Acid−Base Catalysis in the Synthesis of Arylmethylene and Alkylmethine Pyrroles

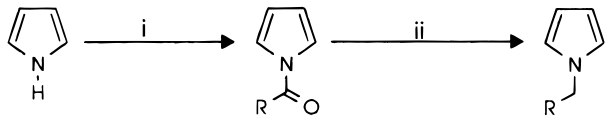
Claudius D'Silva* and Deborah A. Walker

Department of Chemistry & Materials, the Manchester Metropolitan University, Faculty of Science and Engineering, John Dalton Building, Chester Street, Manchester, M1 5GD, U.K.

Received July 24, 1997

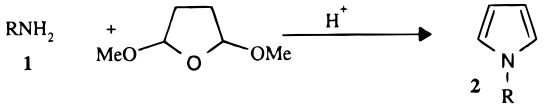
N-Alkyl and arylpyrroles are important intermediates in the formation of modified pyrrole polymers which have found uses in a wide variety of applications.[1,2] Our interest in these materials is in their use in molecular electronics[3] and sensors.[4] The preparation of these compounds traditionally has involved deprotonation of the 1-position of the pyrrole ring under nitrogen in a solution of THF with Na, K,[5] or n-BuLi[6] or under phase transfer conditions with t-BuOK[7] or NaOH followed by reaction of the alkali salt of pyrrole with an equivalent amount of acyl or alkyl halide. The preparation of arylmethylene pyrroles using these methods can prove problematic due to the reactivity of the 2-position[5] which can result in the formation of unreacted 2- and disubstituted pyrroles in addition to the desired 1-substituted product, thus reducing yield and hindering isolation. The above reaction, due to the use of basic conditions, renders itself unsuitable for the preparation of substituted pyrroles containing base labile protecting groups. In an attempt to overcome the problems of existing methods we recently reported a new method to arylmethylene pyrroles based on the reduction of *N*-acylpyrroles[8] (Scheme 1), undertaken in the presence of a Lewis acid, which is suitable for use with base labile and some acid labile protecting groups but involves a two-step reaction. An alternative single-step procedure to pyrroles, a modification of the Paal−Knoor method, involves the condensation of primary amines with 2,5-dimethoxytetrahydrofuran (DMT)[2,9,10] (Scheme 2). This reaction is not as general as it appears, and many compounds fail to produce the desired product due to rearrangement and

Scheme 1



Reagents (i) RCOCl / DMAP; (ii) BF_3:OEt_2, $NaBH_4$

Scheme 2



2a	R=CH_2Ph	(100%)	**2h**	R=CH-CH_2-Ph, COOH	(45%)
2b	CH_2Ph-4-OMe	(45%)	**2i**	CH-CH_2-Ph-4-OH, COOH	(20%)
2c	CH_2Ph-4-Br	(81%)	**2j**	CH-CH_2-CH_2-COOH, COOH	(21%)
2d	CH_2Ph-4-Cl	(17%)	**2k**	CH-CH_2-COOH, COOH	(56%)
2e	CH_2Ph-4-F	(81%)			
2f	CH_2Ph-4-CN	(44%)			
2g	CH_2Ph-4-NO_2	(94%)	**2l**	CH_2-CH_2-SO_3H	(87%)

further condensations[2] the mechanisms of which have not been identified. 1,4-Dichloro-1,4-dimethoxybutane,[11] a reactive functional equivalent of DMT, overcomes some of these problems, but is not readily available and is hydrolytically unstable. The condensation of amines with 1,3-dienes[12] or 2-butyne-1,4-diol[13] using organometallic catalysts affords an alternative approach to pyrrole derivatives, but these methods are not generally applicable and the yields are variable.

The limitations of existing methods for the conversion of amine groups into pyrrole groups led us to seek a general procedure for this conversion under neutral conditions. To demonstrate the effectiveness of the method, we applied the technique to the synthesis of several new *N*-arylmethylene (**2c**−**g**) and *N*-alkylmethine pyrrole (**2h**−**i**) derivatives, many of which were previously inaccessible.[10]

The commercial availability of DMT made it the reagent of choice for further investigations. Clanson−Kaass[14] et al. and Josey[15] achieved reaction of DMT with amines using refluxing AcOH. Schalkhammer et al.[2] reported the use of AcOH solutions or potassium phosphate buffer while Kashima et al.[10] used NaOAc but provided no experimental details. When used for the preparation of *N*-arylmethylene pyrrole derivatives, the above procedures resulted in negligible yields of product due to byproduct formation or solubility problems associated with the use of aqueous buffers. As related enamine type reactions were susceptible to acid−base catalysis,[16] it was decided to investigate the use of acid−base solvent mixtures as buffers in the coupling of benzylamine with DMT, as such mixtures have been used as eluents and

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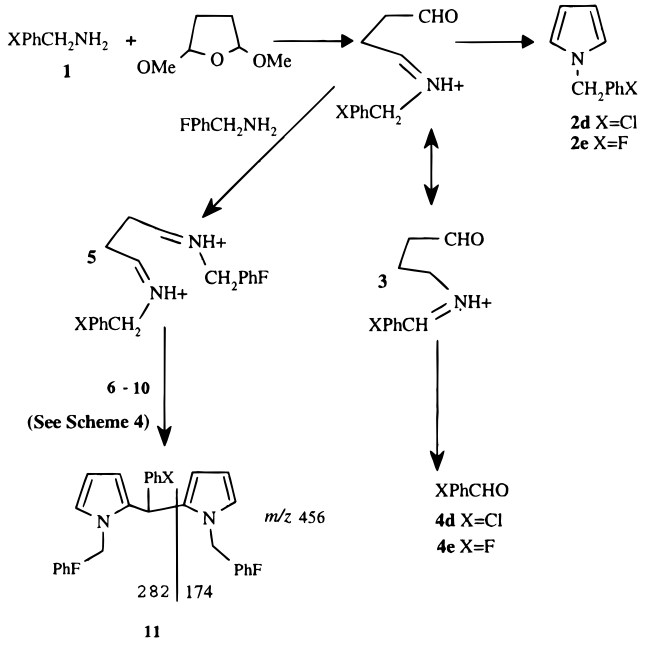
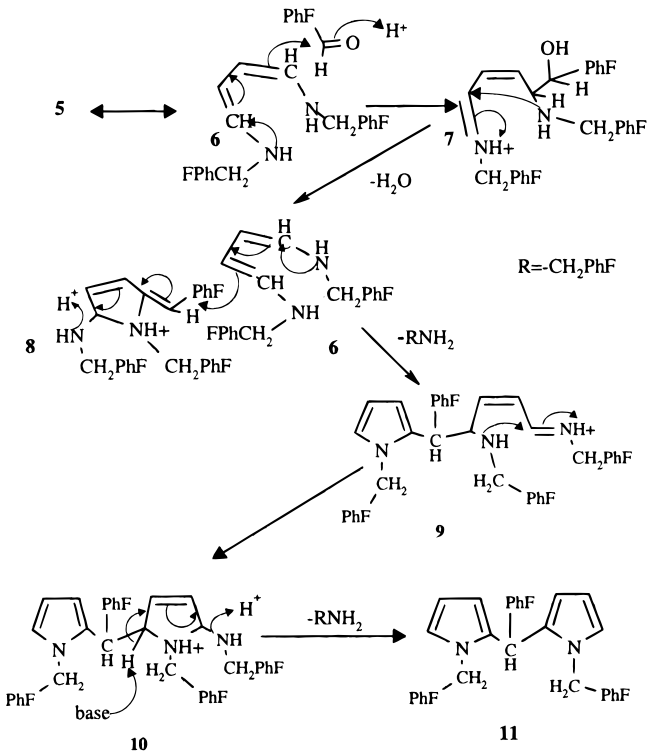
S0022-3263(97)01365-0 CCC: $15.00
Published on Web 08/26/1998

Scheme 3



buffers in ion-exchange chromatography.[17] The results obtained with a 2:1 molar mixture of AcOH (pK_a 4.7) and pyridine (pK_a 5.2) of 100% clearly showed this to be the optimum condition for quantitative coupling comparable with results obtained using 1,4-dichloro-1,4-dimethoxybutane (yield 90%).[11] The use of AcOH alone with a lower temperature of reaction to reduce byproduct formation resulted only in a 7% yield of product. Qualitatively the results obtained correlate well with the requirement for a solvent system buffered between pH 4−6 for optimum reaction,[16] as 2:1 molar acid−base combinations (method A) of AcOH and sodium acetate (pK_a 4.7), imidazole (pK_a 7.0), or triethylamine (TEA) (pK_a 10.9) under the same conditions afforded yields of 69, 70, and 2%, respectively, of product. Although a 2:1 mixture of AcOH and pyridine provided the highest yield, this value was found dependent on reaction time, as longer times resulted in lower yields, probably due to acid-catalyzed self-condensation reactions. To minimize this effect, the acidity of the reaction mixture was altered to a 1:1 ratio of AcOH and pyridine (method B), and in some cases, to enhance the solubility of amines such as amino acids within the mixture small amounts of water were added. The preparation of several new *N*-arylmethylene pyrroles (Scheme 2) such as **2c**, **2e**−**g** were undertaken either via methods A or B using either the free amine or the amine salt, the latter after conversion to the free amine in situ by stirring with aqueous pyridine/DMAP. Both methods generated exclusively the desired products in reasonable yield (see Scheme 2) except in the case of **2d** and **2e.** In the case of **2d** an additional product was isolated and identified by NMR, IR, and MS data as 4-chlorobenzaldehyde (**4d**) (19.5% yield). This product mechanistically can be accounted for if the initial enamine adduct formed between DMT and 4-chlorobenzylamine were to undergo a competing rearrangement (**3**) and hydrolysis reaction (see Scheme 3). In the case of **2e**, 4-fluorobenzaldehyde was not found but a product which analyzed by HRFAB as $C_{29}H_{23}F_3N_2$ (M^+) (calcd: 456.1813 found: 456.1881)

Scheme 4



was isolated, in 7% yield. The compound contained 18 *double bond equivalents* (DBE), and from the ^{1}H, ^{13}C NMR, CIMS (NH_3) data and the nature of reagents used, the structure was assigned to 5-(4-fluorophenyl)-1,1′-bis-((4-fluorophenyl)methyl)-1,1′*H*-dipyrromethane (**11**) which could be formed from the condensation of two 1-((4-fluorophenyl)methyl)-1*H*-pyrrole units and one 4-fluorobenzaldehyde unit. The ^{1}H NMR spectra showed a singlet at δ 5.0 for the methine proton which for related dipyrromethanes appear at δ 5.4−5.5.[18] The condensation of pyrroles with aldehydes to form porphyrins (the Rothemund reaction) has been proposed to involve the intermediate formation of a dipyrromethane derivative.[19] To test the significance of this mechanism to the formation of the dipyrromethane byproduct, 5-(4-fluorophenyl)-1,1′-bis((4-fluorophenyl)methyl)-1,1′*H*-dipyrromethane (**11**) was heated with chlorobenzaldehyde under the same conditions used to prepare **2e**. No dipyrromethane was observed by TLC, suggesting its formation by an alternative mechanism in this case. A mechanism which accounts for the dipyrromethane formed (see Scheme 4) involves the initial formation of a bis-enamine adduct (**5**) from DMT and two molecules of 4-fluorobenzylamine. The rearrangement of the adduct **5** to a diene (**6**), reaction with 4-fluorobenzaldehyde (**4e**), cyclization (**7**), and further reaction with a second molecule of diene **6** produces the dipyrromethane byproduct **11**. Dipyrromethanes are valuable intermediates in the synthesis of *meso*-phenylporphyrinoids;[18,20] the isolation of this byproduct could potentially afford a new route to their synthesis. While the mechanism proposed in Scheme 4 accounts for formation of the byproduct **11**, it is not the only mechanism. A [4 + 2] cycloaddition of intermediate **6** (see

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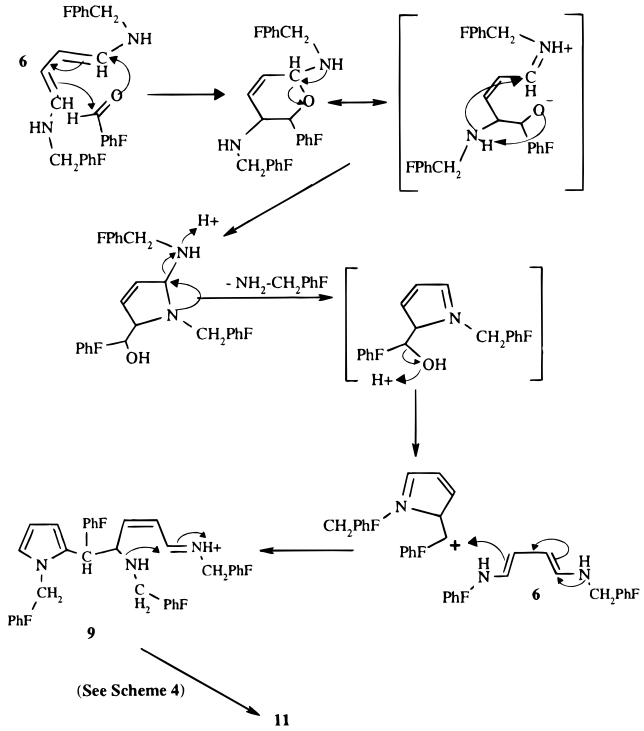
Scheme 5



Scheme 4) with the carbonyl group of 4-fluorobenzaldehyde (**4e**) can be proposed as an alternative mechanism which by a series of cyclizations and rearrangement reactions (see Scheme 5) produces intermediate **9** common to both mechanisms which is converted to **11**, according to Scheme 4. This mechanism (see Scheme 5) overcomes the need to eliminate water (**7** to **8**) which is the most difficult step of Scheme 4.

Although low yields of **2b** and **2d** were obtained via this method, better yields of both compounds of 71 and 79%, respectively, were obtained by the reduction of acylpyrroles[8] (Scheme 1). Bromo-substituted pyrrole derivatives such as **2c** are useful precursors in lithiation and Heck coupling reactions. The preparation of 2−3 g quantities of **2c** and its higher homologue 1-((4-bromophenyl)ethyl)-1*H*-pyrrole were investigated using this method and yields of 62 and 51% obtained, respectively.

To further test the versatility of the new reaction conditions, it was decided to investigate its use in the preparation of several new *N*-alkylmethine pyrroles based on the amino acids phenylalanine, tyrosine, aspartic acid, glutamic acid, and taurine, which were previously reported to be inaccessible using DMT.[2,10] The results obtained in the preparation of compounds **2h**−**l** (see Scheme 2) clearly show the new procedure to produce the desired product, and of the two methods used B produced the highest yields on average due to the milder conditions of reaction.

In summary, the procedures described here have been applied to a range of diverse amines as well as glutathione peptides and amine-functionalized polymers. We have in the course of our studies identified two of the major byproducts produced by this reaction and accounted for their formation.

Experimental Section

General. Commercial reagents were used as received with the exception of AcOH, pyridine, and pyrrole, which were distilled before use. ^{1}H and ^{13}C NMR spectra were recorded at 270.05 and 67.80 MHz, respectively using TMS as an internal standard. Mp's were uncorrected. MS were recorded at 70 eV and ESIMS at 3.5 or −3.0 kV, 70 °C, in a H_2O/MeOH (1:1) matrix. Elemental analysis was performed at the Micro Analytical Service, Manchester Univ, UK. Preparative thin-layer chromatography (PTLC) was performed on silica ($CHCl_3$ as eluent) unless otherwise stated.

Method A (2a). A mixture of amine (4.5 mmol) and DMT (5.0 mmol) was dissolved in a mixture of pyridine (16.1 mmol) and AcOH (34.7 mmol) and heated for 4−20 h on a steam bath. The reaction mixture was then dissolved in EtOAc, washed with $KHSO_4$ solution and water, dried over $MgSO_4$, and reduced in vacuo to give an oil. The residue redissolved in diethyl ether was vacuum filtered through Celite, evaporated, and chromatographed on silica.

Method B (2b−g). A mixture of amine (5.6 mmol) and DMT (5.6 mmol) was dissolved in a mixture of pyridine (94.0 mmol), AcOH (94.0 mmol), and water (3.0 mL) and heated on an oil bath for 4−60 h at 100 °C. The reaction mixture was then reduced in vacuo, triturated with acetone, and filtered, and the compound was confirmed by NMR and MS.

1-(Phenylmethyl)-1*H*-pyrrole (2a). Prepared from benzylamine using method A. PTLC ($CHCl_3$/light petroleum (1:4)) yielded the compound as an oil (100%).[8,11] ^{1}H NMR ($CDCl_3$) δ 5.10 (2 H, s), 6.20 (2 H, t, J = 2.0), 6.70 (2 H, t, J = 2.0), 7.20 (2 H, d, J = 8.1), 7.40 (3 H, m); ^{13}C NMR ($CDCl_3$) δ 52.5, 108.7, 120.9, 121.4, 128.5, 131.7, 137.1; MS m/z 157 (M^+) and 91; HRMS Calcd for $C_{11}H_{11}N$ (M^+) 157.0891, found 157.0891.

1-((4-Methoxyphenyl)methyl)-1*H*-pyrrole (2b). Prepared from 4-methoxybenzylamine using method B, and PTLC yielded the compound as an oil (45%).[8] ^{1}H NMR ($CDCl_3$) δ 3.80 (3 H, s), 5.00 (2 H, s), 6.20 (2 H, t, J = 2.2), 6.65 (2 H, t, J = 2.2), 6.85 (2 H, d, J = 8.2), 7.05 (2 H, d, J = 8.2); ^{13}C NMR ($CDCl_3$) δ 52.8, 55.7, 108.5, 114.0, 121.0, 128.5, 128.9; MS m/z 187 (M^+), 121, and 91; HRMS Calcd for $C_{12}H_{13}NO$ (M^+) 187.0997, found 187.0997.

1-((4-Bromophenyl)methyl)-1*H*-pyrrole (2c). Prepared from 4-bromobenzylamine hydrochloride (9 mmol) after conversion of the salt in situ to the free amine base by dissolving in a mixture of pyridine (0.19 mol), water (3.0 mL), and DMAP (0.9 mol %) and heating at (70 °C; 0.5 h). Then AcOH (0.19 mol) and DMT were added according to method B (70 (C; 50 h), excluding water. PTLC ($CHCl_3$/light petroleum (1:4)) yielded the compound as a brown oil (85%). ^{1}H NMR ($CDCl_3$) δ 5.05 (2 H, s), 6.20 (2 H, t, J = 2.2), 6.65 (2 H, t, J = 2.2), 6.95 (2 H, d, J = 8.9), 7.45 (2 H, d, J = 8.8); ^{13}C NMR ($CDCl_3$) δ 53.2, 108.4, 121.1, 126.9, 127.6, 128.6, 138.1; MS m/z 237/235 (M^+), 171, 169, 156, 154; HRMS Calcd for $C_{11}H_{10}N^{79}Br$ (M^+) 234.9996, found 234.9997. Anal. Calcd for $C_{11}H_{10}NBr$: C, 55.96; H, 4.27; N, 5.93. Found: C, 55.97; H, 4.3; N, 5.93.

1-((4-Chlorophenyl)methyl)-1*H*-pyrrole (2d). Prepared from 4-chlorobenzylamine using method B, excluding water. PTLC yielded the compound as an oil (17%).[8] ^{1}H NMR ($CDCl_3$) δ 5.07 (2 H, s), 6.20 (2 H, t, J = 2.2), 6.70 (2 H, t, J = 2.2), 7.05 (2 H, d, J = 10.4), 7.30 (2 H, d, J = 10.4); ^{13}C NMR ($CDCl_3$) δ 52.8, 108.0, 120.0, 128.1, 128.7; MS m/z 191/193 (M^+), 125/127, 89, 77; HRMS Calcd for $C_{11}H_{10}NCl$ (M^+) 191.0501, found 191.0491.

4-Chlorobenzaldehyde (4d). The compound was isolated as an oil (19.5%) during the preparation of **2d**. IR (film) 3026 (C−H), 2744, 2405, 1705 (CHO), 1598 (C−C), and 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.05 (2 H, d, J = 8.9), 7.85 (2 H, d, J = 8.9), 10.00 (1 H, s); MS m/z 140/142 (M^+), 139, 113, 111, and 75; HRMS Calcd for C_7H_5OCl (M^+) 140.0029, found 140.0029.

1-((4-Fluorophenyl)methyl)-1*H*-pyrrole (2e). Prepared from 4-fluorobenzylamine using method B (70 °C; 60 h), excluding water. PTLC ($CHCl_3$/light petroleum 1:4)) yielded the compound as an oil (81%), ^{1}H NMR ($CDCl_3$) δ 5.00 (2 H, s), 6.20 (2 H, s), 6.68 (2 H, s), 7.00 (2 H, d, J = 9.0), 7.25 (2 H, d, J = 9.0); ^{13}C NMR ($CDCl_3$) δ 52.5, 108.7, 115.3, 115.7, 120.9, 128.6, 128.7, 133.9, 160.4, 164.0; MS m/z 175 (M^+), 157, 109, 91; HRMS Calcd for $C_{11}H_{10}NF$ (M^+) 175.0797, found 175.0797. Anal. Calcd for $C_{11}H_{10}NF$: C, 75.41; H, 5.75; N, 7.99. Found: C, 75.38; H, 5.9; N, 8.13.

5-(4-Fluorophenyl)-1,1′-bis-(4-fluorophenyl)methyl)-1,1′*H*-dipyrromethane (11). The compound was isolated as an oil

(7.0%) during the preparation of **2e.** ^{1}H NMR ($CDCl_3$) δ 4.8 (2H, d, J = 8.4), 4.9 (2H, s), 5.0 (1H, s), 5.75 (1H, m), 5.9 (1H, t, J = 2.4), 6.1 (1H, t, J = 3.6), 6.15 (1H, t, J = 2.4), 6.55 (1H, t, J = 2.4), 6.6 (1H, t, J = 2.4), 6.8 (12H, m); ^{13}C NMR ($CDCl_3$) δ 41.5, 49.8, 52.6, 106.9, 109.1, 109.3, 114.8, 115.1, 115.3, 115.4, 115.6, 115.7, 119.8, 121.2, 121.5, 128.0, 128.2, 128.5, 128.6, 129.8, 129.9, 134.0, 134.3, 136.0, 139.5, 159.6, 160.3, 163.3, 164.1; CIMS (NH_3) m/z 457 ($M + H)^+$, 100), 349, 282, 176, 126, 109; HRFAB Calcd for $C_{29}H_{23}N_2F_3$ (M^+) 456.1813, found 456.1881.

4-Cyanobenzylhexamine Hydrobromide. Condensation of 1-bromomethyl-4-cyanobenzene with hexamethylene tetramine in chloroform according to general procedures[21,22] afforded a colorless solid (97%), mp 230 (C (decom). ^{1}H NMR (DMSO-d_6) δ 4.20 (2 H, s), 4.45 (3 H, d, J = 14.0), 4.60 (3 H, d, J = 14.0), 5.10 (6 H, s), 7.70 (2 H, d, J = 6.7), 8.00 (2 H, d, J = 6.7).

4-Cyanobenzylamine Hydrochloride. Hydrolysis of 4-cyanobenzylhexamine hydrobromide in EtOH/HCl according to general procedures[21,22] afforded a colorless solid (90%), mp 270 °C (dec); ^{1}H NMR ($CDCl_3$) δ 4.10 (2 H, s), 7.67 (2 H, d, J = 9.0), 7.81 (2 H, d, J = 9.0); MS m/z 132 ([M − HCl]$^+$), 131 ([M − H_2-Cl]$^+$), 104, 75, 51, 36; HRMS Calcd for $C_8H_8N_2$ ([M − HCl]$^+$), 132.0687, found 132.0687.

1-((4-Cyanophenyl)methyl)-1*H*-pyrrole (2f). Prepared from 4-cyanobenzylamine hydrochloride (12 mmol) after conversion to the free amine base by dissolving in a mixture of pyridine (0.19 mol), water (2.0 mL), and DMAP (0.9 mol %) and heating at (70 °C; 0.5 h). Then AcOH (0.19 mol) and DMT were added (70 °C; 50 h). PTLC ($CHCl_3$/light petroleum (1:4)) yielded the compound as a colorless solid (44%), mp 46−49 °C; ^{1}H NMR ($CDCl_3$) δ 5.05 (2 H, s), 6.38 (2 H, d, J = 2.1), 6.80 (2 H, d, J = 2.1), 7.22 (2 H, d, J = 9.0), 7.61 (2 H, d, J = 9.0); ^{13}C NMR ($CDCl_3$) δ 52.6, 109.2, 111.4, 118.5, 121.1, 127.2, 132.4, 143.7; MS m/z 182 (M^+), 154, 116, 89; HRMS Calcd for $C_{12}H_{10}N_2$ (M^+) 182.0844, found 182.0844. Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.12; H, 5.49; N, 15.38. Found: C, 78.85; H, 5.38; N, 15.49.

1-((4-Nitrophenyl)methyl)-1*H*-pyrrole (2g). Prepared from 4-nitrobenzylamine hydrochloride (7.8 mmol) after conversion of the salt in situ to the free amine base by dissolving in a mixture of pyridine (0.19 mol), water (6.0 mL), DMAP and (0.16 mol %) and heating at (70 °C; 1.0 h). Then AcOH (0.19 mol) and DMT were added according to method B (78 °C; 48 h), excluding water. PTLC yielded the compound as an off white solid (94%), mp 56−59 °C; ^{1}H NMR ($CDCl_3$) δ 5.30 (2 H, s), 6.40 (2 H t, J = 2.0), 6.90 (2 H, t, J = 2.1), 7.30 (2 H, d, J = 8.9), 8.20 (2 H, d, J = 8.9); ^{13}C NMR ($CDCl_3$) δ 52.4, 109.3, 121.1, 123.8, 127.2, 145.6, 147.3; MS m/z 202 (M^+), 156, 136, 106, 89, 78; HRMS Calcd for $C_{11}H_{10}N_2O_2$ (M^+) 202.0742, found 202.0742. Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.53; H, 4.95; N, 13.86. Found: C, 65.68; H, 5.12; N, 13.92.

***N*-(1-Carboxy-2-phenylethyl)-1*H*-pyrrole (2h).** Prepared from L-phenylalanine using methods A and B, respectively. PTLC yielded the compound as an off brown solid via method A (45%) and via method B (83%), mp 94−97° C. ^{1}H NMR ($CDCl_3$) δ 3.3 (1H, dd, J = 8.8, 8.8), 3.5 (1H, dd, J = 5.0, 5.0), 4.8 (1H, dd, J = 5.0, 5.0), 6.15 (2H, t, J = 2.2), 6.7 (2H, t, J = 2.2), 7.05 (2H, m), 7.25 (3H, m); ^{13}C NMR ($CDCl_3$) δ 39.2, 63.5, 109.1, 120.0, 136.0, 176.0; MS m/z 215 (M^+), 170; HRMS Calcd for $C_{13}H_{13}NO_2$ (M^+) 215.0946, found 215.0946.

***N*-(1-Carboxy-2-(4-hydroxyphenyl)ethyl)-1*H*-pyrrole (2i).** Prepared from L-tyrosine using method A. PTLC yielded the compound as an off white solid (20%), mp 140−144 °C. ^{1}H NMR ($(CD_3)_2CO$) δ 3.3 (1H, dd, J = 8.8, 8.8), 3.45 (1H, dd, J = 5.8, 5.8), 5.0 (1H, dd, J = 5.8, 5.8), 6.1 (2H, t, J = 2.0), 6.8 (2H, d, J = 8.2), 6.9 (2H, t, J = 2.0), 7.0 (2H, d, J = 8.8); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 38.0, 63.3, 107.8, 115.0, 126.6, 129.3, 155.6; MS m/z 231 (M^+), 107; HRMS Calcd for $C_{13}H_{13}NO_3$ (M^+) 231.0895, found 231.0895.

***N*-(1,3-Dicarboxypropyl)-1*H*-pyrrole (2j).** Prepared from L-glutamic acid using methods A and B, respectively, and PTLC to yield the compound as an oil (12%) via method A and (21%) by method B, respectively. ^{1}H NMR ($CDCl_3$) δ 2.35−2.55 (4H, m), 4.8 (1H, dd, J = 5.8, 5.8), 6.2 (2H, s), 6.75 (2H, s); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 27.0, 28.8, 59.6, 107.3, 119.0, 171.0, 173.0; CIMS (NH_3) m/z 198 ($M + H)^+$, 154; HRMS Calcd for $C_9H_{14}NO_4$ ($M + H)^+$ 198.0766, found 198.0766.

(D,L)-*N*-(1,2-Dicarboxyethyl)-1*H*-pyrrole(2k). Prepared from D,L-aspartic acid according to methods A and B respectively and PTLC to yield the compound as an oil via method A (9%) and by method B (56%), respectively. ^{1}H NMR ($(CD_3)_2CO$) δ 3.05 (1H, dd, J = 7.1, 7.1), 3.35 (1H, dd, J = 8.0, 8.0), 5.15 (1H, t, J = 7.1), 6.2 (2H, s), 6.75 (2H, s); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 36.6, 57.7, 107.7, 120.0, 170.4, 170.5; CIMS (NH_3) m/z 184 ($M + H)^+$, 140, 94; HRMS Calcd for $C_8H_{11}NO_4$ ($M + H)^+$ 184.0610, found 184.0610.

2-(Ethylsulfonic acid)-1*H*-pyrrole (2l). Prepared from taurine using method B. The compound was obtained as an off white solid (87%), mp 327−328 °C (dec). ^{1}H NMR (D_2O) δ 3.4 (2H, t, J = 7.1), 4.4 (2H, t, J = 7.1), 6.2 (2H, s), 6.9 (2H, s); ^{13}C NMR (D_2O) δ 49.6, 57.16, 113.2, 126.7; ESIMS m/z 173.5 ([M − H]$^-$, 45.3).

Acknowledgment. Financial support from EPSRC under Grant GR/F 20937 is gratefully acknowledged, and Dr. Ballintine and B. Stein of the EPSRC MS service center, Swansea, for EI/CI, FAB, and ESIMS measurements.

Supporting Information Available: Copies of NMR spectra (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO971365D

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