Synthesis of Pyrrolo[1,2-*c*]imidazol-5-one, Pyrrolo[1,2-*a*]imidazol-5-one and Pyrrolo[1,2-*b*]pyrazol-6-one (Three Isomeric Azapyrrolizinones), by Pyrolysis of Meldrum's Acid Derivatives

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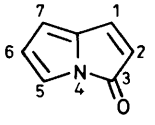
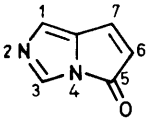
Reaction of Meldrum's acid with the imidazole- and pyrazole-carbaldehydes (**9**)—(**11**) gave the condensation products (**6**), (**7a**), and (**8**) which were pyrolysed in the gas phase to give the title aza-analogues (**2**)—(**4**) of pyrrolizin-3-one (**1**), as air-sensitive yellow solids.

In an earlier paper, we described an efficient synthesis[1] of pyrrolizin-3-one (**1**)[2] by gas-phase pyrolysis of the condensation product (**5**) of Meldrum's acid and pyrrole-2-carbaldehyde. We now report the successful application of this strategy to the parent aza-analogues of pyrrolizin-3-one, (**2**)—(**4**), which are pyrrolo[1,2-*c*]imidazol-5-one, pyrrolo[1,2-*a*]imidazol-5-one,



(**1**)



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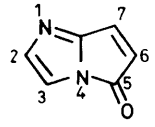

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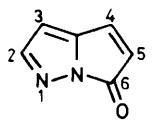
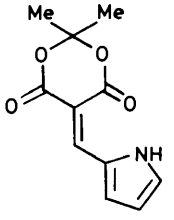
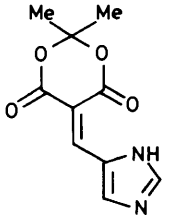


(**4**)

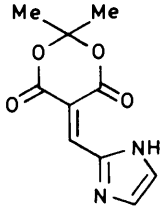
and pyrrolo[1,2-*b*]pyrazol-6-one respectively, and in the following paper, we make a detailed spectroscopic comparison of these systems.[3] There have been no previous reports of these systems or of their simple derivatives, and indeed references to fully oxidised azapyrrolizines of any sort are sparse.[4] However, parent pyrrolo[1,2-*c*]- and [1,2-*a*]-imidazoles are known,[5] as is a dibenzo-derivative,[6] while benzopyrrolo[1,2-*a*]imidazol-5-one and a benzopyrrolo[1,2-*b*]pyrazol-4-one were first reported nearly thirty years ago.[7,8]



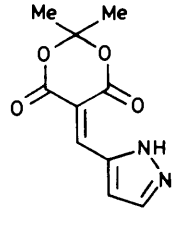
(**5**)



(**6**)



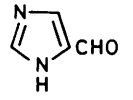
(**7**)



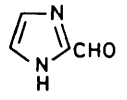
(**8**)

As key intermediates *en route* to the Meldrum's acid derivatives (**6**)—(**8**) good syntheses of the imidazole- and pyrazole-carbaldehydes (**9**)—(**11**) were required. Imidazole-4(5)-carbaldehyde (**9**) is well known, and is best obtained by manganese dioxide oxidation[9] of the corresponding hydroxymethyl compound, which is readily available on a large scale.[10] Several syntheses of imidazole-2-carbaldehyde (**10**) have been developed recently[11] but the four-step method of Godefroi[11] is best adapted to multi-gram quantities. Variable quantities of the diethyl acetal of (**10**) were invariably obtained as a contaminant, but mild acid hydrolysis combined with the recrystallisation step gave a good recovery of the pure carbaldehyde. Surprisingly, for a compound first prepared in 1941,[12] there are but nine references in the literature to pyrazole-3-carbaldehyde (**11**). An excellent three-step procedure, developed by Bredereck[13] was used with trivial modification in the present work (see the Experimental section).

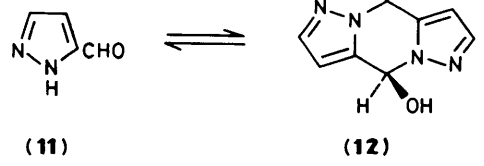
A major difficulty in handling the carbaldehydes (**9**)—(**11**) is



(**9**)



(**10**)



(**11**) (**12**)

their low solubility in common solvents. This is exacerbated in the case of (**11**) by its existence in equilibrium with the dimers[14] (**12**) (2 stereoisomeric forms), which are only partially dissociated even in highly polar solvents (*e.g.* [$^2H_6$]Me_2SO; monomer 67%, dimer isomers 23 and 10% of mixture). However, the mixture is relatively soluble in hot, polar, basic solvents (*e.g.* pyridine) to give solutions of the monomeric carbaldehyde which are stable for many days at room temperature. It is hoped that this simple technique will make the chemistry of pyrazole-3-carbaldehyde more accessible.

Condensation of imidazole-4(5)-carbaldehyde with Meldrum's acid was conveniently effected in pyridine solution, a medium which is generally more applicable to ketone reactions.[15,16] The structure of the 5-ylidene derivative (**6**) followed by spectroscopic comparison with its pyrrole analogue (**5**) (Table 1): absorption maxima at *ca.* 1700 cm^{-1} and > 300 nm in the i.r. and u.v. regions respectively are typical of such

Table 1. Selected spectroscopic data for the Meldrum's acid derivatives (5)—(8)

	$\nu_{max.}$(Nujol)(cm^{-1})	$\lambda_{max.}$(EtOH)(nm)	δ_H (ylidene proton)
(5)	1 690	392	8.25[a]
(6)	1 690	347	8.34[b]
'(7)'	1 570	252	6.61[b]
(8)	1 700	319	8.38[a]

[a] $C[^2H]Cl_3$ solution. [b] $[^2H_6]Me_2SO$ solution

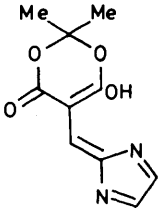
Table 2. I.r. and u.v. absorption maxima of pyrrolizin-3-one (1) and its aza-analogues (2)—(4)

	$\nu_{max.}$(Nujol)(cm^{-1})	$\lambda_{max.}$($CHCl_3$)(nm)
(1)[a]	1 740[b]	292; 416[c]
(2)	1 750	275; 366
(3)	1 760	254; 410
(4)	1 760	295; *ca.* 345sh

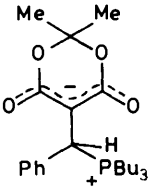
[a] Reference 2. [b] Liquid film. [c] Ethanol solution

structures as is the ^1H n.m.r. chemical shift of the ylidene proton at $\delta_H > 8.0$.

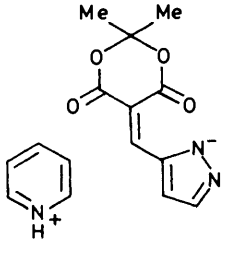
These characteristics were manifestly not fulfilled by the product obtained from reaction of imidazole-2-carbaldehyde with Meldrum's acid in benzene solution, using piperidinium acetate as the catalyst (Table 1). The structure of this material, a colourless solid of extremely low solubility, remains unknown, but it clearly does not possess the carbonyl absorption or the conjugated system expected of compound (7). The analysis was further complicated by mass spectroscopic evidence of impurities (see the Experimental section), although the 'correct' molecular ion was also present. The material could not be recrystallised, and so the elemental analysis is at best only indicative of the molecular formula. It was too insoluble for reliable ^{13}C n.m.r. spectra to be obtained, though exchange effects may contribute to complex spectra even when the structure is well defined [*e.g.* (8) in which the three methine resonances are broad and of low intensity]. It is tentatively suggested that the 2-carbaldehyde condensation product may adopt the enol tautomer (7a), though the reason for this



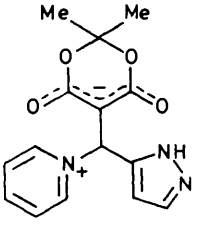
(7a)



(13)



(8a)



(8b)

anomalous behaviour remains obscure. However, the assignment is at least consistent with the u.v. spectrum: spectra of related Michael adducts [*e.g.* (13)] have maxima at *ca.* 260 nm.[17]

Because of problems associated with the dimer (12), the reaction of pyrazole-3-carbaldehyde (11) with Meldrum's acid was carried out in pyridine. The condensation product which precipitated contained, in addition, one mole equivalent of pyridine. This can be associated either as a salt (8a), a Michael adduct (8b) or as a molecular complex. The first is ruled out on the basis of the ^1H n.m.r. chemical shifts, which show no pronounced shielding relative to (8) itself. The Michael adduct (8b) is excluded on the basis of the u.v. and i.r. spectra ($\lambda_{max.}$ 321 nm and $\nu_{max.}$ 1690 cm^{-1} *cf.* Table 1), and so a molecular complex probably represents the correct structure. Decomposition of the complex with dilute acid gave the required condensation product (8) in 64% overall yield, whose spectra are consistent with the assigned structure (Table 1).

Gas-phase pyrolysis of the imidazole-4(5)-carbaldehyde condensation product (6) at 600 °C gave the analytically pure pyrroloimidazolone (2) as a yellow crystalline solid in 79% yield. Attempted recrystallisation was inefficient due to the probable formation of polymeric material on heating. The product may be stored for months at −20 °C, in the absence of air, but is apparently irreversibly hydrated in the atmosphere at room temperature.

Owing to its extreme involatility pyrolysis of the imidazole-2-carbaldehyde condensation product (7a) under standard conditions was unsatisfactory. However, the pyrroloimidazolone (3) could be obtained, in low yield, by dropping the starting material down a *vertical* furnace tube[18] maintained at 600 °C. Separation of the pure heterocycle from quantities of polymeric products was conveniently effected by sublimation *in vacuo* to give orange crystals. In contrast to its isomer (2), compound (3) has high thermal stability and can be re-sublimed over a number of cycles without significant loss. It can be stored at −20 °C, but decomposes in air over a period of hours.

Vertical furnace procedures were also required for the preparation of the pyrrolopyrazolone (4), which was obtained as an analytically pure yellow solid in 18% yield. The material is probably more stable in air than its isomers (2) and (3), but was normally stored at −20 °C.

The spectra of pyrrolizin-3-one (1) and its aza-analogues (2)—(4) show strong resemblences (Table 2). In all cases, the carbonyl stretching frequency in the i.r. region is abnormally high (> 1 740 cm^{-1}) for an amide-type carbonyl, which indicates that normal delocalisation of the lone pair of the bridgehead nitrogen atom is severely impaired (see the following paper). In the u.v. spectra, all the derivatives (1)—(4) show strong absorption in the range 250—300 nm, with a much weaker peak at longer wavelength which is responsible for the colour of the compounds. The shifts which are observed in this peak are comparable in magnitude to those in, for example, pyrazine, pyrimidine, and pyridazine.[19]

The mass spectra of compounds (1)—(3) are also similar, with sequential cleavage of CO and HCN [(1)[1,2] *m/z* 119 (100%), 91 (59), and 64 (41), (2) *m/z* 120 (100%), 92 (12), and 64 (40), and (3) *m/z* 120 (100%), 92 (18), and 65 (32)]. However, these peaks are both of < 3% intensity in the spectrum of the pyrrolopyrazolone (4), which instead exhibits major peaks at ($M^+ - 56$) and ($M^+ - 57$) [*m/z* 64 (36%) and 63 (33%)], probably due to rapid N_2 cleavage after initial loss of CO.

Experimental

^1H N.m.r. spectra were recorded at 80 or 200 MHz and ^{13}C n.m.r. spectra were recorded at 50 MHz, unless otherwise stated.

Imidazole-4(5)-carbaldehyde.—This compound was obtained in 42% yield by oxidation of 4(5)-hydroxymethylimidazole[10] with commercial active manganese dioxide in dioxane,[9a] m.p. 170—172 °C (lit.,[9a] 174—175 °C), δ_H ([$^2H_6$]Me_2SO) 9.74 (1 H, d, *J* 0.70 Hz), 7.98 (1 H, d, *J* 1.0 Hz), and 7.92 (1 H, m); only two peaks were apparent in the ^{13}C n.m.r. spectrum δ_C ([$^2H_6$]Me_2SO) 183.57 ($^1J_{CH}$ *ca.* 175 Hz) and 138.80 ($\Sigma\ ^1J$ *ca.* 219 Hz); a broad peak at *ca.* δ_C 138.3 in the fully coupled spectrum may be due to the C4(5) quaternary.

Imidazole-2-carbaldehyde.—This compound was conveniently prepared on a multi-gram scale by the *Org. Synth.* procedure.[11] However, in our hands the final product was invariably contaminated with up to 40% of the carbaldehyde diethyl acetal, δ_H ([$^2H_6$]Me_2SO) 6.93 (2 H, s), 5.47 (1 H, s), 3.54 (4 H, m), and 1.12 (6 H, t). For hydrolysis and purification, the crude mixture of aldehyde and acetal (12.2 g) was dissolved in the minimum amount of hot hydrochloric acid (1M; 50 ml), and the solution was heated under reflux for 1 h. The cooled solution was neutralised with sodium hydrogen carbonate as described[11] to give the aldehyde (8.0 g) as a fawn precipitate, m.p. 200—202 °C (lit.,[11] 206—207 °C), δ_H ([$^2H_6$]Me_2SO) 9.65 (1 H, t, *J* 0.5 Hz), and 7.41 (2 H, d, *J* 0.5 Hz); δ_C ([$^2H_6$]Me_2SO) 181.08 ($^1J_{CH}$ 182.2 Hz), 145. 61 (q), and 127.13 ($^1J_{CH}$ 190.7 Hz).

Pyrazole-3-carbaldehyde.—(*a*) *4-Dimethylamino-1,1-dimethoxybut-3-en-2-one.* This was obtained in 62% yield from pyruvaldehyde dimethyl acetal and dimethylformamide diethyl acetal in an identical manner to that described for the diethyl acetal,[13] and had b.p. 128—131 °C (0.8 Torr) (Found: C, 55.65; H, 8.75; N, 8.2. $C_8H_{15}NO_3$ requires C, 55.5; H, 8.65; N, 8.1%); δ_H (C[^{2}H]Cl_3; 100 MHz) 7.69 (1 H, d), 5.32 (1 H, d), 4.55 (1 H, s), 3.38 (6 H, s), and 3.09 and 2.86 (6 H, 2 × br s).

(*b*) *Pyrazole-3-carbaldehyde dimethyl acetal.* Treatment of the above acrolein with hydrazinium sulphate in dilute aqueous sodium hydroxide as described for the diethyl acetal[13] gave an 85% yield of the pyrazole, b.p. 95—98 °C (0.1 Torr) (Found: M^+, 142.0742. $C_6H_{10}N_2O_2$ requires *M*, 142.0742); δ_H (C[^{2}H]Cl_3; 100 MHz) 7.58 (1 H, d), 6.34 (1 H, d), 5.62 (1 H, s), and 3.37 (6 H, s). This product was used without purification for the synthesis of the carbaldehyde dimer: distillation on a large scale resulted in considerable losses, with little or no improvement in quality.

(*c*) *Dimer of pyrazole-3-carbaldehyde.* Hydrolysis of the above acetal proceeded in the same way as that of the diethyl acetal,[13] to give, after 24 h, a 66% yield of the carbaldehyde dimer, m.p. 145—146 °C (lit.,[13] 146—147 °C) as a grey, insoluble solid, *m/z* 192.

(*d*) in situ *Generation of pyrazole-3-carbaldehyde.* A mixture of the above dimer (50 mg) and [$^2H_5$]pyridine (0.3 ml) was heated until all the solid had dissolved (*ca.* 5 min). The resulting solution, which was stable for many days at room temperature, contained the monomeric carbaldehyde, δ_H ([$^2H_5$]pyridine) 10.38 (1 H, apparent t, *J ca.* 0.5 Hz), 7.95 (1 H, dd, *J* 2.4 and 0.7 Hz), and 7.06 (1 H, d, *J* 2.4 Hz); δ_C ([$^2H_5$]pyridine) 186.28 ($^1J_{CH}$ 177.0 Hz), 151.20 (q), 132.46 ($^1J_{CH}$ 193.2 Hz), and 105.95 ($^1J_{CH}$ 184.6 Hz).

5-[Imidazol-4(5)-ylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione.—A solution of imidazole-4(5)-carbaldehyde (0.96 g, 10 mmol) in the minimum quantity of pyridine (50 ml) was treated with Meldum's acid (1.44 g, 10 mmol). After 2 h, the precipitated solid (0.84 g) was filtered off. After 20 h, the pyridine mother liquors were concentrated to give a second crop of brown solid, which was conveniently purified by washing it with water to yield the *title imidazol-4(5)-ylidenedioxanedione*, which was analytically pure, (1.29 g, 58% total), m.p. 222—228 °C (decomp.) (Found: C, 53.9; H, 4.75; N, 12.85. $C_{10}H_{10}N_2O_4$ requires C, 54.05; H, 4.5; N, 12.6%); δ_H ([$^2H_6$]Me_2SO) 8.63 (1 H, br s), 8.34 (1 H, s), 8.10 (1 H, s), and 1.71 (6 H, s); $\lambda_{max.}$(EtOH) 347 nm; $\nu_{max.}$(Nujol) 1 690 cm^{-1}; *m/z* 222 (M^+, 14%), 164 (52), 120 (100), 92 (20), and 65 (18).

Condensation Product of Meldrum's Acid and Imidazole-2-carbaldehyde.—Meldrum's acid (2.88 g, 20 mmol), was added to a solution of imidazole-2-carbaldehyde (1.92 g, 20 mmol) in the minimum amount of boiling benzene (850 ml) containing piperidine (20 drops) and acetic acid (20 drops). The mixture was set aside to cool overnight, and the fine solid which formed was then filtered off and dried overnight at 0.1 Torr, to give a free-flowing cream-coloured solid (3.82 g, *ca.* 86%), m.p. 190—193 °C (decomp). The identity of this material remains unknown. It is essentially insoluble in organic solvents, and could not be recrystallised. The ^1H n.m.r. spectra of different batches show the presence of variable trace amounts of residual benzene, δ_H ([$^2H_6$]Me_2SO) 7.36 which may account for some variation in chemical shift of the methine resonances. Typical values are δ_H ([$^2H_6$]Me_2SO) 7.41 (1 H, d, *J* 1.84 Hz), 7.25 (1 H, d, *J* 1.84 Hz), 6.61 (1 H, s), and 1.53 (*ca.* 6 H, s). Its u.v. and i.r. spectra [$\lambda_{max.}$ (EtOH) 252 nm, with very weak absorption at 370 nm, and $\nu_{max.}$ (Nujol) 1 570 cm^{-1}] are inconsistent with a typical 5-ylidene-1,3-dioxane-4,6-dione (see Discussion section). Nevertheless, the e.i. mass spectrum shows a consistent peak at *m/z* 222 (18%) (Found: M^+, 222.0640. $C_{10}H_{10}N_2O_4$ requires *M*, 222.0641) with anticipated breakdown peaks at *m/z* 164 (45%), 120 (100), 92 (28) and 65 (17). In addition, a reproducible peak at *m/z* 247 (8%) (Found: 247.1312) which corresponds to either of the unlikely formulae $C_{11}H_{15}N_6O$ (requires 247.1307) or $C_{13}H_{17}N_3O_2$ (requires 247.1321), was always present, together with other fragment ions at *m/z* 135 (36%), 84 (31), and 58 (70). Microanalysis gave results which were almost acceptable for the condensation product (Found: C, 53.5; H, 4.9; N, 12.4. $C_{10}H_{10}N_2O_4$ requires C, 54.05; H, 4.5; N, 12.6%), and exclude the *m/z* 247 material (*e.g.* $C_{13}H_{17}N_3O_2$ requires C, 63.15; H, 6.9; N, 17.0%). Broadly similar results were obtained when pyridine was used as the solvent for the condensation.

2,2-Dimethyl-5-(pyrazol-3-ylidene)-1,3-dioxane-4,6-dione.—Pyrazole-3-carbaldehyde dimer (0.96 g, 10 mmol of monomer) was heated under reflux in pyridine (20 ml) until all the solid had dissolved (*ca.* 5 min). The solution was cooled to room temperature and Meldrum's acid (1.44 g, 10 mmol) was added. After 18 h, the precipitated solid (2.22 g) was filtered, washed with light petroleum (b.p. 40—60 °C), and dried at 0.1 Torr. From its spectra and microanalysis, this material was identified as a 1:1 *complex* of pyridine and the required ylidenedioxanedione (74% yield), m.p. 121—122 °C (decomp.) (Found C, 59.9; H, 5.0; N, 14.1. $C_{10}H_{10}N_2O_4 \cdot C_5H_5N$ requires C, 59.8; H, 5.0; N, 13.95%); δ_H([$^2H_6$]Me_2SO) 8.59 (2 H, m), 8.33 (1 H, s), 7.75—7.95 (2 H, m), 7.35—7.55 (3 H, m), and 1.72 (6 H, s). {A similar experiment using [$^2H_5$]pyridine enabled the pyrazole ring proton resonances to be identified: δ_H([$^2H_6$]Me_2SO) 8.32 (1 H, s), 7.93 (1 H, d, *J* 2.3 Hz), 7.55 (1 H, d, *J* 2.3 Hz), and 1.72 (6 H, s)}; $\lambda_{max.}$(EtOH) 321 nm; $\nu_{max.}$(Nujol) 1 690 cm^{-1}; *m/z* 222 (16%), 164 (61), 120 (25), 79 (25), 64 (30), 58 (39), 44 (98), and 43 (100).

Decomposition of the complex was effected with dilute acid, as follows. A solution of the complex (1.86 g, 6 mmol) in water (6 ml) was treated with hydrochloric acid (1M; 10 ml). The white precipitate was filtered off, washed with water, and dried thoroughly *in vacuo*, to give the analytically pure *ylidenedioxanedione* (1.14 g, 86%; 64% overall yield from the carbaldehyde dimer), m.p. 108–110 °C (decomp.) (Found: C, 53.9; H, 4.5; N, 12.6. $C_{10}H_{10}N_2O_4$ requires C, 54.05; H, 4.5; N, 12.6%); δ_H(C[^{2}H]Cl_3) 8.38 (1 H, s), 7.78 (1 H, d, *J* 1.9 Hz), 6.97 (1 H, d, *J* 1.9 Hz), and 1.80 (6 H, s); $\lambda_{max.}$(EtOH) 319 nm;

$\nu_{max.}$(Nujol) 1 700 cm^{-1}; *m/z* 222 (M^+, 3%), 164 (14), 120 (9), 79 (12), 58 (30), 44 (74), and 43 (100).

Pyrrolo[1,2-c]*imidazol-5-one*.—The imidazol-4(5)-ylidenedioxanedione (0.44 g, 2 mmol) was sublimed at 170—180 °C and 1—2 m Torr into a horizontal silica furnace tube (35 × 2.5 cm) which was maintained at 600 °C. The products were trapped in a 'U'-tube, cooled by liquid nitrogen, which was situated at the exit point of the furnace. After the pyrolysis, which required 30—40 min, the trap was allowed to warm to room temperature. The pyrolysate consisted of three fractions. The volatile (liquid) fraction was removed from the trap with a dropper, and was discarded. A tarry, polymeric fraction, which collected at the furnace joint, was removed with a tissue soaked in methylene chloride. The major fraction, which was a yellow solid, was dissolved in acetone and the solution was filtered through a plug of cotton wool. Removal of the solvent at the oil pump (10^{-1} Torr) gave a yellow crystalline residue (0.19 g, 79%) which was pure *pyrrolo*[1,2-c]*imidazol-5-one*, m.p. >300 °C, after significant decomposition at 100—120 °C (Found: C, 60.25; H, 3.55; N, 23.45. $C_6H_4N_2O$ requires C, 60.0; H, 3.35; N, 23.35%); δ_H (C[^{2}H]Cl_3) 7.76 (1 H, apparent s), 7.32 (1 H, dd), 6.81 (1 H, s), and 5.86 (1 H, d); $\lambda_{max.}$($CHCl_3$) 275 and 366 nm; $\nu_{max.}$(Nujol) 1 750, 1 190, 1 080, 800 and 620 cm^{-1}; *m/z* 120 (M^+, 100%), 92 (12), 65 (40), and 38 (35).

Pyrrolo[1,2-a]*imidazol-5-one*.—The solid condensation product of Meldrum's acid and imidazole-2-carbaldehyde (0.44 g, *ca.* 2 mmol) was dropped, during a period of 10—15 min, down a vertical furnace tube (30 × 2.5 cm) at 600°C and 10−30 mTorr. A *loose* plug of silica wool was positioned at the centre of the tube. The products were trapped by a similar arrangement to that used for the horizontal pyrolyses (see above). When all the solid had been added, the liquid nitrogen was removed from the U-tube trap and the volatiles were evaporated under reduced pressure into the pump trap. The remaining material in the U-tube was dissolved in methylene chloride, the solvent was evaporated at 0.1 Torr, and the residue was sublimed (Kugelrohr) at 90 °C (0.1 Torr). The orange-red crystals so obtained were pure *pyrrolo*-[1,2-a]*imidazol-5-one* (0.014 g, 5.8%), m.p. 93—95 °C (Found: C, 58.9; H, 3.35; N, 22.9. $C_6H_4N_2O{\cdot}0.1H_2O$ requires C, 59.1; H, 3.45; N, 23.0%); δ_H (C[^{2}H]Cl_3) 7.23 (1 H, d), 7.03 (1 H, d), 6.96 (1 H, m), and 6.02 (1 H, dd); $\lambda_{max.}$($CHCl_3$) 254 and 410 nm; $\nu_{max.}$(Nujol) 1 760, 1 240, 1 100, 1 040, 760, and 670 cm^{-1}; *m/z* 120 (M^+, 100%), 92 (18), 65 (33), and 38 (27).

Pyrrolo[1,2-b]*pyrazol-6-one*.—Attempted pyrolyses of the pyrazolylidenedioxanedione (0.44 g, 2 mmol) under standard horizontal-tube conditions, gave poor results with substantial inlet residues (30—40%). However, use of the vertical furnace on a similar scale at 600 °C (10—30 mTorr), as described above for pyrrolo[1,2-*a*]imidazol-5-one, gave a dense yellow solid pyrolysate (0.043 g) after evaporation of the volatiles under reduced pressure. This was scraped out of the trap with a spatula, and was identified as pure *pyrrolo*[1,2-b]*pyrazol-6-one* (18%), m.p. 36—38 °C (Found: C, 59.75; H, 3.45; N. 23.25. $C_6H_4N_2O$ requires C, 60.0; H, 3.35; N, 23.35%); δ_H(C[^{2}H]Cl_3) 7.61 (1 H, apparent s), 7.19 (1 H, d), 6.12 (1 H, d), and 5.97 (1 H, dd); $\lambda_{max.}$($CHCl_3$) 295 and *ca.* 345sh nm; $\nu_{max.}$(Nujol) 1 760, 1 270, 1 180, 800, and 670 cm^{-1}; *m/z* 120 (M^+, 100%), 64 (36), 63 (33), and 38 (17) (Found: M^+, 120.032. $C_6H_4N_2O$ requires *M*, 120.032).

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