Azepinones. Part 1.[1] Formation of Simple 1*H*-Azepin-3(2*H*)-ones by Gas-phase Pyrolysis: Crystal and Molecular Structure of 1-Phenyl-1*H*-azepin-3(2*H*)-one

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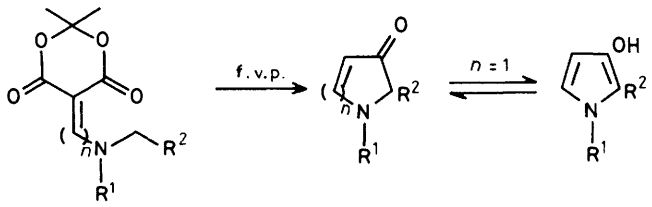
Flash vacuum pyrolysis of the Meldrum's acid derivatives (**4**)—(**6**) at 500 °C (10^{-3} Torr) gives good yields of the 1*H*-azepin-3(2*H*)-ones (**7**)—(**9**) respectively. *X*-Ray crystallography of the 1-phenylazepinone (**8**) shows that the dienaminone conjugated system is approximately planar though the seven-membered ring as a whole is markedly non-planar. The coalescence temperature for ring-inversion of the 2,2-dimethyl derivative (**9**) is −96 °C, corresponding to a $\Delta G^{\ddagger}$ of 36.4 kJ mol^{-1}.

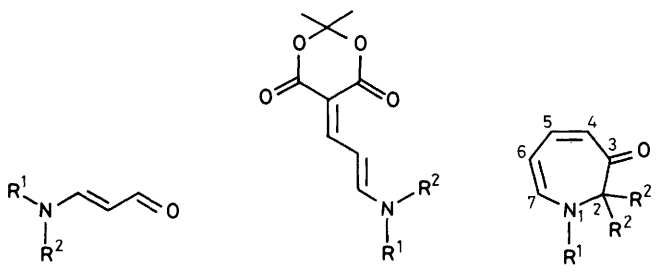
We have recently discovered that the sensitive 1*H*-pyrrol-3(2*H*)-one (3-hydroxypyrrole) nucleus can be prepared in the gas phase, on a preparatively useful scale, by pyrolysis of aminomethylene derivatives of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) (Scheme, $n = 1$).[2,3] Here we report the



Scheme.

successful extension of this approach to the vinylogous case (Scheme, $n = 2$) which has given the first rational synthesis[4] of the novel 1*H*-azepin-3(2*H*)-one system.[1] In the present paper, we describe the simplest *N*-alkyl and *N*-aryl derivatives, which serve as typical examples, together with the full structural characterisation of the ring system by *X*-ray crystallography. In addition, the flexibility of the ring system is investigated by variable temperature n.m.r. spectroscopy. The scope and mechanism of the synthesis,[1] and the chemical[5] and spectroscopic properties of these azepinones will be considered in later Parts of this series.

The required azepinone precursors are the 5-aminopropenylidene derivatives of Meldrum's acid (**4**)—(**6**) which should, in principle, be accessible by Knoevenagel reaction of Meldrum's acid with the enaminals (**1**)—(**3**), which themselves can be obtained in moderate yield by well-established general methods.[6,7] In the event, standard 'aldehyde' conditions for the condensation which we had applied to aza analogues of (**4**)—(**6**)[8] proved unsuccessful, though the reaction proceeded well, in the absence of a catalyst, when pyridine was used as solvent.[8]



(**1**) R^1=R^2=Me
(**2**) R^1=Ph, R^2=Me
(**3**) R^1=Ph, R^2=Pr^i

(**4**) R^1=R^2=Me
(**5**) R^1=Ph, R^2=Me
(**6**) R^1=Ph, R^2=Pr^i

(**7**) R^1=Me, R^2=H
(**8**) R^1=Ph, R^2=H
(**9**) R^1=Ph, R^2=Me

Because of their low solubility, the yields of the *N*-aryl derivatives (**5**) and (**6**) were particularly high, but all three are yellow crystalline solids with high melting points. In the ^{1}H n.m.r. spectra, the signals due to the conjugated portion appear as two doublets and a double doublet at δ_H 6.5—8.0 [partially superimposed on the aromatic signals in the cases of (**5**) and (**6**)] with large coupling constants which indicate the *trans*-s-*trans* configuration: this has been confirmed by *X*-ray crystallography.[9] There is an indication of the existence of two rotamers (about the C–N bond) in the *N*-phenyl-*N*-isopropyl compound (**6**). In the ^{13}C n.m.r. spectra, the 1- and 3-propenylidene positions are considerably deshielded (δ_C 158—162), with the resonance of the electron-rich central position occurring at δ_C 101—104.

The mass spectra of the propenyl compounds (**4**)—(**6**) are unusual, since they show intense molecular ions and do not show significant cleavage of $Me_2CO + CO_2$ which is the favoured breakdown pattern for most Meldrum's acid derivatives.[8,10] This suggests that side-chain ionisation may be preferred, and indeed the base peak in all three cases may be due to a pyridinium ion derived from the *N*-alkylamino group and the propenyl chain, plus the C-5 atom of the Meldrum's acid ring. Thus the *N*,*N*-dimethyl compound (**4**) shows a base peak at *m*/*z* 94 (corresponding to *N*-methylpyridinium), the *N*-methyl-*N*-phenyl compound (**5**) has its base peak at *m*/*z* 156 (*N*-phenylpyridinium) while the *N*-isopropyl-*N*-phenyl compound (**6**) must lose a methyl group in the aromatisation to give the base peak at *m*/*z* 170 (2-methyl-*N*-phenylpyridinium).

Flash vacuum pyrolysis (f.v.p.) of the Meldrum's acid precursors (**4**)—(**6**) at *ca.* 500 °C gave the azepinones (**7**)—(**9**) in 65—75% yield. Because of the possibility of side reactions,[1] the pyrolysis conditions were much more critical than for the pyrrolones,[2,3] and the optimum temperature was *ca.* 100 °C lower than for the 5-membered ring examples. The azepinones (**7**)—(**9**) are bright yellow materials, owing to the extended conjugation, and were characterised by their ^{1}H n.m.r. spectra which showed two pairs of doublets and two pairs of double doublets in the olefinic region (δ_H 5—7). The 1*H*-azepin-3(2*H*)-one tautomer was present exclusively, in a wide range of solvents: tautomerisation to the 3-hydroxyazepine would generate an 8π-electron counter-Hückel species. The ^{13}C n.m.r. spectra confirm the dienaminone conjugation with two methine signals corresponding to electron-rich carbon atoms (C-4 and C-6, δ_C *ca.* 125 and *ca.* 100 respectively) and two corresponding to electron-deficient centres (C-5 and C-7, δ_C 140—150). In their mass spectra, significant molecular ions are obtained, with the major breakdown being loss of CO and aromatisation to give the same pyridinium species found in the spectra of the corresponding Meldrum's acid derivatives (above) [(**7**); *m*/*z* 94 (100%); (**8**), *m*/*z* 156 (100%); (**9**), *m*/*z* 170 (58%)]. An alternative cleavage, particularly important for the *N*-aryl examples,

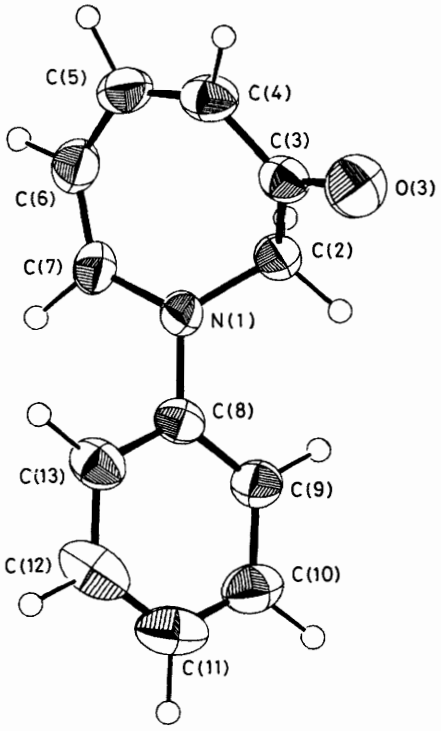


Figure 1. ORTEP diagram of the azepinone (**8**) showing crystallographic numbering system.

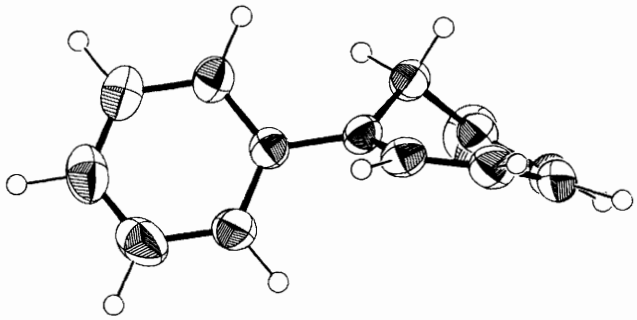


Figure 2. Side view of the azepinone (**8**)

generates an iminium radical cation from the N(1)–C(2) fragment [(**8**), $PhN^{+\bullet}=CH_2$, *m/z* 105 (53%); (**9**), $PhN^{+\bullet}=CMe_2$, *m/z* 133 (100%)].

Intense maxima are observed in the u.v. spectra of (**7**)—(**9**) at *ca.* 420 nm. The 1-methylazepinone (**7**) and the 2,2-dimethyl-1-phenyl compound (**9**) have almost indentical maxima (414 and 413 nm respectively) which indicates that the aryl substituent is twisted out-of-plane by the adjacent methyl groups and is therefore unable to conjugate efficiently. Even in the case of the parent 1-phenylazepinone (**8**) the bathochromic shift due to the *N*-aryl group (14 nm) is considerably less than that found in the 1*H*-pyrrol-3(2*H*)-one series[11] (*ca.* 25 nm), and therefore an increased dihedral angle between the two rings would be predicted (see below).

In view of the unusual nature of the thermal hydrogen transfer-cyclisation process which gives rise to these 1*H*-azepin-3(2*H*)-ones, and because of their novel conjugated system, it was desirable to confirm the structure by *X*-ray crystallography. The *N*-phenyl derivative (**8**) gave satisfactory crystals, and the structural parameters so obtained are listed in Tables 1—4. Figures 1 and 2 are ORTEP plots displaying different projections, while Figure 3 shows selected data for (**8**) and related model compounds.

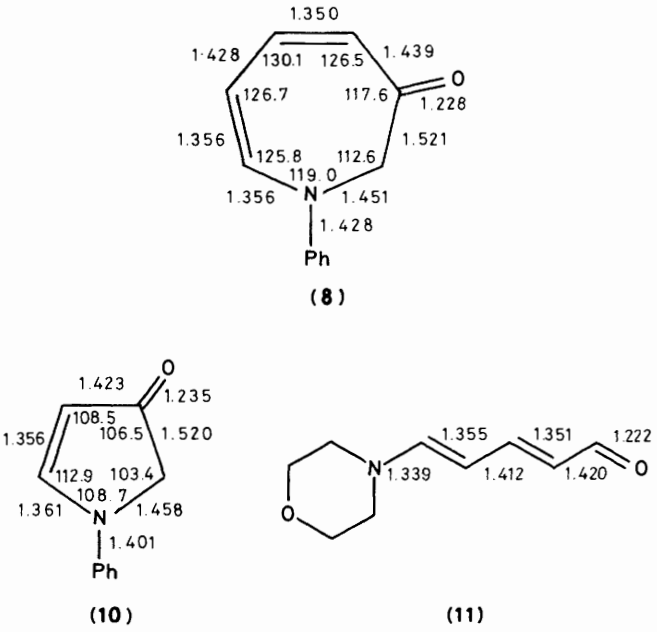


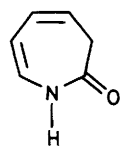
Figure 3. Selected structural parameters for the azepinone (**8**) and related model compounds

It is clear from Figure 2 in particular that the seven-membered ring as a whole is non-planar, in contrast to the 1*H*-pyrrol-3(2*H*)-one (**10**). However, the geometry approximates to that of an almost planar dienaminone conjugated system [from N(1) through C(7)–C(3) to O(3)] bridged by a methylene group which has pseudo-axial and pseudo-equatorial substituents. The bond lengths in the dienaminone unit are uniformly similar to those in the 1*H*-pyrrol-3(2*H*)-one analogue[11] (**10**) and to those in the open-chain dienaminone[12] (**11**). Thus the average lengths of the formal C=C, C–C, and C=O bonds in this unit in all three structures are 1.354 ± 0.003 Å, 1.424 ± 0.015 Å and 1.228 ± 0.007 Å: the C–N bond lengths of (**8**) and (**10**) are also closely similar (1.359 ± 0.003 Å) while the shorter value for the open-chain compound (**11**) is most likely due to its *N*-alkyl rather than *N*-aryl substitution.[2,11] A consequence of the enforced planarity of the conjugated portion of the azepinone (**8**) is that the bond angles are distorted (usually increased) from 120°: as in the pyrrolone (**10**) the N(1)–C(2)–C(3) and C(2)–C(3)–C(4) bond angles are the most acute in the ring system.

Whereas the *N*-aryl ring and the pyrrolone system in (**10**) are almost coplanar[11] (dihedral angle 13°), the dihedral angle between the *N*-aryl ring and the conjugated system of the azepinone (**8**) is some 47.9°. This result was expected on the basis of the u.v. spectra (above), and is presumably due to an increase in the steric repulsion between H(2A), H(7), and H(9), H(13), caused by the larger bond angles in the 7-membered ring. Conjugative interaction between the lone pair on the nitrogen atom and the aryl ring is consequently reduced in the azepinone case and this is reflected by an increase in the *N*-aryl bond length by an amount >6 standard deviations [(**8**), *N*-aryl, 1.428 Å; (**10**), *N*-aryl, 1.401 Å].

The non-planarity of the ring was not apparent in the room temperature n.m.r. spectra of the 1*H*-azepin-3(2*H*)-ones (**7**)—(**9**), in which the 2-substituent signals appear as sharp singlets owing to rapid ring inversion in solution. Though considerable broadening of the H(2) resonance of the *N*-phenyl derivative (**8**) was observed at low temperature ([$^2H_6$]acetone solvent, 360 MHz), coalescence had not been reached even at −105 °C. However, partial separation of the pseudo-axial and pseudo-

equatorial methyl groups of the 2,2-dimethyl compound (**9**) was successfully achieved at −104 °C ([$^2H_2$]methylene dichloride solvent, 360 MHz). The coalescence temperature (T_c −96 °C) and half-height line-width at T_c (33 Hz) allow[13] an estimate of the free energy of activation[14] for the ring inversion ($\Delta G^{\ddagger}$) as 36.4 kJ mol^{-1}. Since the gem-dimethyl substitution is unlikely to affect $\Delta G^{\ddagger}$ significantly (*cf.* cyclohexane and 1,1-dimethylcyclohexane, $\Delta G^{\ddagger}$ 42.9 and 44.0 kJ mol^{-1} respectively[15]), this value may be taken as a good approximation to that of the 1*H*-azepin-3(2*H*)-one system in general. Indeed it is remarkably close to that estimated for the ring inversion of the parent isomeric 1*H*-azepin-2(3*H*)-one (**12**)[16] ($\Delta G^{\ddagger}$ *ca.* 35.6 kJ mol^{-1}),[14] and available data for typical 3*H*- and 4*H*-azepines are of similar magnitude [*e.g.* (**13**), $\Delta G^{\ddagger}$ 57.4 kJ mol^{-1};[17] (**14**), $\Delta G^{\ddagger}$ 42.7 kJ mol^{-1};[14] (**15**), $\Delta G^{\ddagger}$ <40 kJ mol^{-1}.[18]].



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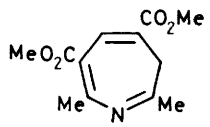

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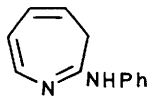

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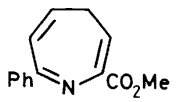

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Experimental

^1H and ^{13}C N.m.r. spectra were recorded at 200 and 50 MHz respectively, for solutions in [^2H]chloroform.

3-Aminopropenal Derivatives.—3-(*N,N*-Dimethylamino)-prop-2-enal (**1**) was obtained commercially or was prepared by a literature method.[6] It was found that extraction of the product from the aqueous alkaline medium of the final hydrolysis step was not complete after six extractions and the use of a continuous extractor may increase the yield of this preparation.

Other *N,N*-disubstituted prop-2-enals were prepared as follows:[7] the appropriate secondary amine (30 mmol) was added to a solution of prop-2-ynol (2.9 ml, 25 mmol) in benzene (40 ml). The reaction mixture was cooled on an ice bath and manganese dioxide (6.25 g, 70 mmol) was added in portions, over a period of 30 min, to the stirred solution. The suspension was then allowed to warm to room temperature and was stirred overnight. The remaining solid was filtered off and the filtrate evaporated under reduced pressure. The residue was purified by bulb-to-bulb distillation. In cases where the starting amine was relatively involatile, care was required during the distillation to give reasonable separation. The amount of amine which remained as contaminant could be calculated if necessary from the ^1H n.m.r. spectrum and this material could be used without further purification. The following prop-2-enals were prepared: 3-(*N*-methyl-*N*-phenyl) (**2**) (49%), b.p. 130 °C (0.3 Torr) [lit.,[19] 144 °C (0.8 Torr)]; 3-(*N*-isopropyl-*N*-phenyl) (**3**) (26%), b.p. 150—155 °C (0.1 Torr), m.p. 82—83 °C (from cyclohexane) (Found: C, 76.1; H, 8.1; N, 7.5. $C_{12}H_{15}NO$ requires C, 76.2; H, 7.95; N, 7.4%); δ_H 9.09 (1 H, d, ^3J 8.3 Hz), 7.2—7.5 (5 H, m), 7.10 (1 H, d, ^3J 7.3 Hz), 5.00 (1 H, br s), 3.93 (1 H, septet), and 1.25 (6 H, d); δ_C 189.52, 157.98, 140.90 (q), 129.45, 127.87, 127.58, 103.68, 56.39 (br), and 21.52; *m/z* 189 (M^+, 100%), 174 (40), 146 (84), 118 (72), 104 (37), and 77 (64).

5-(Aminopropenylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione Derivatives.—2,2-Dimethyl-1,3-dioxane-4,6-dione (2.2 g, 15 mmol) was dissolved in pyridine (10 ml)[8] and a solution of the appropriate aldehyde (15 mmol) in pyridine (5 ml) was added. The reaction mixture rapidly became a deep red and was stirred overnight at room temperature. This produced the condensation product as a precipitate which was filtered off and recrystallised. In order to obtain a reasonable yield of the dimethylamino derivative, the filtrate was concentrated under reduced pressure and the residue was triturated with ethanol to yield a further quantity of product. The condensation could not be accomplished using the method generally applied to aldehydes which uses benzene as solvent with catalytic amounts of piperidine and acetic acid.[8]

The following 5-[(3-N,N-*disubstituted-amino)propenylidene*]-2,2-*dimethyl*-1,3-*dioxane*-4,6-*diones* were prepared: N,N-*dimethyl* (**4**) (57%) m.p. 173—175 °C (from ethanol) (Found: C, 58.8; H, 6.75; N, 6.05. $C_{11}H_{15}NO_4$ requires C, 58.65; H, 6.65; N, 6.2%); δ_H 7.94 (1 H, d, ^3J 13.2 Hz), 7.29 (1 H, d, ^3J 12.1 Hz), 6.88 (1 H, dd, ^3J 12.1 and 13.2 Hz), 3.11 (3 H, s), 3.26 (3 H, s), and 1.67 (6 H, s); δ_C 165.20 (q), 163.19 (q), 162.97, 158.36, 102.94 (q), 101.95, 94.38 (q), 45.11, 38.12, and 26.86; *m/z* 225 (M^+, 83%), 168 (25), 139 (12), 123 (13), 108 (25), and 94 (100); N-*methyl*-N-*phenyl* (**5**) (93%), m.p. 218—219 °C (from ethanol) (Found: C, 67.0; H, 5.95; N, 5.15. $C_{16}H_{17}NO_4$ requires C, 66.9; H, 5.9; N, 4.9%); δ_H 8.07 (1 H, d, ^3J 12.9 Hz), 7.66 (1 H, d, ^3J 12.3 Hz), 7.0—7.5 (6 H, m) (central olefinic resonance superimposed on aromatics), 3.52 (3 H, s), and 1.67 (6 H, s); δ_C 164.74 (q), 162.78 (q), 159.11, 158.64, 145.43 (q), 129.85, 126.89, 120.89, 104.23, 103.34 (q), 98.19 (q), 38.12, and 27.06; *m/z* 287 (M^+, 73%), 230 (27), 184 (80), 159 (40), 158 (67), 157 (40), 156 (100), 144 (27), 132 (60), and 131 (60); N-*isopropyl*-N-*phenyl* (**6**) (72%), m.p. 235—237 °C (from ethanol) (Found: C, 68.7; H, 6.9; N, 4.5. $C_{18}H_{21}NO_4$ requires C, 68.55; H, 6.65; N, 4.45%); δ_H (major rotamer only) 7.98 (1 H, d, ^3J 13.0 Hz), 7.1—7.6 (6 H, m), 6.50 (1 H, t, ^3J 13.0 Hz), 3.99 (1 H, septet), 1.61 (6 H, s), and 1.34 (6 H, d); δ_C (major rotamer only) 165.14 (q), 162.58 (q), 160.81, 158.73, 138.86 (q), 129.98, 129.05, 126.90, 103.86, 102.80 (q), 95.13 (q), 59.78, 26.87, and 21.97; *m/z* 315 (M^+, 83%), 258 (10), 198 (14), 171 (95), 170 (100), 143 (28), 133 (47), 118 (32), and 77 (72).

Table 1. Bond lengths (Å) with standard deviations

N(1)–C(2)	1.451(4)	C(6)–C(7)	1.356(4)
N(1)–C(7)	1.356(4)	C(8)–C(9)	1.393(4)
N(1)–C(8)	1.428(3)	C(8)–C(13)	1.382(4)
C(2)–C(3)	1.521(4)	C(9)–C(10)	1.389(5)
C(3)–O(3)	1.228(4)	C(10)–C(11)	1.373(5)
C(3)–C(4)	1.439(4)	C(11)–C(12)	1.380(5)
C(4)–C(5)	1.350(4)	C(12)–C(13)	1.403(5)
C(5)–C(6)	1.428(4)		

Table 2. Angles (°) with standard deviations

C(2)–N(1)–C(7)	118.99(23)	N(1)–C(7)–C(6)	125.8(3)
C(2)–N(1)–C(8)	120.92(21)	N(1)–C(8)–C(9)	120.51(24)
C(7)–N(1)–C(8)	118.82(22)	N(1)–C(8)–C(13)	119.15(24)
N(1)–C(2)–C(3)	112.61(23)	C(9)–C(8)–C(13)	120.3(3)
C(2)–C(3)–O(3)	118.5(3)	C(8)–C(9)–C(10)	119.9(3)
C(2)–C(3)–C(4)	117.61(25)	C(9)–C(10)–C(11)	120.0(3)
O(3)–C(3)–C(4)	123.8(3)	C(10)–C(11)–C(12)	120.6(3)
C(3)–C(4)–C(5)	126.5(3)	C(11)–C(12)–C(13)	120.2(3)
C(4)–C(5)–C(6)	130.1(3)	C(8)–C(13)–C(12)	119.1(3)
C(5)–C(6)–C(7)	126.7(3)		

Table 3. Torsion angles (°) with standard deviations

C(7)–N(1)–C(2)–C(3)	77.4(3)	C(3)–C(4)–C(5)–C(6)	14.6(6)
C(8)–N(1)–C(2)–C(3)	−115.6(3)	C(4)–C(5)–C(6)–C(7)	10.7(6)
C(2)–N(1)–C(7)–C(6)	−28.5(4)	C(5)–C(6)–C(7)–N(1)	−19.1(5)
C(8)–N(1)–C(7)–C(6)	164.2(3)	N(1)–C(8)–C(9)–C(10)	−177.7(3)
C(2)–N(1)–C(8)–C(9)	−38.1(4)	C(13)–C(8)–C(9)–C(10)	−0.9(4)
C(2)–N(1)–C(8)–C(13)	145.1(3)	N(1)–C(8)–C(13)–C(12)	177.6(3)
C(7)–N(1)–C(8)–C(9)	128.9(3)	C(9)–C(8)–C(13)–C(12)	0.7(4)
C(7)–N(1)–C(8)–C(13)	−47.9(4)	C(8)–C(9)–C(10)–C(11)	0.2(5)
N(1)–C(2)–C(3)–O(3)	122.1(3)	C(9)–C(10)–C(11)–C(12)	0.7(5)
N(1)–C(2)–C(3)–C(4)	−61.9(3)	C(10)–C(11)–C(12)–C(13)	−0.8(6)
C(2)–C(3)–C(4)–C(5)	9.1(5)	C(11)–C(12)–C(13)–C(8)	0.1(5)
O(3)–C(3)–C(4)–C(5)	−175.1(3)		

Table 4. Fractional co-ordinates of atoms with standard deviations

	x	*y*	*z*
N(1)	0.336 56(18)	0.719 02(18)	0.084 9(3)
C(2)	0.292 15(24)	0.803 73(22)	0.219 6(4)
C(3)	0.177 33(22)	0.835 81(21)	0.162 7(5)
O(3)	0.106 28(18)	0.824 93(23)	0.292 4(4)
C(4)	0.159 80(24)	0.884 18(24)	−0.036 5(5)
C(5)	0.232 49(25)	0.891 40(24)	−0.190 1(5)
C(6)	0.333 4(3)	0.835 88(24)	−0.216 5(4)
C(7)	0.371 58(24)	0.749 29(23)	−0.104 0(5)
C(8)	0.364 34(18)	0.611 12(22)	0.161 3(4)
C(9)	0.410 59(23)	0.599 3(3)	0.354 8(5)
C(10)	0.440 75(25)	0.494 2(3)	0.424 2(6)
C(11)	0.425 26(25)	0.402 4(3)	0.301 9(7)
C(12)	0.380 9(3)	0.413 5(3)	0.109 1(7)
C(13)	0.349 72(22)	0.518 95(24)	0.037 0(5)

1H-*Azepin*-3(2H)-*ones*.—These compounds were made on 0.5—2.0 g scale by sublimation of the appropriate propenylidene Meldrum's acid derivative through a silica furnace tube (35 × 2.5 cm) at *ca.* 10^{-3} Torr. The products were collected in a U-tube cooled by liquid nitrogen, and positioned at the exit point of the furnace.

The crude azepinone was generally purified by bulb-to-bulb distillation but, if required, chromatography on alumina with ethyl acetate–hexane (75:25) as eluant was also possible.

The following 1H-*azepin*-3(2H)-*ones* were prepared. The 5-(3-aminopropenylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione substrate, furnace temperature, and inlet temperature are reported. 1-*Methyl* (**7**) (*N*,*N*-dimethyl, 500 °C, 200 °C) (64%); b.p. 92 °C (0.3 Torr) (Found: M^+, 123.068. C_7H_9NO requires M^+ 123.068); δ_H 6.84 (1 H, dd, ^3J 9.1 and 11.0 Hz), 6.72 (1 H, d, ^3J 7.2 Hz), 6.17 (1 H, d, ^3J 11.0 Hz), 5.17 (1 H, dd, ^3J 7.2 and 9.0 Hz), 3.57 (2 H, s), and 3.20 (3 H, s); δ_C 180.21 (q), 147.19, 142.01, 123.33, 99.41, 62.65, and 44.04; $\lambda_{max.}(CHCl_3)$ 414 nm; *m*/*z* 123 (M^+, 61%), 95 (12), and 94 (100); 1-*phenyl* (**8**) (*N*-methyl-*N*-phenyl, 500 °C, 210 °C) (75%), m.p. 79—81 °C (from methanol) (Found: C, 77.9; H, 5.95; N, 7.25. $C_{12}H_{11}NO$ requires C, 77.85; H, 5.95; N, 7.55%); δ_H 7.05—7.35 (5 H, m), 6.99 (1 H, d, ^3J 8.0 Hz), 6.89 (1 H, dd, ^3J 11.2 and 8.6 Hz), 6.34 (1 H, d, ^3J 11.2 Hz), 5.49 (1 H, apparent t, ^3J 8.4 Hz), and 4.14 (2 H, s); δ_C 182.87 (q), 144.11 (q), 141.54, 140.16, 129.18, 126.71, 124.73, 119.77, 103.86, and 59.38; $\lambda_{max.}(CHCl_3)$ 428 nm; *m*/*z* 185 (M^+, 67%), 156 (100), 105 (53), and 77 (40); 2,2-*dimethyl*-1-*phenyl* (**9**) (*N*-isopropyl-*N*-phenyl, 525 °C, 200 °C), (70%), b.p. 152—154 °C (0.1 Torr) (Found: C, 78.8; H, 7.1; N, 6.55. $C_{14}H_{15}NO$ requires C, 78.9; H, 7.05; N, 6.55%); δ_H 7.0—7.4 (5 H, m), 6.75 (1 H, dd, ^3J 11.5 and 8.5 Hz), 6.68 (1 H, d, ^3J 8.5 Hz), 6.30 (1 H, d, ^3J 11.5 Hz), 5.28 (1 H, apparent t, ^3J 8.5 Hz), and 1.22 (6 H, s); δ_C 185.79 (q), 145.07 (q), 142.53, 138.14, 128.96 (2 peaks superimposed), 127.65, 123.34, 100.84, 64.50 (q), and 22.59; $\lambda_{max.}(CHCl_3)$ 413 nm; *m*/*z* 213 (M^+, 56%), 170 (58), 133 (100), 118 (78), and 77 (54).

Crystal Data.—$C_{12}H_{11}NO$, M = 185.23, orthorhombic, space group $P2_12_12_1$, a = 12.399(20), b = 11.982(13), c = 6.523(13) Å, U = 969 Å^3 (from diffractometer angles of 11 reflections with $10 < 2\theta < 36°$), Z = 4, D_c = 1.270 g cm^{-3}, Mo-K_α radiation, $\bar{\lambda}$ = 0.710 73 Å, crystal size 0.28 × 0.40 × 0.88 mm, μ = 0.76 cm^{-1}, $F(000)$ = 392.

Data collection and processing. STADI-2 diffractometer, graphite-monochromated Mo-K_α X-radiation, ω scans, 1 015 data ($2\theta_{max.}$ 50°, $+h$, $+k$, $+l$), of which 823 with $F > 6\sigma(F)$ were used in all calculations.

Structure analysis and refinement. SHELX84[20] direct methods located all non-H atoms, which were then refined anisotropically, with H atoms in fixed, calculated positions.[21] At final convergence, R, wR = 0.0410, 0.0621, S = 0.603 for 127 parameters and the final difference Fourier synthesis showed no feature above 0.19 e Å^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.010\,73F^2$ gave satisfactory agreement analyses and $(\Delta/\sigma)_{max.}$ in the final cycle was 0.16.

Selected molecular geometry parameters are listed in Tables 1—3 and refined fractional co-ordinates in Table 4. Thermal parameters, calculated H-atom positions and full structural parameters are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for the paper.*

Acknowledgements

We are indebted to Dr. D. Reed for the variable-temperature n.m.r. measurements, which were obtained through the S.E.R.C. supported Edinburgh University high-field n.m.r. service. We are also grateful to the S.E.R.C. for support, for a Research Studentship (to L. C. M.), and to Lonza Ltd. for a generous gift of Meldrum's acid.

* See 'Instructions for Authors (1989)', *J. Chem. Soc., Perkin Trans. 1*, 1989, Issue 1.

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Received 23*rd May* 1988; *Paper* 8/02036A