3-Hydroxypyrroles and 1*H*-Pyrrol-3(2*H*)-ones. Part 13.[1] Reactions of Methoxymethylene Meldrum's Acid with 3-Hydroxypyrroles, with 3-Methoxypyrroles and with other Active Substrates, and Pyrolytic Heterocyclisations of the Products

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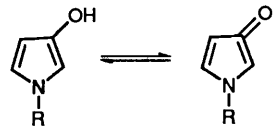
Methoxymethylene Meldrum's acid **2** in acetonitrile solution acts as a useful *C*-electrophile for active substrates such as pyrrole, indole or tertiary enaminones to give substitution products (*e.g.* **5**, **6** or **12**, respectively). Primary enaminones react exclusively at the nitrogen atom under these conditions. The effect of ring substituents on the regiochemistry of electrophilic substitution of 3-hydroxypyrroles and 3-methoxypyrroles was studied using methoxymethylene Meldrum's acid as the electrophile. Flash vacuum pyrolysis of the Meldrum's acid derivatives obtained in many of these reactions gave access to a range of heterocyclic systems, including the pyridone **48**, quinolinedione **43**, benzazepinedione **41** and fused pyrones **50**, **52** and **54**.

The chemistry of the 3-hydroxypyrrole system is controlled by the tautomerism shown in Scheme 1, in which the pyrrole-like



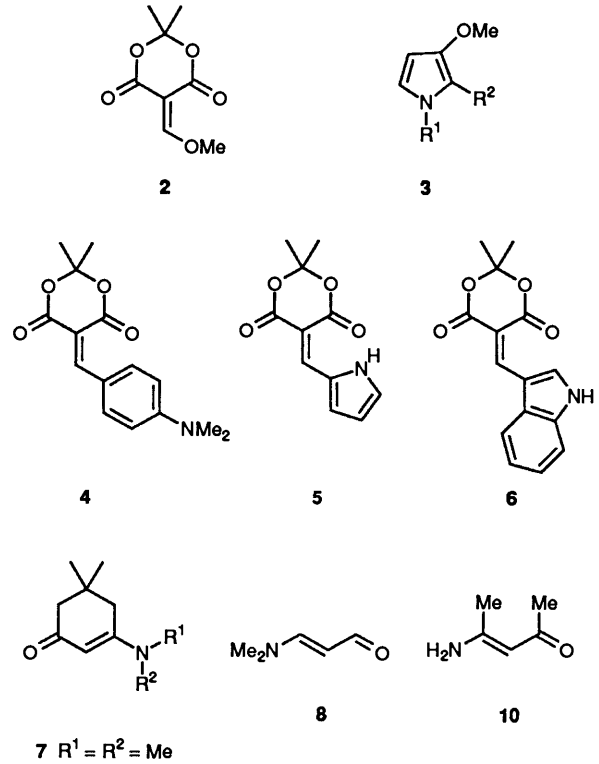
1E **1K**

Scheme 1

reactivity of the enol **1E** competes with the enaminone reactivity of the keto form **1K**.[2] We have previously demonstrated that 2,2-disubstituted pyrrolones (in which tautomerism is not possible) undergo electrophilic substitution at the 4-position,[3] and that methoxymethylene Meldrum's acid **2**[4] (2,2-dimethyl-1,3-dioxane-4,6-dione) is a useful *C*-electrophile for such active substrates.[3] Here we extend this work to *N*-substituted and *N*-unsubstituted 3-hydroxypyrroles capable of tautomerism, and explore the reactivity of model pyrrole and enaminone systems to the reagent **2**. The synthetic potential of these products is demonstrated by their pyrolysis reactions which lead to heterocyclic systems including pyridones, azepinones, and fused pyrones. In addition, the reaction of **2** with simple 3-alkoxypyrroles **3** is explored. No systematic studies of electrophilic substitution in these highly active substrates have been reported, and it was hoped that reaction with **2** would take place under mild conditions and lead to stable crystalline products.

Although methoxymethylene Meldrum's acid **2** is a relatively weak electrophile, it reacts readily with *N*,*N*-dimethylaniline, pyrrole or indole in acetonitrile solution to give the substitution products **4**–**6**, respectively, in *ca.* 70% yield. This provides a direct route to methylene Meldrum's acid derivatives without the need for prior formylation of the (hetero)aromatic substrate. However, closely related substrates such as *N*-methylpyrrole, thiophene, or furan, proved to be unreactive under these standard conditions.

In view of the reactivity of cyclic enaminones towards methoxymethylene Meldrum's acid **2**,[3] we also studied its reaction with the tertiary enaminones **7** and **8**, the primary enaminones **9** and **10** and the secondary enaminone **11**. The tertiary substrates followed the same mode of reaction as 2,2-disubstituted pyrrolones and the *C*-substitution products **12** and **13** were obtained in 52 and 6% yield respectively. Clearly **8**

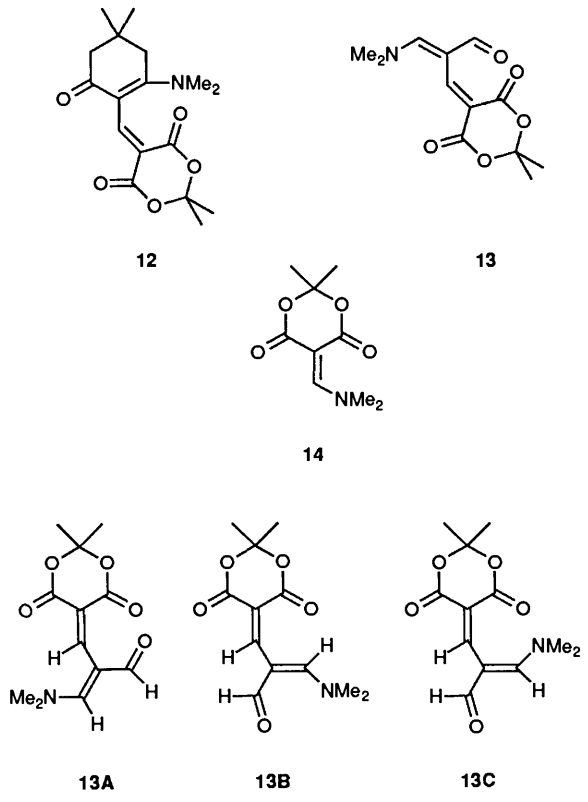


2 **3** **4** **5** **6** **8** **10**

7 $R^1 = R^2 = Me$
9 $R^1 = R^2 = H$
11 $R^1 = Ph$, $R^2 = H$

is barely active enough to give products, but more vigorous conditions usually caused decomposition of the methoxymethylene Meldrum's acid.

A series of NOE experiments was carried out to assign the configuration of the exocyclic portion of **13**. Irradiation of the *N*-methyl group(s) affected one alkene proton (at δ_H 8.60) only, whereas irradiation of the aldehyde proton (δ_H 9.20) affected the remaining alkene proton (δ_H 8.24) and *vice versa*. Configurations such as **13A** are ruled out by these results. Only **13B** and **13C** are consistent with the data though the latter is highly improbable on steric grounds (Fig. 1): even dimethylaminomethylene Meldrum's acid **14** is severely distorted owing to steric interaction between an *N*-methyl group and the adjacent carbonyl function.[5]



12 13 14

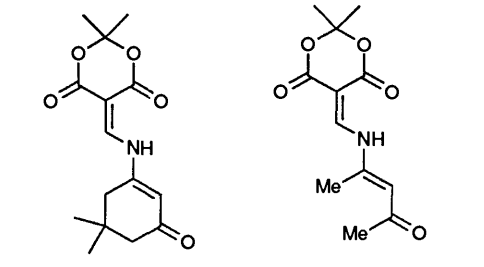
13A 13B 13C

Fig. 1 Some configurations of **13**

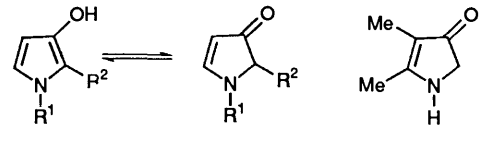
In contrast, the primary enaminones **9** and **10** react with **2** at the nitrogen atom to give the aminomethylene derivatives **15** and **16** in moderate yield. The ability of these vinylogous amides to act as *N*-nucleophiles was initially unexpected: however, a similar reaction of 3-aminocyclohexenone with methoxymethylene Meldrum's acid in refluxing ethanol has been recently reported,[6] though the yield was lower than in our example, and substantial amounts of a by-product were formed.

The phenylamino compound **11** did not react with **2** even after extended reaction times.

In the 3-hydroxypyrrole series, we studied the behaviour of a range of 1-substituted and 1,2-disubstituted compounds **17**–**21**,



15 16

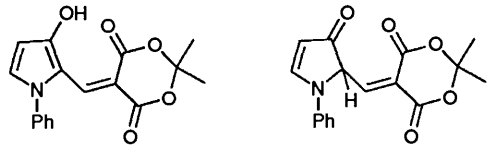


E K 22

17 R^1 = Ph, R^2 =H
18 R^1 = Bu^t, R^2 = H
19 R^1 = Me, R^2 = Ph
20 R^1 = Bu^t, R^2 = Ph
21 R^1 =Ph, R^2 = Me

which were made by the Meldrum's acid pyrolysis route,[7,8] and the *N*-unsubstituted compound **22** which was made by Bauer's method.[9]

The 1-phenyl and 1-*tert*-butyl compounds **17** and **18** gave contrasting results on overnight treatment with methoxymethylene Meldrum's acid in acetonitrile at room temperature. The *N*-aryl example **17** gave the 2-substitution product **23** (62%), a mode of reaction which was found previously for an azo-coupling process.[10] The structure and tautomerism of the product followed from its NMR spectra. Thus, the coupling constant between the two remaining pyrrole ring protons (J 2.9 Hz) is typical of $^3J_{4,5}$ in 3-hydroxypyrroles,[11] and larger than would be expected of $^4J_{2,4}$ or $^4J_{2,5}$. The reaction must, therefore, have taken place at the 2-position, and the presence of an OH resonance at δ_H 10.92 further confirms that the product adopts the hydroxypyrrole tautomer **23A**, rather than



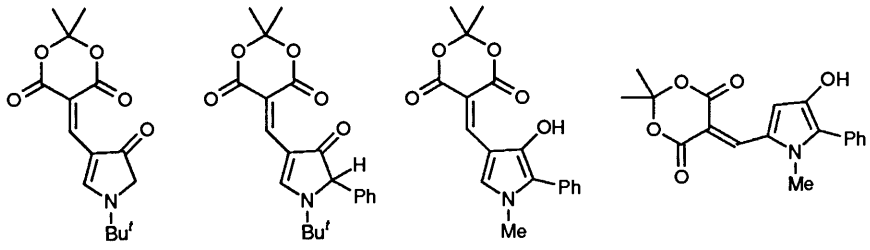
23A 23B

the pyrrolone **23B**. In contrast, the *N*-*tert*-butyl compound **18** gives the 4-substitution product **24** (75%) as shown by the two proton signals at δ_H 4.02 (due to the 2-position) and the characteristically deshielded resonance (δ_H 10.15) corresponding to the 5-position of 1*H*-pyrrol-3(2*H*)-ones, in the ^{1}H NMR spectrum of the product. These assignments were confirmed by an NOE experiment: irradiation of the *N*-*tert*-butyl signal caused enhancement at δ_H 10.15 (15%) and 4.02 (1%) as expected.

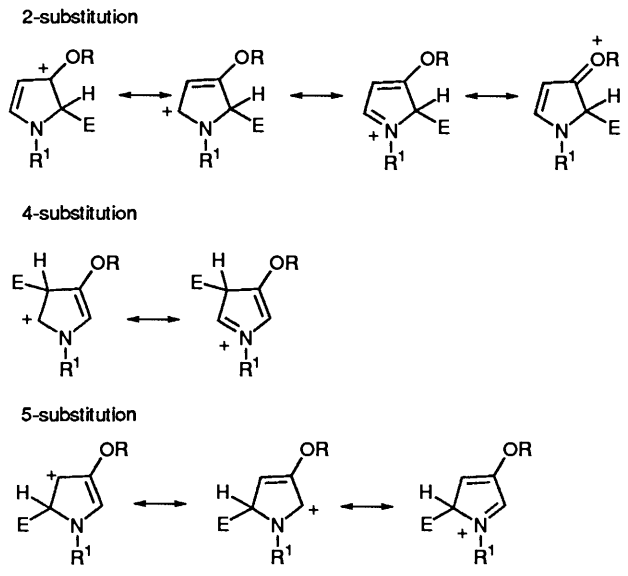
The dramatic difference in regioselectivity between **17** and **18** may arise from the tautomeric form in which they react. The *N*-phenyl compound presumably reacts *via* the hydroxypyrrole tautomer **17E**, since the 2-position is activated by electron donation from N and O.[10] In contrast, the *N*-*tert*-butyl derivative probably reacts *via* the pyrrolone tautomer **18K** which behaves as an electron-rich enaminone in a similar fashion to 2,2-disubstituted pyrrolones.[3] The 2-position of the hydroxypyrrole form **18E** in this case is relatively deactivated by the presence of the bulky *N*-substituent.[12,13]

The reactivity of three 1,2-disubstituted 3-hydroxypyrroles **19**–**21** was also studied. As expected, the *N*-*tert*-butyl-2-phenyl compound **20** gave the 4-substituted product **25** (75%) in a similar fashion to its 2-unsubstituted analogue. It was evident from the ^{1}H NMR spectrum that the product had adopted the keto tautomeric form (δ_H 4.97 = 2-H) and the assignment was confirmed by an NOE experiment [irradiation at *N*-*tert*-butyl resonance caused enhancement at δ_H 10.45 (20%) (5-position) and 4.97 (9%) (2-position)].

The *N*-methyl derivative **19** reacted cleanly to give a single product (68%). This was clearly in the hydroxypyrrole form because of the broad OH singlet in the ^{1}H NMR spectrum at δ_H 9.70, but it was not possible by inspection to distinguish between the 4- and 5-substituted isomers **26** and **27**. An NOE experiment established that the *N*-methyl group and the proton which gives rise to the singlet at δ_H 8.17 are adjacent (28% enhancement on irradiation at δ_H 3.75), and this was assigned as the exocyclic methylene proton by analogy with the corresponding methoxypyrrole, for which unambiguous assignment was possible (see below). The product is, therefore, the 5-substituted isomer **27**. Unfortunately, the *N*-phenyl compound **21** decomposed under the standard conditions, and no methylene Meldrum's substitution product could be obtained.



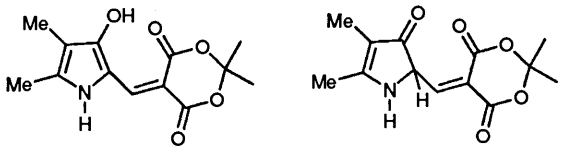
24 25 26 27



Scheme 2

Taken together, these results establish that the 'normal' pattern of reactivity for 1-substituted 3-hydroxypyrroles with electrophiles is: 2 position > 5-position > 4-position, and that reactions take place *via* the enol (hydroxypyrrole) tautomers (Scheme 2, R=H). For the special case in which a bulky 1-substituent sterically deactivates the α-(2,5)-positions, then 4-substitution [probably *via* the keto (pyrrolone) tautomer] can compete.

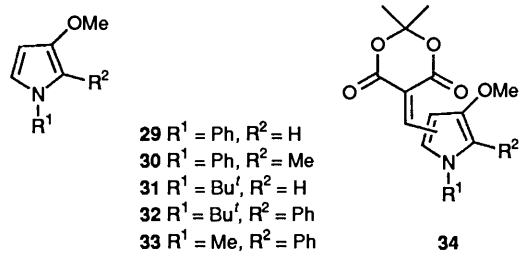
The 1-unsubstituted pyrrolone **22** shows no trace of hydroxypyrrole tautomer, even in solution in [$^2H_6$]DMSO which is known to favour enolisation in these systems,[14] and so it was expected that this might react with methoxymethylene Meldrum's acid at the 1-position, as found for the related enaminones **9** and **10**. In the event, the standard 2-substitution product **28** was isolated in 50% yield; this product clearly adopted the hydroxypyrrole form **28A** in [$^2H_6$]DMSO



28A **28B**

solution, since there is no resonance corresponding to the 2-methine carbon atom of the alternative isomer **28B**, in the ^{13}C NMR spectrum of the product.

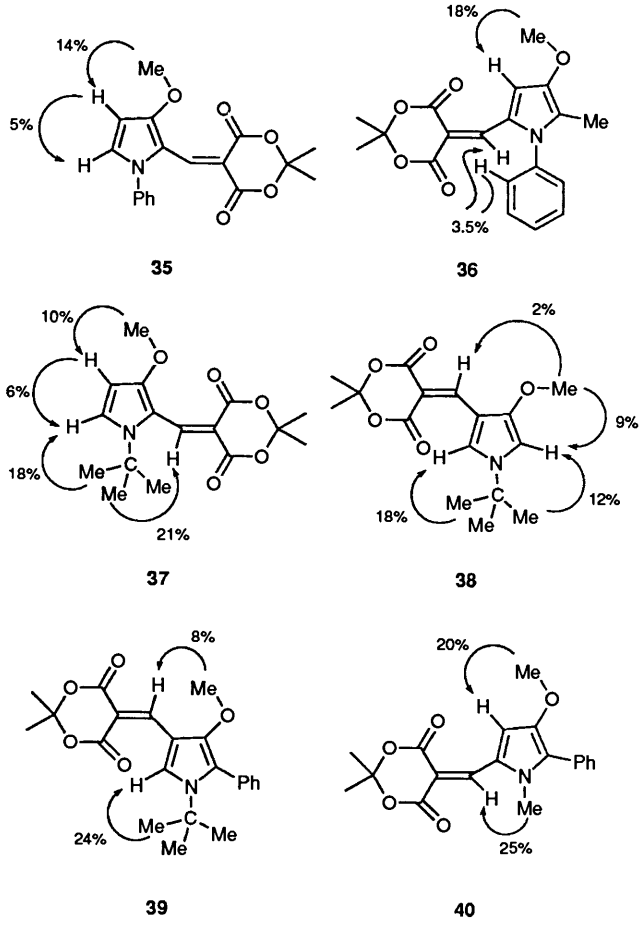
The alkoxypyrroles **29–33** which were used were prepared by regiospecific *O*-methylation[8] of the corresponding hydroxypyrroles [1*H*-pyrrol-3(2*H*)-ones]. All were sufficiently reactive to give clean crystalline products **34** on treatment with methoxymethylene Meldrum's acid **2** in acetonitrile solution,



29 R^1 = Ph, R^2 = H
30 R^1 = Ph, R^2 = Me
31 R^1 = Bu^t, R^2 = H
32 R^1 = Bu^t, R^2 = Ph
33 R^1 = Me, R^2 = Ph

34

typically after 18 h at room temperature. Yields were generally greater than 60%. Assignment of the regiochemistry in these cases relied heavily on the results of NOE experiments, which are shown collectively in Fig. 2.



35 **36** **37** **38** **39** **40**

Fig. 2 NOE data for the Meldrum's acid derivatives **35–40**

As predicted by extrapolation from the hydroxypyrrole results (*e.g.* Scheme 2, R=Me), the 1-phenyl compound **29** gave the 2-substituted product **35** (65%) exclusively, on treatment with the reagent **2**. The vicinal coupling constant ($^3J_{4,5}$ 3.2 Hz) is larger than would be expected for $^4J_{2,4}$ or $^4J_{2,5}$[11] and the assignment was confirmed by irradiation of the

pyrrole ring proton at δ_H 6.09 which caused enhancement of a doublet which could be identified (at 360 MHz) at the low frequency side of the aromatic resonances (δ_H 7.23). Further irradiation of the methoxy group established that the peak at δ_H 6.09 corresponds to the 4-H resonance (Fig. 2).

The incorporation of the methylene Meldrum's substituent at the 2-position has a dramatic deshielding effect at the 5-position, both in ^1H and ^{13}C NMR spectra. The chemical shifts of the exocyclic methylene group were at characteristic high frequency (δ_H 8.00 and δ_C 138.76); the latter signal was identified as a simple doublet in the ^1H-coupled spectrum ($^1J_{CH}$ 155.8 Hz), in contrast to the aromatic and pyrrole carbon resonances all of which showed further long-range coupling.[11]

Assignment of the regiochemistry of the product from **30** was more complex, since the remaining pyrrole proton and the exocyclic methylene proton had similar chemical shifts (δ_H 8.13 and 7.68). However, ^1H–^{13}C correlation experiments showed that the proton at *higher* frequency corresponded to the unsubstituted ring position (δ_C 108.1) and the proton at δ_H 7.68 corresponded to the carbon atom of higher chemical shift (δ_C 139.4)—a typical position for the exocyclic methine carbon atom signal (see above). Subsequent NOE experiments (Fig. 2) confirmed the assignment as the 5-substituted compound **36** (65%). As predicted, therefore, the reaction is diverted to the free α-position when the 2-position is blocked. In addition, the NOE experiments showed the preferred orientation of the 5-substituent since irradiation of the methine proton enhanced the *o*-hydrogen atom signals of the *N*-Ph group, and not the 4-H of the pyrrole ring.

Two products in 5:1 ratio were obtained by reaction of the *N*-*tert*-butylmethoxypyrrole **31** with the electrophile **2**, and these were readily separated by chromatography on silica. The major product (72%) was identified (as above) as the 2-substituted product **37** (see Fig. 2). Irradiation of the *N*-*tert*-butyl group signal of the minor isomer (15%) caused enhancement of *both* mutually-coupled (^4J 2.2 Hz) pyrrole ring protons (Fig. 2), which establishes that the substitution had taken place in the 4-position to give **38**. Clearly, in this case, the reaction is finely balanced between the electronic activation of the 2-position and its steric overcrowding which forces the electrophile into the β-position; reaction at the other α-position does not compete. It is of interest that in the corresponding hydroxypyrrole, β-substitution (presumably *via* the pyrrolone tautomer) is observed exclusively.

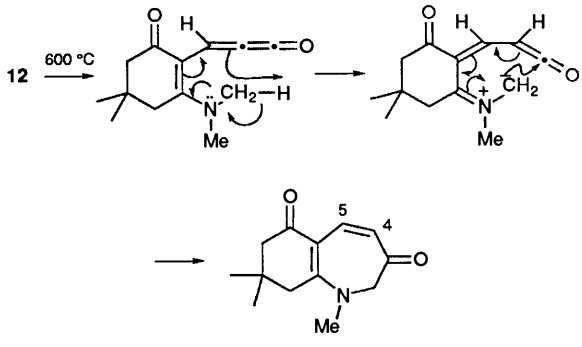
When the 2-position of a 1-*tert*-butylmethoxypyrrole is blocked—as in compound **32**—it is, therefore, not surprising that substitution is much slower than usual and that the reaction is diverted exclusively to the 4-position, to give **39** in 30% yield after chromatography. The assignment was again based on a sequence of $^{13}C/^1H$ correlations and NOE experiments, as follows. First, the exocyclic methine carbon atom resonance was identified by a fully coupled spectrum as the signal at δ_C 147.11 (d, $^1J_{CH}$ 152.9 Hz) and that this correlated with the singlet proton resonance at δ_H 8.51. The other methine ^1H resonance at δ_H 8.81 was associated with the carbon signal at δ_C 128.6 which must be due to the remaining pyrrole position. The results of the NOE experiment (Fig. 2) completed the assignment.

The final experiment in this series was carried out to confirm that small *N*-alkyl groups promote 5- rather than 4-substitution when the 2-position is blocked, and the 1-methyl-2-phenyl derivative **33** was used for this purpose. A single product was isolated in 70% yield, but the assignment was complicated by the similarity in chemical shift of both the *N*-methyl and *O*-methyl groups (δ_H 3.84 and 3.78) and the two methine protons (δ_H 8.32 and 8.11). A 2D proton–carbon correlation experiment established that the exocyclic methine carbon atom signal (δ_C 137.9, $^1J_{CH}$ 147.4 Hz) and the resonance at δ_H 8.32 were connected, and similarly the remaining pyrrole methine signal (δ_C 108.2) was associated with the peak at δ_H 8.11. The same experiment showed that the high frequency methyl resonance correlated with the carbon signal at δ_C 57.8 (OMe) and the low frequency peak correlated with the carbon signal at δ_C 32.2 (NMe). The NOE data (Fig. 2) based on these assignments confirmed that the structure is the 5-substituted product **40**.

This study has completed the first systematic investigation of electrophilic substitution reactions of 3-alkoxypyrroles, and has rigorously established the regiochemistry of the process. The results confirm the predictions of simple resonance theory (Scheme 2), with the reactivity of the 2-position > 5-position > 4-position under normal circumstances. However, large *N*-substituents can divert the reaction to the 4(β)-position, as often found in the chemistry of simple pyrroles.

The reactions described so far in this paper have led to a number of functionalised Meldrum's acid derivatives, whose gas phase pyrolytic reactions would be expected to generate highly reactive methyleneketene intermediates[15] which might undergo novel cyclisation processes. Such reactions of the pyrrole and indole derivatives **5**[16] and **6**[17] have been previously reported.

Flash vacuum pyrolysis of the dienylidene derivative **12** at 600 °C (10^{-2} to 10^{-3} Torr) gave a 45% yield of the fused azepinone **41** after chromatography on alumina. As with other cases of azepinone formation from dialkylaminodienylidene Meldrum's acid derivatives,[18] the reaction probably takes place by a hydrogen shift–electrocyclisation mechanism (Scheme 3).



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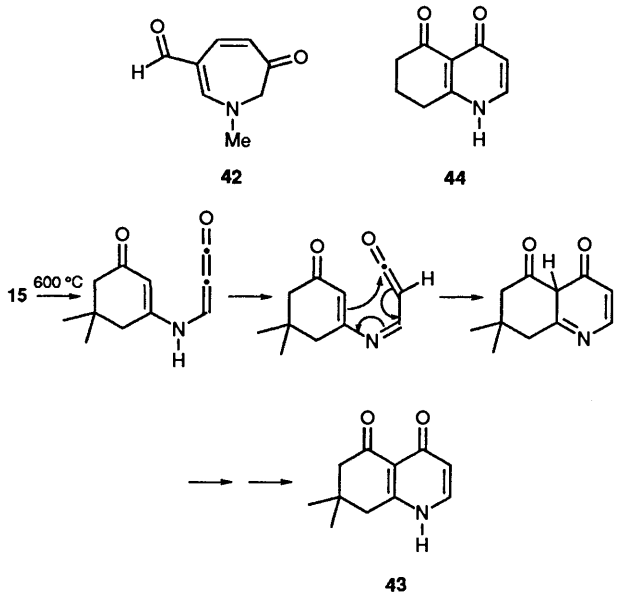
Scheme 3

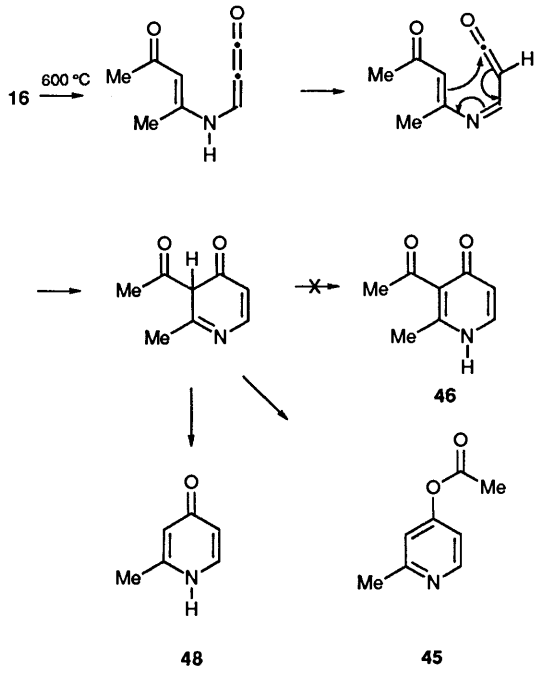
The structure of the product followed from its ^1H NMR spectrum; in particular, the vicinal coupling $^3J_{4,5}$ (11.5 Hz) is typical of such systems.[19] The 6-formylazepinone **42** was also tentatively identified from a small-scale pyrolysis of the Meldrum's acid derivative **13**, but was not fully characterised.

Aminomethyleneketenes with a free NH generally undergo 1,3-shift of this hydrogen atom to generate an iminoketene which leads to products.[20,21] In the case of **15**, electrocyclisation of the iminoketene followed by H-shift generates the quinolinedione derivative **43** (83%) (Scheme 4) whose spectroscopic data are closely similar to the 7,7-unsubstituted analogue **44** made by Gatta *et al.* from a solution-phase pyrolysis of an analogous Meldrum's acid derivative.[6] In particular, the coupling constant $^3J_{2,3}$ (5.9 Hz) is typical of such quinolinedione derivatives.[6]

Pyrolysis of the open-chain analogue **16** was more complex, and three products were formed in 5:5:1 ratio. The most volatile was identified as the acetoxypyridine **45** (20%) from its mass spectrum [*m*/*z* 151 (M^+), 109 ($M-CH_2CO$)], ^{13}C NMR spectrum [which confirmed the presence of the acyl group (δ_C 167.67)] and ^1H NMR spectrum, whose coupling pattern was typical of a 2,4-disubstituted pyridine ($^3J_{5,6}$ 5.5 Hz).[22] The

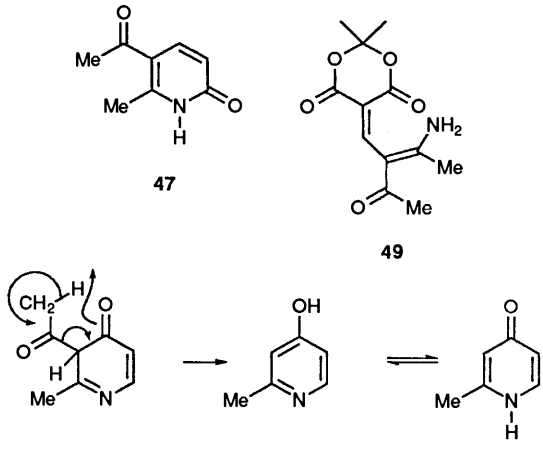


Scheme 4



Scheme 5

remaining products condensed at the exit point of the furnace and proved to be too polar for chromatographic separation. However, extraction of the mixture from water gave the second component (*m/z* 151) isomeric with **45**, which showed just two mutually coupled methine protons in the ^{1}H NMR spectrum and was originally assigned the 3-acetylpyridone structure **46** (10%). However, the vicinal coupling constant (^3J 9.6 Hz) is inconsistent with this assignment ($^3J_{5,6}$ in pyridin-4-ones is *ca.* 7–8 Hz[23]) and is more in keeping with $^3J_{3,4}$ of a pyridin-2-one,[24] such as **47**. The assignment of this regioisomer can also be rationalised on mechanistic grounds (see below). The remaining component, obtained in pure form by recrystallisation, was a deacylated derivative of **45**, and showed a closely similar ^{13}C NMR spectrum to that of an authentic sample of pyridin-4-one, which suggests that the product is 2-methylpyridin-4-one **48** (25%) [*cf.* $^3J_{5,6}$ (**47**) 7.1 and $^3J_{5,6}$ (pyridin-4-one) 7.6 Hz[23]].



Scheme 6

Products **45** and **48** of this pyrolysis are probably derived from a common intermediate (Scheme 5) which may be transformed into **45** by acyl shift and into **48** by loss of ketene. This process may be concerted, and assisted by the carbonyl group (Scheme 6), though homolysis and subsequent hydrogen atom abstraction cannot be excluded. Hydrogen shift (to give **46**) apparently does not compete with either of these mechanisms.

The most likely source of the pyridin-2-one **47** is by rearrangement of the starting material **16** to its *C*-substituted isomer **49**. Since there is no trace of an isomer of this type in the NMR spectrum of the starting material, it is possible that the rearrangement takes place in the inlet system at the high temperature (190 °C) required for its sublimation. Cyclisation of analogues of **49** to give fused pyridin-2-ones has been reported.[6]

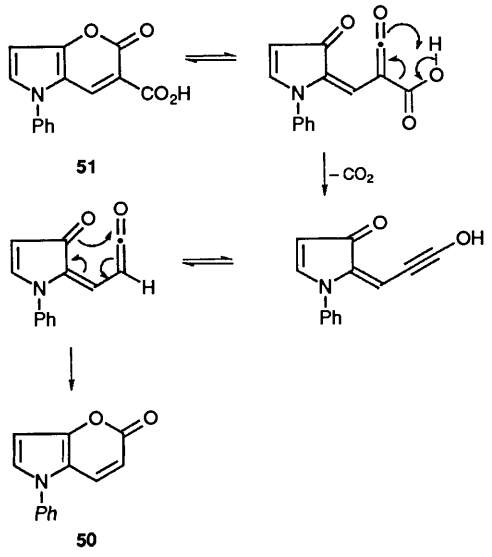
These results suggest that pyrolysis of cyclic enaminone derivatives (*e.g.* **15**) is likely to give a generally useful route to fused pyridin-4-ones such as **43** or **44**,[6] but extension to the monocyclic system is less efficient owing to possible rearrangements, and to the variety of routes which are open to 3*H*-pyridinone intermediates (Scheme 5).

Pyrolysis of the hydroxypyrrole derivative **23** at 600 °C gave a quantitative yield of the pyranopyrrole **50**, though at lower temperatures a mixture of **50** and the carboxylic acid **51** was obtained. The formation of **51** must clearly precede the methyleneketene stage of the Meldrum's acid pyrolysis mechanism, and its further decarboxylation may be assisted by ring-opening to a ketene (Scheme 7).

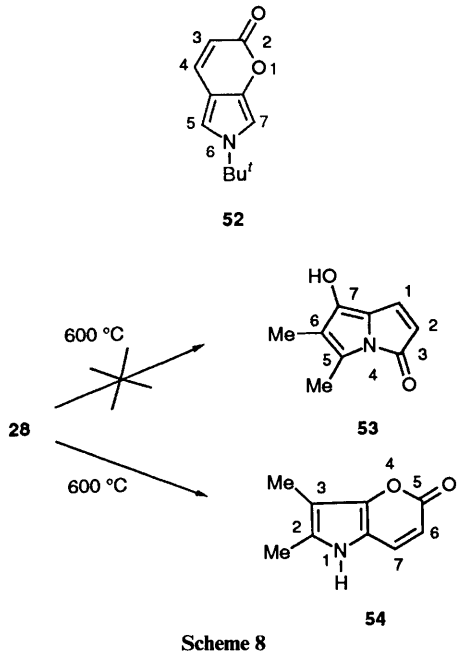
Pyrolysis of the *N-tert*-butyl compound **24** at 650 °C gave rise to the pyrano[2,3-*c*]pyrrole derivative **52**, though only in 25% yield. The assignment was confirmed by typical[25] α-pyrone coupling $^3J_{3,4}$ (9.7 Hz), and an NOE experiment, in which irradiation of the *N-tert*-butyl resonance caused enhancement of the other two methine protons [at δ_H 6.83 (17%) and 6.58 (19%)]. Small long-range couplings ($^4J_{5,7}$ 1.8 Hz and $^6J_{3,7}$ 0.8 Hz) are also observed in this ring system.

Two well-precedented cyclisation routes may be followed by the *N*-unsubstituted pyrrole **28** on pyrolysis (Scheme 8) which can lead to the pyrrolizin-3-one system[16] **53** or the pyranopyrrole **54**. In the event, the 6-membered ring **54** was formed exclusively, and again the vicinal coupling constant $^3J_{HH}$ was crucial to the assignment. The observed value of 9.2 Hz is typical of a pyranopyrrole (see above), whereas a much smaller value (< 6 Hz) is expected of the corresponding $^3J_{1,2}$ in the pyrrolizinone system.[26] Ring-strain factors are presumably involved in this regiospecific cyclisation behaviour.

A number of conclusions may be drawn from the work described in this paper. First, methoxymethylene Meldrum's



Scheme 7



Scheme 8

acid is a useful *C*-electrophile in electrophilic substitution reactions of highly active systems. Second, we have used this reagent to establish the factors which affect regioselectivity in reactions of 3-hydroxypyrroles [1*H*-pyrrol-3(2*H*)-ones] and 3-methoxypyrroles with electrophiles. Finally, we have demonstrated the synthetic utility of this sequence by pyrolysis reactions of the 'Meldrumsated' products which give convenient access to a variety of heterocyclic systems.

Experimental

Unless otherwise stated, ^{1}H NMR spectra were recorded at 80 or 200 MHz, and ^{13}C NMR spectra at 50 MHz, for solutions in [^{2}H]chloroform. *J* Values are recorded in Hz.

Electrophilic Substitution Reactions with Methoxymethylene Meldrum's Acid.—Freshly prepared methoxymethylene Meldrum's acid[4] **2** (5 mmol) was dissolved in acetonitrile and the substrate (5.5 mmol) was added. The reaction was either stirred at room temperature [in which case a minimum amount of solvent (8 cm^3) was used] or heated to reflux (16 cm^3 solvent). The precise reaction conditions are given with individual examples. The precipitated products were filtered off, whilst others were obtained by evaporation of solvent. The following 2,2-dimethyl-1,3-dioxane-4,6-diones were prepared: 5-[(*p*-(dimethylamino)benzylidene]-**4** (from *N*,*N*-dimethylaniline at reflux for 2 h) (74%), m.p. 172–174 °C (from methanol) (lit.,[27] 175 °C): 5-(pyrrol-2-ylmethylene)-**5** (from pyrrole, overnight at room temperature (73%), m.p. 179–181 °C (from ethanol) (lit.,[27] 182 °C): 5-(indol-3-ylmethylene)-**6** (from indole, at reflux for 40 min (68%), m.p. 245–246 °C (from ethanol) (lit.,[27] 246 °C): *N*-methylpyrrole, was recovered unchanged after 5 h at reflux: 5-(*2-dimethylamino-4,4-dimethyl-6-oxocyclohex-1-enyl)methylene*-**12** [from 5,5-dimethyl-2-(dimethylamino)cyclohex-2-enone,[28] at reflux for 3 h] (52%), m.p. 218–220 °C (from methanol) (Found: C, 63.6; H, 7.3; N, 4.45. $C_{17}H_{23}NO_5$ requires C, 63.55; H, 7.15; N, 4.35%); δ_H 8.84 (1 H, s), 3.08 (6 H, s), 2.72 (2 H, s), 2.30 (2 H, s), 1.70 (6 H, s) and 1.09 (6 H, s); δ_C(quaternary signal missing) 194.01 (q), 178.31 (q), 164.53 (q), 161.08 (q), 150.36, 109.61 (q), 102.57 (q), 95.74 (q), 50.54, 45.55, 43.32, 29.59 and 26.88; *m*/*z* 321 (M$^+$, 100%), 264 (56), 248 (27), 236 (27) and 219 (90): 5-[(*3-dimethylamino-1-oxoprop-2-en-2-yl)methylene*]-**13** [from 3-(dimethylamino)propenal, room temperature for 6 h] (6%), m.p. 203 °C (from toluene) (Found: C, 56.75; H, 6.0; N, 5.65. $C_{12}H_{15}NO_5$ requires C, 56.9; H, 5.95; N, 5.55%); δ_H 9.20 (1 H, s), 8.60 (1 H, br s), 8.24 (1 H, s), 3.59 (3 H, s), 3.22 (3 H, s) and 1.69 (6 H, s); δ_C 187.14, 168.03, 164.35 (q), 163.40 (q), 156.73, 109.59 (q), 102.99 (q), 94.60 (q), 48.22, 43.70 and 26.82; *m*/*z* 253 (M$^+$, < 5%), 225 (42), 195 (100), 167 (53), 152 (19), 151 (28) and 139 (90): 5-[(*4-oxopent-2-en-2-ylamino)methylene*]-**16** (from 4-aminopent-3-en-2-one,[29] room temperature, overnight) (60%), m.p. 185–187 °C (from methanol) (Found: C, 56.9; H, 5.95; N, 5.6. $C_{12}H_{15}NO_5$ requires C, 56.9; H, 5.95; N, 5.55%); δ_H 13.7–14.0 (1 H, br s), 8.32 (1 H, d, ^3J 14.0), 5.71 (1 H, br s), 2.23 (3 H, s), 2.19 (3 H, d, ^4J 0.9) and 1.25 (6 H, s); δ_C 198.45 (q), 163.13 (q), 162.37 (q), 150.43, 148.08 (q), 109.33, 104.57 (q), 90.55 (q), 30.37, 26.90 and 17.63; *m*/*z* 253 (M$^+$, 40%), 195 (100), 167 (20), 149 (85), 136 40) and 135 (30): 5-[(*5,5-dimethyl-3-oxocyclohex-1-enylamino)methylene*]-**15** (from 3-amino-5,5-dimethylcyclohex-2-enone,[30] room temperature, overnight) (45%), m.p. 202–203 °C (from ethanol) (Found: C, 61.95; H, 6.65; N, 4.75. $C_{15}H_{19}NO_5$ requires C, 61.45; H, 6.5; N, 4.8%); δ_H 10.91 (1 H, br d, ^3J 13.8), 8.34 (1 H, d, ^3J 13.8), 5.85 (1 H, s), 2.43 (2 H, s), 2.34 (2 H, s), 1.67 (6 H, s) and 1.08 (6 H, s); δ_C (one quaternary signal not observed), 164.56 (q), 162.23 (q), 152.19 (q), 150.40, 111.95, 105.36 (q), 90.54 (q), 50.38 (q), 38.82, 32.73, 28.12 and 26.96; *m*/*z* 293 (M$^+$, 66%), 236 (29), 235 (100), 217 (54), 191 (71), 189 (73) and 188 (24): attempted reaction with 3-anilino-5,5-dimethylcyclohex-2-enone[30] (at reflux for 6 h) resulted only in recovered starting material.

Reactions of 3-Hydroxypyrroles and 3-Methoxypyrroles with Methoxymethylene Meldrum's Acid.—Using the same general conditions as reported above the following reactions were carried out. All were stirred overnight at room temperature. 3-Hydroxy-1-phenylpyrrole[7] gave 5-[(*3-hydroxy-1-phenylpyrrol-2-yl)methylene*]-*2,2-dimethyl-1,3-dioxane-4,6-dione* **23** (62%), m.p. 160–162 °C (from toluene) (Found: C, 65.0; H, 4.8; N, 4.45. $C_{17}H_{15}NO_5$ requires C, 65.2; H, 4.8; N, 4.45%); δ_H 10.92 (1 H, s), 8.10 (1 H, s), 7.2–7.6 (5 H, m), 7.47 (1 H, d, ^3J 2.9), 6.12 (1 H, d, ^3J 2.9) and 1.74 (6 H, s); δ_C 167.04 (q), 163.57 (q), 163.04 (q), 139.49, 139.34, 137.45 (q), 129.79, 128.91, 126.52, 121.09 (q), 103.86 (q), 102.24, 95.17 (q) and 26.78; *m*/*z* 313 (M$^+$, 15%), 255 (100), 211 (39), 210 (24), 183 (30), 182 (21), 138 (24) and 77 (22): 1-*tert*-butyl-3-hydroxypyrrole[7] gave 5-[(1-tert-*butyl*-1,2-*dihydro-3-oxopyrrol-4-yl)methylene*]-*2,2-dimethyl-1,3-dioxane-4,6-dione* **24** (75%), m.p. 192–194 °C (from isopropyl alcohol) (Found: C, 61.2; H, 6.6; N, 4.65. $C_{15}H_{19}NO_5$ requires C, 61.4; H, 6.5; N, 4.8%); δ_H 10.15 (1 H, t of d, ^4J 1.3 and 0.5), 8.22 (1

H, d, ^4J 0.5), 4.02 (2 H, d, ^4J 1.3), 1.65 (6 H, s) and 1.48 (9 H, s); δ_C 194.39 (q), 168.39, 164.07 (q), 163.01 (q), 144.42, 110.55 (q), 103.24 (q), 99.95 (q), 58.58 (q), 54.80, 28.12 and 26.99; *m/z* 293 (M^+, 25%), 235 (40), 191 (5), 179 (50), 163 (25), 135 (100) and 107 (50): 3-hydroxy-1-methyl-2-phenylpyrrole[7] gave 5-[(3-*hydroxy*-1-*methyl*-2-*phenylpyrrol*-5-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione*, **27** (68%), m.p. 246–247 °C (from isopropyl alcohol) (Found: C, 65.8; H, 5.3; N, 4.2. $C_{18}H_{17}NO_5$ requires C, 66.1; H, 5.2; N, 4.3%); δ_H([$^2H_6$]-DMSO) 9.70 (1 H, br s), 8.17 (1 H, s), 7.85 (1 H, s), 7.58–7.53 (5 H, m), 3.75 (3 H, s) and 1.68 (6 H, s); δ_C([$^2H_6$]-DMSO) (one quaternary missing), 164.40 (q), 160.60 (q), 145.59, 137.45 (q), 136.59 (q), 129.96, 128.94, 128.34, 126.75 (q), 110.50, 102.66 (q), 97.78 (q), 31.99 and 26.62; *m/z* 327 (M^+, 80%), 269 (30), 225 (100), 196 (13) and 168 (16): 1-*tert*-butyl-3-hydroxy-2-phenylpyrrole[8] gave 5-[(1-tert-*butyl*-1,2-*dihydro*-3-*oxo*-2-*phenylpyrrol*-4-*yl*)*methylene*)]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **25** (75%), m.p. 202–203 °C (from isopropyl alcohol) (Found: C, 68.4; H, 6.4; N, 3.7. $C_{21}H_{23}NO_5$ requires C, 68.3; H, 6.25; N, 3.8%); δ_H 10.45 (1 H, s), 8.23 (1 H, s), 7.31–7.12 (5 H, m), 4.97 (1 H, s), 1.67 (6 H, s) and 1.33 (9 H, s); δ_C 195.73 (q), 170.36, 163.92 (q), 163.02 (q), 144.91, 133.94 (q), 129.13, 128.83, 126.96, 108.63 (q), 103.28 (q), 100.85 (q), 70.89, 60.43 (q), 29.45 and 27.06; *m/z* 369 (M^+, 10%), 311 (40), 255 (75), 211 (100), 183 (25) and 155 (15): the analogous reaction with 3-hydroxy-2-methyl-1-phenylpyrrole[7] was repeatedly unsuccessful, probably due to the sensitivity of the starting pyrrole: 4,5-dimethyl-1*H*-pyrrol-3-(2*H*)-one[9] gave 5-[(3-*hydroxy*-4,5-*dimethylpyrrol*-2-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **28** (50%), m.p. 214–217 °C (decomp.) (from ethanol) (Found: M^+, 265.0947. $C_{13}H_{15}NO_5$ requires M^+, 265.0950); δ_H([$^2H_6$]-DMSO) 11.8 (1 H, br s), 7.95 (1 H, s), 2.32 (3 H, s), 1.88 (3 H, s) and 1.64 (6 H, s); δ_C([$^2H_6$]-DMSO) (one quaternary missing) 164.62 (q), 159.92 (q), 149.02 (q), 131.38, 118.00 (q), 106.54 (q), 102.78 (q), 90.00 (q), 26.48, 13.32 and 7.01; *m/z* 265 (M^+, 62%), 207 (100), 163 (46), 135 (78), 134 (28), 54 (43) and 53 (37).

3-Methoxy-1-phenylpyrrole[8] gave 5-[(3-*methoxy*-1-*phenylpyrrol*-2-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **35** (65%), m.p. 202–204 °C (from ethanol) (Found: C, 65.9; H, 5.2; N, 4.3. $C_{18}H_{17}NO_5$ requires C, 66.0; H, 5.2; N, 4.3%); δ_H 8.00 (1 H, s), 7.46–7.23 (6 H, m), 6.09 (1 H, d, ^3J 3.2), 3.97 (3 H, s) and 1.71 (6 H, s); δ_C 163.91 (q), 160.30 (q), 159.24 (q), 138.76, 138.65 (q – visible in ^{1}H-coupled spectrum only), 132.48, 129.59, 127.85, 124.75, 118.07 (q), 103.16 (q), 102.97 (q), 96.88, 58.07 and 26.95; *m/z* 327 (M^+, 56%), 269 (50), 225 (100), 224 (59), 182 (33), 128 (33), 77 (43) and 43 (27); 3-methoxy-2-methyl-1-phenylpyrrole[8] gave 5-[(3-*methoxy*-2-*methyl*-1-*phenylpyrrol*-5-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **36** (65%), m.p. 240 °C (decomp.) (from ethanol) (Found: C, 67.2; H, 5.8; N, 4.15. $C_{19}H_{19}NO_5$ requires C, 66.9; H, 5.6; N, 4.1%); δ_H 8.13 (1 H, s), 7.68 (1 H, s), 7.50–7.15 (5 H, m), 3.84 (3 H, s), 2.03 (3 H, s) and 1.62 (6 H, s); δ_C 164.64 (q), 161.39 (q), 148.99 (q), 139.46, 134.70 (q), 134.64 (q), 129.64, 129.46, 128.31, 127.65 (q), 108.15, 102.69 (q), 97.53 (q), 57.57, 26.88 and 10.09; *m/z* 341 (M^+, 61%), 239 (25), 224 (67), 105 (50), 85 (54) and 84 (100): 1-*tert*-butyl-3-methoxypyrrole[8] gave 5-[(1-tert-*butyl*-3-*methoxypyrrol*-2-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **37** and 5-[(1-tert-*butyl*-3-*methoxypyrrol*-4-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **38** (isomer ratio ~5:1 respectively, separated by dry flash chromatography on silica using hexane and ethyl acetate as eluents), 2-substituted isomer (72%), m.p. 200.5–201.5 °C (from ethanol) (Found: C, 62.7; H, 7.1; N, 4.55. $C_{16}H_{21}NO_5$ requires C, 62.5; H, 6.85; N, 4.55%); δ_H 8.43 (1 H, s), 7.15 (1 H, d, ^4J 3.1), 5.80 (1 H, d, ^4J 3.1), 3.85 (3 H, s), 1.76 (6 H, s) and 1.64 (9 H, s); δ_C 164.64 (q), 160.64 (q), 158.56 (q), 139.95, 129.25, 117.86 (q), 103.12 (q), 102.91 (q), 94.14, 57.84 (q), 57.77, 31.07 and 27.00; *m/z* 307 (M^+, 50%), 249 (40), 218 (25), 205 (20), 193 (15), 166 (10), 149 (100) and 120 (75); 4-substituted isomer (15%), m.p. 199.5–201.5 °C (from ethanol) (Found: C, 62.7; H, 7.0; N, 4.55. $C_{16}H_{21}NO_5$ requires C, 62.5; H, 6.85; N, 4.55%); δ_H 8.61 (1 H, d, ^4J 2.2), 8.55 (1 H, s), 6.27 (1 H, d, ^4J 2.2), 3.78 (3 H, s), 1.71 (6 H, s) and 1.55 (9 H, s); δ_C 164.60 (q), 162.01 (q), 151.94 (q), 146.87, 128.30, 109.35 (q), 103.10 (q), 102.27 (q), 99.08, 57.66, 56.96 (q), 29.66 and 27.05; *m/z* 307 (M^+, 25%), 249 (90), 205 (20), 149 (40), 121 (100) and 93 (80): 1-*tert*-butyl-3-methoxy-2-phenylpyrrole[8] gave 5-[(1-tert-*butyl*-3-*methoxy*-2-*phenylpyrrol*-4-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **39** (60 °C, 24 h, 30%, after dry flash chromatography on silica using ethyl acetate and hexane as eluents), m.p. 193–195 °C (Found: M^+, 383.1735. $C_{22}H_{25}NO_5$ requires M^+, 383.1733); δ_H 8.81 (1 H, s), 8.51 (1 H, s), 7.40 (5 H, br s), 3.44 (3 H, s), 1.73 (6 H, s) and 1.43 (9 H, s); δ_C 164.53 (q), 162.00 (q), 149.08 (q), 147.11, 133.00, 132.26 (q), 128.76, 128.56, 127.87, 123.13 (q), 109.71 (q), 103.24 (q), 103.16 (q), 62.46, 59.96 (q), 30.80 and 27.11; *m/z* 383 (M^+, 2%), 325 (5), 269 (7), 225 (10), 197 (20), 192 (15) and 104 (100): 3-methoxy-1-methyl-2-phenylpyrrole[8] gave 5-[(3-*methoxy*-1-*methyl*-2-*phenylpyrrol*-5-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **40** (70%), m.p. 181–183 °C (from ethanol) (Found: M^+, 341.1263. $C_{19}H_{19}NO_5$ requires M^+, 341.1263); δ_H 8.32 (1 H, s), 8.11 (1 H, s), 7.50–7.42 (5 H, m), 3.84 (3 H, s), 3.78 (3 H, s) and 1.74 (6 H, s); δ_C 165.22 (q), 161.28 (q), 149.04 (q), 137.92, 136.15 (q), 129.92, 129.19, 128.49, 128.06 (q), 127.17 (q), 108.43, 103.11 (q), 98.98 (q), 57.73, 31.95 and 27.05; *m/z* 341 (M^+, 20%), 340 (85), 238 (6), 224 (100), 196 (30) and 118 (20).

Pyrolysis Experiments.—The substrate was sublimed or distilled, at 10^{-2}–10^{-3} Torr unless otherwise stated, into a silica tube (35 × 2.5 cm), which was maintained at the required temperature by an electrically heated furnace. The products were collected in a U-tube, cooled by liquid nitrogen, at the exit point of the furnace. The parameters are quoted as follows: quantity of substrate, furnace temperature, inlet temperature, and pyrolysis time.

8,8-*Dimethyl*-2,3,6,7,8,9-*hexahydro*-1H-*benzazepine*-3,6-*dione* **41**. Obtained by pyrolysis of the Meldrum's acid derivative **12** (0.30 g, 0.93 mmol, 600 °C, 220 °C, 2 h), the crude product was purified by chromatography on alumina using ethyl acetate–hexane (3:1) as eluent. The pure *benzazepinedione* (0.091 g, 45%) had m.p. 119–120 °C (from toluene) (Found: C, 71.25; H, 7.9; N, 6.6. $C_{13}H_{17}NO_2$ requires C, 71.25; H, 7.75; N, 6.4%); δ_H 7.75 (1 H, d, ^3J 11.5), 6.13 (1 H, d, ^3J 11.5), 3.59 (2 H, s), 3.22 (3 H, s), 2.56 (2 H, s), 2.25 (2 H, s) and 1.03 (6 H, s); δ_C 194.48 (q), 182.40 (q), 164.66 (q), 140.45, 122.12, 112.00 (q), 64.69, 49.82, 42.13, 40.49, 30.70 (q) and 28.34; *m/z* 219 (M^+, 50%), 191 (21), 190 (100), 188 (12) and 186 (12).

A small-scale pyrolysis of 5-[(3-dimethylamino-1-oxoprop-2-en-2-yl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione **13** (41 mg, 0.16 mmol, 500 °C, 200 °C, 30 min) was also carried out. The ^{1}H NMR spectrum of the pyrolysate was consistent with the formation of 6-formyl-1-methyl-1*H*-azepin-3(2*H*)-one **42**, δ_H 9.28 (1 H, s), 7.52 (1 H, s), 7.43 (1 H, d, ^3J *ca.* 12, additional fine coupling also observed), 6.27 (1 H, d, ^3J 11.6), 3.85 (2 H, s) and 3.43 (3 H, s), but there was insufficient material for characterisation.

6,7,8,8a-*Tetrahydro*-7,7-*dimethyl*-1H-*quinoline*-4,5-*dione* **43**. Pyrolysis of the aminocyclohexenone derivative **15** (0.21 g, 0.70 mmol, 600 °C, 195 °C, 3 h) followed by bulb-to-bulb distillation of the pyrolysate, gave the *quinolinedione* (0.11 g, 83%), m.p. 191–192 °C (from ethanol) (Found: C, 68.0; H, 6.9; N, 7.25. $C_{11}H_{13}NO_2 \cdot 0.2H_2O$ requires C, 67.8; H, 6.9; N, 7.2%) (analyses reproducibly as a partial hydrate); δ_H 8.36 (1 H, d, ^3J 5.9), 6.73 (1 H, d, ^3J 5.9), 2.93 (2 H, s), 2.55 (2 H, s) and 1.10 (6 H, s); δ_C 186.52 (q), 168.00 (q), 164.32 (q), 154.76, 113.12 (q), 111.41, 51.56, 46.18, 32.79 (q) and 28.00; *m/z* 191 (M^+, 41%), 176 (26), 163 (12), 135 (100) and 125 (35).

Pyrolysis of 5-[(4-*oxopent*-2-*en*-2-*ylamino*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **16**. Flash vacuum pyrolysis of the Meldrum's acid derivative **16** (0.50 g, 2.0 mmol, 600 °C, 190 °C, 2.5 h) gave products consisting of two fractions. The first fraction, obtained from the liquid nitrogen trap, was purified by bulb-to-bulb distillation to yield 4-*acetoxy*-2-*methylpyridine* **45** (20%), b.p. 84 °C (0.2 Torr) (Found: M^+, 151.062. $C_8H_9NO_2$ requires M^+, 151.063); δ_H 8.42 (1 H, d, ^3J 5.4), 6.91 (1 H, s with unresolved fine coupling), 6.86 (1 H, dd, ^3J 5.6 and ^4J 1.8), 2.51 (3 H, s) and 2.25 (3 H, s); δ_C 167.67 (q), 160.27 (q), 157.64 (q), 150.16, 115.88, 113.79, 23.94 and 20.73; *m/z* 151 (M^+, 15%), 109 (100) and 58 (90).

The second fraction from the pyrolysis, obtained from the exit point of the furnace, consisted of two crystalline compounds after distillation, one of which was very insoluble and was obtained in pure form by recrystallisation from ethanol. This was 2-methylpyridin-4(1*H*)-one **48** (25%), m.p. 179–180 °C (from ethanol) (lit.,[31] b.p. 350–360 °C); δ_H 7.52 (1 H, d, ^3J 7.1), 6.29 (1 H, dd, ^3J 7.1 and ^4J 2.4), 6.22 (1 H, br s) and 2.31 (3 H, s); δ_C([$^2H_6$]-DMSO) 176.38 (q), 148.95 (q), 138.85, 115.14, 114.20 and 19.22; *m/z* 109 (M^+, 8%), 108 (100), 79 (10) and 70 (16). The second compound was obtained by dissolution of the mixture in water (10 cm^3) and extraction with methylene dichloride (3 × 15 cm^3) to give a compound which was tentatively identified as 5-*acetyl*-6-*methylpyridin*-2(1H)-*one* **47** (10%), m.p. 164–165 °C (Found: M^+, 151.064. $C_8H_9NO_2$ requires M^+, 151.063); δ_H 7.88 (1 H, d, ^3J 9.6), 6.44 (1 H, d, ^3J 9.6), 2.70 (3 H, s) and 2.47 (3 H, s); δ_C 195.39 (q), 164.66 (q), 152.62 (q), 142.15, 116.42 (q), 115.79, 28.60 and 20.04; *m/z* 151 (M^+, 60%), 136 (100), 109 (13) and 108 (13).

A small-scale pyrolysis (600 °C, 180 °C, 20 min) was carried out and the crude products were examined by ^1H NMR spectroscopy. The ratio of 4-acetoxy-2-methylpyridine **45** to 5-acetyl-6-methylpyridin-2(1*H*)-one **47** to 2-methylpyridin-4-(1*H*)-one **48** was 5:1:5.

Pyrolysis of 5-[(3-*Hydroxy*-1-*phenylpyrrol*-2-*yl*)*methylene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione* **23**. Large-scale pyrolysis of the Meldrum's acid derivative **23** (0.80 g, 2.6 mmol, 550 °C, 180 °C, 30 min) gave a mixture of the pyranopyrrolecarboxylic acid **51** and its decarboxylated analogue **50**. These were separated by dissolving the mixture in aqueous sodium hydrogen carbonate which caused the acid to precipitate as its sodium salt. The salt was filtered off, dissolved in dilute hydrochloric acid (15 cm^3) and the acid solution was extracted with methylene dichloride (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give 5-*oxo*-1-*phenyl*-1,5-*dihydropyrano*[3,2-b]*pyrrole*-6-*carboxylic acid* **51** (175 mg, 27%), m.p. 204–205 °C (from acetonitrile) (Found: C, 65.8; H, 3.5; N, 5.7. $C_{14}H_9NO_4$ requires C, 65.9; H, 3.55; N, 5.5%); δ_H 8.71 (1 H, d, ^5J 0.8), 7.52 (1 H, d, ^3J 3.1), 7.3–7.5 (5 H, m) and 6.47 (1 H, dd, ^3J 3.1 and ^5J 0.8); δ_C 165.68 (q), 164.39 (q), 151.88 (q), 137.65, 136.55 (q), 133.01, 130.26, 129.05, 124.40, 118.06 (q), 104.53 (q) and 98.18; *m/z* 255 (M^+, 100%), 183 (41), 182 (37), 154 (41), 129 (48), 128 (52) and 103 (37).

The aqueous sodium hydrogen carbonate from above was extracted with methylene dichloride (3 × 20 cm^3), and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give 1-*phenylpyrano*[3,2-b]*pyrrol*-5(1H)-*one* **50** (201 mg, 38%), m.p. 108–109 °C (from acetone) (Found: C, 73.7; H, 4.25; N, 6.75. $C_{13}H_9NO_2$ requires C, 73.95; H, 4.25; N, 6.65%); δ_H 7.58 (1 H, dd, ^3J 9.7 and ^5J 0.8), 7.3–7.55 (5 H, m), 7.13 (1 H, d, ^3J 3.2), 6.28 (1 H, dd, ^3J 3.2 and ^5J 0.8) and 6.01 (1 H, d ^3J 9.7); δ_C 162.52 (q), 148.68 (q), 137.81 (q), 131.92, 129.80, 127.71, 125.79, 123.88, 116.12 (q), 107.16 and 97.64; *m/z* 211 (M^+, 100%), 183 (40), 182 (37), 154 (41), 129 (48), 128 (52) and 103 (37). This product was formed exclusively when the pyrolysis was carried out at 600 °C.

6-tert-*Butylpyrano*[2,3-c]*pyrrol*-2(6H)-*one* **52**. Large-scale pyrolysis of the Meldrum's acid derivative **24** (0.5 g, 1.7 mmol, 600 °C, 170 °C, 8 × 10^{-4} Torr, 2 h) gave 6-tert-*butylpyrano*-[2,3-c]*pyrrol*-2(6H)-*one* **52** (25%), m.p. 125–127 °C (from isopropyl alcohol) (Found: C, 67.5; H, 6.6; N, 7.2. $C_{11}H_{13}NO_2 \cdot 0.25H_2O$ requires C, 67.5; H, 6.9; N, 7.15%); δ_H 7.49 (1 H, d, ^3J 9.7), 6.82 (1 H, d, ^4J 1.8), 6.59 (1 H, dd, ^4J 1.8 and ^6J 0.8), 5.81 (1 H, dd, ^3J 9.7 and ^6J 0.8) and 1.43 (9 H, s); δ_C 162.88 (q), 142.21 (q), 138.88, 111.50, 109.53, 106.67 (q), 100.72, 56.26 (q) and 30.20; *m/z* 191 (M^+, 35%), 135 (100) and 107 (16).

2,3-*Dimethylpyrano*[3,2-b]*pyrrol*-5(1H)-*one* **54**. Pyrolysis of the Meldrum's acid derivative **28** (0.039 g, 0.15 mmol, 600 °C, 150–200 °C, 55 min) gave a solid pyrolysate which consisted exclusively of the *pyranopyrrolone* **54** (Found: M^+, 163.0629. $C_9H_9NO_2$ requires M^+, 163.0633); δ_H([$^2H_6$]-DMSO) 11.20 (1 H, br s), 7.65 (1 H, d, ^3J 9.2), 5.69 (1 H, d, ^3J 9.2), 2.23 (3 H, s) and 1.96 (3 H, s); δ_C([$^2H_6$]-DMSO) 162.56 (q), 147.25 (q), 133.59, 133.17 (q), 113.64 (q), 102.19, 101.86 (q), 11.63 and 6.51; *m/z* 163 (M^+, 100%), 135 (34), 134 (40), 54 (27) and 53 (22).

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