Pergamon

Tetrahedron, Vol. 52, No. 9, pp. 3163-3170, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)01102-1

Synthesis of 2-Substituted 1,3-Oxazin-6-ones by Gas-phase Pyrolysis

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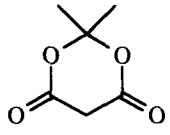
Key words: Oxazinones: flash vacuum pyrolysis; Meldrum's acid; ^{13}C NMR spectroscopy; ketene intermediates

Abstract: *Acylaminomethylene Meldrum's acid derivatives* **5** *are prepared either by direct reaction of methoxymethylene Meldrum's acid* **4** *with primary amides, or by acylation of aminomethylene Meldrum's acid* **6**. *Pyrolysis of the substrates* **5** *under FVP conditions gives the title compounds* **8** *in good yields.*

In recent years we have been studying transformations of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) **1**[1] derivatives into other heterocyclic ring systems using pyrolytic methodology.



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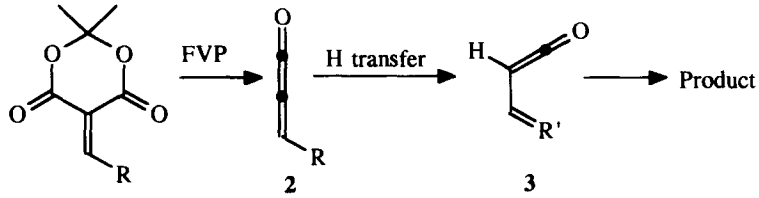
The strategy has involved the design of appropriate substrates so that hydrogen transfer in the key methyleneketene intermediate **2** (first identified by Brown and co-workers[2]) leads to a conjugated ketene **3** which collapses to give the product (Scheme 1).

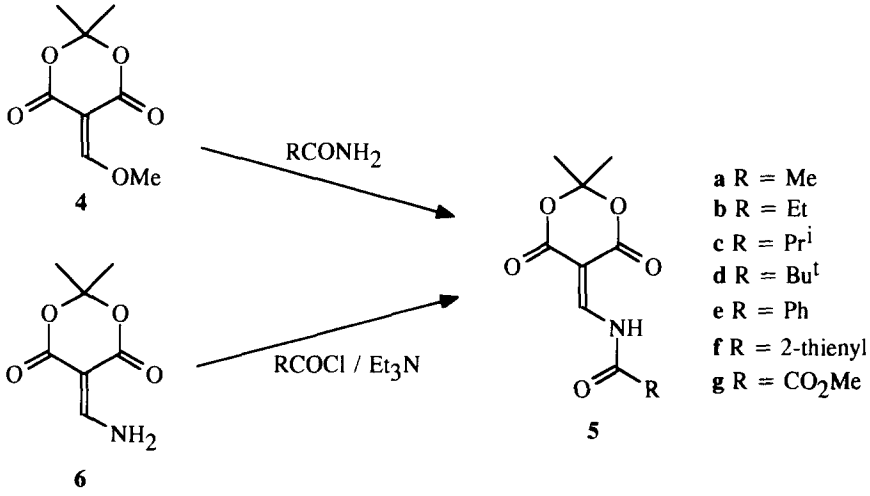


2 **3**

Scheme 1

In this way, we have synthesised a range of monocyclic (pyridazin-3-ones,[3] 3-hydroxypyrroles,[4] 3-hydroxythiophenes,[5] azepin-3(2*H*)-ones[6] *etc.*) and bicyclic (pyrrolizin-3-ones[7] and their aza-analogues,[8] pyrazolo[1,2*a*]1,2,3-triazinium-4-olate[9] *etc.*) heterocyclic systems, generally in good yield and in preparatively useful quantities. Here we present an extension of this work which has led to the first general route to 2-substituted 1,3-oxazin-6-ones, which themselves are important substrates in heterocycle transformations.[10]

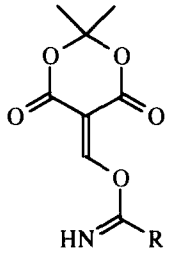
Methoxymethylene Meldrum's acid **4** is a very reactive electrophilic reagent for both nitrogen[4] and carbon nucleophiles.[11] We have now found that even primary amides react as *N*-nucleophiles with this reagent to give the acylamino derivatives **5** (Scheme 2), though extended reaction times (up to 96 h) in refluxing acetonitrile may be required (see Experimental section). Aliphatic, aromatic and heterocyclic amides can be used, but although the products could be isolated without chromatography, the yields are only moderate (*ca.* 50%). The reaction of formamide itself with **4** is still under investigation, but the room temperature NMR spectrum of the product indicates that exchange processes are taking place in this compound which are not found with the other examples. Some amides were poorly soluble under the standard conditions which resulted in very low yields. However, the synthesis of these products could be improved by direct acylation of aminomethylene Meldrum's acid **6** using the appropriate acyl chloride in the presence of triethylamine in refluxing acetonitrile (Scheme 2). In this way, the yield of **5c** was improved from 24% to 70% and this is the method of choice for more complex acylamino derivatives such as the carbomethoxy compound **5g**. Yamamoto and co-workers were unable to *N*-acylate aminomethylene Meldrum's acid derivatives substituted at the methine carbon atom,[12] which may represent a limitation of this route.



Scheme 2

The products **5** were characterised by their ^{1}H NMR spectra which showed typical coupling constants of ^3J 12-13 Hz from the exocyclic methine position to the *N-H*. This confirms that the amide is acting as an *N*-nucleophile, since the most likely alternative product **7** would not show such a three bond

coupling. The size of the coupling constant also confirms that the configuration about the C-N single bond is *s-trans*, as expected from the potential hydrogen bonding with the ring carbonyl group. In agreement with this, both ring carbonyl groups give distinct peaks in the ^{13}C NMR spectra. These assignments have been further confirmed by X-ray crystallography.[13] All the derivatives **5** show significant molecular ions in their electron impact mass spectra, with loss of *m/z* 57 or 58 [corresponding to (acetone - H) or acetone] as the initial breakdown peak.[14] Loss of carbon dioxide or of alkyl substituents compete for the later fragmentations.



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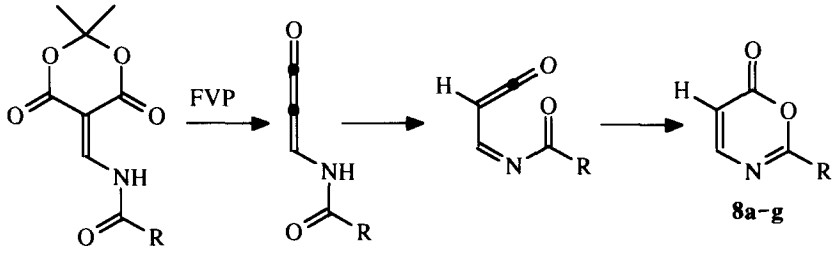
Flash vacuum pyrolysis (FVP) of the Meldrum's acid derivatives **5a-g** at 500-550 °C and 0.01 Torr gave the 2-substituted 1,3-oxazin-6-ones **8a-g** in 62-80% yield (Scheme 3). The method is compatible with primary, secondary and tertiary substituents at the 2-position (**8a-d**) as well as aromatic (**8e**), heterocyclic (**8f**) and functional (**8g**) substituents. Although 2-aryl oxazinones have been previously prepared,[15] earlier methods have been shown to fail for 2-alkyl substituents. The present method is therefore the first route to 2-alkyloxazinones, as well as being applicable to other substituents.



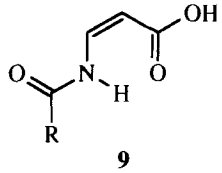
Scheme 3

2,4-Disubstituted oxazinones have been made previously by liquid-phase thermolysis of appropriately substituted Meldrum's acid derivatives,[12] (either in solution or in the melt) but the yields and

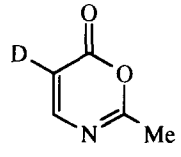
reaction conditions were dependent on the substitution pattern. We therefore believe that the gas-phase method reported here is more reliable and generally applicable.

The characterisation of the products **8** follows from comparison of their ^{1}H NMR spectra with that of the unsubstituted compound previously reported.[16] Thus the protons at the 4- and 5-positions resonate at δ_H 7.5-7.8 and 6.0-6.2 (^3J *ca.* 6.8 Hz) respectively [*c.f.* δ_H 7.78 and 6.38 (^3J 7.2 Hz)[16] reported for the parent compound]. Stájer *et al.* quote a coupling constant of ^3J 6.8 Hz for a range of 2-aryl-1,3-oxazinones.[17] The mass spectra of the oxazinones **8** generally show relatively weak molecular ions with characteristic loss of *m/z* 28 (CO). In addition, most have significant peaks at *m/z* 96 due to loss of the 2-substituent.

As found for the parent 1,3-oxazin-6-one,[16] alkyl-substituted compounds **8** are susceptible to slow hydrolysis in [^{2}H]chloroform solution to give the open-chain products **9**, which were identified by their characteristic enamide protons at *ca.* δ_H 5.1 (^3J *ca.* 9 Hz) and 7.5 (^3J *ca.* 9 and 11.5 Hz) in the ^{1}H NMR spectra. After 2 weeks in solution in [^{2}H]chloroform at room temperature the methyl derivative **9a** (R = Me) was formed to the extent of 12%. In contrast, the 2-thienyl derivative **8f** was apparently stable in solution over a period of 8 weeks.



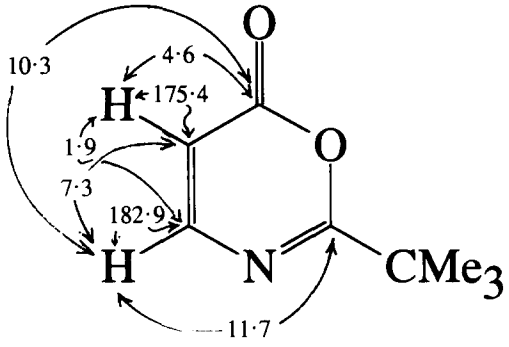
9



8a'

Formation of the oxazin-6-ones presumably follows from the mechanism in Scheme 1, with the final step being the electrocyclisation of an acyliminoketene intermediate (Scheme 3). We have established the hydrogen transfer step leading to the acyliminoketene by a deuterium labelling experiment; exchange of the *N-H* of **5a** with deuterium was accomplished by heating in [^{2}H] methanol, and immediate pyrolysis after removal of solvent gave the oxazin-6-one **8a'** specifically labelled in the 5-position, as shown by the absence of the signal at δ_H 6.0, in agreement with the proposed mechanism.

The ^{13}C NMR spectra of some 2-aryloxazinones have been reported,[17] and our data are in agreement with the previous work (see Experimental section). The t-butyl derivative **8d** was used to determine the major proton-carbon coupling parameters as follows. C(5) (109.31 p.p.m.) and C(4) (153.89 p.p.m.) appeared as doublets of doublets due to one bond (175.4 and 182.9 Hz respectively) and two bond (7.3 and 1.9 Hz respectively) couplings. The quaternary C(6) (158.80 p.p.m.) also showed two couplings (10.3 and 4.6 Hz); examination of the ^{1}H coupled spectrum of the deuterium labelled compound **8a'** showed that the major interaction to be a three bond coupling with the proton on C(4). The other quaternary C(2) is complex due to coupling with the substituent, but again **8a'** enabled assignment of one significant interaction (^3J 11.7 Hz) with H(4). These data are summarised in the Figure.



Figure

EXPERIMENTAL

^1H NMR spectra were recorded at 200 or 250 MHz, and ^{13}C NMR spectra at 50 or 63 MHz for solutions in [^2H]chloroform unless otherwise stated. Quaternary signals in the ^{13}C NMR spectra are indicated (q).

5-N-(AMIDO)METHYLENE-2,2-DIMETHYL-1,3-DIOXANE-4,6-DIONES

Method 1

To a well stirred solution of 5-methoxymethylene-2,2-dimethyl-1,3-dioxane-4,6-dione **4** (1.86g, 10 mmol) in acetonitrile (50 ml) was added the amide (10 mmol). The mixture was heated under reflux for the time quoted, and the solvent was removed under reduced pressure to give the crude product which could be recrystallised.

The following 5-*N*-(amido)methylene-2,2-dimethyl-1,3-dioxane-4,6-diones **5** were prepared. The reflux time for each example is given in brackets.

5-*N*-(Acetamido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5a (24h), (62%), m.p. 138-140 °C (from ethanol), (Found: C, 50.75; H, 5.35; N, 6.55. $C_9H_{11}NO_5$ requires C, 50.7; H, 5.2; N, 6.55%); δ_H 10.94 (1H, broad d), 8.70 (1H, d, ^3J 12.5 Hz), 2.27 (3H, s) and 1.64 (6H, s); δ_C 168.06(q), 163.81(q), 161.62(q), 149.76, 105.35(q), 93.13(q), 26.98 and 23.48; *m/z* 213 (M^+, 26%), 198(14), 171(28), 160(23), 156(54), 155(15), 114(52), 111(24), 51(15) and 57(100).

5-*N*-(Propionamido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5b (24h), (58%), m.p. 141-142 °C (from ethanol), (Found: C, 52.8; H, 5.8; N, 6.05. $C_{10}H_{13}NO_5$ requires C, 52.85; H, 5.75; N, 6.15%); δ_H 10.94 (1H, broad d), 8.72 (1H, d, ^3J 12.8 Hz), 2.51 (2H, q, ^3J 7.4 Hz), 1.62 (6H, s) and 1.13 (3H, t, ^3J 7.4 Hz); δ_C 171.68(q), 163.86(q), 161.62(q), 159.76, 105.24(q), 92.90(q), 29.70, 26.91 and 7.93; *m/z* 227 (M^+, 27%), 170(37), 169(41), 141(18), 140(28), 125(17), 114(54), 69(20) and 57(100).

5-*N*-(iso-Butyramido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5c (48h), (24%), m.p. 100-102 °C (from ethanol), (Found: C, 54.45; H, 5.9; N, 5.7. $C_{11}H_{15}NO_5$ requires C, 54.75; H, 6.25; N, 5.8%); δ_H 11.12 (1H, broad d), 8.80 (1H, d, ^3J 12.7 Hz), 2.66 (1H, septet, ^3J 6.9 Hz), 1.68 (6H, s) and 1.22 (6H, d, ^3J 6.9 Hz); δ_C 174.70(q), 164.24(q), 161.68(q), 150.27, 105.45(q), 93.29(q), 35.77, 27.09 and 18.33; *m/z* 241 (M^+, 8%), 184(9), 183(8), 140(18), 114(20), 96(10), 71(45), 70(20) and 43(100).

5-*N*-(Trimethylacetamido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5d (72h), (48%), m.p. 99-100 °C (from ethanol), (Found: C, 56.1; H, 7.05; N, 5.45. $C_{12}H_{17}NO_5$ requires C, 56.5; H, 6.7; N, 5.5%); δ_H 11.46 (1H, broad d), 8.79 (1H, d, ^3J 12.6 Hz), 1.67 (6H, s) and 1.25 (9H, s); δ_C 176.27(q), 164.48(q), 161.62(q), 150.71, 105.45(q), 93.40(q), 39.58(q), 27.09 and 26.44; *m/z* 255 (M^+, 4%), 198(13), 140(12), 114(8), 85(11), 69(10), 59(11) and 57(100).

5-*N*-(Benzamido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5e (48h), (48%), m.p. 153-154 °C (from ethanol), (Found: C, 61.0; H, 4.85; N, 4.95. $C_{14}H_{13}NO_5$ requires C, 61.1; H, 4.75; N, 5.1%); δ_H 12.08 (1H, broad d), 9.02 (1H, d, ^3J 12.4 Hz), 7.94 (2H, m), 7.58 (3H, m) and 1.72 (6H, s); δ_C 164.56(q), 163.62(q), 161.48(q), 150.62, 134.15, 129.92(q), 129.04, 128.01, 105.54(q), 94.03(q) and 27.06; *m/z* 275 (M^+, 3%), 218(3), 173(2), 106(8), 105(100), 77(42) and 51(15).

5-*N*-(Thienyl-2-carboxamido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5f (96h), (51%), m.p. 121-122 °C (from ethanol), (Found: C, 51.0; H, 4.0; N, 5.25. $C_{12}H_{11}NO_5S$ requires C, 51.25; H, 3.9; N, 5.0%); δ_H ([$^2H_6$] DMSO) 11.71 (1H, broad d), 8.65 (1H, d, ^3J 12.5 Hz), 8.16 (1H, dd, ^3J 4.8 Hz, ^4J 1.0 Hz), 7.92 (1H, dd, ^3J 3.8 Hz, ^4J 1.0 Hz), 7.33 (1H, dd, ^3J 4.8 and 3.8 Hz) and 1.71 (6H, s); δ_C ([$^2H_6$] DMSO) 163.84(q), 161.74(q), 158.54(q), 149.59, 136.85, 134.79(q), 133.22, 129.40, 105.73(q), 93.97(q) and 26.87; *m/z* 281 (M^+, 18%), 224(10), 223(18), 111(100) and 83(7).

Method 2

To a well stirred solution of 5-aminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione[18] **6** (1.71g, 10 mmol) and triethylamine (10 mmol) in acetonitrile (90 ml) was added the acid chloride (10 mmol) in acetonitrile (10 ml) dropwise over a period of 10 min. The mixture was heated under reflux for the time quoted, and the solvent was then removed under reduced pressure. The crude product was redissolved in dichloromethane. and the solution was washed with water (3 x 50 ml) and dilute HCl (2M, 1 x 50 ml). The combined aqueous washings were back extracted with dichloromethane (2 x 50 ml). The combined organic layers were then dried ($MgSO_4$) and the solvent was evaporated under reduced pressure to give the crude product which could then be recrystallised.

The following 5-*N*-(amido)methylene-2,2-dimethyl-1,3-dioxane-4,6-diones **5** were prepared. The precursor acid chloride and reflux time for each example are given in parentheses.

5-*N*-(iso-Butyramido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5c (isobutyryl chloride, 2h), (70%), m.p. 100-101 °C (from ethanol). Spectra obtained were identical with those reported above.

5-*N*-(2-Carbomethoxyamido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5g (methyl oxalyl chloride, 8h), (56%), m.p. 136-137 °C (from ethanol), (Found: C, 46.9; H, 4.7; N, 5.75. $C_{10}H_{11}NO_7$ requires C, 46.7; H, 4.3; N, 5.45%); δ_H 12.08 (1H, broad d), 8.70 (1H, d, ^3J 12.7 Hz), 3.98 (3H, s) and 1.71 (6H, s); δ_C 163.21(q), 161.02(q), 158.03(q), 154.42(q), 147.78, 105.98(q), 97.32(q), 54.47 and 27.30; *m/z* 257 (M^+, 3%), 200(31), 198(26), 140(80), 114(54), 96(17), 70(27) and 69(100).

2-SUBSTITUTED-6H-1,3-OXAZIN-6-ONES 8

The amidomethylene Meldrum's acid derivative **5** was sublimed or distilled at low pressure through an empty silica furnace tube (2.5 x 35 cm) maintained at 500-550 °C, and products were collected in a liquid nitrogen trap. Involatile solid products which condensed at the exit point of the furnace were

scraped from the trap, whereas volatile solids and liquids were washed from the trap with solvent. After the solvent had been removed under reduced pressure, the crude pyrolysate was purified by either recrystallisation or bulb-to-bulb distillation. The following 2-substituted 6*H*-1,3-oxazin-6-ones **8** were prepared by pyrolysis; the amidomethylene Meldrum's acid precursor **5** and pyrolysis conditions (furnace temperature, inlet temperature, average pressure, pyrolysis time and amount of substrate) are given for each example in parentheses.

2-Methyl-6*H*-1,3-oxazin-6-one 8a [5-*N*-(acetamido-) **5a**, 500 °C, 150 °C, 0.01 Torr, 22 min, 0.5 g], (77%), b.p. 35-40 °C (0.15 Torr), (Found: M^+, 111.0321. $C_5H_5NO_2$ requires M, 111.0320); δ_H 7.55 (1H, d, ^3J 6.8 Hz), 6.09 (1H, d, ^3J 6.8 Hz) and 2.36 (3H, s); δ_C 168.31(q), 158.39(q), 153.83, 109.39 and 21.46; *m/z* 111 (M^+, 31%), 96(19), 86(38), 84(48), 83(32), 69(17), 49(29) and 43(100).

2-Ethyl-6*H*-1,3-oxazin-6-one 8b [5-*N*-(propionamido-) **5b**, 500 °C, 160 °C, 0.01 Torr, 37 min, 0.5 g], (62%), b.p. 40-45 °C (0.20 Torr), (Found: M^+, 125.0473. $C_6H_7NO_2$ requires M, 125.0477); δ_H 7.53 (1H, d, ^3J 6.8 Hz), 6.03 (1H, d, ^3J 6.8 Hz), 2.54 (2H, q, ^3J 7.5 Hz) and 1.16 (3H, t, ^3J 7.5 Hz); δ_C 171.79(q), 158.23(q), 153.58, 109.23, 27.89 and 9.49; *m/z* 125 (M^+, 36%), 97(11), 96(75), 87(12), 70(26), 69(11) and 57(100).

2-iso-Propyl-6*H*-1,3-oxazin-6-one 8c [5-*N*-(iso-butyramido-) **5c**, 550 °C, 165 °C, 0.01 Torr, 31 min, 0.5 g], (68%), b.p. 40-45 °C (0.40 Torr), (Found: M^+, 139.0638. $C_7H_9NO_2$ requires M, 139.0633); δ_H 7.58 (1H, d, ^3J 6.9 Hz), 6.06 (1H, d, ^3J 6.9 Hz), 2.79 (1H, septet, ^3J 7.0 Hz) and 2.22 (6H, d, ^3J 7.0 Hz); δ_C 174.80(q), 158.53(q), 153.82, 109.35, 34.03 and 19.21; *m/z* 139 (M^+, 11%), 121(9), 119(10), 96(47), 88(22), 86(74), 84(100) and 71(11).

2-t-Butyl-6*H*-1,3-oxazin-6-one 8d [5-*N*-(trimethylacetamido-) **5d**, 550 °C, 135 °C, 0.02 Torr, 25 min, 0.5 g], (70%), b.p. 45-50 °C (0.40 Torr), (Found: M^+, 153.0783. $C_8H_{11}NO_2$ requires M, 153.0790); δ_H 7.64 (1H, d, ^3J 6.8 Hz), 6.10 (1H, d, ^3J 6.8 Hz) and 1.32 (9H, s); δ_C 176.70(q), 158.80(q), 153.89, 109.31, 38.23(q) and 27.45; *m/z* 153 (M^+, 15%), 138(8), 125(6), 110(9), 96(45), 84(7), 70(14), 69(9) and 57(100).

2-Phenyl-6*H*-1,3-oxazin-6-one 8e [5-*N*-(benzamido-) **5e**, 550 °C, 150 °C, 0.01 Torr, 77 min, 0.5 g], (79%), m.p. 85-87 °C (from hexane/toluene), (lit.,[15] 85-87 °C); δ_H 8.19 (2H, m), 7.78 (1H, d, ^3J 6.7 Hz), 7.47 (3H, m) and 6.18 (1H, d, ^3J 6.7 Hz); δ_C 164.46(q), 158.08(q), 154.44, 133.24, 129.34(q), 128.62, 128.31 and 109.28; *m/z* 173 (M^+, 10%), 146(8), 106(8), 105(100), 77(42) and 58(25).

2-(2-Thienyl)-6*H*-1,3-oxazin-6-one 8f [5-*N*-(thienyl-2-carboxamido-) **5f**, 550 °C, 180 °C, 0.01 Torr, 52 min, 0.5 g], (72%), m.p. 109-110 °C (from ethanol), (Found: C, 53.4; H, 2.85; N, 7.9. $C_8H_5NO_2S$ requires C, 53.6; H, 2.8; N, 7.8%); δ_H 7.91 (1H, dd, ^3J 3.8 Hz, ^4J 1.2 Hz), 7.71 (1H, d, ^3J 6.8 Hz), 7.63 (1H, dd, ^3J 5.0 Hz, ^4J 1.2 Hz), 7.14 (1H, dd, ^3J 5.0 and 3.8 Hz) and 6.10 (1H, d, ^3J 6.8 Hz); δ_C 160.98(q), 157.60(q), 154.75, 133.74, 133.34(q), 132.76, 128.52 and 108.36; *m/z* 179 (M^+, 59%), 151(27), 127(19), 113(13), 112(18), 111(100), 83(22) and 57(14).

2-Carbomethoxy-6*H*-1,3-oxazin-6-one 8g [5-*N*-(2-carbomethoxyamido-) **5g**, 500 °C, 225 °C, 0.01 Torr, 37 min, 0.5 g], (80%), m.p. 93-95 °C [after distillation at 155 °C (0.5 Torr)], (Found: C, 46.25; H, 3.65; N, 9.1. $C_6H_5NO_4$ requires C, 46.45; H, 3.25; N, 9.05%); δ_H ([$^2H_6$] DMSO) 7.98 (1H, d, ^3J 6.8 Hz), 6.66 (1H, d, ^3J 6.8 Hz) and 3.88 (3H, s); δ_C ([$^2H_6$] DMSO) 157.66(q), 157.02(q), 153.69,

153.53(q), 114.50 and 53.75; *m/z* 155 (M^+, 3%), 154(10), 128(17), 114(10), 96(100), 95(28), 70(13), 69(12) and 59(10).

2-Methyl-5-[^{2}H]-6*H*-1,3-oxazin-6-one 8a' (*c.f.* ref 19) 5-*N*-(Acetamido)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione **5a** (0.21 g, 1 mmol) was dissolved in deuteriated methanol (CH_3OD, 10 ml) by heating. The solution was allowed to stand for 15 min and the solvent was then removed under reduced pressure at the oil pump. The crude deuteriated solid was immediately pyrolysed (inlet tube flame dried, 500 °C, 150 °C, 0.02 Torr, 12 min). The product was extracted with deuteriated chloroform and shown by NMR spectroscopy to be the desired 2-methyl-5-[^{2}H]-6*H*-1,3-oxazin-6-one, with 93% deuterium incorporation. Spectra are reported in the Discussion section.

ACKNOWLEDGEMENTS

We are most grateful to the EPSRC for the award of an Earmarked Studentship (GRJ/73094) to K.W, and to Lonza Ltd. for a generous gift of Meldrum's acid.

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(*Received* 14 *August* 1995; *accepted* 6 *November* 1995)