Gas-Phase Synthesis of N-Unsubstituted 3-Hydroxypyrroles and 1*H*-Pyrrol-3(2*H*)-ones

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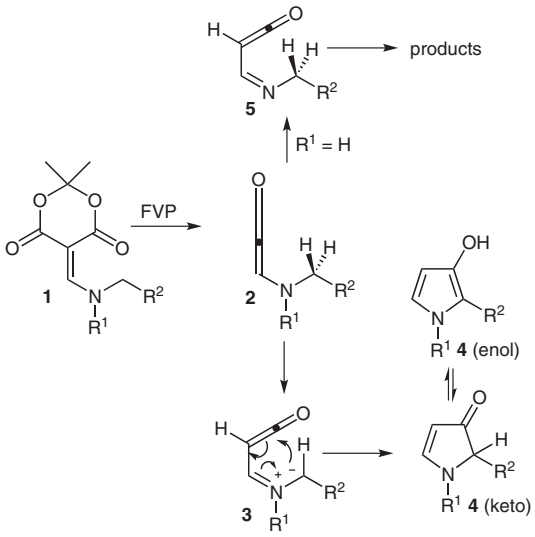
Abstract: Flash vacuum pyrolysis (FVP) at 600 °C of methylaminomethylene derivatives of Meldrum's acid bearing electron-withdrawing substituents on the methyl group, provides N-unsubstituted 3-hydroxypyrroles and/or 1*H*-pyrrol-3(2*H*)-ones in high yield.

Key words: gas-phase reactions, pericyclic reactions, heterocycles, pyrroles, regioselectivity

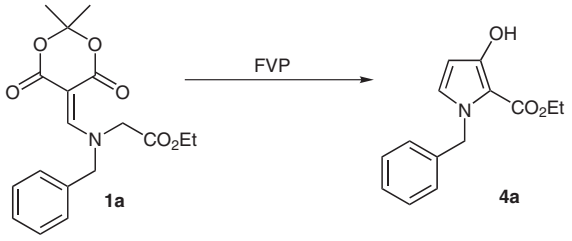
In previous papers[1] we have shown that flash vacuum pyrolysis (FVP) at 600 °C of N,N-disubstituted aminomethylene derivatives of Meldrum's acid **1** provides a convenient synthetic route to sensitive 1-substituted,[2] 1,2-disubstituted,[2] 1,2,2-trisubstituted[2] and 1,2,5-trisubstituted[3] 3-hydroxypyrroles **4** (enol) and/or 1*H*-pyrrol-3(2*H*)-ones **4** (keto) (Scheme 1). The mechanism involves creation of the methyleneketene intermediates **2**, followed by a sigmatropic 1,4-hydrogen transfer to provide azomethine ylides **3** which collapse to **4** by electrocyclisation.[4,5] In the case of **1** (R^1 = H), an alternative 1,3-hydrogen atom shift at the methyleneketene stage provides an imidoylketene **5**, which leads to alternative products (Scheme 1).[6]



Scheme 1

Formation of N-unsubstituted 3-hydroxypyrroles by the Meldrum's route has been unsuccessful, despite the exploration of various possible N-protecting groups.[7,8] The synthesis of such compounds still relies on multistep condensation sequences.[1a,9]

We have also shown that in the cases where the group R^1 (Scheme 1) also contains an α-hydrogen atom, the H-shift step can be highly selective.[2] Thus, for **1** (R^1 = Me, R^2 = CH_2Ph) hydrogen transfer from the benzyl group (leading to 1-methyl-2-phenyl-3-hydroxypyrrole) takes place exclusively.[2] We have now discovered that an ester substituent activates the hydrogen transfer even more than a benzyl group; FVP of **1a** (R^1 = CH_2Ph, R^2 = CO_2Et) gives ethyl 1-benzyl-3-hydroxypyrrole-2-carboxylate (**4a**) exclusively in 30% isolated yield (Scheme 2).



Scheme 2

Taken together, these results suggest that an ester group might be capable of activating the 1,4-hydrogen shift by four orders of magnitude or more. Therefore, in the R^1 = H case, this mode of reaction might be able to compete with the 1,3-H shift leading to the imidoylketenes. This idea is supported by DFT calculations at B3LYP/6-31G** level,[10] which show that the 1,4-H shift (leading to the pyrrolone) is preferred by approximately 50 kJ mol^{-1} over the 1,3-shift leading to the imidoylketene (Figure 1).

The predictions have been borne out in practice (Figure 2). The precursors **1b–e** were first made in 89–97% yield by treatment of methoxymethylene Meldrum's acid **6** with the hydrochloride salt of the appropriate amino acid esters in acetonitrile containing triethylamine. Yields of the nitrile **1f** and the trifluoromethyl compound **1g** were 89% and 95%, respectively.

FVP of **1b** at 600 °C gave the known ethyl 3-hydroxypyrrole-2-carboxylate (**4b**) (85%) as a yellow solid (2 steps; 81% overall). The two known routes[9] to this compound

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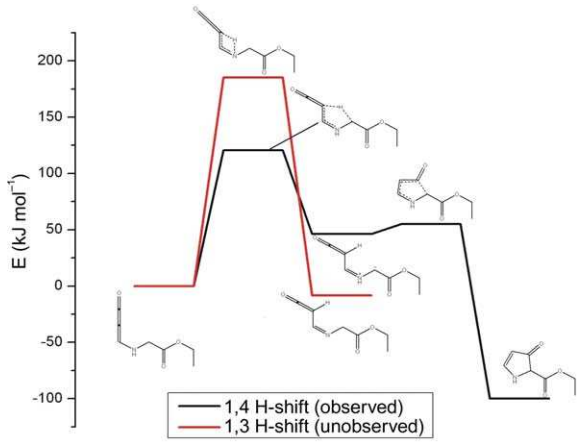

Figure 1 Energy surface for pyrrolone formation and (in red) imidoylketene formation (cf. Scheme 1, $R^2 = CO_2Et$)

both require four steps (11 and 28% overall yields, respectively). In order to confirm that the N-*H* does not migrate during the pyrolysis, the N-*D* analogue **1b′** was generated in situ in the inlet tube. No deuterium incorporation at C(4) or C(5) of **4b** could be detected by ^{1}H NMR spectroscopy.

The other amino acid ester derivatives **1c–e** gave the new pyrrolones **4c–e** in 65–99% yields. The nitrile **4f** was obtained in 74% yield, and exists exclusively as the hydroxypyrrole tautomer in $CDCl_3$.

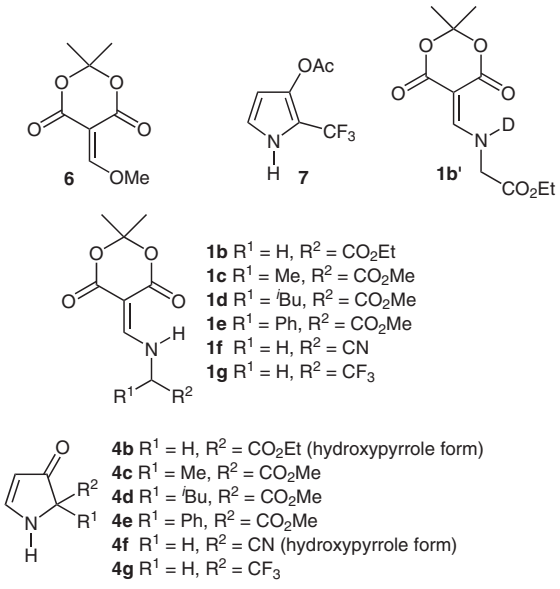

Figure 2

All the previous examples have employed a conjugative electron-withdrawing group to stabilize the site of high electron density in the azomethine ylide **3**. In order to explore if a strong inductive electron-withdrawing group can fulfill this role, the trifluoromethyl compound **1g** was synthesized and pyrolysed at 600 °C. The ^{1}H NMR spectrum of the pyrolysate showed that at least four significant components were formed, but the pyrrole **4g** could be identified as a 54:46 mixture of its hydroxypyrrole [δ = 5.84 ppm (^3J and ^4J = 3.0 Hz; $^5J_{HF}$ = 1.0 Hz); 6.61 (^3J = 3.2 Hz and $^5J_{HF}$ = 0.7 Hz)] and pyrrolone (δ = 5.30 and 8.09 ppm) tautomers in $CDCl_3$. The hydroxypyrrole was present exclusively in DMSO-d_6 (δ = 5.70 and 6.69 ppm). This product was characterized as its acetoxy derivative **7**.

In conclusion, the work described here provides a convenient two-step synthesis of 1-unsubstituted 3-hydroxypyrroles and pyrrol-3(2*H*)-ones bearing conjugative, or strong inductively electron-withdrawing groups at the 2-position. The application of this methodology to provide a two-step route to 3-hydroxypyrrole itself is reported in the following paper.[11]

^{1}H and ^{13}C NMR spectra were recorded at 250 MHz and 63 MHz respectively unless otherwise stated. Chemical shifts are given in ppm relative to TMS. ^{13}C NMR signals refer to one CH unless otherwise stated. Mass spectra were recorded under electron impact conditions. Flash vacuum pyrolysis (FVP) reactions were carried out by distillation of the substrate in vacuo through an electrically heated silica furnace tube (35 × 2.5 cm). Products were trapped in a U-tube situated at the exit point of the furnace and cooled with liquid N_2. Pyrolysis conditions are quoted as follows: substrate, quantity (*w*), furnace temperature (T_f), inlet temperature (T_i), pressure range (*P*), pyrolysis time (*t*) and product(s).

Aminomethylene Derivatives of Meldrum's Acid 1

Method A:[7] Et_3N (0.28 mL per mmol) was added to a solution of the amine salt (1 equiv) in MeCN (15 mL per mmol). Methoxymethylene Meldrum's acid **6** (1 equiv) was added and the solution stirred for 2.5 h at r.t. The solvent was removed, the residue dissolved in CH_2Cl_2 and washed with HCl (2 M, 100 mL). The organic layer was dried ($MgSO_4$) and the solvent removed to give the product.

Method B:[2] To a solution of the amine (1 equiv) dissolved in the minimum amount of MeCN, was added methoxymethylene Meldrum's acid **6** (1 equiv). The mixture was allowed to stand for 15 min and the solvent removed to give the product.

Ethyl [(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)benzylamino]acetate (1a)

Using general method B, *N*-benzylglycine ethyl ester (1.93 g, 10 mmol) gave **1a** as a yellow solid (2.60 g, 75%); mp 88–89 °C (from EtOH).

^{1}H NMR ($CDCl_3$): δ (2 rotamers, 9:1; major rotamer) = 8.24 (s, 1 H), 7.27–7.14 (m, 5 H), 4.63 (s, 2 H), 4.47 (s, 2 H), 4.02 (q, ^3J = 7.1 Hz, 2 H), 1.55 (s, 6 H), 1.09 (t, ^3J = 7.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ (major rotamer) = 166.80 (C_q), 165.29 (C_q), 160.49 (C_q), 159.59, 132.70 (C_q), 128.73 (2 CH), 127.90 (2 CH), 102.53 (C_q), 86.12 (C_q), 64.37 (CH_2), 61.18 (CH_2), 52.53 (CH_2), 26.06 (2 CH_3), 13.51 (CH_3) (one CH overlapping).

MS: *m*/*z* (%) = 228 [(M – 119)$^+$, 17], 271 (39), 216 (17), 91 (100).

Anal. Calcd for $C_{18}H_{21}NO_6$: C, 62.2; H, 6.05; N, 4.05. Found: C, 62.0; H, 6.1; N, 4.15.

Ethyl [(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)amino]acetate (1b)

Using general method A, glycine ethyl ester hydrochloride (1.396 g, 10 mmol) gave **1b** as a yellow solid (2.432 g, 95%); mp 125–126 °C (from EtOH).

^{1}H NMR ($CDCl_3$): δ = 9.65 (br s, 1 H), 8.09 (d, ^3J = 14.5 Hz, 1 H), 4.25 (q, ^3J = 7.2 Hz, 2 H), 4.19 (d, ^3J = 6.1 Hz, 2 H), 1.69 (s, 6 H), 1.30 (t, ^3J = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 167.35 (C_q), 165.23 (C_q), 163.63 (C_q), 160.21, 104.52 (C_q), 86.06 (C_q), 62.34 (CH_2), 50.24 (CH_2), 26.90 (2 CH_3), 14.04 (CH_3).

MS: *m*/*z* (%) = 257 (M^+, 49), 200 (55), 155 (61), 126 (100).

Anal. Calcd for $C_{11}H_{15}NO_6$: C, 51.35; H, 5.85; N, 5.45. Found: C, 51.4; H, 5.85; N, 5.45.

Methyl 2-[(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)amino]propionate (1c)

Using general method A, alanine methyl ester hydrochloride (0.349 g, 2.5 mmol) gave **1c** as a yellow solid (0.623 g, 97%); mp 125–126 °C (from EtOH).

^{1}H NMR ($CDCl_3$): δ = 9.74 (br s, 1 H), 8.11 (d, ^3J = 14.8 Hz, 1 H), 4.23 (quint, ^3J = 7.3 Hz, 1 H), 3.78 (s, 3 H), 1.67 (s, 6 H), 1.59 (d, ^3J = 7.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 170.46 (C_q), 165.15 (C_q), 163.67 (C_q), 158.29, 104.72 (C_q), 85.73 (C_q), 57.02, 53.06 (CH_3), 26.88 (2 CH_3), 18.74 (CH_3).

MS: *m*/*z* (%) = 257 (M^+, 30), 200 (30), 199 (13), 155 (18), 140 (100), 96 (55).

Anal. Calcd for $C_{11}H_{15}NO_6 \cdot 0.1H_2O$: C, 51.0; H, 5.8; N, 5.4. Found: C, 50.95; H, 5.75; N, 5.4.

Methyl 2-[(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)amino]-4-methylpentanoate (1d)

Using general method A, leucine methyl ester hydrochloride (0.454 g, 2.5 mmol) gave **1d** as a yellow solid (0.687 g, 92%); mp 106–107 °C (from EtOH).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.64 (br m, 1 H), 8.08 (d, ^3J = 14.5 Hz, 1 H), 4.13 (td, ^3J = 9.0, 5.5 Hz, 1 H), 3.80 (s, 3 H), 1.79 (m, 2 H), 1.71 (s, 6 H), 1.66 (m, 1 H), 0.97 (d, ^3J = 7.0 Hz, 3 H), 0.96 (d, ^3J = 7.0 Hz, 3 H).

^{13}C NMR (90 MHz, $CDCl_3$): δ = 170.34 (C_q), 165.20 (C_q), 163.63 (C_q), 158.67, 104.76 (C_q), 85.70 (C_q), 60.70 (CH_3), 52.89, 41.53 (CH_2), 26.90 (CH_3), 26.82 (CH_3), 24.34, 22.50 (CH_3), 21.41 (CH_3).

MS: *m*/*z* (%) = 299 (M^+, 16), 240 (15), 182 (100), 138 (18), 96 (15).

Anal. Calcd for $C_{14}H_{21}NO_6$: C, 56.2; H, 7.0; N, 4.75. Found: C, 56.4; H, 7.0; N, 4.75.

Methyl [(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)amino]phenylacetate (1e)

Using general method A, phenylglycine methyl ester hydrochloride (2.060 g, 10 mmol) gave **1e** as a yellow solid (2.828 g, 89%); mp 178–181 °C (from EtOH).

^{1}H NMR ($CDCl_3$): δ = 10.32 (dd, ^3J = 14.5, 6.6 Hz, 1 H), 8.08 (d, ^3J = 14.5 Hz, 1 H), 7.45–7.32 (m, 5 H), 5.21 (d, ^3J = 6.6 Hz, 1 H), 3.80 (s, 3 H) 1.45 (s, 3 H), 1.43 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 168.75 (C_q), 164.93 (C_q), 163.46 (C_q), 158.05, 134.21 (C_q), 129.50, 129.41 (2 CH), 127.14 (2 CH), 104.68 (C_q), 86.29 (C_q), 64.52, 53.26 (CH_3), 26.77 (2 CH_3).

MS: *m*/*z* (%) = 319 (M^+, 31), 260 (72), 202 (100), 158 (100).

Anal. Calcd for $C_{16}H_{17}NO_6$: C, 60.55; H, 5.35; N, 4.40. Found: C, 60.25; H, 5.05; N, 4.35.

[(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)amino]acetonitrile (1f)

Using general method A, aminoacetonitrile hydrogen sulfate (1.54 g, 10 mmol) gave **1f** as a yellow solid (1.86 g, 89%); mp 182–184 °C (from EtOH).

^{1}H NMR (DMSO-d_6): δ = 9.89 (s, 1 H), 8.34 (s, 1 H), 4.62 (s, 2 H), 1.62 (s, 6 H).

^{13}C NMR (DMSO-d_6): δ = 160.71, 117.03, 104.16, 85.77, 37.76 (CH_2), 26.75 (2 CH_3), two carbonyl signals not apparent due to restricted rotation.

MS: *m*/*z* (%) = 211 (M^+, 71), 210 (60), 153 (100), 109 (16), 108 (45).

Anal. Calcd for $C_9H_{10}N_2O_4$: C, 51.45; H, 4.75; N, 13.35. Found: C, 51.75; H, 4.6; N, 13.0.

2,2-Dimethyl-5-[(2,2,2-trifluoroethylamino)methylene]-1,3-dioxane-4,6-dione (1g)

Using general method B, 2,2,2-trifluoroethylamine (1.98 g, 20 mmol) gave **1g** as an orange solid (4.82 g, 95%); mp 161–163 °C (from EtOH).

^{1}H NMR ($CDCl_3$): δ = 9.60 (br s, 1 H), 8.17 (d, ^3J = 13.7 Hz, 1 H), 3.99 (quint, ^3J = 8.3 Hz, 2 H), 1.73 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 165.16 (C_q), 163.11 (C_q), 160.92, 122.67 (C_q, q, $^1J_{HF}$ = 281.4 Hz), 105.18 (C_q), 87.58 (C_q), 50.42 (q, $^2J_{HF}$ = 33.7 Hz, CH_2), 26.88 (2 CH_3).

MS: *m*/*z* (%) = 253 (M^+, 81), 196 (100), 167 (99), 151 (46), 123 (32).

Anal. Calcd for $C_9H_{10}F_3NO_4$: C, 42.7; H, 3.95; N, 5.55. Found: C, 42.85; H, 3.85; N, 5.45.

Ethyl 1-Benzyl-3-hydroxypyrrole-2-carboxylate (4a)

FVP of **1a** (*w* 0.35 g, T_f 600 °C, T_i 200 °C, *P* 10^{-3} Torr, *t* 1 h) gave **4a** as a yellow solid (0.074 g, 30%); (decomposed on attempted distillation).

^{1}H NMR ($CDCl_3$): δ = 7.35–7.19 (m, 3 H), 7.05–7.0 (m, 2 H), 6.66 (d, ^3J = 3.0 Hz, 1 H), 5.82 (d, ^3J = 3.0 Hz, 1 H), 5.29 (s, 2 H), 4.25 (q, ^3J = 7.1 Hz, 2 H), 1.21 (t, ^3J = 7.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 162.52 (C_q), 155.85 (C_q), 138.21 (C_q), 128.30 (2 CH), 127.86, 127.28, 126.24 (2 CH), 105.78 (C_q), 96.59, 59.81 (CH_2), 52.84 (CH_2), 14.18 (CH_3).

MS: *m*/*z* (%) = 245 (M^+, 24), 200 (10), 199 (19), 91 (100).

HRMS: *m*/*z* calcd for $C_{14}H_{15}NO_3$ (M^+): 245.1052; found: 245.1046.

Ethyl 3-Hydroxypyrrole-2-carboxylate (4b)

FVP of **1b** (*w* 1.09 g, T_f 600 °C, T_i 200 °C, *P* 3.6–3.8 × 10^{-2} Torr, *t* 5 min) gave a brown oil (0.718 g), which was purified by Kugelrohr distillation to give **4b** as a yellow solid (0.558 g, 85%); mp 37–38 °C, bp 72 °C (0.5 mmHg) [lit.[9a] 110 °C (0.05 Torr)]

^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.30 (br s, 1 H), 7.74 (br s, 1 H), 6.71 (br s, 1 H), 5.87 (t, ^3J = 2.9 Hz, 1 H), 4.35 (q, ^3J = 7.1 Hz, 2 H), 1.37 (t, ^3J = 7.1 Hz, 3 H).

MS: *m*/*z* (%) = 155 (53), 109 (100), 81 (41).

Deuteriation Experiment

Compound **1b** (0.124 g) was heated in methanol-d_4 (ca. 1 mL) and the solvent removed under high vacuum. Pyrolysis of the resulting solid (T_f 600 °C, T_i 200 °C, *P* 2.8 – 3.2 × 10^{-2} Torr, *t* 8 min) gave a brown oil. The product **4b** was dissolved in $CDCl_3$. By ^{1}H NMR spectroscopy, no deuterium incorporation at C(4) or C(5) of **4b** could be detected.

Methyl 2-Methyl-3-oxo-2,3-dihydro-1*H*-pyrrole-2-carboxylate (4c)

FVP of **1c** (*w* 0.306 g, T_f 600 °C, T_i 200 °C, *P* 2.3–2.4 × 10^{-2} Torr, *t* 7 min) gave an orange oil, which solidified on concentration from an acetone solution to give **4c** as an orange solid (0.182 g, 99%); mp 79–81 °C.

^{1}H NMR ($CDCl_3$): δ = 8.10 (s, 1 H), 6.65 (br s, 1 H), 5.09 (d, ^3J = 3.5 Hz, 1 H), 3.71 (s, 3 H), 1.57 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 198.19 (C_q), 168.28 (C_q), 165.48, 97.63, 69.32 (C_q), 53.16 (CH_3), 20.99 (CH_3).

MS: *m*/*z* (%) = 155 (M^+, 100), 96 (87), 112 (23).

HRMS: *m*/*z* calcd for $C_7H_9NO_3$ (M^+): 155.05769; found: 155.05791.

Methyl 2-Isobutyl-3-oxo-2,3-dihydro-1*H*-pyrrole-2-carboxylate (4d)

FVP of **1d** (*w* 0.450 g, T_f 600 °C, T_i 170 °C, *P* 2.6–4.2 × 10^{-2} Torr, *t* 24 min) gave **4d** as an orange solid (0.240 g, 81%); mp 91–92 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (t, ^3J = 3.5 Hz, 1 H), 6.11 (br s, 1 H), 5.16 (d, ^3J = 3.5 Hz, 1 H), 3.76 (s, 3 H), 2.16 (q, ^3J = 9.0 Hz, 1 H), 1.73 (m, 2 H), 0.91 (d, ^3J = 7.0 Hz, 3 H), 0.90 (d, ^3J = 7.0 Hz, 3 H).

^{13}C NMR (90 MHz, $CDCl_3$): δ = 196.86 (C_q), 168.02 (C_q), 165.50, 99.02, 73.29 (C_q), 53.11, 43.99 (CH_2), 25.39, 23.47 (CH_3), 23.03 (CH_3).

MS: *m*/*z* (%) = 197 (M^+, 11), 154 (53), 141 (100), 126 (22), 109 (32), 94 (69).

HRMS: *m*/*z* calcd for $C_{10}H_{15}NO_3$ (M^+): 197.10464; found: 197.10460.

Methyl 3-Oxo-2-phenyl-2,3-dihydro-1*H*-pyrrole-2-carboxylate (4e)

FVP of **1e** (*w* 1.050 g, T_f 600 °C, T_i 220 °C, *P* 4.2–5.5 × 10^{-2} Torr, *t* 10 min) gave **4e** as a brown solid (0.463 g, 65%); mp 177–179 °C (from toluene).

^{1}H NMR (DMSO-d_6): δ = 9.41 (br s, 1 H), 8.56 (br s, 1 H), 7.57–7.35 (m, 5 H), 4.88 (s, 1 H), 3.67 (s, 3 H).

^{13}C NMR (DMSO-d_6): δ = 194.41 (C_q), 167.04, 166.91 (C_q), 135.13 (C_q), 127.92 (2 CH), 127.85, 126.31 (2 CH), 94.09, 73.24 (C_q), 52.88 (CH_3).

MS: *m*/*z* (%) = 217 (M^+, 17), 185 (20), 130 (22), 105 (47), 84 (100).

HRMS: *m*/*z* calcd for $C_{12}H_{11}NO_3$ (M^+): 217.07334; found: 217.07334.

2-Hydroxy-3-cyanopyrrole (4f)

FVP of **1f** (*w* 0.208 g, T_f 600 °C, T_i 200 °C, *P* 2.3–2.9 × 10^{-2} Torr, *t* 10 min) gave **4f** as an off-white solid (0.0877 g, 74%); mp 92–94 °C.

^{1}H NMR ($CDCl_3$): δ = 11.23 (br s, 1 H), 9.72 (br s, 1 H), 6.78 (d, ^3J = 2.5 Hz, 1 H), 5.65 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 154.07 (C_q), 123.07, 114.78 (C_q), 97.85, 85.11 (C_q).

MS: *m*/*z* (%) = 108 (M^+, 100), 84 (31), 53 (47).

HRMS: *m*/*z* calcd for $C_5H_4N_2O$ (M^+): 108.03181; found: 108.03181.

3-Acetoxy-2-trifluoromethylpyrrole (7)

Pyrolysis of **1g** (*w* 1.0126 g, T_f 600 °C, T_i 200 °C, *P* 3.0–3.2 × 10^{-2} Torr, *t* 22 min) gave an orange oil which contained **4g** as a mixture of tautomers (see discussion). The oil was dissolved in CH_2Cl_2 (20 mL), Et_3N (0.7 mL) and AcCl (0.5 mL) were added and the mixture stirred for 2.5 h at r.t. The solution was washed with HCl (2 M; 2 × 40 mL) and $NaHCO_3$ (sat.; 40 mL). The organic layer was dried ($MgSO_4$) and the solution concentrated to give an orange oil. Kugelrohr distillation gave **7** as a pale yellow oil (0.2208 g, 28%); bp 64–66 °C (2 Torr).

^{1}H NMR (360 MHz, $CDCl_3$): δ = 8.69 (br s, 1 H), 6.72 (td, ^3J = 3.3 Hz, ^4J = 0.7 Hz, 1 H), 6.16 (td, ^3J = 3.2 Hz, ^4J = 0.7 Hz, 1 H), 2.28 (s, 3 H).

^{13}C NMR (90 MHz, $CDCl_3$): δ = 164.84 (C_q), 136.47 (C_q), 120.51 (C_q, q, $^1J_{HF}$ = 264.8 Hz), 118.35, 103.81, 20.45 (CH_3), one C_q not apparent.

MS: *m*/*z* (%) = 193 (M^+, 30), 151 (100), 131 (63).

HRMS: *m*/*z* calcd for $C_7H_6F_3NO_2$ (M^+): 193.03451; found: 193.03477.

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