylpyridine (0.02 mol) in ethanol (20 ml). The mixture was heated under reflux and divinyl sulfone (1.18 g, 0.01 mol) was added dropwise over 30 min and then refluxed for further 12h. The precipitated product was separated from the orange solution, washed with cold ethanol (10 ml) and diethyl ether (10 ml), and purified either by chromatography from silica gel (ethyl acetate:diethyl ether; 1:1) or by recrystallisation from ethanol.

Method D: The appropriate formylpyridine (0.033 mol), 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (1.35 g, 0.005 mol) and dry triethylamine (1.01 g, 0.01 mol) in dry dioxane (70 ml) were heated at 90 - 100°C under nitrogen. Divinyl sulfone (1.89 g, 0.016 mol) was added dropwise slowly over a period of 1h, and the mixture was then stirred at 90 - 100°C for 12h. The mixture was cooled to room temperature and the solvent was removed under vacuum. Water (100 ml) was added to the residue and the aqueous suspension was extracted with dichloromethane (3 x 50 ml). The combined organic extracts were dried ($MgSO_4$). Evaporation of the solvent gave the crude product, which was purified either by chromatography from silica gel (ethyl acetate-petroleum ether; 1:1), or by recrystallisation from ethanol.

Method E: Triethylamine (0.068 g, 6.7 mmol) and the appropriate formylpyridine (8.4 mmol) in DMF (2 ml) was added dropwise under nitrogen at 85°C to the appropriate 3-dimethylamino-1-arylpropan-1-one (10 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium bromide (0.2 g, 0.79 mmol) in DMF (10 ml) over a period of 20 - 30 min using a gas tight syringe. The reaction mixture was stirred until all of the starting material had been consumed (as indicated by tlc analysis) and then poured into water (25 ml) The aqueous mixture was made alkaline and then extracted with dichloromethane (3 x 50 ml), dried (Na_2SO_4) and evaporated. The crude product was purified by chromatography from silica gel.

Method F: The appropriate formylpyridine (7.8 mmol) in DMF (8 ml) was added dropwise under nitrogen at 35°C to sodium cyanide (0.83 g, 17 mmol) in DMF (8 ml) over a period of 20 min and the mixture was stirred for a further 15 min. The appropriate 3-dimethylamino-1-arylpropan-1-one (7.8 mmol) in DMF (10 ml) was then added at 35°C over a period of 30 min using a gas-tight syringe. The reaction mixture was stirred for 4 h and then poured into water (30 ml). The aqueous mixture was extracted with dichloromethane (3 x 90 ml), dried (Na_2SO_4), and evaporated. The crude product was purified by chromatography from silica gel, using ethyl acetate as the eluant.

1-(2-Pyridyl)pentan-1,4-dione **1a** (66%), m.p. 43 - 44°C (lit.,[16] m.p. 45 - 46°C) δ_H 2.22 (3H, s), 2.87 (2H, t), 3.50 (2H, t), 7.45 (1H, dt), 7.70 - 8.00 (2H, m), 8.63 (1H, dd); δ_C 29.8 (q), 31.9 (t), 37.2 (t), 121.6 (d), 127.2 (d), 136.8 (d), 149.0 (d), 153.2 (s), 200.1 (s), 206.9 (s), 1-(3-pyridyl)-pentan-1,4-dione **1e** (62%) b.p. 137 -138°C at 1.0 mm Hg (lit.,[17] b.p. 112 - 113°C at 0.25 mm Hg) δ_H 2.25 (3H, s), 2.92 (2H, t), 3.26 (2H, t), 7.39 (1H, dd), 8.24 (1H, dd), 8.77 (1H, dd), 9.18 (1H, d); δ_C 29.7 (q), 32.5 (t), 36.7 (t), 123.5 (d), 131.8 (s), 135.2 (d), 149.2 (d), 153.2 (d), 197.3 (s), 206.7 (s), and 1-(4-pyridyl)pentan-1,4-dione **1h** (68%) b.p. 70.8 - 73°C (lit.,[17] b.p. 75°C) δ_H 2.22 (3H, s), 2.84 (2H, t), 3.50 (2H, t), 7.77 (2H, dd), 8.81 (2H, dd); δ_C 29.8 (q), 32.6 (t), 36.7 (t), 120.9 (d), 142.4 (s), 150.8 (d), 198.0 (s), 206.5 (s) were obtained by the standard literature procedure from the 2-, 3- and 4-formylpyridines, respectively, using Method A.

1-Phenyl-4-(2-pyridyl)butan-1,4-dione **1b** (72%) m.p. 71 - 72°C (lit.,[16] m.p. 72°C) δ_H 3.48 (2H, m), 3.66 (2H, m), 7.50 - 8.00 (8H, m), 8.67 (1H, m); δ_C 31.9 (t), 32.7 (t), 121.7 (d), 127.1 (d), 128.0 (d), 128.5 (d), 133.0 (d), 136.8 (d), 149.0 (d), 153.2(s), 198.5 (s), 200.4 (s), 1-phenyl-4-(3-pyridyl)butan-1,4-dione **1f** (49%) m.p. 97 - 99°C (lit.,[17,18] m.p. 100°C) δ_H 3.46 (4H, s), 7.35 - 7.60 (4H, m), 8.00 (2H, d), 8.27 (1H, d), 8.50 - 8.80 (1H, m), 9.26 (1H, s); δ_C 32.4 (t), 32.8 (t), 123.6 (d), 128.1(d), 128.7(d), 132.3 (s), 133.3 (d), 135.4(d), 136.6 (s), 149.7 (d), 153.6(d), 197.6 (s), 198.2 (s) and *1-phenyl-4-(4-pyridyl)butan-1,4-dione* **1i** (7.3%) m.p. 116°C (Found: C, 75.1; H, 5.4; N, 5.7 $C_{15}H_{13}NO_2$ requires C, 75.3; H, 5.5; N, 5.85%) δ_H 3.40 (4H m), 7.35 - 7.61 (3H, m), 7.75 (2H, d), 7.96 - 8.06 (2H, m), 8.77 (2H, d); δ_C 32.5 (t), 32.8 (t), 121.1 (d), 128.1 (d), 128.7 (d), 133.3 (d), 136.5 (s), 142.7 (s), 150.9 (d), 198.1 (s), 198.3 (s) were obtained from the 2-, 3- and 4-formylpyridines and 3-dimethyl-amino-1-phenylpropan-1-one,[19] respectively, using Method E or F.

2-Formyl-6-methylpyridine gave *1-(6-methyl-2-pyridyl)pentan-1,4-dione* **7a** (45%, Method A), b.p. 144 - 147°C at 20 mm Hg (Found: C, 68.8; H, 7.1; N, 7.2 $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.9; N, 7.3%). δ_H 2.20 (3H, s), 2.52 (3H, s), 2.84 (2H, t), 3.46 (2H, t), 7.20 - 7.30 (1H, m), 7.60 - 7.70 (2H, m); δ_C 24.2 (q), 29.7 (q), 31.9 (t), 37.0 (t), 118.5 (d), 126.8 (d), 137.0 (d), 152.6 (s), 157.9 (s), 200.1 (s), 206.8 (s).
1-(6-Methyl-2-pyridyl)-5-acetoxypentan-1,4-dione **7b** (26.5 g, 75%), m.p. 36 - 38°C (Found: C, 62.8; H, 6.1; N, 5.8 $C_{13}H_{15}N_2O_4$ requires C, 62.6; H, 6.1; N, 5.6%) was obtained by Method A from 2-formyl-6-methylpyridine, using Method A with 1-acetoxybut-3-en-2-one[20] in place of but-2-en-1-one. δ_H 2.16 (3H, s), 2.59 (3H, s), 2.82 (2H, t), 3.59 (2H, t), 4.81 (2H, s), 7.31 (1H, d), 7.60 - 7.80 (m, 2H); δ_C 20.5 (q), 24.4 (q), 31.7 (t), 32.5 (t), 68.1 (t), 118.8 (d), 126.9 (d), 136.9 (d), 152.4 (s), 158.1 (s), 170.2 (s), 200.2 (s), 203.1 (s).

Using Methods C and D, 2-formylpyridine gave *1,4-di(2-pyridyl)butan-1,4-dione* **1c** (17 %, Method C; 28%, Method D) m.p., 141 - 142°C (lit.,[15,21] m.p. 140 - 141°C) (Found: C, 69.8; H, 5.0; N, 11.6 Calc. for $C_{14}H_{12}N_2O_2$ C, 70.0; H, 5.0; N, 11.7%). δ_H 3.70 (4H, s), 7.50 - 8.10 (6H, m), 8.68 (2H, m); δ_C 32.1 (t), 121.8 (d), 127.1 (d), 136.8 (d), 149.0 (d), 153.3 (s), 200.4 (s) and 1,2-di(2-pyridyl)ethan-1,2-dione (20%, Method C; 41% Method D), m.p. 156 - 157°C (lit.,[22,23] m.p. 154 - 155°C*) (Found: C, 67.9; H, 3.7; N, 13.2. Calc. for $C_{12}H_8N_2O_2$: C, 67.9; H, 3.8; N, 13.2%). ν_{max} 1710, 1690 cm^{-1}; δ_H 7.20 - 8.20 (m, 3H), 8.52 (d, 1H); δ_C 122.6 (d), 127.9 (d), 137.2 (d), 149.4 (d), 151.7 (s), 197.0 (s); m/z 213 (M^+). [*2-Pyridoin is also reported[23] to have m.p. 156 °C.]
Using Method E, 2-formylpyridine and 3-dimethylamino-1-(2-pyridyl)propan-1-one[19] gave only 1,4-di(2-pyridyl)butan-1,4-dione (36%), and 2-bromopyridine gave the butan-1,4-dione (22%), using Method B.

1-(2-Pyridyl)-4-(3-pyridyl)butan-1,4-dione **1d** (30%), m.p. 64 - 66°C (Found: C, 69.9; H, 5.05; N, 11.95 $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.0; N, 11.7%) was obtained from 3-formylpyridine and 3-dimethylamino-1-(2-pyridyl)propan-1-one[19a] using Method F. δ_H 3.49 (2H, t), 3.71 (2H, t), 7.40 - 8.80 (7H, m), 9.26 (1H, s); δ_C 31.8 (t), 32.9 (t), 121.8 (d), 122.9 (d), 123.6 (d), 127.3(d), 132.1 (s),135.4 (d), 136.9 (d), 149.1 (d), 153.1 (s), 153.5 (d), 197.6 (s), 200.1 (s).

1,4--Di(3-Pyridyl)butan-1,4-dione **1g** (13 %, Method C; 40%, Method D) had m.p. 165 - 167°C (Found: C, 69.9; H, 5.0; N, 11.6. $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.0; N, 11.7%). ν_{max} 1695 cm^{-1} ; δ_H 3.47 (4H, s), 7.35 - 7.50 (2H, m), 8.00 - 8.60 (2H, m), 8.82 (2H, dd), 9.26 (2H, dd); δ_C 32.6 (t), 123.7 (d), 132.0 (s), 135.4 (d), 149.7 (d), 153.7 (d), 197.2 (s).

1,4-Di(4-pyridyl)butan-1,4-dione **1j** (32 %, Method C) had m.p. 197 - 198°C (Found: C, 69.6; H, 5.1; N, 11.2 $C_{14}H_{12}N_2O_2$ requires C, 69.7; H, 5.0; N, 11.6%). δ_H 3.81 (4H, s), 7.81 - 7.93 (4H, m), 8.80 - 8.90 (4H, m); δ_C 32.4 (t), 120.7 (d), 142.2 (s), 150.8 (d), 197.5 (s).

2,6-Di(4-phenyl-1,4-dioxobutyl)pyridine **3a** (45%) m.p. 115 - 117°C (Found: C, 75.0; H, 5.4; N, 3.3 $C_{25}H_{21}NO_4$ requires C, 75.2; H, 5.3; N, 3.5%) was obtained from 2,6-diformylpyridine and 3-dimethyl-amino-1-phenylpropan-1-one[19] using Method E. δ_H 3.30 - 3.60 (4H, m), 3.70 - 3.90 (4H, m), 7.30 - 8.30

(13H, m); δ_C 31.9 (t), 32.9 (t), 125.0 (d), 128.1 (d), 128.6 (d), 133.1 (d), 136.8 (s), 138.0 (d), 152.3 (s), 198.5 (s), 199.7 (s).

2,6-Di[4-(2-pyridyl)-1,4-dioxobutyl]pyridine **3b** (15%), m.p. 144 - 145°C (Found: C, 68.5; H, 4.95; N, 10.1 $C_{23}H_{19}N_3O_4$ requires C, 68.8; H, 4.8; N, 10.5%) was obtained from 2-formyl-pyridine and 2,6-bis(3-dimethylamino-1-oxopropyl)pyridine[9] using Method E. δ_H 3.78 (8H, s), 7.40 - 8.30 (9H, m), 8.71 (2H, d); δ_C 32.0 (t)*, 121.8 (d), 125.0 (d), 127.2 (d), 136.9 (d), 138.0 (d), 149.4 (d), 152.4 (s)*, 199.8 (s), 200.4 (s).

Using Method E, 1,4-bis(3-dimethylamino-1-oxopropyl)benzene[24] and 2-formylpyridine gave *1,4-di[4-(2-pyridyl)-1,4-dioxobutyl]benzene* **5b** (32%), m.p. 178 - 180°C (Found: C, 71.6; H, 5.1; N, 6.7 $C_{24}H_{20}N_2O_4$ requires C, 72.0; H, 5.0; N, 7.0%). δ_H (pyridine-d_6, 70°C) 3.55 (4H, t), 3.85 (4H, t), 7.20 - 8.20 (10H, m), 8.68 (2H, m); δ_C (pyridine-d_6, 70°C) 32.6 (t), 33.5 (t), 121.8 (d), 127.5 (d), 128.6 (d), 137.1 (d), 140.6 (s), 149.4 (d), 153.8 (s), 198.6 (s), 200.4 (s).

Reaction of 2,6-diformylpyridine and 1,4-bis(3-dimethylamino-1-oxopropyl)benzene.
1,4-Bis(3-dimethylamino-1-oxopropyl)benzene[24] (2.5 g, 9 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium bromide (0.42 g, 1.7 mmol) in DMF (12 ml) were heated under nitrogen to 85°C. Triethylamine (1.5 g, 9.4 mmol) and 2,6-diformylpyridine (1.2 g, 8.8 mmol) in DMF (7 ml) was were added over a period of 25 min and the mixture was stirred at 85°C until it became very viscous. The mixture was allowed stand at room temperature for 15 h and then extracted with water (5 x 50 ml). The solid polymer was collected and washed sequentially with benzene (25 ml), ethyl acetate (25 ml) and dichloromethane (25 ml) to yield the *polymeric diketone* **14**, (1.73 g) m.p. > 300°C (Found: C, 68.2; H, 5.3; N, 6.0 $(C_{19}H_{15}NO_4)_n$ requires C, 71.0; H, 4.7; N, 4.4%).

Reaction of 2,6-diformylpyridine and 2,6-bis(3-dimethylamino-1-oxopropyl)pyridine.
2,6-Bis(3-dimethylamino-1-oxopropyl)pyridine[9] (20 g, 5.7 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium bromide (0.29 g, 1.2 mmol) in DMF (8 ml) were heated under nitrogen to 85°C. Triethylamine (2.1 g, 13 mmol) and 2,6-diformylpyridine (0.77 g, 5.7 mmol) in DMF (4 ml) were added over a period of 20 min and the mixture was stirred at 85°C for 8 h until it became very viscous. The mixture was allowed stand at room temperature for 15 h and then extracted with water (5 x 50 ml). The solid polymer was collected and washed sequentially with benzene (25 ml), ethyl acetate (25 ml) and dichloromethane (25 ml) to yield the *polymeric diketone* **17**, (1.16 g) m.p. > 300°C (Found: C, 63.8; H, 5.1; N, 8.9 $(C_9H_7NO_2)_n$ requires C, 67.1; H, 4.4; N, 8.7%). δ_C (solid state) 34.9, 125.6, 137.8, 151.4, 199.7.

General procedure for the conversion of the 1,4-diones into pyrroles.
Method A: The appropriate dione (*ca.* 1.25 mmol) was heated with an excess of ammonium acetate (1.93 g, 12.5 mmol) at 125°C for 1.5 - 2 h and the cooled to room temperature and poured into water (40 ml). The aqueous mixture was extracted with dichloromethane (3 x 100 ml); the organic extracts were dried (Na_2SO_4) and evaporated to yield the pyrrolyl derivative, which was purified by chromatography from silica gel, using dichloromethane:ethyl acetate (10:1) as the eluant.

Method B: The appropriate dione (*ca.* 1.25 mmol) in ethanol (10 ml) was heated under reflux with ammonium carbonate (0.55 g) for 2 - 3 h. The volatile material was removed under reduced pressure and the product was either collected and washed with ethyl acetate, or purified by chromatography as for Method A.

Using Method B, 1-(2-pyridyl)pentan-1,4-dione **1a** gave 2-(5-methylpyrrol-2-yl)pyridine **2a** (94%), m.p. 72 - 73°C (lit.,[25] m.p. 74°C). δ_H 2.28 (3H, s), 5.95 (1H, m), 6.60 (1H, m), 6.91 - 7.03 (1H, m), 7.49 - 7.59 (2H, m), 8.37 (1H, m), 9.72 (1H, br, s); δ_C 13.1 (q), 108.0 (d), 108.4 (d), 117.8 (d), 119.8 (d), 129.9 (s), 130.8 (s), 136.5 (d), 148.3 (d), 150.5 (s).

1-(6-Methyl-2-pyridyl)pentan-1,4-dione **7a** gave *6-methyl-2-(5-methylpyrrol-2-yl)pyridine* **8a** (45%, Method B), b.p. 129 - 130°C at 2 mm Hg. (Found: C, 76.4; H, 7.0; N, 16.4 $C_{11}H_{12}N_2$ requires C, 76.7; H, 7.0; N, 16.3%). δ_H 2.08 (3H, s), 2.48 (3H, s), 5.92 (1H, s), 6.55 (1H, s), 6.50 - 6.80 (1H, m), 7.30 - 7.40 (2H, m), 10.20 (1H, br, s); δ_C 12.6 (q), 24.1 (q), 107.6 (d), 108.0 (d), 114.7 (d), 119.1 (d), 130.3 (s)*, 136.6 (d), 150.3 (s), 157.2 (s).

1-(3-Pyridyl)pentan-1,4-dione **1e** gave *3-(5-methylpyrrol-2-yl)pyridine* **2h** (47%, Method B), m.p. 156 - 158°C (Found: C, 75.5; H, 6.3; N, 17.5 $C_{10}H_{10}N_2$ requires C, 75.9; H, 6.4; N, 17.7%). δ_H 2.33 (3H, s), 5.98 (1H, t), 6.47 (1H, t), 7.23 (1H, dd), 7.72 (1H, dt), 8.35 (1H, dd), 8.75 (1H, d), 9.11 (1H, br s); δ_C 13.1 (q), 107.6 (d), 108.3 (d), 123.8 (d), 127.2 (s), 129.3 (s), 130.6 (d), 130.7 (s), 144.5 (d), 146.0 (d).

1-(4-Pyridyl)pentan-1,4-dione **1h** gave *4-(5-methylpyrrol-2-yl)pyridine* **2l** (71%, Method B), m.p. 220 - 222°C. (Found: C, 75.8; H, 6.3; N, 17.5 $C_{10}H_{10}N_2$ requires C, 75.9; H, 6.4; N, 17.7%). δ_H (DMSO-d_6) 3.55 (3H, s), 5.90 (1H, d), 6.69 (1H, d), 7.52 (2H, dd), 8.43 (2H, dd), 11.33 (1H, br, s); δ_C (DMSO-d_6) 12.8 (q), 108.3 (d), 109.2 (d), 116.8 (d), 126.9 (s), 131.7 (s), 139.5 (s), 149.7 (d).

1-Phenyl-4-(2-pyridyl)butan-1,4-dione **1b** gave *2-(5-phenylpyrrol-2-yl)pyridine* **2e** (90%, Method A), m.p. 106 - 107°C. (Found: C, 81.6; H, 5.5; N, 12.7 $C_{15}H_{12}N_2$ requires C, 81.8; H, 5.5; N, 12.7%). δ_H 6.50 - 7.60 (10H, m), 8.37 (1H, d), 10.20 (1H, br, s); δ_C 108.2 (d), 109.3 (d), 118.4 (d), 120.6 (d), 124.3 (d), 126.7 (d), 129.0 (d), 132.4 (s),132.6 (s), 134.3 (s), 136.6 (d), 148.9 (d), 150.5 (s).

1-Phenyl-4-(3-pyridyl)butan-1,4-dione **1f** gave *3-(5-phenylpyrrol-2-yl)pyridine* **2j** (90% Method B), m.p. 190 - 201°C. (Found: C, 81.4; H, 5.3; N, 12.4 $C_{15}H_{12}N_2$ requires C, 81.8; H, 5.5; N, 12.7%). δ_H (pyridine-d_5) 6.89 (1H, t), 6.91 (1H, t), 7.16 - 7.22 (2H, m), 7.34 (2H, t), 7.87 (2H, d), 8.00 - 8.10 (1H, m), 8.52 (1H, d), 9.33 (1H, d), 10.60 (1H, br, s); δ_C (pyridine-d_5) 108.9 (d), 109.7 (d), 123.5 (s), 125.1 (d), 126.6 (d), 129.2 (d), 129.6 (s), 131.4 (d), 133.6 (s), 146.6 (d), 147.3 (d).

1-Phenyl-4-(4-pyridyl)butan-1,4-dione **1i** gave *4-(5-phenylpyrrol-2-yl)pyridine* **2n** (67%, Method A), m.p. 260 - 261°C (Found: C, 81.9; H, 5.3; N, 12.7 $C_{15}H_{12}N_2$ requires C, 81.8; H, 5.5; N, 12.7%). δ_H (DMSO -d_6) 6.64 - 6.74 (1H, m), 6.88 7.00 (1H, m), 7.20 - 7.60 (4H, m), 7.72 - 7.94 (3H, m), 8.56 (2H, d); δ_C 108.3 (d), 110.7 (d), 117.8 (d), 124.4 (d), 126.5 (d), 128.6 (s), 130.1 (s), 132.0 (d), 135.2 (s), 139.0 (s), 149.8 (d).

1,4-Di(2-pyridyl)butan-1,4-dione **1c** gave *2-(5-(2-pyridyl)pyrrol-2-yl)pyridine* **2f** (90%, Method A), m.p. 90.5 - 92°C (Found: C, 75.8; H, 5.0; N, 18.6 $C_{14}H_{11}N_3$ requires C, 76.0; H, 5.0; N, 19.0%). δ_H 6.70 - 7.50 (8H, m), 8.47 (m, 2H), 10.60 (1H, br, s); δ_C 109.0 (d), 118.4 (d), 120.8 (d), 133.2 (s), 136.3 (d), 149.1 (d), 150.1 (s).

1-(2-Pyridyl)-4-(3-pyridyl)butan-1,4-dione **1d** gave *2-(5-(3-pyridyl)pyrrol-2-yl)pyridine* **2g** (85%, Method A), m.p. 140 - 141°C (Found: C, 75.8; H, 5.1; N, 18.8 $C_{14}H_{11}N_3$ requires C, 76.0; H, 5.0; N, 19.0%). δ_H 6.70 - 7.80 (7H, m), 8.40 (2H, m), 8.86 (1H, s), 10.60 (1H, br, s); δ_C 109.0 (d), 109.3 (d), 118.5 (d)*, 120.9 (d), 123.5 (d), 128.3 (s), 130.8 (s), 131.0 (d), 133.5 (s), 136.6 (d), 145.8 (d), 148.8 (d), 150.0 (s).

1,4-Di(3-pyridyl)butan-1,4-dione **1g** gave *3-(5-(3-pyridyl)pyrrol-2-yl)pyridine* **2k** (95%, Method A), m.p. 137 - 139°C (Found: C, 76.1; H, 4.9; N, 18.9 $C_{14}H_{11}N_3$ requires C, 76.0; H, 5.0; N, 19.0%). δ_H 6.58 - 6.61 (2H, m), 7.72 - 7.85 (4H, m), 8.39 (2H, d), 8.83 (2H, d); δ_C 109.4 (d), 117.6 (d), 123.7 (d), 130.7 (s), 131.3 (d), 145.4 (d), 147.5 (s).

Using Method A, 1,4-di(4-pyridyl)butan-1,4-dione **1j** gave *4-(5-(4-pyridyl)pyrrol-2-yl)pyridine* **2o** (85%), isolated as the monohydrate, m.p. 262°C (Found: C, 70.4; H, 5.4; N, 17.55 $C_{14}H_{11}N_3.H_2O$ requires C, 70.3; H, 5.5; N, 17.6%). δ_H (DMSO-d_6) 7.00 (2H, s), 7.84 (4H, d) 8.64 (4H, d) 11.80 (1H, br, s); δ_C (DMSO-d_6) 111.0 (d), 118.4 (d), 132.1 (s), 138.6 (d), 150.0 (s).

Using Method A, 2,6-di(4-phenyl-1,4-dioxobutyl)pyridine **3a** gave *2,6-di(5-phenylpyrrol-2-yl)pyridine* **4a** (90%), m.p. 225 - 227°C (Found: C, 82.6; H, 5.5; N, 11.2 $C_{25}H_{19}N_3$ requires C, 83.1; H, 5.3; N, 11.6%). δ_H (pyridine-d_5) 6.80 (4H, m), 7.00 - 7.80 (13H, m); δ_C (pyridine-d_5) 108.8 (d), 110.3 (d), 115.7 (d), 125.3 (d), 126.6 (d), 129.0 (s), 133.4 (s), 133.9 (d), 135.1 (d), 137.3 (d).

Using Method A, 2,6-di(2-pyridyl-1,4-dioxobutyl)pyridine **3b** gave *2,6-di[5-(2-pyridyl)pyrrol-2-yl]pyridine* **4b** (90%), m.p. 184 - 186°C (Found: C, 75.6; H, 4.5; N, 18.95 $C_{23}H_{17}N_5$ requires C, 76.0; H, 4.7; N, 19.3%). δ_H 6.70 - 6.95 (4H, m), 7.00 - 7.70 (9H, m), 8.65 (2H, d), 11.14 (2H, s br); δ_C 109.0 (d), 109.7 (d), 115.6 (d), 119.0 (d), 120.7 (d), 132.7 (s), 133.9 (s), 136.6 (d)*, 148.8 (d), 149.5 (s), 150.4 (s).

Using Method A, 1,4-di(2-pyridyl-1,4-dioxobutyl)benzene **5b** gave *1,4-di[5-(2-pyridyl)pyrrol-2-yl]benzene* **6b** (90%), m.p. 238 - 240°C (Found: C, 78.65; H, 5.1; N, 15.0 $C_{24}H_{18}N_4$ requires C, 79.5; H, 5.0; N, 15.5%). δ_H (pyridine-d_5) 6.90 -7.00 (4H, m), 7.10 - 7.70 (6H, m); δ_C (pyridine-d_5) 108.9 (d), 110.4 (d), 118.6 (d), 120.7 (d), 125.5 (d), 131.4 (s), 133.9 (s), 136.7 (d), 149.3 (d), 151.4 (s).

2-Hydroxymethyl-5-(6-methyl-2-pyridyl)pyrrole:

1-(6-Methyl-2-pyridyl)-5-acetoxypentan-1,4-dione **7b** (6.0 g, 0.24 mol) and ammonium carbonate (10.8 g) were heated at 70 - 80°C for 2h. A further amount of ammonium carbonate (10.8 g) was added and the mixture was heated for a further 2h. The reaction mixture was then cooled and water (300 ml) was added. The resulting suspension was extracted with ethyl acetate (3 x 200 ml) and the combined organic extracts were dried

($MgSO_4$) and evaporated. Purification of the crude product by chromatography from silica gel (1:1) gave two fractions. The first fraction (0.7 g) was further separated by radial chromatography using a Chromatotron to give *bis[5-(6-methyl-2-pyridyl)pyrrol-2-yl] ether* **11** m.p. 87 - 88°C (Found: C, 73.9; H, 6.2; N, 4.0 $C_{22}H_{22}N_4O$ requires C, 73.7; H, 6.2; N, 3.9%). δ_H 2.55 (6H, s), 3.66 (4H, s), 6.18 (2H, d), 6.63 (2H, d), 6.60 (2H, m), 6.90 (4H, m), 10.20 (2H, s, br); δ_C 24.3 (q), 49.9 (t), 107.5 (d), 109.8 (d), 115.1 (d), 119.6 (d), 131.0 (s), 131.5 (s), 136.6 (d), 150.2 (s), 157.3 (s), and *bis[5-(6-methyl-2-pyridyl)pyrrol-2-yl]methane* **10** m.p. 103 - 104.5°C (Found: C, 76.7; H, 6.2; N, 16.9 $C_{21}H_{20}N_4$ requires C, 76.8; H, 6.1; N, 17.0%). δ_H 2.37 (6H, s), 3.75 (2H, s), 5.86 (2H, m), 6.50 (2H, m), 6.75 (2H, m), 7.10 - 7.50 (4H, m), 10.10 (2H, s, br); δ_C 24.1 (q), 26.7 (t), 107.6 (d), 108.5 (d), 114.9 (d), 119.4 (d), 131.2 (s), 131.4 (s), 136.6 (d), 150.2 (s), 157.4 (s). The second fraction gave *2-(5-hydroxymethylpyrrol-2-yl)-6-methylpyridine* **9** (0.25 g, 11%), m.p. 119 - 120°C (Found: C, 70.2; H, 6.4; N, 14.7 $C_{11}H_{12}N_2O_4$ requires C, 70.2; H, 6.4; N, 14.9%). δ_H 2.52 (3H, s), 4.76 (2H, s), 5.00 (1H s br,), 6.10 (1H, d), 6.58 (1H, d), 6.84 (1H, d), 7.20 - 7.60 (2H, m), 10.60 (1H, s br); δ_C 23.9 (q), 57.5 (t), 108.1 (d)*, 115.8 (d), 119.9 (d), 131.3 (s), 133.8 (s), 137.0 (d), 150.2 (s), 157.0 (s).

***Conversion of Polymeric Diketone* 14 *into Pyrrole:Pyridine Polymer* 15.**

The polymeric diketone **14** (0.5 g) and liquid ammonia (*ca.* 5 ml) were sealed in a thick-walled glass tube (capacity *ca.* 15 ml) and heated in an autoclave at 150°C for 16 h. The mixture was cooled to 0°C, before the tube was opened and the *pyrrole:pyridine polymer* **15** was collected (0.43 g) m.p. > 300°C (Found: C, 75.8; H, 4.4; N, 14.6 $(C_{19}H_{13}N_3)_n$ requires C, 80.5; H, 4.6; N, 14.8%).

***Conversion of Polymeric Diketone* 17 *into Pyrrole:Pyridine Polymer* 18.**

Using a method analogous to that for the preparation of polymer **15**, the polymeric diketone **17** (0.5 g) was converted into *polymer* **18** (0.43 g), m.p. > 300°C (Found: C, 68.4; H, 5.6; N, 18.1 $(C_9H_6N_2)_n$ requires C, 76.0; H, 4.25; N, 19.7%). δ_C (solid state) 109.3, 119.9, 130.2, 136.5, 148.7.

***Preparation of N-alkylpyrroles*:**

The appropriate 1,4-dione (0.1 mol) in ethanol (40 ml) was refluxed with an excess of the appropriate alkylamine (*ca.* 0.5 mol) for 3h. The mixture was cooled to room temperature and extracted with dichloromethane (3 x 50 ml). The extracts were dried ($MgSO_4$) and evaporated to yield the crude pyrrole, which was distilled under reduced pressure.

Reaction of 1-(2-pyridyl)pentan-1,4-dione **1a** with, respectively, aqueous methylamine (30%), ethylamine, and aniline gave 2-(1,5-dimethylpyrrol-2-yl)pyridine **2b** (66%), b.p. 114 - 120°C at 2 mm Hg (lit.,[25] b.p. 125 - 130°C at 1.6 mm Hg) δ_H 2.20 (3H, s), 3.80 (3H, s), 5.92 (1H, d), 6.43 (1H, d), 6.84 - 6.97 (1H, m), 7.36 - 7.50 (2H, m), 8.51 (1H, m); δ_C 12.6 (q), 32.5 (q), 106.9 (d), 110.0 (d), 119.7 (d), 121.3 (d), 131.9 (s)*, 138.0 (d), 148.3 (d), 153.0 (s); *2-(1-ethyl-5-methyl-pyrrol-2-yl)pyridine* **2c** (80%), b.p. 114 -118°C at 1 mm Hg (Found: C, 77.2; H, 7.6, N, 14.9 $C_{12}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%) δ_H 1.22 (3H, t), 2.25 (3H, s), 4.42 (2H, q), 5.88 (1H, d), 6.42 (1H, d), 6.82 - 6.96 (1H, m), 7.35 - 7.50 (2H, m), 8.41 (1H, d); 2-(5-methyl-1-phenylpyrrol-2-yl)pyridine **2d** (75%), m.p. 68 - 69°C (lit.,[26] m.p. 71°C) δ_H 2.11 (3H, s), 6.11 (1H, dd), 6.70 - 7.40 (9H, m), 8.30 - 8.40 (1H, m).

Reaction of 1-(6-methyl-2-pyridyl)pentan-1,4-dione **7a** with methylamine gave *6-methyl-2-(1,5-dimethyl-pyrrol-2-yl)pyridine* **8b** (55%), b.p. 135 - 142°C at 0.15 mm Hg (Found: C, 77.5; H, 7.9; N, 15.1 $C_{12}H_{14}N_2$ requires C, 77.3; H, 7.6; N, 15.0%). δ_H 2.17 (3H, s), 2.47 (3H, s), 3.76 (3H, s), 5.91 (1H, d), 6.39 (1H, d), 6.70 - 6.80 (1H, m), 7.15 - 7.42 (2H, m); δ_C 12.5 (q), 24.4 (q), 32.4 (q), 106.8 (d), 109.9 (d), 119.0 (d), 118.2 (d), 131.9 (s), 132.5 (s), 136.3 (d), 152.5 (s), 156.6 (s).

Reaction of 1-(3-pyridyl)pentan-1,4-dione **1e** with aqueous methylamine (30%) gave *3-(1,5-dimethylpyrrol-2-yl)pyridine* **2i** (62%), as an oil (Found: C, 76.2; H, 7.0; N, 15.1 $C_{11}H_{12}N_2$ requires C, 76.7; H, 7.0; N, 15.2%). δ_H 2.27 (3H, s), 3.47 (3H, s), 5.97 (1H, d), 6.16 (1H, d), 7.22 - 7.27 (1H, m), 7.59 - 7.64 (1H, dq), 8,46 (1H, dt), 8.64 (1H, s); δ_C 12.7 (q), 31.6 (q), 106.9 (d), 108.6 (d), 123.1 (d), 129.1 (s), 130.2 (s), 131.5 (s), 135.2 (d), 147.3 (d), 149.2 (d).

Reaction of 1-(4-pyridyl)pentan-1,4-dione **1h** with aqueous methylamine (30%) gave *4-(1,5-dimethylpyrrol-2-yl)pyridine* **2m** (99%), m.p. 75.5 - 78°C (Found: C, 76.2; H, 7.0; N, 15.1 $C_{11}H_{12}N_2$ requires C, 76.5; H, 7.0; N, 15.0%). δ_H 2.30 (3H, s), 3.58 (3H, s), 5.99 (1H, d), 6.32 (1H, d), 7.26 (2H, d), 8.55 (2H, d); δ_C 12.8 (q), 32.1 (q), 107.5 (d), 109.9 (d), 121.9 (d), 131.2 (s), 133.3 (s), 140.9 (s), 149.8 (d).

1,4-Di(4-pyridyl)butan-1,4-dione **1j** and methylamine gave *4-(1-methyl-5-(4-pyridyl)pyrrol-2-yl)pyridine* **2p** (71%), m.p. 126 - 127°C (Found: C, 76.3; H, 5.5; N, 17.7 $C_{15}H_{13}N_3$ requires C, 76.6; H, 5.6; N, 17.9%). δ_H 3.75 (3H, s) 6.55 (2H, s), 7.40 (4H, d), 8.70 (4H, d); δ_C 34.9 (q), 111.4 (d), 122.4 (d), 136.1 (s), 140.0 (d), 150.1 (s).

N-Methylpyridinium Salts:

Method A: The appropriate pyridine (*ca.* 0.5 mmol) was heated under reflux in ethanol (5 ml) with an excess of iodomethane (1 ml) for 1 - 2h. The reaction was monitored by tlc and, on completion, the volatile material was removed by evaporation under reduced pressure and the crude product was recrystallised from ethanol.

Method B: The appropriate pyridine (*ca.* 0.01 mol) was heated at 120°C in a sealed tube with iodomethane (20 g) for 5 - 10h. The mixture was allowed to cool to room temperature over a period of 12h to yield the methiodide salt, which was crystallised from ethanol.

Using Method B, 2-(5-methylpyrrol-2-yl)pyridine gave *1-methyl-2-(5-methylpyrrol-2-yl)pyridinium iodide* (98%), m.p. 201 - 202°C (Found: C, 44.1; H, 4.4; N, 9.4; I, 42.4 $C_{11}H_{13}N_2I$ requires C, 44.0; H, 4.4; N, 9.3; I, 42.3%). δ_H (DMSO-d_6) 2.37 (3H, s), 4.34 (3H, s), 6.30 - 6.40 (1H, m), 7.00 - 7.11 (1H, m), 7.60 - 8.50 (m, 3H), 8.84 (1H, d); δ_C (DMSO-d_6) 12.7 (q), 47.6 (q), 110.8 (d), 119.5 (d)*, 121.7 (d), 125.4 (s), 137.5 (s), 142.9 (d), 145.6 (d), 146.4 (s).

Using Method A, 2-(1,5-dimethylpyrrol-2-yl)pyridine gave *1-methyl-2-(1,5-dimethylpyrrol-2-yl)pyridinium iodide* (35%), m.p. 184 - 185°C (Found: C, 46.4; H, 4.8; N, 8.9 $C_{12}H_{15}N_2I$ requires C, 45.9; H, 4.8; N, 8.9%). δ_H (DMSO-d_6) 2.32 (3H, s), 3.51 (3H, s), 4.24 (3H, s), 6.18 (1H, d), 6.70 (1H, d), 7.98 (2H, m), 9.08 (1H, d); δ_C (DMSO-d_6) 12.3 (q), 31.0 (q), 48.8 (q), 108.3 (d), 115.3 (d), 121.6 (d), 124.6 (d), 129.6 (s), 135.7 (s), 143.8 (d), 146.7 (d), 147.0 (s).

Using Method B, 6-methyl-2-(5-methylpyrrol-2-yl)pyridine gave *1,6-dimethyl-2-(5-methylpyrrol-2-yl) pyridinium iodide* (56%), m.p. 147 - 148°C (Found: C, 45.9; H, 4.8; N, 8.8 $C_{13}H_{17}N_2I$ requires C, 45.9; H, 4.8; N, 8.9%). δ_H (DMSO-d_6) 2.35 (3H, s), 2.82 (3H, s), 4.22 (3H, s), 6.19 (1H, t), 6.89 (1H, t), 7.50 - 8.00 (2H, m), 8.32 (1H, t), 11.86 (1H, s, br); δ_C (DMSO-d_6) 12.7 (q), 21.7 (q), 42.9 (q), 110.0 (d), 118.2 (d), 120.4 (d), 124.0 (d), 124.4 (s), 136.0 (s), 142.3 (d), 147.9 (s), 155.2 (s).

Using Method A, 6-methyl-2-(1,5-dimethylpyrrol-2-yl)pyridine gave *1,6-dimethyl-2-(1,5-dimethylpyrrol-2-yl) pyridinium iodide* (30%), m.p. 130 - 131°C (Found: C, 47.2; H, 5.4; N, 8.5 $C_{13}H_{17}N_2I$ requires C, 47.6; H, 5.2; N, 8.5%). δ_H (DMSO-d_6) 2.15 (3H, s), 2.70 (3H, s), 3.62 (3H, s), 4.00 (3H, s), 6.30 (1H, d), 6.68 (1H, d), 7.50 - 7.96 (2H, m), 8.16 - 8.50 (1H, m); δ_C (DMSO-d_6) 12.4 (q), 19.8 (q), 32.4 (q), 42.6 (q), 108.4 (d), 115.0 (d), 123.1 (d), 124.2 (d), 127.9 (s), 136.9 (s), 144.5 (d), 153.8 (s), 156.5 (s).

Using Method A, 3-(5-methylpyrrol-2-yl)pyridine gave *1-methyl-3-(5-methylpyrrol-2-yl)pyridinium iodide* (77%), m.p. 239 - 240°C (Found: C, 43.9; H, 4.0; N, 9.2 $C_{11}H_{13}N_2I$ requires C, 44.0; H, 4.4; N, 9.3%). δ_H (DMSO-d_6) 2.29 (3H, s), 4.35 (3H, s), 5.98 (1H, br, s), 6.86 (1H, t), 8.01 (1H, dd), 8.57 (1H, d), 8.62 (1H, dd), 9.24 (1H, s), 11.56 (1H, br s); δ_C (DMSO-d_6) 12.7 (q), 48.0 (q), 108.9 (d), 111.1 (d), 122.9(s), 127.5 (s), 132.4 (s), 133.4 (d), 135.4 (d), 139.2 (d), 139.6 (d).

Using Method A, 3-(1,5-dimethylpyrrol-2-yl)pyridine gave *1-methyl-3-(1,5-dimethylpyrrol-2-yl)pyridinium iodide* (52%) at the hemi-hydrate, m.p. 99 - 101°C (Found: C, 44.5; H, 4.9; N, 8.5 $C_{12}H_{15}N_2I$ $0.5H_2O$ requires C, 44.6; H, 5.0; N, 8.7%). δ_H (DMSO-d_6) 2.28 (3H, s), 3.65 (3H, s), 4.38 (3H, s), 6.02 (1H, d), 6.54 (1H, d), 8.15 (1H, dd), 8.57 (1H, d), 8.83 (1H, d), 9.08 (1H, s); δ_C (DMSO-d_6) 12.5 (q), 32.1 (q), 48.1 (q), 107.8 (d), 111.6 (d), 125.7 (s), 127.3 (s), 132.5 (d), 134.3 (s), 141.1 (d), 141.3 (d), 142.5 (d).

Using Method A, 4-(5-methylpyrrol-2-yl)pyridine gave *1-methyl-4-(5-methylpyrrol-2-yl)pyridinium iodide* (99%), m.p. 221 - 222°C (Found: C, 43.9; H, 4.0; N, 9.2 $C_{11}H_{13}N_2I$ requires C, 44.0; H, 4.4; N, 9.3%). δ_H (DMSO-d_6) 2.40 (3H, s), 4.11 (3H, s), 6.15 (1H, d), 7.25 (1H, d), 7.97 (2H, d), 8.60 (2H, d), 11.96 (1H, br, s); δ_C (DMSO-d_6) 12.9 (q), 45.8 (q), 111.5 (d), 117.3 (s), 117.6 (d), 125.2 (s), 138.8 (s), 144.1 (d), 144.6 (d).

Using Method A, 4-(1,5-dimethylpyrrol-2-yl)pyridine gave *1-methyl-4-(1,5-dimethylpyrrol-2-yl)pyridinium iodide* (80%), m.p. 234 - 236°C (Found: C, 45.9; H, 4.6; N, 8.8 $C_{12}H_{15}N_2I$ requires C, 45.9; H, 4.8; N, 8.9%). δ_H (DMSO-d_6) 2.33 (3H, s), 3.76 (3H, s), 4.21 (3H, s), 6.16 (1H, d), 7.04 (1H, d), 7.97 (2H, d), 8.67 (2H, d); δ_C (DMSO-d_6) 12.5 (q), 33.0 (q), 45.7 (q), 109.8 (d), 116.9 (d), 120.5 (d), 127.5 (s), 139.9 (s), 143.6 (d), 144.9 (s).

Using Method A, 3-(5-phenylpyrrol-2-yl)pyridine gave *1-methyl-3-(5-phenylpyrrol-2-yl)pyridinium iodide* (92%), m.p. 223-225°C. (Found: C, 52.8; H, 4.1; N, 7.5. $C_{16}H_{15}N_2I$ requires C, 53.1; H, 4.1; N, 7.7%). δ_H 3.34 (3H, s), 6.78 (1H, d), 7.07 (1H, d), 7.30 (1H, t), 7.46 (2H, t), 7.79 (2H, d), 8.10 (1H, dd), 8.68 (1H, d), 8.83 (1H, d), 9.35 (1H, s).

Using Method A, 4-(5-phenylpyrrolyl-2-yl)pyridine gave *1-methyl-4-(5-phenylpyrrol-2-yl)pyridinium iodide* (87%), m.p. 307 - 310°C. (Found: C, 52.9; H, 4.2; N, 7.6. $C_{16}H_{15}N_2I$ requires C, 53.1; H, 4.1; N, 7.7%). δ_H (DMSO-d_6) 4.23 (3H, s), 6.90 -7.02 (1H, m), 7.44 - 7.60 (4H, m), 7.86 - 8.04 (2H, m), 8.81 (4H, m); δ_C (DMSO-d_6) 46.0 (q), 110.6 (d), 117.9 (d), 118.8 (d), 125.2 (d), 127.7 (s), 128.0 (d), 128.8 (d), 130.6 (s), 140.3 (s), 144.3 (d), 144.5 (s).

Using Method A, 4-(5-(4-pyridyl)pyrrol-2-yl)pyridine gave *2,5-di(4-pyridyl)pyrrole bismethiodide* (72%), m.p. 200°C (decomp.) (Found: C, 38.3; H, 3.5; N, 8.3 $C_{16}H_{17}N_3$. $0.5H_2O$ requires C, 38.65; H, 3.8; N, 8.0%). δ_H 4.30 (6H, s), 7.58 (2H, s), 8.50 (4H, d), 8.97 (4H, d); δ_C 46.9 (q), 117.4 (d), 121.0 (d), 133.0 (s), 144.0 (d), 145.3 (s).

Using Method A, 4-(1-methyl-5-(4-pyridyl)pyrrol-2-yl)pyridine gave *1-methyl-2,5-di(4-pyridyl)pyrrole bismethiodide* (84%), as its hemihydrate, m.p. 266 - 267°C (Found: C, 38.7; H, 3.7; N, 7.7 $C_{17}H_{19}N_3I_2$ $0.5H_2O$ requires C, 38.7; H, 3.8; N, 8.0%). δ_H 4.02 (3H, s), 4.40 (6H, s), 7.27 (2H, s), 8.36 (4H, d), 9.08 (4H, d); δ_C 36.3 (q), 47.1 (q), 116.8 (d), 124.2 (d), 136.4 (s), 144.6 (d), 145.1 (s).

Using Method A, 2-(5-(3-pyridyl)pyrrol-2-yl)pyridine gave *1-methyl-3-(5-(2-pyridyl)pyrrol-2-yl)pyridinium iodide* (95%), m.p. 221°C. (Found: C, 50.8; H, 4.5; N, 11.2. $C_{16}H_{17}N_3I$ requires C, 50.8; H, 4.5; N, 11.1%); δ_H (DMSO-d_6) 4.38 (3H, s), 7.08 - 7.14 (2H, m), 7.34 - 7.39 (1H, m), 7.94 - 8.08 (1H, m), 8.11 (1H, dd), 8.64 (1H, dt), 8.76 (1H, d), 8.94 (1H, d), 9.52 (1H, s), 12.30 (1H, s br); δ_C 48.0 (q), 111.1 (d), 112.5 (d), 119.5 (d), 122.0 (d), 127.5 (d), 131.7 (s),* 134.6 (d), 137.9 (d), 138.3 (d), 140.9 (d), 141.4 (d), 147.9 (d), 148.5 (s). Method B failed to give the bismethiodide.

ACKNOWLEDGEMENTS

Financial support for this research from NATO Science Programme (for MK), the Fijian Government (for TNV), the Turkish Government (for PUC and OO), the EC ERASMUS Programme (for AF), the University of East Anglia (for JPS), and the SERC and Ciba-Geigy (for APW) is gratefully acknowledged.

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(*Received in USA* 8 *April* 1996; *revised* 3 *May* 1996; *accepted* 4 *May* 1996)