Pyrrolizine-1,3-dione†

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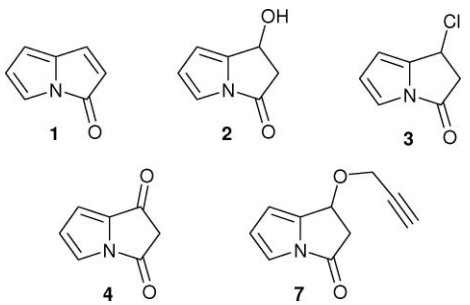
Pyrrolizine-1,3-dione **4** was made by oxidation of the alcohol **2** using pyridinium chlorochromate. The dione **4** shows ketone properties (*e.g.* formation of DNP derivative **11**) and, in common with other pyrrolizinones, the lactam unit is readily ring-opened by methanol under basic conditions. The active methylene unit of **4** couples readily with diazonium salts to provide the hydrazone **15** whose structure was confirmed by X-ray crystallography. The 'Meldrumsated' derivative **18** exists exclusively as the tautomer **18F**; flash vacuum pyrolysis (FVP) of **18** at 700 °C gives the pyronopyrrolizine **20** exclusively. Reaction of **4** with DMF acetal gives the dimethylaminomethylene derivative **22** which exists as a mixture of rotamers at room temperature.

Introduction

In previous papers, we have reported facile routes to pyrrolizin-3-ones **1** using flash vacuum pyrolysis (FVP) as the key step.[1] We have also shown that the 1-hydroxy derivative **2** is easily made from pyrrolizin-3-one by sequential addition of HCl and quenching of the highly reactive 1-chloro compound **3** by water.[2] Here, we report an optimised method for the oxidation of **2** into pyrrolizine-1,3-dione **4** and our studies of the properties of this unusual dione. Compound **4** potentially shows pyrrole, ketone, amide and active methylene functionality. Open-chain analogues such as pyrrolyl β-ketoanilides have been used as yellow couplers with potential applications in colour photography.[3] However, **4** is a unique system; electron donation from the bridgehead nitrogen atom into the lactam system is compromised by its contribution to the 6π system of the pyrrole (and its associated 1-keto functionality). The carbonyl groups are therefore likely to show unusual properties.

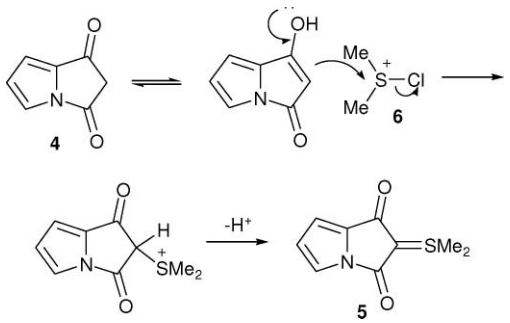


Results and discussion

Our optimised route to **4** involves oxidation of the secondary alcohol functionality of **2** with pyridinium chlorochromate (PCC),[4] providing **4** in 68% yield. Efficient agitation of the reaction mixture throughout the oxidation is essential for good yields and this is best achieved by a combination of magnetic stirring and bubbling nitrogen through the solution. The dione **4** is characterised by its methylene signal at δ_H 3.54 in the ^{1}H NMR spectrum. Pyridinium dichromate oxidation of **2** was also successful but the yield was significantly lower.

Other oxidation methods met with little success (ESI†). For example, Dess–Martin conditions[5] gave unidentified decomposition products and manganese dioxide oxidation[6] showed only low conversion to **4**. Swern oxidation[7] gave the ylide **5** in 3% yield. This compound was characterised by the *S*–Me singlet at δ_H 3.01 (*cf.* ref. 8) and by the ylide carbon resonance at δ_C 64.87; although the value of latter parameter is variable in sulfonium ylides,[9,10] the observed figure occurs in the expected range for dicarbonyl-stabilised examples.[9]

The ylide **5** is likely to be formed by initial oxidation to the dione **4** followed by *in situ* reaction with an activated Swern intermediate such as **6** (Scheme 1).



Scheme 1

We have also explored two potential gas-phase routes to **4**. The anticipated retro-ene decomposition of **7** (*cf.* ref. 11) by FVP at 750 °C gave only a trace of the dione **4** together with some pyrrolizin-3-one **1** and higher molecular-weight products. Dehydration to pyrrolizin-3-one **1** was the only process when the alcohol **2** was subjected to FVP at 200 °C over a plug of zinc oxide, conditions which generally promote dehydrogenation of secondary alcohols to ketones.[12]

In contrast to pyrrolizinones which are generally highly coloured, pyrrolizine-1,3-dione **4** is a slightly yellow, highly crystalline solid. It shows carbonyl absorptions at 1698 and 1760 cm^{-1}. Since dihydropyrrolizin-1-one **8** is reported[13] to have

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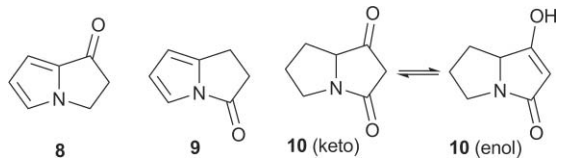
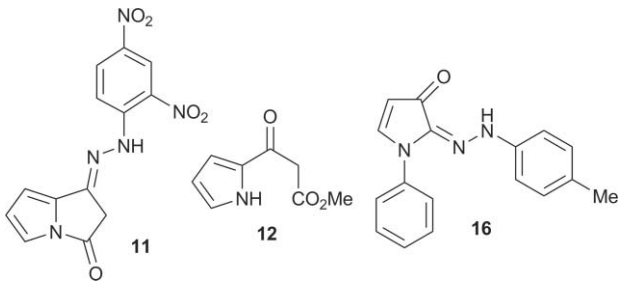
† Electronic supplementary information (ESI) available: Experimental, V.T. NMR data for **22**. X-Ray structure table. CCDC reference numbers 777142–777143. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00116c

ν_{max} 1705 cm^{-1} and the isomeric dihydropyrrolizin-3-one[14] **9** has ν_{max} 1734 cm^{-1}, it seems likely that the lactam carbonyl of **4** has ν_{max} 1760 and the ketone ν_{max} 1698 cm^{-1}. This appears to be an unusual example of a lactam having a higher frequency absorption than a ketone in a similar structural environment. Crystals are disordered (see Experimental section) but the results of an X-ray crystallographic analysis confirm the planarity of the system and show that the dione is the major tautomeric form in the solid state.

In solution, pyrrolizine-1,3-dione **4** appears to adopt the keto tautomer exclusively. In contrast, the tetrahydro-derivative **10** is known to exist as a 1 : 1 mixture of keto and enol tautomers in DMSO solution[15] though it apparently exists as the keto tautomer in chloroform.[16]



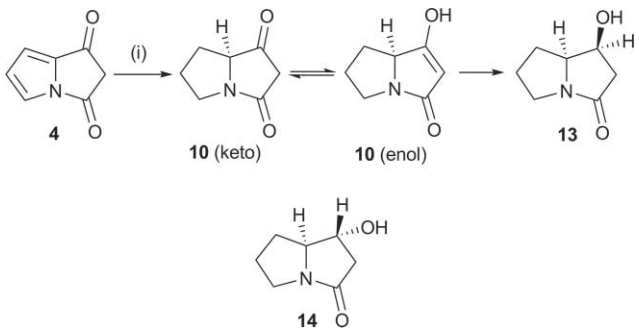
Under appropriate conditions, pyrrolizine-1,3-dione **4** can show typical ketone properties; for example reaction with Brady's reagent gives the hydrazone **11** (89%). The amide functionality survives the acid conditions used in this reaction. Unusually for typical lactams, but in common with other pyrrolizin-3-ones (such as **1**), the dione **4** is very reactive under basic conditions and quantitative ring opening to the β-ketoester **12** occurs in methanol containing a drop of Hünig's base.



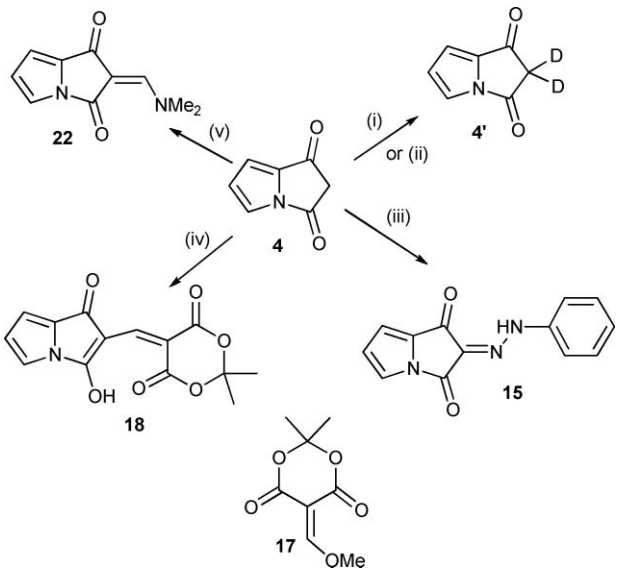
Pyrrolizin-3-ones can be readily hydrogenated under mild heterogeneous catalytic conditions[17] and the dione **4** behaves similarly, providing a 88 : 12 mixture of **10** and **13** (Pd/C, 3 atm H_2 in ethyl acetate). The isomers **13** and **14** can be readily distinguished by their characteristic NMR spectra,[18] and it was clear that the *trans*-isomer **14** was not formed. A possible mechanism involves initial hydrogenation of the pyrrole ring to the tetrahydro compound **10** followed by reduction of the ketone function *via* a small amount of the enol tautomer at its less hindered face (Scheme 2).[17]

The dione **4** shows extensive active methylene chemistry. The CH_2 group exchanges rapidly in [$^2H_4$]methanol but rather more slowly under acidic conditions ([^{2}H]TFA; $t_{\frac{1}{2}}$ *ca.* 3 h). Under neutral conditions, the exchange presumably takes place *via* traces of an enol tautomer, which suggests that keto-enol tautomerism is rapid. Chemical shifts are almost unchanged in TFA solution (see Experimental section), which suggests that relatively little protonation takes place under these conditions.

Azo-coupling of **4** with benzenediazonium tetrafluoroborate in dichloromethane containing a trace of Hünig's base provides the hydrazone **15** quantitatively (Scheme 3). Its crystal structure (Fig. 1) shows internal hydrogen bonding between H(3) and O(1) [H(3)–O(1), 2.20 Å; N(3)–O(1), 2.8588(12) Å, angle at H 131°].



Scheme 2 Reagents and conditions: (i), H_2/Pd/C/ethanol (one of the enantiomeric pairs shown).



Scheme 3 Reagents and conditions: (i) [$^2H_4$]methanol; (ii) [^{2}H]TFA; (iii) benzenediazonium tetrafluoroborate, Hünig's base, CH_2Cl_2; (iv) methoxymethylene Meldrum's acid **17**, Hünig's base, CH_2Cl_2; (v) DMF dimethyl acetal, $CHCl_3$.

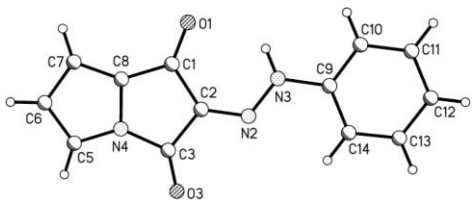
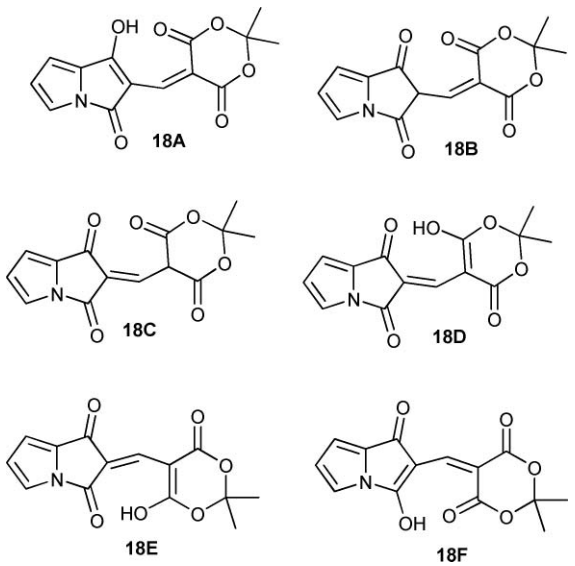


Fig. 1 Plot of the hydrazone **15**, showing the crystallographic numbering scheme.

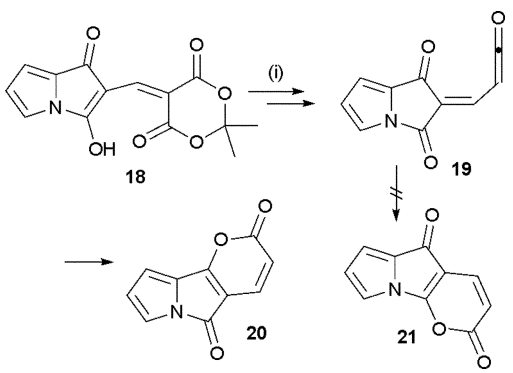
The C(1)–O(1) bond distance [1.2236(14) Å] is significantly longer than that of the 3-carbonyl group [C(3)–O(3), 1.2023(14) Å]. This is an unusual example of a ketone carbonyl bond length being longer than an amide in similar structural environments,[19] but is consistent with the I. R. data reported above. The molecule as a whole is planar [mean deviation from best plane 0.062 Å; maximum deviation from best plane 0.20 Å at O(1)]. By comparison with pyrrolizin-3-one **1** itself,[20] the formal single bonds in the 'pyrrole' ring [N(4) through to C(8)] of **15** are shorter, and the formal double bonds are longer owing to conjugation of the N(4) lone pair through the pyrrole ring to the 1-carbonyl group.

Structural parameters for the ketohydrazone unit of **15** as a whole [N(3)–N(2)–C(2)–C(1)–O(1)] are broadly comparable to those of related compounds, such as the hydrazonopyrrolone **16**.[21]

Reaction of the dione **4** with methoxymethylene Meldrum's acid **17** in dichloromethane containing a drop of Hünig's base provides the 'Meldrumsated' product **18** (81%) (Scheme 3).[22] Various tautomeric structures of this product are possible (**18A–F**). ^{13}C NMR spectroscopy shows only 4 CH resonances which eliminates the non-conjugated tautomers **18B** and **18C**. Two carbonyl quaternary signals at δ_C 162.42 are in the region expected for the dioxanedione moiety (thereby eliminating **18D** and **18E**). The 1-hydroxy tautomer **18A** would be expected to show a 'normal' pyrrolizin-3-one lactam resonance[23] at about δ_C 165 and since the two remaining C–O quaternaries are at δ_C 177.81 and 176.91 the tautomeric structure of **18** is most likely to be **18F**.

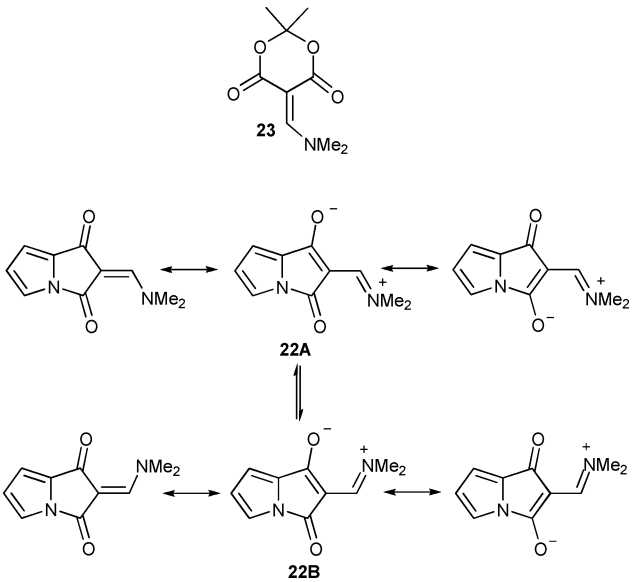


By comparison with the FVP reactions of other Meldrum's acid derivatives,[24] FVP of **18** was expected to generate the ketene intermediate **19** which could electrocyclise onto either of the carbonyl groups to give one (or both) of the pyronopyrrolizinones **20** and **21** (Scheme 4).[22] In the event, FVP of **18** at 700 °C provided the single pyronopyrrolizinone **20** (96%), the first example of this ring system. In this case, the presence of a typical pyrrolizin-3-one carbonyl resonance at δ_C 166.81, and the absence of a pyrrolizin-1-one carbonyl signal at *ca.* δ_C 180, are particularly diagnostic. The ketene **19** therefore cyclises onto the ketone carbonyl group of the pyrrolizinedione rather than its lactam carbonyl group, with very high selectivity.



Scheme 4 Reagents and conditions: (i) FVP, 700 °C.

When the dione **4** is allowed to stand in a chloroform solution of DMF dimethyl acetal, at room temperature, the dimethylaminomethylene product **22** is obtained in 95% yield (Scheme 3). In a similar fashion to dimethylaminomethylene Meldrum's acid **23**,[25] which shows restricted rotation around C–N and C=C bonds, compound **22** can exist in potentially interconverting *Z* and *E* isomers (**22A** and **22B** respectively), both of which can undergo C–N rotation. Its room temperature ^{1}H NMR spectrum shows two pairs of signals for the *N*-methyl groups due to restricted C–N rotation of the two isomers and one pair for the exocyclic methine proton due to restricted C=C rotation; each pair coalesces to a single resonance at higher temperatures. These parameters are discussed in the ESI.†



Conclusions

We conclude that pyrrolizine-1,3-dione **4** can be conveniently made in two steps from pyrrolizin-3-one **1**. The dione is stable under acidic conditions but rapidly ring opens in the presence of base. The two carbonyl groups of **4** have anomalous IR stretches, and their unusual nature is also reflected in the crystal structure of the hydrazone **15**. Dione **4** displays chemical properties typical of β-ketoamides – in particular a rich variety of active methylene chemistry. Its synthetic utility is exemplified by a two-step transformation into the tricycle **20**, the first example of this ring system.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 250 or 63 MHz respectively for solutions in [^{2}H]chloroform unless otherwise stated. Coupling constants are quoted in Hz. ^{13}C NMR signals refer to one CH resonance unless otherwise stated. Mass spectra were recorded under electron impact conditions.

Pyrrolizine-1,3-dione 4

A solution of 1,2-dihydro-1-hydroxypyrrolizin-3-one **2**[2] (0.10 g, 0.7 mmol) in dichloromethane (5 cm^3) was added dropwise to a vigorously stirred suspension of pyridinium chlorochromate (0.63 g, 2.9 mmol) in dichloromethane (5 cm^3).[4] The flask was wrapped in aluminium foil to ensure the absence of light, and a flow of nitrogen was constantly bubbled through the suspension to keep it mobile. The mixture was allowed to stir at room temperature for 1 h and was then filtered through a 1 cm silica plug. The filtrate was concentrated, the resulting solid was washed with hexane, and dried *in vacuo* to give pure pyrrolizine-1,3-dione **4** 0.069 g (68%) as a yellow crystalline solid, mp 150–151 °C (from ethyl acetate), (Found: M^+ 135.0321. $C_7H_4NO_2$ requires *M* 135.0320) (Found: C 61.5; H 3.9; N 9.9%. $C_7H_4NO_2$ requires C 62.2; H 3.7; N 10.4%); δ_H 7.44 (1H, dd, ^3J 2.9 and ^4J 0.9), 6.89 (1H, dd, ^3J 3.5, ^4J 0.9), 6.75 (1H, dd, ^3J 3.5, 2.9) and 3.55 (2H, s); δ_C 182.07 (quat), 165.11 (quat), 136.14 (quat), 121.03, 118.55, 112.09 and 44.62 (CH_2); δ_H ([^{2}H]TFA) 7.39 (1H, dd, ^3J 3.0, ^4J 0.8), 6.93 (1H, dd, ^3J 3.7, ^4J 0.8), 6.67 (1H, dd, ^3J 3.7 and 3.0) and 3.64 (2H, s); δ_C ([^{2}H]TFA) 186.24 (quat), 167.25 (quat), 134.77 (quat), 122.36, 120.97, 116.03 and 43.64 (CH_2); *m*/*z* 135 (M^+, 100%), 94 (52), 93 (84) and 65 (42); ν_{max} 3111, 2959, 2360, 1760, 1698, 1551, 1432, 1361, 1289, 1251, 1130, 1022, 937, 915, 893, 857, 775 and 601 cm^{-1}.

Oxidation of a solution of **2** (0.10 g, 0.7 mmol) in DCM (1.25 cm^3) with PDC (0.44 g) under similar conditions for 3 h yielded pyrrolizine-1,3-dione **4** (0.025 g, 25%) after workup.

1-(2,4-Dinitrophenylhydrazono)-1,2-dihydropyrrolizin-3-one 11

Brady's reagent (2 drops) was added to a solution of pyrrolizine-1,3-dione **4** (20 mg, 0.15 mmol) in ethyl acetate. The precipitate was filtered off to give 1-(2,4-dinitrophenylhydrazono)-1,2-dihydropyrrolizin-3-one **11** (42 mg, 89%); mp 189 °C; (Found: M^+ 315.0605. $C_{13}H_9N_5O_5$ requires *M* 315.0604) δ_H 11.41 (1H, s), 9.19 (1H, d, ^3J 9.2), 8.40 (1H, dd, ^3J 9.5 and ^4J 2.5), 8.08 (1H, d, ^3J 9.5), 7.45 (1H, d, ^3J 3.0), 7.23 (1H, d, ^3J 3.7), 6.83 (1H, m) and 3.54 (2H, s); δ_C 166.0 (quat), 144.7 (quat), 139.1 (quat), 130.2, 123.4, 121.1, 116.5, 116.4, 111.7 and 40.7 (CH_2) (3 quaternary signals not apparent); *m*/*z* 315 (M^+, 86%), 193 (45) and 84 (100).

Methyl 3-oxo-3-(1*H*-pyrrol-2-yl)-propionate 12

Pyrrolizine-1,3-dione **4** (20 mg, 0.15 mmol) was dissolved in methanol (1 cm^3) and *N*,*N*-di-isopropylethylamine (1 drop) was added. The solution became deep red in colour, then the solvent was removed to yield methyl 3-oxo-3-(1*H*-pyrrol-2-yl)-propionate **12** (25 mg, 99%), bp 65 °C (0.3 Torr), as a red oil; (Found: M^+ 167.0577. $C_8H_9NO_3$ requires *M* 167.0577) δ_H 9.73 (1H, br. s), 7.10 (1H, m), 6.96 (1H, m), 6.31 (1H, dt, ^3J 3.9 and 2.3), 3.82 (2H, s) and 3.75 (3H, s); δ_C 181.74 (quat), 167.98 (quat), 131.13 (quat), 125.97, 118.11, 111.23, 52.50 (CH_3) and 45.13 (CH_2); *m*/*z* 167 (M^+ 19%), 94 (100), 66 (38) and 44 (35).

Hydrogenation of Pyrrolizine-l,3-dione 4

Palladium on charcoal (5%, 10 mg) was added to a solution of pyrrolizine-1,3-dione **4** (20 mg, 0.15 mmol) in ethyl acetate (20 cm^3) and the mixture was hydrogenated at 3 atm for 3 h. The catalyst was filtered (celite) and the solvent removed to give a mixture of products which was not separated. From the NMR spectra of the mixture, these products were identified as pyrrolizidine-1,3-dione **10** (88%) δ_H 4.09 (1H, m), 3.83 (1H, m), 3.26 (1H, d, ^2J 21.2), 3.13 (1H, m), 2.89 (1H, dd, ^2J 21.2, ^nJ 1.5), 1.80–2.15 (3H, m) and 1.60 (1H, m); δ_C 205.84 (quat), 170.34 (quat), 69.99, 45.49 (CH_2), 43.21 (CH_2), 26.47 (CH_2) and 25.80 (CH_2) (spectra compatible with literature data[15,16,26]) and *cis*-1-hydroxypyrrolizidin-3-one **13** (12%) δ_C 173.19 (quat), 67.87, 66.84, 45.49 (CH_2) 41.40 (CH_2), 27.10 (CH_2) and 22.92 (CH_2) (spectrum compatible with literature data[17,18]).

2-(Phenylhydrazono)-pyrrolizine-1,3-dione 15

Benzenediazonium tetrafluoroborate (28 mg, 0.15 mmol) was added to a solution of pyrrolizine-1,3-dione **4** (20 mg, 0.15 mmol) in dichloromethane (0.5 cm^3). *N*,*N*-Di-isopropylethylamine was added dropwise to this stirred suspension until all solid had dissolved. After 15 min stirring a precipitate had formed, so the solvent was evaporated and the organic material was dissolved in ether leaving behind all inorganic material. Removal of the solvent yielded 2-(phenylhydrazono)-pyrrolizine-1,3-dione **15** as an intense orange solid (43 mg, 99%), (Found: M^+ 239.0695. $C_{13}H_9N_3O_2$ requires *M* 239.0695); mp 113 °C: δ_H 13.22 (1H, s), 7.43–7.51 (3H, m), 7.38 (2H, t, ^3J 7.3), 7.21 (1H, t, ^3J 7.3), 6.91 (1H, d, ^3J 3.4) and 6.60 (1H, t, ^3J 3.3); δ_C 176.00 (quat), 158.34 (quat), 140.83 (quat), 132.53 (quat), 129.39 (2CH), 127.15 (quat), 126.00, 119.73, 118.78, 115.95 (2CH) and 113.40; *m*/*z* 169 (M^+ 100%), 162 (10), 147 (63), 103 (20), 94 (98), 77 (100) and 51 (46).

5-(3-Hydroxy-1-oxo-1*H*-pyrrolizin-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione 18

5-Methoxymethylene-2,2-dimethyl-1,3-dioxane-4,6-dione **17** (28 mg, 0.15 mmol) was added to a solution of pyrrolizine-1,3-dione **4** (20 mg, 0.15 mmol) in dichloromethane (1 cm^3). The solution was stirred for 15 min then hexane (5 cm^3) was added until a red oil settled; the yellow solvent layer was discarded. The red oil was then treated with dilute hydrochloric acid (2M, 2 cm^3) and the organics extracted into dichloromethane. Removal of the solvent yielded 5-(3-hydroxy-1-oxo-1*H*-pyrrolizin-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **18** (42 mg, 81%) as a red solid, mp 156 °C; (Found: M^+ 289.0589. $C_{14}H_{11}NO_6$ requires *M* 289.0581); δ_H 8.42 (1H, s), 7.47 (1H, d, ^3J 2.5), 6.98 (1H, d, ^3J 3.4), 6.58 (1H, dd, ^3J 3.4 and 2.5) and 1.78 (6H, s); δ_C 177.81 (quat), 176.91 (quat), 162.42 (2 quat), 144.62, 130.97 (quat), 122.78, 119.47, 117.72, 104.98 (2 quat), 96.18 (quat) and 26.75 ($2CH_3$); *m*/*z* 289 (M^+, 5%), 231 (57), 159 (100), 94 (38) and 57 (61).

4-Oxa-8a-azacyclopenta[*a*]indene-5,8-dione 20

5-(3-Hydroxy-1-oxo-1*H*-pyrrolizin-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **18** (20 mg, 0.07 mmol) was sublimed at 110 °C (0.034 Torr) over 15 min through a silica furnace tube held at 700 °C by an electrical tube furnace. 4-Oxa-8a-azacyclopenta[*a*]indene-5,8-dione **20** was collected in a liquid nitrogen trap situated at the exit point of the furnace, as a dark orange solid (13 mg, 96%), mp 168 °C (decomp); (Found: M^+ 187.0264. $C_{10}H_5NO_3$ requires *M* 187.0271); δ_H 7.51 (1H, d, ^3J 9.5), 7.15 (1H, dd, ^3J 4.0 and ^4J 0.8), 6.51 (1H, dd, ^3J 4.0 and ^4J 0.8), 6.21 (1H,

t, ^3J 4.0) and 6.03 (1H, d, ^3J 9.5); δ_C 166.81 (quat), 159.12 (quat), 158.80 (quat), 137.98, 127.65 (quat), 121.47, 116.75, 114.26, 108.90 and 106.77 (quat); *m/z* 187 (M^+, 71%), 159 (100), 103 (32) and 94 (39).

2-(1-Dimethylaminomethylene)-pyrrolizine-1,3-dione 22

DMF dimethyl acetal (3 drops) was added to a solution of pyrrolizine-1,3-dione **4** (20 mg, 0.015 mmol) in chloroform (1 cm^3). The solution instantly became black and the solvent was removed leaving a black solid. The residue was dissolved in dichloromethane and decolourising charcoal (0.5 g) was added; after filtration through celite the solvent was removed to give 2-(1-dimethylaminomethylene)-pyrrolizine-1,3-dione **22** (27 mg, 95%), mp 103–104 °C as an off white solid. This was a 1 : 1 mixture of the *E*/*Z* isomers; (Found: M^+ 190.0742. $C_{10}H_{10}N_2O_2$ requires *M* 190.0742); δ_H 7.82 (1H, s), 7.72 (1H, s), 7.65–7.67 (2H, m), 7.05–7.08 (2H, m), 6.86 (2H, m), 4.13 (3H, m), 4.03 (3H, s) and 3.85 (6H); δ_C 184.1 (quat), 183.7 (quat), 167.2 (2 quat), 135.6 (quat), 134.5 (quat), 122.9, 121.3, 120.0, 119.4, 118.5, 116.3, 115.3, 27.6 ($2CH_3$), 26.5 (CH_3) and 25.7 (CH_3) (other signals broad or overlapping); *m/z* 190 (M^+, 68%), 94 (100), 85 (42) and 65 (38).

Crystallography

Crystal data for 4. $C_7H_5NO_2$, *M* = 135.12, orthorhombic, space group *Pbcn*. *a* = 5.1445(9), *b* = 14.134(2), *c* = 8.0639(15) Å, *V* = 586.35(17) $Å^3$ at *T* = 150 K. *Z* = 4. Data were collected with Cu-Kα radiation on a Stoe Stadi-4 four circle diffractometer equipped with an Oxford Cryosystems low temperature device. The structure was solved by direct methods (SIR92)[27] and refined against F^2 using all data (Shelxl-97).[28] The final *R* factor based on *F* and data with $F > 4\sigma(F)$ was 0.0325. The molecule is disordered about a crystallographic two-fold axis which passes through the atoms C2 and C6. This averages the lengths and angles formed between chemically inequivalent atoms, and so these should not be interpreted. This determination is used only to show that **4** is planar and to establish the tautomeric form in the solid-state.

Crystal data for 15. $C_{13}H_9N_3O_2$ *M* = 239.23, monoclinic, space group $P2_1/c$. *a* = 6.1911(3), *b* = 7.8957(4), *c* = 21.7772(10) Å, *β* = 91.924(3)°, *V* = 1063.94(9) $Å^3$ at *T* = 150 K. *Z* = 4. Data were collected with Mo-Kα radiation on a Bruker Apex CCD diffractometer equipped with an Oxford Cryosystems low temperature device. The structure was solved by direct methods (SIR92) and refined against F^2 using all data (Crystals).[29]

In both structures non-H atoms were modelled with anisotropic displacement parameters and H-atoms were placed in calculated positions. Further crystal and refinement data are available in the ESI.†

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