Methylene Meldrum's Acid Derivatives of Indoxyl and Their Cyclization Reactions under Flash Vacuum Pyrolysis Conditions

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Abstract: Pure indoxyl can be obtained in 75% yield by flash vacuum pyrolysis (FVP) of 2′-azidoacetophenone at 650 °C. Reaction of indoxyl with methoxymethylene Meldrum's acid takes place at the 1-position, and FVP of the resulting derivative provides 1-hydroxy-9*H*-pyrrolo[1,2-*a*]indol-9-one (54%). FVP of the isomeric 2-methylene compound gives pyrano[3,2-*b*]indol-2(5*H*)-one (42%).

Key words: gas-phase reactions, cyclisations, heterocycles, pyrolysis, ketenes

We report the synthesis and flash vacuum pyrolysis (FVP) behaviour of the two possible methylene-2,2-dimethyl-1,3-dioxane-4,6-dione derivatives, **1** and **2**[1] of indoxyl **3** (Figure 1). We have carried out similar reactions in the 3-hydroxypyrrole series,[2] but, in extending the work to the indole series we were surprised to discover that synthetic routes to indoxyl (3-hydroxy-1*H*-indole, **3**) are themselves poorly defined, perhaps because it is highly prone to aerial oxidation to indigo.[3] Indoxyl (**3**) is often generated in situ[4] and, indeed, its melting point has been recorded only five times in the *Beilstein* database (and two values are clearly in error). We have, therefore, developed a practical gas-phase route to indoxyl (**3**) by FVP of 2′-azidoacetophenone (**4**). A similar strategy was employed for our recent synthesis of the first heteroindoxyl.[5] FVP is an excellent technique for making such air-sensitive compounds because solvent, workup, and the presence of oxygen during the transformation are all avoided.

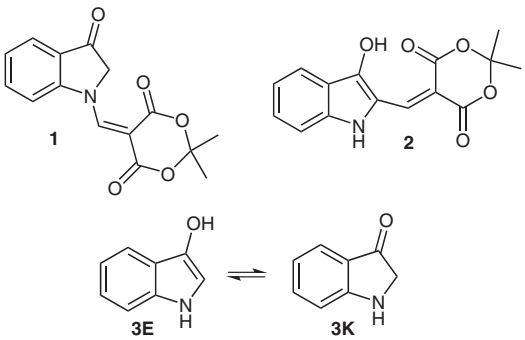
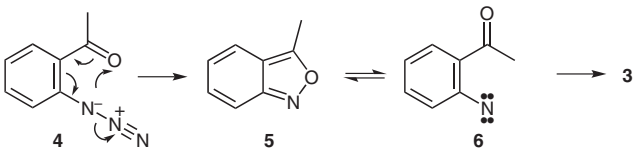


Figure 1

Solution-phase thermolysis of 2′-azidoacetophenone (**4**) is known to give anthranil **5**.[6] Although it has been reported that further pyrolysis provides indoxyl (**3**),[7a] attempts to replicate this process by spray pyrolysis provided indoxyl (isolated as indigo) in only 15% yield.[7b] Under FVP conditions, decomposition of **4** is essentially complete around 300 °C and anthranil **5** is indeed the major product between 300–400 °C (Scheme 1). The temperature profile (Figure 2) shows that above 400 °C indoxyl **3K** begins to appear, identified by the CH_2 resonance (δ = 3.89) in its ^{1}H NMR spectrum.[4] For preparative purposes, FVP of **4** at 650 °C provided indoxyl (**3**) in 75% yield, sufficiently pure for further reactions (Scheme 1).



Scheme 1

The formation of indoxyl (**3**) is likely to involve a CH insertion reaction of 2-acetylphenylnitrene (**6**), but the anthranil **5** may be formed either via the nitrene or by anchimeric assistance by the acetyl group in the nitrogen elimination. This issue has been thoroughly explored in the solution-phase reaction.[8]

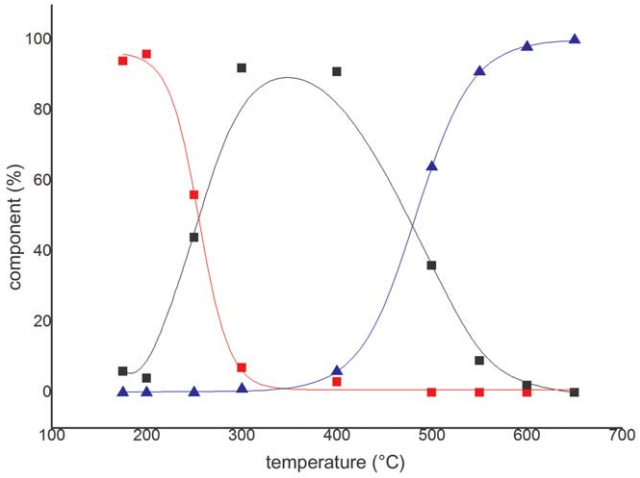


Figure 2 Temperature-conversion graph for FVP of **4** (shown in red) detailing the formation of **5** (kinetic product; shown in black) and **3** (thermodynamic product; shown in blue)

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Decomposition of the isomeric 4′-azidoacetophenone (**7**) cannot take place via anchimeric assistance so the temperature dependence of the decomposition of **7** was briefly studied. It is clear from Figure 3 that key points of the temperature profile lie ca. 50 °C higher in the case of the *para*-isomer **7**. Hence, we favour the anchimeric assistance mechanism (Scheme 1) for the formation of **3**, as previously found under other conditions.[8]

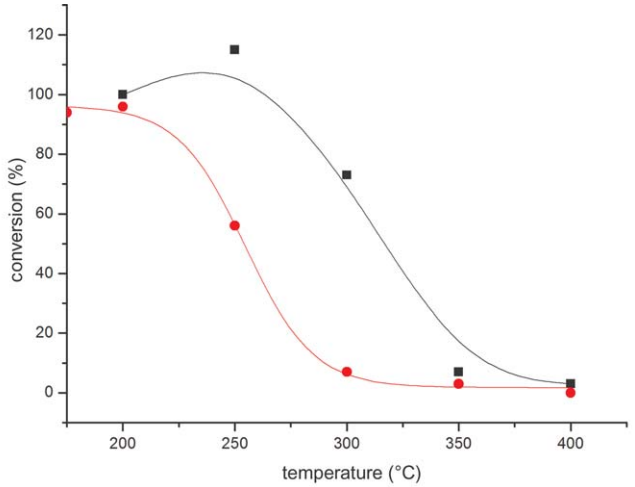


Figure 3 Temperature-conversion graph for FVP of **4** (shown in red) and **7** (shown in black)

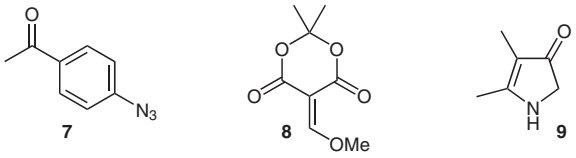
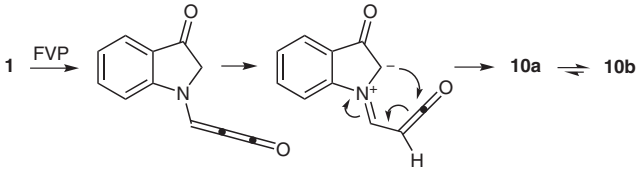


Figure 4

Reaction of methoxymethylene Meldrum's acid **8** with 4,5-dimethyl-1,2-dihydro-3*H*-pyrrol-3-one (**9**) in acetonitrile solution takes place at the 2-position (Figure 4).[2] In contrast indoxyl (**3**) behaves as a typical secondary amine and reaction takes place at the nitrogen atom to provide **1** in 63% yield. FVP of most (dialkylamino)methylene derivatives of Meldrum's acid provide 1,2-dihydro-3*H*-pyrrol-3-ones by 1,4-hydrogen shift and electrocyclisation.[9,10] A similar process indeed occurs with **1** (Scheme 2) to give 1-hydroxypyrrolo[1,2-*a*]indol-9-one **10** (54%). This ring system is not widely known[11] and **10** is the first example of a pyrrolo[1,2-*a*]indol-9-one with an electron-donating group in the 1-position.

Compound **10** can adopt three possible tautomeric forms, **10a**, **10b**, and **10c** (Figure 5). The dione form **10a** is easily



Scheme 2

eliminated by its ^{13}C NMR spectrum, which shows only six CH resonances. The indolone **10b** and the pyrrolone **10c** were distinguished by the absence of the widely spaced doublets expected for H2 and H3 of a pyrrolone structure such as **10c**,[12] and the correspondence of the ^{13}C NMR chemical shift for C9 (δ_C = 175.13) with that of pyrrolo[1,2-*a*]indol-9-one itself (δ_C = 175.04).[13] Therefore, the available evidence is consistent with the hydroxypyrrole structure **10b**.

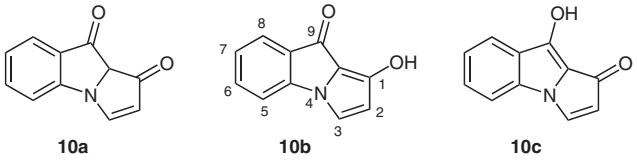
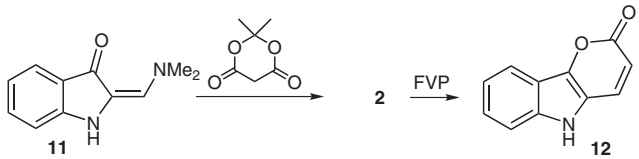


Figure 5

In principle 1-hydroxypyrrolo[1,2-*a*]indol-9-one (**10b**) can participate in intramolecular hydrogen bonding, which is common in analogous fused six-membered rings.[14] The OH signal of **10b** occurs at δ_H = 6.97 showing that the appropriate bond angles in two fused five-membered rings are too large for effective hydrogen bonding.

The 2-methylene Meldrum's derivative of indoxyl **2** is known,[1] but the precursor (dimethylamino)methylene compound **11** was obtained directly from indoxyl (**3**) rather than from its N-acetyl derivative[15] and gave **2** in 40% overall yield (Scheme 3). FVP of **2** at 650 °C proceeded in analogous fashion to the corresponding pyrrolone[2] and provided pyrano[3,2-*b*]indol-2(5*H*)-one (**12**) in 42% yield by cyclisation of the intermediate ketene onto the carbonyl group (Scheme 3), rather than the isomeric 9-hydroxypyrrolo[1,2-*a*]indol-3-one which would have been obtained by cyclisation onto the nitrogen atom. The pyrone ring of **12** was characterized by its vicinal coupling constant (^3J = 9.3 Hz), which is much larger than the corresponding coupling in the five-membered ring of the pyrrolo[1,2-*a*]indol-3-one structure. This is the first report of the parent member of the pyrano[3,2-*b*]indol-2-one heterocyclic system; derivatives are also rare.[16]



Scheme 3

In summary, we have developed a robust, gas-phase method for the preparation of indoxyl (**3**) which provides an efficient, controllable alternative to in situ solution-phase methods. Synthesis and FVP of the two Meldrum's acid derivatives **1** and **2** provides access to unusual heterocyclic systems **10** and **12**, respectively. The former shows interesting tautomerism and hydrogen-bonding properties

and the latter, formed regiospecifically in the pyrolysis, is the parent member of an unusual tricyclic system.

^{1}H and ^{13}C NMR spectra were generally recorded at 250 MHz and 63 MHz, respectively. Chemical shifts are given in ppm relative to TMS and refer to one CH resonance unless otherwise stated. Mass spectra were recorded under electron impact conditions.

Flash Vacuum Pyrolysis Experiments; General Procedure

The precursor was volatilized through an empty, electrically heated silica tube (35 × 2.5 cm) and the products were collected in a U-tube, cooled with liquid N_2, situated at the exit point of the furnace. CAUTION: for the azide precursors described below, a metal sublimation oven was used under rotary pump pressure (ca. 0.02 Torr) and the scale was limited to a maximum of a few hundred mg. We experienced no problems with pyrolyses of the azides reported here, but clearly every precaution must be taken in handing such potentially explosive materials. Upon completion of the pyrolysis, the trap was allowed to warm to r.t. under an N_2 atmosphere. The entire pyrolysate was dissolved in solvent and removed from the trap. The precursor, pyrolysis conditions [quantity of precursor, furnace temperature (T_f), inlet temperature (T_i), pressure (P) and pyrolysis time (t)] and products are quoted.

For the Meldrum's acid derivatives, the pyrolyses proceeded more smoothly under diffusion pump pressure (ca. 10^{-5} Torr) to minimize decomposition in the inlet tube.

Temperature Profile of FVP of 2′-Azidoacetophenone (4)

Small-scale FVP reactions of 2′-azidoacetophenone (**4**)[17] were carried out (typically 20 mg, 0.12 mmol; T_i 40 °C; P 2.2×10^{-2} Torr; t 10 min) at the temperatures shown in Figure 2, with the following peaks in the ^{1}H NMR spectrum of the pyrolysate used to calculate the product ratio: 2′-azidoacetophenone (**4**) [δ = 2.55 (s, 3 H, CH_3)], 3-methyl-2,1-benzisoxazole (**5**) [δ = 2.72 (s, 3 H, CH_3)], and indoxyl (**3**) [δ = 3.89 (s, 2 H, CH_2)]. Data are shown in Figures 2 and 3.

Indoxyl (3) by FVP of 2′-Azidoacetophenone (4)

FVP of 2′-azidoacetophenone (**4**, 125 mg, 0.78 mmol; T_f 650 °C; T_i 40 °C; P 2×10^{-2} Torr; t ~50 min) gave indoxyl (**3**, 82 mg, 75%); mp 85–87 °C (Lit.[18] 84 °C),

MS: m/z (%) = 133 (M^+, 100), 105 (53), 104 (90), 78 (67), 77 (29), 51 (18).

***Keto tautomer* 3K**

^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 2 H, CH_2), 6.84 (ddd, J = 0.8, 7.1, 7.8 Hz, 1 H, Ar-H), 6.92 (dd, J = 0.8, 8.3 Hz, 1 H, Ar-H), 7.45 (ddd, J = 1.3, 7.1, 8.3 Hz, 1 H, Ar-H), 7.62 (dd, J = 1.3, 7.8 Hz, 1 H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 54.08 (CH_2), 112.92, 118.98, 121.87 (C_q), 124.19, 136.88, 162.57 (C_q), 200.51 (C_q).

***Enol tautomer* 3E**

^{1}H NMR (DMSO-d_6): δ = 6.70 (d, J = 2.1 Hz, 1 H, H2), 6.88 (ddd, J = 1.0, 6.9, 7.9 Hz, 1 H, Ar-H), 7.00 (ddd, J = 1.3, 6.9, 8.1 Hz, 1 H, Ar-H), 7.21 (dd, J = 1.0, 8.1 Hz, 1 H, Ar-H), 7.50 (dd, J = 1.3, 7.9 Hz, 1 H, Ar-H), 10.26 (s, 1 H, OH).

^{13}C NMR (DMSO-d_6): δ = 106.86, 111.05, 116.98, 117.18, 119.67 (C_q), 120.69, 133.47 (C_q), 135.69 (C_q).

3-Methyl-2,1-benzisoxazole (5) by FVP of 2′-Azidoacetophenone (4)

FVP of 2′-azidoacetophenone (**4**, 50 mg, 0.31 mmol; T_f 400 °C; T_i 40 °C; P 2×10^{-2} Torr; t 20 min) gave a mixture containing **5** (91%), **4** (7%), and **3** (1%) (by ^{1}H NMR spectroscopy).

3-Methyl-2,1-benzisoxazole (5)

^{1}H NMR ($CDCl_3$): δ = 2.72 (s, 3 H, CH_3), 6.76 (dt, 1 H, Ar-H), 6.84 (dd, 1 H, Ar-H), 7.37 (dt, 1 H, Ar-H), 7.55 (dd, 1 H, Ar-H); consistent with literature data.[19]

Temperature Profile of FVP of 4′-Azidoacetophenone (7)

4′-Azidoacetophenone[20] (**7**, 50 mg, 0.31 mmol) was pyrolysed at the temperatures shown in Figure 3 (typical conditions T_i 40 °C; P 2.6×10^{-2} Torr; t 10 min). The pyrolysate was washed out carefully with DMSO-d_6, along with 1,4-dinitrobenzene (15 mg, 0.91 mg) to act as internal standard. The integral of the 1,4-dinitrobenzene peak compared with the two peaks for the aromatics from remaining 4′-azidoacetophenone (**7**) was then measured. This value was then normalized against the value obtained for pyrolysis at 200 °C (the temperature at which no pressure increase was noted during reaction, i.e. all azide remained unreacted). Data are shown in Figure 3.

2,2-Dimethyl-5-(3-oxo-2,3-dihydro-1*H*-indol-1-ylmethylene)-1,3-dioxane-4,6-dione (1)

Methoxymethylene Meldrum's acid (**8**, 184 mg, 0.99 mmol) and indoxyl (**3**, 159 mg, 1.20 mmol) were dissolved in the minimum amount of MeCN and stirred for 16 h. The resulting precipitate was collected and identified as **1** (178 mg, 63%); mp 212–214 °C (MeOH).

^{1}H NMR ($CDCl_3$): δ = 1.76 (s, 6 H, 2 CH_3), 4.72 (s, 2 H, CH_2), 7.42 (m, 1 H, Ar-H), 7.64 (m, 1 H, Ar-H), 7.80 (m, 2 H, 2 Ar-H), 8.74 (s, 1 H, alkene).

^{13}C NMR ($CDCl_3$): δ = 26.82 (2 CH_3), 59.66 (CH_2), 90.98 (C_q), 103.89 (C_q), 112.78, 124.66, 124.87, 126.91 (C_q), 137.21, 147.45, 156.64 (C_q), 159.61 (C_q), 164.66 (C_q), 193.41 (C_q).

MS: m/z (%) = 287 (M^+, 17), 229 (65), 185 (66), 157 (52), 129 (64), 43 (100).

HRMS: m/z $[M]^+$ calcd for $C_{15}H_{13}NO_5$: 287.0794; found: 287.0796.

1-Hydroxy-9*H*-pyrrolo[1,2-*a*]indol-9-one (10b)

FVP of **1** (158 mg, 0.55 mmol; T_f 650 °C; T_i 140 °C; P 9×10^{-6} Torr; t 2 h) gave **10b** (55 mg, 54%).

^{1}H NMR (acetone-d_6): δ = 5.85 (d, J = 2.9 Hz, 1 H, H2), 6.97 (br s, 1 H, OH), 7.14 (m, 1 H, H6), 7.39 (d, J = 2.9 Hz, 1 H, H3), 7.41 (m, 1 H, H4), 7.50 (m, 1 H, H7), 7.54 (m, 1 H, H5).

^{13}C NMR (90 MHz, acetone-d_6): δ = 104.37 (C2), 109.54 (C4), 115.87 (C_q, C8a), 121.15 (C3), 122.48 (C7), 123.35 (C6), 129.89 (C_q, C7a), 132.48 (C5), 141.91 (C_q, C3b), 149.82 (C_q, C1), 175.13 (C_q, C8); (signals identified by HSQC and HMBC experiments).

MS: m/z (%) = 185 (M^+, 48), 86 (87), 84 (100), 51 (74), 49 (100), 47 (53).

HRMS: m/z $[M]^+$ calcd for $C_{11}H_7NO_2$: 185.0479; found: 185.0473.

2-[(Dimethylamino)methylene-1,2-dihydro-3*H*-indol-3-one (11)

Indoxyl (**3**, 128 mg, 0.96 mmol) was dissolved in toluene (3 mL) and *N*,*N*-dimethylformamide diethyl acetal (512 mg, 3.48 mmol) was added. The mixture was stirred at r.t. for 1 h, then heated under reflux for 1 h. The solvent was removed by rotary evaporation, and EtOAc (2 mL) was added. This was stirred for 30 min, the resulting precipitate filtered off and washed with *i*-PrOH followed by Et_2O to give **11** (108 mg, 60%); mp 223 °C (dec) [Lit.[15] 215 °C (dec)].

^{1}H NMR (DMSO-d_6): δ = 3.19 [s, 6 H, $N(CH_3)_2$], 6.79 (ddd, J = 0.7, 7.2, 7.7 Hz, 1 H, Ar-H), 7.02 (s, 1 H, alkene), 7.09 (dd, J = 0.7, 8.2 Hz, 1 H, Ar-H), 7.33 (ddd J = 0.5, 7.2, 8.2 Hz, 1 H, Ar-H), 7.48 (dd, J = 0.5, 7.7 Hz, 1 H, Ar-H), 8.99 (s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 42.08 (2 CH_3), 112.39, 114.12 (C_q), 117.21, 122.31, 131.53, 133.62, 148.86 (C_q), 179.93 (C_q) (1 C_q overlapping).

MS: *m*/*z* (%) = 188 (M^+, 100), 173 (48), 158 (23), 147 (35), 146 (65).

2,2-Dimethyl-5-(3-oxo-2,3-dihydro-1*H*-indol-2-ylmethylene)-1,3-dioxane-4,6-dione (2)

Following the literature method,[1] a soln of **11** (87 mg, 0.47 mmol) and Meldrum's acid (136 mg, 0.95 mmol) in *i*-PrOH (2 mL) was stirred at r.t. for 5 h to give **2** (67 mg, 51%); mp 204–206 °C [Lit.[1] >210 °C (dec)].

^{1}H NMR (DMSO-d_6): δ = 1.79 (s, 6 H, 2 CH_3), 6.98 (m, 1 H, Ar-H), 7.40 (m, 1 H, Ar-H), 7.55 (m, 1 H, Ar-H), 7.83 (m, 1 H, Ar-H), 8.30 (s, 1 H), 10.75 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 26.41 (2 CH_3), 96.28 (C_q), 103.17 (C_q), 113.79, 116.04 (C_q), 119.18, 121.54, 131.12, 134.00, 141.11 (C_q), 157.30 (C_q), 163.42 (C_q) (2 C_q overlapping).

MS: *m*/*z* (%) = 262 (M^+, 17), 185 (100), 157 (38), 129 (83), 102 (22), 76 (35).

Pyrano[3,2-*b*]indol-2(5*H*)-one (12)

After FVP of **2** (55 mg, 0.21 mmol; T_f 650 °C; T_i 120 °C; P 9×10^{-6} Torr; *t* 2 h) the U-tube trap was first washed through with $CHCl_3$ to remove soluble impurities, leaving **12** (ca. 20 mg, 42%).

^{1}H NMR (acetone-d_6): δ = 6.11 (d, J = 9.4 Hz, 1 H, alkene), 7.07 (m, 1 H, Ar-H), 7.23 (m, 1 H, Ar-H), 7.41 (d, J = 9.4 Hz, 1 H, alkene), 7.66 (m, 1 H, Ar-H), 7.88 (m, 1 H, Ar-H).

^{13}C NMR (DMSO-d_6): δ = 110.76, 112.63, 114.58 (C_q), 117.55, 119.04 (C_q), 119.98, 125.54, 128.26 (C_q), 135.04, 136.27 (C_q), 161.34 (C_q).

MS: *m*/*z* (%) = 185 (M^+, 70), 157 (45), 129 (41), 102 (20), 76 (16), 58 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{11}H_7NO_2$: 185.0477; found: 185.0473.

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