Supplementary Information: McNab, Montgomery, Parsons and Tredgett

Pyrrolizine-1,3-dione

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Supplementary Information

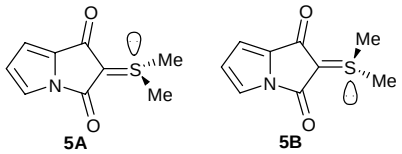
Attempted oxidation of 1,2-dihydro-l-hydroxypyrrolizin-3-one 2.

(i) Compound **2** (58 mg, 0.42 mmol) was dissolved in DCM (0.32 cm^3), to this a solution of DMP Dess-Martin periodinane (117 mg, 0.28 mmol) in DCM (1.2 cm^3) was added and stirred for 20 min.[1] After workup, the ^1H NMR spectrum showed evidence of complete decomposition.

(ii) Manganese dioxide (250 mg, 2.9 mmol) was added to a stirred solution of **2** (100 mg, 0.73 mmol) in chloroform (20 cm^3) at room temperature.[2] After 24 h, the presence of **4** was shown by its NMR signal at δ_H 3.47 (2H, s), but conversion was only 10%.

(iii) A solution of dimethylsulfoxide (0.74 g, 9.6 mmol) in dichloromethane (2 cm^3) was added dropwise over 5 min to a solution of oxalyl chloride (0.56 g, 4.4 mmol) in dichloromethane (5 cm^3) at -60 °C.[3] After stirring for 10 min, a solution of **2** (0.27 g, 2 mmol) in dichloromethane (2 cm^3) was added dropwise and the solution was stirred for 30 min. Triethylamine (1.01 g, 10 mmol) was added over 5 min and then the temperature was allowed to rise to 20 °C. Water (6 cm^3) was added, the organic layer was separated and the aqueous phase was extracted with dichloromethane (4 cm^3). The combined organic layers were washed with dilute HCl (4 cm^3), water (4 cm^3), dilute sodium bicarbonate (4 cm^3), water (20 cm^3), dried (Na_2SO_4) and the solvent removed. Dry-flash chromatography on silica, eluting with ethyl acetate/ethanol (3:1) gave 2-(dimethyl-λ^4-sulfanylidene)-pyrrolizine-1,3-dione **5** (12 mg, 3%), (Found (ESI): M^+ 196.0432. $C_9H_{10}NO_2S$ requires *M* 196.0433); δ_H 7.08 (1H, dd, ^3J 3.1 and ^4J 0.9), 6.46 (1H, dd, ^3J 3.1 and ^4J 0.9), 6.23 (1H, t, ^3J 3.1) and 3.01 (6H, s); δ_C 181.48 (quat), 167.85 (quat), 131.06 (quat), 125.76, 117.73, 111.09, 64.39 (quat) and 30.82; *m/z* 195 (M^+, 69%), 180 (19), 94 (100), 87 (27), 78 (17) and 59 (17).

In the ^1H NMR spectrum, the *S*-methyl singlet is unchanged at -35 °C which suggests that **5** adopts one of the symmetrical structures **5A** or **5B** as found for other sulfonium ylides.[4]



1,2-Dihydro-1-propargyloxypyrrolizin-3-one 7.

1-Chloro-1,2-dihydropyrrolizin-3-one[5] **3** (0.78 g, 5 mmol) was dissolved in dichloromethane (5 cm^3) and propargyl alcohol (0.96 g, 17 mmol, 1 cm^3) was added. The mixture was stirred at room temperature for 1 h. The solution was extracted with dichloromethane (3 × 10 cm^3) and washed with water (10 cm^3). The solution was dried (Na_2SO_4) and the solvent was removed. Kugelrohr distillation gave 1,2-dihydro-1-propargyloxypyrrolizin-3-one **7** (0.177 g, 22%), b.p. 95 °C (0.4 Torr) (Found: M^+ 175.0631. $C_{10}H_9NO_2$ requires *M* 175.0633); δ_H 7.07 (1H, dd, ^3J 3.1 and ^4J 0.9), 6.47 (1H, t, ^3J 3.1), 6.27 (1H, dt, ^3J 3.1, ^4J 0.9 and 0.9), 5.18 (1H, ddd, ^3J 6.8 and 1.8, ^4J 0.9), 4.25 (2H, d, ^4J 2.4), 3.37 (1H, dd, ^3J 6.8 and 1.8), 3.01 (1H, dd, ^3J 6.8 and 1.9) and 2.50 (1H, t, ^4J 2.4); δ_C 168.97 (quat), 137.85 (quat), 118.76, 112.26, 107.80, 78.75, 75.14, 76.41, 55.53 and 42.91 ; *m/z* 175 (M^+, 20%), 135 (15), 133 (100), 121 (27), 120 (88), 119 (20), 104 (35) and 93 (21).

Flash vacuum pyrolysis (FVP) experiments.
The substrate was sublimed under vacuum into a horizontal silica furnace tube (35 × 2.5 cm) heated by an electrical furnace. Products were collected in a U-tube, cooled by liquid nitrogen, situated at the exit point of the furnace. When the pyrolysis was complete, the trap was allowed to warm to room temperature under an atmosphere of dry nitrogen. Pyrolysis parameters are quoted as follows: quantity of substrate, inlet temperature (T_i), furnace temperature (T_f), pressure range (P) and time of pyrolysis (t).

FVP of 1,2-Dihydro-1-propargyloxypyrrolizin-3-one 7.
FVP of **7** [175 mg (1.0 mmol), T_i 75 °C, T_f 750 °C, P 0.005 Torr, t 52 min.] gave pyrrolizine-1,3-dione **4** (spectra consistent with those reported in main paper), pyrrolizin-3-one **1** δ_H 7.07 (1H, dd), 6.90 (1H, dt), 5.99 (2H, d) and 5.66 (1H, d); *m/z* 119 (M^+, 94%), and an unidentified species δ_H 8.04-6.48; *m/z* 252 (M^+, 100%).

FVP of 2 over zinc oxide.
Compound **2** (56.4 mg) was subjected to FVP with a plug of zinc oxide (10 g) inserted between two silica wool stoppers, at the centre of the furnace. The catalyst was conditioned by heating in air at 600 °C for 30 min, then cooled, and the FVP was carried out (T_f 200 ºC, P 0.028 Torr, t 40 min). The pyrolysate consisted entirely of pyrrolizin-3-one **1**, spectra as above.

VT-NMR spectra of 22

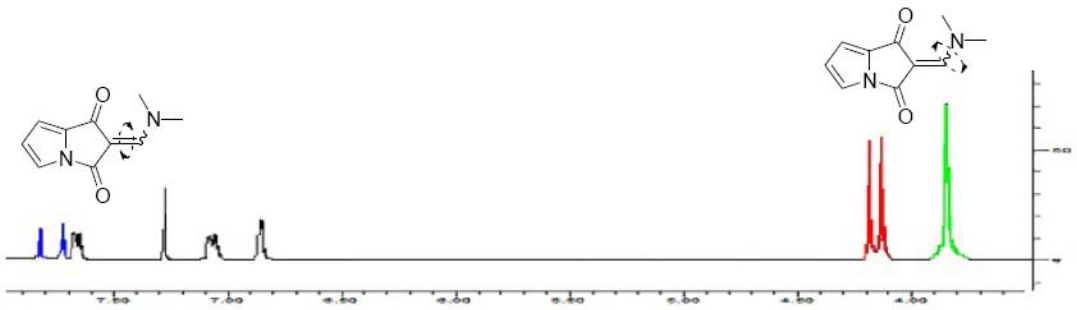


Figure S1. Room temperature ^{1}H NMR spectrum of **22**.

The room temperature ^{1}H NMR spectrum of **22** (Figure S1) shows two pairs of signals for the *N*-methyl groups (shown in red and green) due to restricted C-N rotation of the two isomers and one pair of signals (shown in blue) for the exocyclic methine proton due to restricted C=C rotation. As shown in Figure S2, each pair coalesces to a single resonance at higher temperatures.

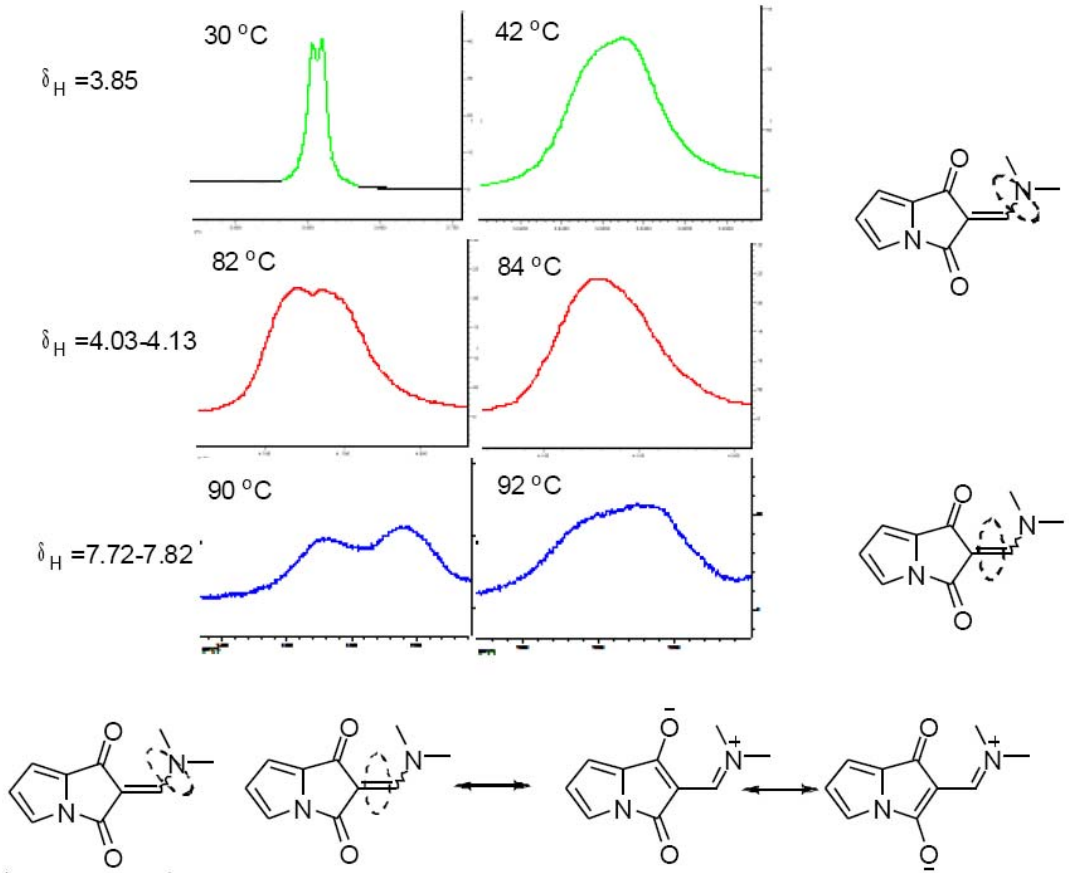


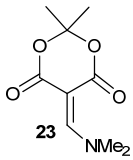
Figure S2. Coalescence behaviour of signals at δ_H 3.85 (note difference in horizontal scale) and δ_H 4.03-4.13 due to *N*-methyl groups and at δ_H 7.72-7.82 due to the exocyclic methine proton of **22**.

Using the equation:[6] $\Delta G^{\ddagger} = 19.13T_c(9.97 + \log_{10}T_c/\Delta\nu)$ kJ mol^{-1} (where $\Delta G^{\ddagger}$ is the activation energy for the process in kJ mol^{-1}, T_c is the coalescence temperature in K and $\Delta\nu$ is the maximum separation of the two signals in Hz), the following data were obtained:

$$\Delta G^{\ddagger}(\text{C-N}) = 73.7 \text{ kJ mol}^{-1}$$
$$\Delta G^{\ddagger}(\text{C-N}) = 77.1 \text{ kJ mol}^{-1}$$
$$\Delta G^{\ddagger}(\text{C=C}) = 77.7 \text{ kJ mol}^{-1}$$

For comparison, the corresponding data[7] for the Meldrum's acid derivative **23** are as follows:

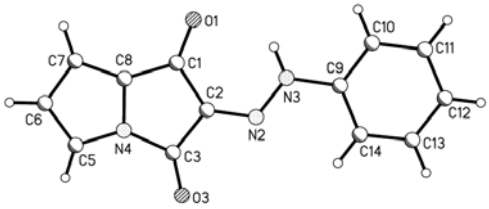
$$\Delta G^{\ddagger}(\text{C-N}) = 90.5 \text{ kJ mol}^{-1}$$
$$\Delta G^{\ddagger}(\text{C=C}) = 53.5 \text{ kJ mol}^{-1}$$



23

These results show that the C-N bond has much more double bond character in the Meldrum's acid derivative **23** and therefore that the dioxanedione ring behaves as a much better electron withdrawing group than the pyrrolizinedione.

Table S1. Bond lengths and angles for hydrazone 15.



Bond lengths	Bond angles
C1 . O1 . 1.2236(14)	O1 . C1 . C2 . 126.40(10)
C1 . C2 . 1.4761(15)	O1 . C1 . C8 . 129.00(10)
C1 . C8 . 1.4512(15)	C2 . C1 . C8 . 104.58(9)
C2 . C3 . 1.4774(16)	C1 . C2 . C3 . 109.83(9)
C2 . N2 . 1.3045(14)	C1 . C2 . N2 . 129.90(10)
C3 . O3 . 1.2023(14)	C3 . C2 . N2 . 120.26(10)
C3 . N4 . 1.4260(14)	C2 . C3 . O3 . 130.96(11)
N4 . C5 . 1.3685(15)	C2 . C3 . N4 . 103.50(9)
N4 . C8 . 1.3852(14)	O3 . C3 . N4 . 125.53(11)
C5 . C6 . 1.3730(16)	C3 . N4 . C5 . 137.44(10)
C6 . C7 . 1.4141(17)	C3 . N4 . C8 . 112.91(9)
C7 . C8 . 1.3711(16)	C5 . N4 . C8 . 109.63(9)
N2 . N3 . 1.3091(13)	N4 . C5 . C6 . 106.97(10)
N3 . C9 . 1.4106(14)	C5 . C6 . C7 . 108.80(10)
C9 . C10 . 1.3857(16)	C6 . C7 . C8 . 106.71(11)
C9 . C14 . 1.3936(15)	C1 . C8 . N4 . 109.12(9)
C10 . C11 . 1.3883(16)	C1 . C8 . C7 . 142.98(11)
C11 . C12 . 1.3871(16)	N4 . C8 . C7 . 107.89(10)
C12 . C13 . 1.3812(18)	C2 . N2 . N3 . 119.28(10)
C13 . C14 . 1.3845(17)	N2 . N3 . C9 . 119.12(9)
	N3 . C9 . C10 . 118.16(10)
	N3 . C9 . C14 . 120.82(10)
	C10 . C9 . C14 . 121.02(10)
	C9 . C10 . C11 . 119.20(11)
	C10 . C11 . C12 . 120.46(11)
	C11 . C12 . C13 . 119.51(11)
	C12 . C13 . C14 . 121.17(11)
	C9 . C14 . C13 . 118.63(11)

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