Preparation and pyrolysis of some N-protected derivatives of aminomethylene Meldrum’s Acid

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Dedicated to Professor Otto Meth-Cohn on the occasion of his 65th birthday
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Abstract
The syntheses of new N-protected aminomethylene Meldrum’s acid derivatives have been achieved and their gas-phase pyrolyses under flash vacuum pyrolysis (FVP) conditions have been studied. The pyrolyses were dominated by polymerisation and radical-cleavage pathways rather than by intramolecular cyclisation mechanisms.

Keywords: Meldrum’s acid, pyrolysis, free radicals

Introduction

An inspiring young chemist, Meth-Cohn,
Over all Lakeland fell-sides would roam,
But unlike Katritzky
(Or even Suschitzky?),
He always could find his way home.

This selfsame ‘young’ fellow called Otto,
Was of voce which none could call sotto,
For his sixty-fifth year,
We wrote this paper here,
(Though not everything did what it ought-to.)

In previous papers we have shown that flash vacuum pyrolysis (FVP) of N,N-disubstituted aminomethylene derivatives of Meldrum’s acid 1 provides a straightforward synthetic route to N-alkyl- or N-aryl-3-hydroxypyrroles 2 (R^1 = alkyl or aryl), by a hydrogen transfer-cyclisation mechanism from the initial methyleneketene intermediate (Scheme 1).^1,2 Because of their electron rich nature and sensitivity to oxidation, 3-hydroxypyrroles are often difficult to obtain by other means. However, this route is not directly applicable to the preparation of N-unsubstituted hydroxypyrroles 2 (R^1 = H), since the pyrolysis takes
an alternative course (Scheme 1). Because of current interest in the prodigiosin series of antibiotics and immunosuppressants, which contain an \(N\)-unsubstituted 3-alkoxy pyrrole function, we have explored routes to some \(N\)-protected Meldrum’s acid precursors which we hoped would lead to \(N\)-protected 3-hydroxy pyrroles. Although, in the event, the precursors described here (\(N\)-silylated materials, hydrazines and hydroxylamines, and \(N\)-dimethylbenzyl derivatives) either could not be obtained or did not give cyclisation products on pyrolysis, the strategy ultimately proved partially successful and a limited range of \(N\)-unsubstituted-3-hydroxy pyrroles has been obtained.

Scheme 1

Our route to the precursors involves the reaction of methoxymethylene Meldrum’s acid (MMMA) 3 with an appropriate protected amine (Scheme 1, \(R^1\) = protecting group) in acetonitrile solution. Reaction conditions are mild (room temperature, 5-10 min) and methanol is the only co-product.
Silyl protection of amines using classical silylation reagents is often unsuccessful because of the extreme hydrolytic instability of the products. However, the use of \(N\)-t-butyldiphenylsilyl derivatives has been advocated; these are generally stable under neutral and basic conditions and require 80% acetic acid for deprotection. Compounds 4-6 were made by standard methods, and were reacted with MMMA 3 in acetonitrile, but the only products which could be isolated, generally in excellent yield, were the \(N\)-unsubstituted compounds 7-9. These were easily identified from the characteristic doublet at \(\delta H 8.2\) (\(J 15\) Hz) due to the methylene proton which shows trans-coupling to the adjacent NH. Compounds 7 and 9 have been previously made by direct reaction of MMMA 3 with the appropriate amine. The facile loss of the protecting group under essentially anhydrous, mildly basic conditions was most surprising, and may be connected with the sterically congested nature of the expected products, which are vinylogous amides rather than amines. It is perhaps significant that when the reaction was carried out using a non-polar solvent (cyclohexane), only recovered starting materials were obtained, even after extended reaction times.

In principle, weak bonds from nitrogen to heteroatoms (N or O) may be cleaved under reductive conditions. We therefore targeted the hydrazone 10 and the hydroxylamine derivative 11 as potential pyrolysis precursors.
The N-benzyl substituent was chosen because of the high reactivity of benzyl-type hydrogen atoms to the transfer-cyclisation process, and so the known N-benzylhydrazine 12 was synthesised and reacted with MMMA 3 to give the pyrolysis precursor 10 in 44% yield. N,O-Dimethylhydroxylamine is commercially available as its hydrochloride salt; without isolation of the free base, this salt was allowed to react with MMMA 3 in dilute solution in acetonitrile, in the presence of one equivalent of triethylamine, to give 11 in high yield after aqueous work-up. These conditions should be generally applicable to the reactions of other unstable amines, provided they are available as salts.

Scheme 2

No cyclisation products were obtained from the pyrolys of either 10 or 11. In the former case, much insoluble polymer was generated and the only isolable product was bibenzyl 13 (38%), obtained by dimerisation of benzyl radicals formed by radical cleavage of the C-N
bond. At first sight it is surprising that the C-N bond cleaves rather than the N-N bond (Scheme 2), but the relative stability of both the benzyl radical 14 (over the dimethylaminyl radical 15) and the captodative residue 16 (over the aminyl residue 17) is apparently sufficient to favour the unwanted C-N rupture.

The major product from the pyrolysis of the hydroxylamine derivative 11 at 500, 550 or 600 °C was again an insoluble polymer. A minor, soluble component showed a number of resonances in the region $\delta_H$ 3.45 – 5.30 but no constituent compound could be characterised; it was clear that no pyrrolone had been formed. It is possible that methoxy-group migration on the methyleneketene energy surface (which is known to be a facile process$^{10,11}$) leads to iminoketene intermediates, which polymerise on warming. Matrix isolation experiments would be required to confirm this hypothesis.

In addition, the secondary derivatives 18 and 19 were also synthesised (see Experimental section) but again both gave polymeric material on pyrolysis. In the case of the hydrazine 18, it was hoped that, by analogy with the cyclisation of unsaturated hydrazinoesters 20 discovered by Chuche and co-workers (Scheme 3),$^{12}$ unusual pyrazole derivatives might be formed via analogous ketene intermediates (c.f. 21 and 22). The failure of our cyclisation suggests that the presence of the electron withdrawing group may be essential for the success of the hydrazinoester process.

Hydrogenolysis of $N$-benzyl groups is a common means of deprotection which has been used in the alkoxyprrole series.$^{13}$ Because pyrolysis of $N$-alkyl-$N$-benzylaminomethylene Meldrum’s acid derivatives always leads to $N$-alkyl-2-phenyl-3-hydroxypyroles via hydrogen transfer from the benzyl CH$_2$ group,$^1$ we hoped that the dimethylbenzyl group would provide required protection (Scheme 4).
Scheme 3

$N,\alpha,\alpha$-Trimethylbenzylamine 23 was made by the literature method,\textsuperscript{14} and was reacted with MMMA 3 to give the product 24 in 45% yield. Unfortunately the only product from the pyrolysis of 24 at 600 °C was $\alpha$-methylstyrene 25, which is clearly formed by an initial radical cleavage of the C-N bond. Pyrolysis at lower temperatures (500 and 550 °C) gave only 24 and 25 in differing proportions.
Scheme 5

Radical cleavage of this type was an unfortunate and unexpected result, since pyrolysis of $N$-benzyl and $N$-$\alpha$-methylbenzyl derivatives of aminomethylene Meldrum’s acid give rise to 3-hydroxypyrrroles [or pyrrol-3(2$H$)-ones] without complications.\textsuperscript{1,2}

Scheme 6
We therefore briefly investigated the temperature profile of the pyrolyses of N-methylbenzylamine 26 (which gives bibenzyl), N-α-dimethylbenzylamine 27 (which gives styrene) and N,α,α-trimethylbenzylamine 23 (which gives α-methylstyrene) (Figure 1, series 3, 2 and 1 respectively). All of these decompositions are presumably initiated by a radical C-N cleavage mechanism (Scheme 6). The temperatures for 50% conversion to products for 26, 27 and 23 are >800 °C, 790 °C and 690 °C respectively. It is clear that the second C-methyl group in 23 has a greater effect in lowering the temperature for radical cleavage than the first C-substitution. In addition, the temperature for quantitative conversion of 23 to products was >800 °C (by comparison with quantitative decomposition of the Meldrum’s acid derivative 24 at ca. 600 °C) which suggests that the aminomethylene Meldrum’s acid moiety stabilises the co-formed N-centred radical more effectively than a simple methylaminyl function.

In conclusion, we have had no success in our attempts to extend our hydroxypyrrole synthesis to N-unsubstituted examples by using the range of different N-protected precursors described here. In subsequent work the use of amide (lactam) precursors gave a restricted access to these targets and these results will be reported in a later paper.

**Experimental Section**
General Procedures. $^1$H and $^{13}$C NMR spectra were recorded at 200 or 250 MHz and 50 or 63 MHz respectively for solutions in deuteriochloroform. Coupling constants are quoted in Hz. Mass spectra were obtained under electron impact conditions.

Silylation of primary amines$^{6,7}$
To a stirred solution of the appropriate amine (freshly distilled and dried over potassium hydroxide pellets, 2 mmol) in dry acetonitrile (6 cm$^3$), under nitrogen, was added triethylamine (0.304 g, 3.5 mmol) and t-butyldiphenylsilyl chloride (0.550 g, 2 mmol). The mixture was stirred at room temperature for the time quoted below and the solvent was removed under reduced pressure. The residue was dissolved in a mixture of 4:1 hexane/ethyl acetate (25 cm$^3$) and washed with aqueous sodium hydrogen carbonate (1M, 3 x 25 cm$^3$). The combined aqueous washings were back extracted with 4:1 hexane/ethyl acetate and the combined organic layers were dried (MgSO$_4$). The solvent was then removed under reduced pressure to give the desired product as an opaque oil. The following compounds were prepared in this manner. The amine used and reaction time are given for each example in parentheses.

$N$-(t-Butyldiphenylsilyl)cyclohexylamine$^6$ (4). (cyclohexylamine, 3 h), (76%), bp 190 °C (1.1 Torr); $\delta^H$ 7.75-7.69 (4H, m), 7.41-7.30 (6H, m), 2.57 (1H, br), 1.88-0.91 (11H, m) and 1.06 (9H, s); $\delta^C$ 136.11 (quat), 135.92, 128.83, 127.17, 50.65, 38.44, 27.51, 25.68, 25.41 and 18.32 (quat).

$N$-(t-Butyldiphenylsilyl)benzylamine (5). (benzylamine, 24 h), (82%), bp 170 °C (0.3 Torr), (Found: $M^+$, 345.1914. C$_{23}$H$_{27}$NSi requires $M^+$, 345.1913); $\delta^H$ 7.78-7.71 (5H, m), 7.42-7.31 (10H, m), 3.96 (2H, s), 1.25 (1H, br) and 1.06 (9H, s); $\delta^C$ 143.60 (quat), 135.76, 135.02 (quat), 129.11, 128.19, 127.47, 126.90, 126.39, 46.58, 27.43 and 18.55 (q); $m/z$ 345 ($M^+$, 1%), 288 (100), 271 (15), 259 (54), 210 (19), 199 (33), 183 (34), 181 (21) and 105 (15).

$N$-(t-Butyldiphenylsilyl)-1-phenylethylamine$^7$ (6). ($\alpha$-methylbenzylamine, 24 h), (75%), bp 165 °C (0.1 Torr) [lit.,$^7$ 180 °C (0.5 Torr)]; $\delta^H$ 7.68-7.62 (3H, m), 7.48-7.43 (2H, m), 7.34-7.03 (10H, m), 3.85 (1H, br m), 1.58 (1H, br), 1.23 (3H, d, $^3J$6.6) and 0.93 (9H, s); $\delta^C$ 148.83 (quat), 136.02, 135.89, 135.74 (quat), 134.83 (quat), 129.01, 128.87, 128.00, 127.32, 127.11, 126.39, 125.98, 51.80, 28.07, 27.45 and 18.48 (quat); $m/z$ 302 ($M^+$ - C$_4$H$_9$, 100%), 259 (41), 199 (39), 183 (19), 181 (14), 105 (17) and 77 (8).

In all of the reactions, the use of “wet” acetonitrile, or “wet” amines resulted in a dramatic reduction in yield of the desired product and the production of t-butyldiphenylsilanol, mp 61-62 °C (from toluene) (lit.,$^{15}$ 62-64 °C); $\delta^H$ 7.75-7.69 (4H, m), 7.45-7.34 (6H, m), 2.25 (1H, s) and 1.08 (9H, s); $\delta^C$ 135.06 (quat), 134.70, 129.48, 127.57,
26.44 and 18.85 (quat); m/z 256 (M⁺, 25%), 201 (78), 200 (93), 199 (62), 198 (83), 181 (75), 152 (17), 137 (30), 121 (52), 78 (57) and 77 (100).

2-Benzyl-1,1-dimethylhydrazine (12)⁹. (a) To a stirred, ice-cooled solution of 1,1-dimethylhydrazine (18.62 g, 0.31 mol) in acetonitrile (30 cm³) was added benzyl chloride (39.24 g, 0.31 mol) dropwise over a period of 45 min. The mixture was then heated under reflux for 3 h, and the solvent was removed under reduced pressure to give 1-benzyl-1,1-dimethylhydraziniumchloride (41.3 g, 71%); δ_H 7.78-7.38 (5H, m), 6.90 (2H, br s), 5.21 (2H, s) and 3.59 (6H, s). (b) 1-Benzyl-1,1-dimethylhydrazinium chloride (3.0 g, 16 mmol) and crushed potassium hydroxide pellets (2.25 g, 40 mmol) were well mixed, and then distilled by Kugelrohr (200-300 °C, 30 Torr) to give the title compound 12 (2.00 g, 83%), bp 50 °C (1.0 Torr) (lit.,⁹ 206-208 °C); δ_C 138.85 (quat), 128.16, 126.84, 52.78 and 47.53.

N,a,a-Trimethylbenzylamine (23)¹⁴. This compound was prepared in three steps from 2-phenylpropan-2-ol, via 2-chloro-2-phenylpropane (55%), and 2-isothiocyanato-2-phenylpropane (68%). Reduction of the latter derivative with lithium aluminium hydride in dry ether gave N,a,a-trimethylbenzylamine 23¹⁴ (46%); δ_H 7.32 (5H, m), 2.14 (3H, s) and 1.45 (6H, s); δ_C 147.09 (quat), 128.00, 126.04, 125.60, 55.72 (quat), 29.50 and 28.75; m/z 149 (M⁺, 2%), 134 (100), 120 (14), 105 (28), 91 (12), 72 (28), 60 (28), 44 (28), 39 (28) and 77 (11).

N,a-Dimethylbenzylamine (27)¹⁶. Alkylation of α-methylbenzylamine (2.0 g, 16.5 mmol) with iodomethane (2.34 g, 16.5 mmol) in diethyl ether (20 cm³) at room temperature overnight gave, after chromatography on alumina, N,a-dimethylbenzylamine 27¹⁶ (0.26 g, 12%); δ_H 7.3 (5H, m), 3.62 (1H, q), 2.30 (3H, s) and 1.35 (3H, d); δ_C 145.19 (quat), 128.24, 126.74, 126.43, 60.07, 34.35 and 23.71; m/z 135 (M⁺, 3%) 120 (100), 105 (14), 86 (28), 84 (39) and 77 (11).

Preparation of aminomethylene Meldrum’s acid derivatives¹

To a solution of 2,2-dimethyl-5-methoxymethylene-1,3-dioxane-4,6-dione¹⁷ 3 (5-methoxymethylene Meldrum’s acid) (1.86 g, 10 mmol) in acetonitrile (50 cm³) was added the appropriate amine, hydrazine or hydroxylamine (10 mmol) and the mixture was stirred at room temperature for 10 min.¹ The solvent was then removed under reduced pressure to give the crude product which was recrystallised. The following aminomethylene derivatives were prepared.

Reactions of N-Silyl Protected Amines: (0.5 mmol scale)

Examination of the crude product by ¹H NMR spectroscopy showed the product was not the desired N-protected aminomethylene Meldrum’s acid derivative, but that it was a mixture of t-butyldiphenylsilanol and the deprotected aminomethylene Meldrum’s acid compound.
2,2-Dimethyl-5-(N-cyclohexylaminomethylene)-1,3-dioxane-4,6-dione (7). \[N-(t\text{-}
\text{butyldiphenylsilyl})\text{cyclohexylamine}\] (55%), mp 150-151 °C (from ethanol) (lit., 149-151 °C); \(\delta_H\) 9.48 (1H, br), 8.16 (1H, d, \(J_{14.8}\)), 3.27 (1H, br), 1.71 (6H, s) and 2.08-1.02 (10H, m).

2,2-Dimethyl-5-(N-benzylaminomethylene)-1,3-dioxane-4,6-dione (8). \[N-(t\text{-}
\text{butyldiphenylsilyl})\text{benzylamine}\] (80%), mp 166-167 °C (from ethanol) (Found: C, 63.9; H, 5.8; N, 5.35. \(\text{C}_{14}\text{H}_{15}\text{NO}_4\) requires C, 64.35; H, 5.8; N, 5.35%); \(\delta_H\) 9.75 (1H, br), 8.18 (1H, d, \(J_{14.8}\)), 7.36-7.19 (5H, m), 4.55 (2H, d, \(J_{6.0}\)) and 1.61 (6H, s); \(\delta_C\) 165.35 (quat), 163.72 (quat), 159.41, 134.70 (quat), 128.97, 128.47, 127.50, 104.48 (quat), 84.66 (quat), 53.79 and 26.65; \text{m/z} 261 (M\(^{+}\), 18%), 204 (16), 203 (21), 175 (10), 174 (30), 159 (18), 130 (45), 97 (12), 91 (100), 77 (18) and 69 (30).

2,2-Dimethyl-5-\[N-(\alpha\text{-}methylbenzyl)aminomethylene\]-1,3-dioxane-4,6-dione (9). \[N-(t\text{-}
\text{butyldiphenylsilyl})\text{-}1\text{-phenylethylamine}\] (81%), mp 113-115 °C (from ethanol), (lit., 3 113-116 °C); \(\delta_H\) 9.76 (1H, br), 8.16 (1H, d, \(J_{14.4}\)), 7.47-7.23 (5H, m), 4.70 (1H, m), 1.68 (6H, s) and 1.66 (3H, d, \(J_{6.9}\)).

In an alternative method, \(\text{N-(t\text{-}butyldiphenylsilyl})\text{-}1\text{-phenylethylamine}\) 6 (0.179 g, 0.5 mmol) was dissolved in cyclohexane (10 cm\(^3\)) and 5-methoxymethylene Meldrum’s acid 3 (0.093 g, 0.5 mmol) was added with stirring. The mixture was heated under reflux for 24 h and the solvent was removed under reduced pressure to give a yellow solid. Examination of the crude product by \(^1\text{H NMR spectroscopy showed only unreacted starting material.}

Reactions of hydrazines and hydroxylamine derivatives:

2,2-Dimethyl-5-\[N\text{(benzyl-N-dimethylamino)aminomethylene}\]-1,3-dioxane-4,6-dione (10). (1-benzyl-2,2-dimethylhydrazine), (44%), mp 111-113 °C (from cyclohexane), (Found: C, 63.2; H, 6.3; N, 9.0. \(\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4\) requires C, 63.15; H, 6.6; N, 9.2%); \(\delta_H\) 8.45 (1H, s), 7.30-7.13 (5H, m), 5.16 (2H, s), 2.70 (6H, s) and 1.27 (6H, s); \(\delta_C\) (2 quaternaries missing), 156.61, 133.92 (quat), 128.51, 128.20, 127.68, 102.72 (quat), 85.14 (quat), 52.08, 44.96 and 25.85; \text{m/z} 304 (M\(^{+}\), 3%), 247 (34), 246 (30), 203 (16), 155 (50), 139 (17), 130 (15) and 91 (100).

2,2-Dimethyl-5-\[N\text{(dimethylamino)aminomethylene}\]-1,3-dioxane-4,6-dione (18). (1,1-dimethylhydrazine), (79%), mp 188-190 °C (from ethanol), (Found: C, 50.5; H, 6.6; N, 13.15. \(\text{C}_{9}\text{H}_{14}\text{N}_2\text{O}_4\) requires C, 50.45; H, 6.6; N, 13.1%); \(\delta_H\) 9.76 (1H, br d), 8.19 (1H, d, \(J_{11.7}\)), 2.55 (6H, s), and 1.52 (6H, s); \(\delta_C\) 164.49 (quat), 162.99 (quat), 157.56, 104.00 (quat), 82.12 (quat), 47.79 and 26.33; \text{m/z} 214 (M\(^{+}\), 2%), 194 (16), 157 (20), 156 (100), 83 (10) and 70 (58).

A slightly different procedure was used for the hydroxylamine derivatives. The hydroxylamine hydrochloride (10 mmol) was suspended in acetonitrile (150 cm\(^3\)), and triethylamine (1.01 g, 10 mmol) was added. The mixture was stirred at room temperature
for 30 min before addition of methoxymethylene Meldrum’s acid 3 (10 mmol), then stirred for a further 2.5 h at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in dichloromethane and washed with dilute hydrochloric acid (1 M). The organic fraction was dried (MgSO₄), and concentrated to give the product. The following derivatives were made in this way:

**2,2-Dimethyl-5-(N-methyl-N-methoxyaminomethylene)-1,3-dioxane-4,6-dione (11).** (N,O-dimethylhydroxylamine hydrochloride) (89%), mp 82-84 °C (from ethanol), (Found: C, 50.55; H, 6.3; N, 6.45. C₈H₁₅NO₅ requires C, 50.25; H, 6.1; N, 6.5%); δH 8.39 (1H, s), 3.85 (3H, s), 3.66 (3H, s) and 1.66 (6H, s); δC 164.63 (quat), 160.29 (quat), 155.28, 103.15 (quat), 81.62 (quat), 63.28, 42.05 and 26.53; m/z 215 (M⁺, 17%), 157 (24), 126 (100) and 82 (36).

**2,2-Dimethyl-5-(N-methoxyaminomethylene)-1,3-dioxane-4,6-dione (19).** (O-methylhydroxylamine hydrochloride) (79%), mp 112-114 °C (from ethanol), (Found: C, 48.1; H, 5.75; N, 6.85. C₈H₁₅NO₅ requires C, 47.75; H, 5.5; N, 6.95%); δH 8.39 (1H, s), 3.89 (3H, s) and 1.68 (6H, s); δC 164.20 (2 quat), 154.12, 104.98 (quat), 81.34 (quat), 65.77 and 26.71; m/z 201 (M⁺, 14%), 143 (100), 99 (81) and 68 (31).

**Reactions of amines:**

5-[(N-Methyl-N-(α,α-dimethylbenzyl)aminomethylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (24). (N,a,a-trimethylbenzylamine) (45%) mp 118-120 °C (from ethanol), (Found: C, 66.75; H, 7.3; N, 4.8. C₁₇H₂₁NO₄ requires C, 67.3; H, 7.0; N, 4.6%); δH 8.62 (1H, s), 7.32 (5H, m), 3.00 (3H, s), 1.81 (6H, s) and 1.73 (6H, s); δC (2 quaternary signals missing) 157.52, 142.40 (quat), 129.97, 127.98, 124.96, 102.64 (quat), 84.03 (quat), 68.30 (quat), 40.03, 28.46 and 26.39; m/z 303 (M⁺, 4%), 245 (7), 185 (3), 119 (100) and 91 (31).

**Flash vacuum pyrolysis experiments**

The appropriate derivative was sublimed, under vacuum, through the furnace tube and the product(s) were collected in a trap cooled by liquid nitrogen. Upon completion of the pyrolysis the trap was allowed to warm to room temperature under an atmosphere of nitrogen. The entire pyrolysate was then dissolved in solvent to enable removal from the trap. Pyrolysis parameters are given in the order: furnace temperature, inlet temperature, pressure range, pyrolysis time, quantity of precursor. The following derivatives were pyrolysed, with the pyrolysis parameters given in brackets.

**Pyrolyses of aminomethylene Meldrum’s acid derivatives**

2,2-Dimethyl-5-[(N-benzyl-N-dimethylamino)aminomethylene]-1,3-dioxane-4,6-dione (10). (475 °C, 270 °C, 0.01 Torr, 20 min, 0.609 g). The pyrolysis generated black, insoluble polymeric material. The minor, soluble product(s) were removed from the trap with dichloromethane and subjected to dry flash chromatography, eluting with a mixture of n-hexane and ethyl acetate. The only identifiable product obtained was bibenzyl 13 [70
mg, 38% (based on 1 mole of starting material giving 0.5 moles of product), mp 46-49 °C (lit., 18 50-53 °C; δ_H 7.25 (10H, m) and 2.96 (4H, s); δ_C 141.65 (quat), 128.32, 128.21, 125.79 and 37.82; m/z 182 (M^+, 54%) and 91 (100).

**2,2-Dimethyl-5-(N-methyl-N-methoxyaminomethylene)-1,3-dioxane-4,6-dione (11).** (600 °C, 135 °C, 0.005 Torr, 20 min, 0.05 g). The major product was an insoluble yellow-brown polymer. The (minor) soluble fraction showed signals at δ_H 5.30, 4.40, 3.75, 3.50 and 3.45 but no components could be identified. Similar results were obtained at furnace temperatures of 500 and 550 °C.

**2,2-Dimethyl-5-[(N-dimethylamino)aminomethylene]-1,3-dioxane-4,6-dione (18).** (600 °C, 210 °C, 0.01 Torr, 17 min, 1.00 g). Pyrolysis again generated mainly insoluble, polymeric material. The very minor soluble portion of the product yielded no identifiable products, even after silica dry flash column chromatography.

**2,2-Dimethyl-5-(N-methoxyaminomethylene)-1,3-dioxane-4,6-dione (19).** (550 °C, 185 °C, 0.001 Torr, 25 min, 0.05 g). A bright yellow insoluble polymer was obtained.

**5-[N-Methyl-N-(a,a-dimethylbenzyl)aminomethylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (24).** (600 °C, 160 °C, 0.005 Torr, 20 min, 0.058 g). This pyrolysis gave only α-methylstyrene δ_H 7.31 (5H, m), 5.38 (1H, s), 5.09 (1H, s) and 2.17 (3H, s); δ_C 143.09 (quat), 141.02 (quat), 128.06, 127.24, 125.32, 112.26 and 21.67 (spectra compatible with literature data19). Pyrolyses at 500 and 550 °C gave a mixture of α-methylstyrene and starting material.

**Pyrolyses of the amines 26, 27 and 23**

*N-Methylbenzylamine (26)* was pyrolysed at 50 °C intervals from 700-950 °C to give varying proportions of bibenzyl and starting material. Results are shown in Figure 1.

*N,a-Dimethylbenzylamine (27)* was pyrolysed at 50 °C intervals from 700-900 °C to give styrene and unreacted starting material. Results are shown in Figure 1.

*N,a,a-Trimethylbenzylamine 23* was pyrolysed at 50 °C intervals from 600-850 °C to give α-methylstyrene and unreacted starting material. Results are shown in Figure 1.

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