Thermal Cyclisation Reactions of Vinylogous Aminomethylene Meldrum's Acid Derivatives

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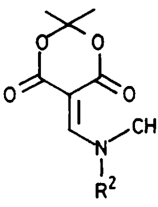
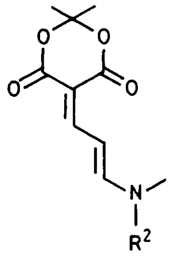
Flash vacuum pyrolysis of vinylogous aminomethylene derivatives of Meldrum's acid leads to new cyclisation reactions; one additional double bond results in the formation of 1*H*-azepin-3(2*H*)-ones, while two additional double bonds lead to benzamide derivatives.

Gas-phase pyrolysis of aminomethylene derivatives of Meldrum's acid (**1**) has provided an efficient route to simple 1*H*-pyrrol-3(2*H*)-ones (3-hydroxypyrroles)[1—3] and has given access to exceptionally stable methyleneketenes.[4] Our investigations of the vinylogous systems (**2**) and (**3**), reported here, have uncovered new cyclisation reactions of these intermediates, which lead, respectively, to an unusual heterocyclic system and to a new synthesis of benzenoid derivatives from acyclic precursors.[5]

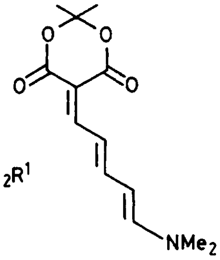
The thermolysis precursors (**2**)† and (**3**)† were readily obtained in 50—70% yield by condensation of the appropriate enaminone[6] or dienaminone[7] with Meldrum's acid in pyridine solution.



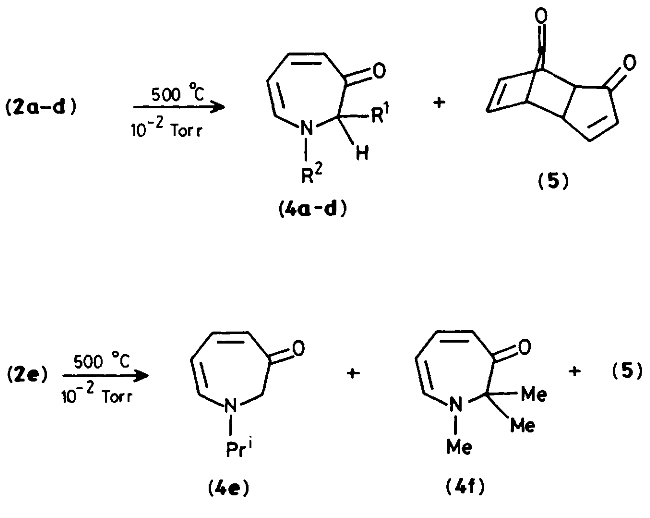
(**1**)



(**2**)



(**3**)

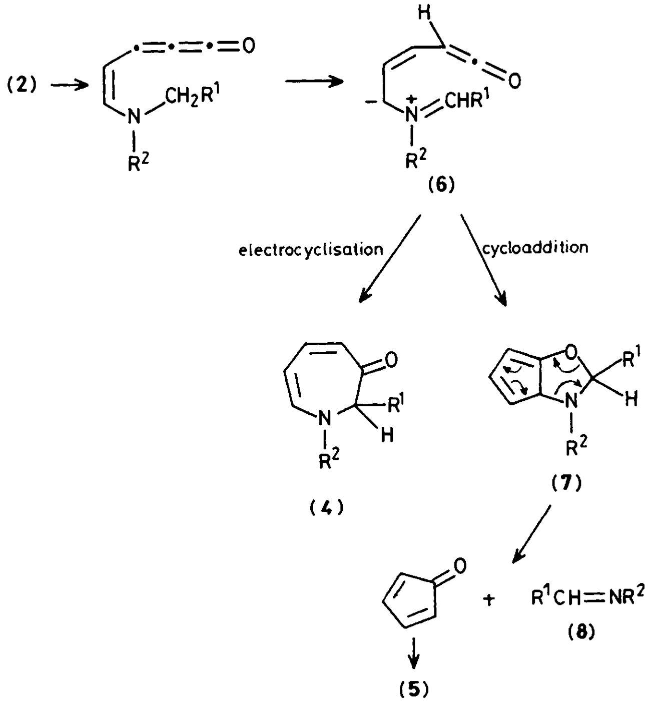


a; R¹ = H, R² = Me
b; R¹ = H, R² = Ph
c; R¹ = Me, R² = Et
d; R¹ = R² = Ph
e; R¹ = H, R² = Prⁱ

Scheme 1

Flash vacuum pyrolysis of (**2**) leads to the 1*H*-azepin-3-(2*H*)-ones (**4**) in *ca.* 60% yield,‡ contaminated by a small amount of cyclopentadienone dimer (**5**) which can be separated by chromatography on alumina. This method provides the first generally applicable synthesis of simple 1*H*-azepin-3(2*H*)-ones (Scheme 1), which have been hitherto unobtainable. The only previously reported derivative is a highly substituted example isolated in low yield (16%) by an approach which is apparently incapable of generalisation.[8] The pyrolytic cyclisation can take place at *N*-methyl groups (Scheme 1, examples **a**, **b**, and **e**), *N*-methylene groups (examples **c** and **d**), or *N*-methine groups (example **f**) leading to 1-substituted, 1,2-disubstituted, and 1,2,2-trisubstituted derivatives respectively. In a competitive case reaction takes place with little regioselectivity [*e.g.* pyrolysis of (**2e**) (Scheme 1)] though the products are readily separated by chromatography on alumina. The chemical properties of these new materials are discussed in the following Communication.[9]

The formation of (**4**) and (**5**) can be rationalised by the mechanism of Scheme 2. Hydrogen transfer in the methyleneketene leads to a dipolar intermediate (**6**) similar to that



Scheme 2

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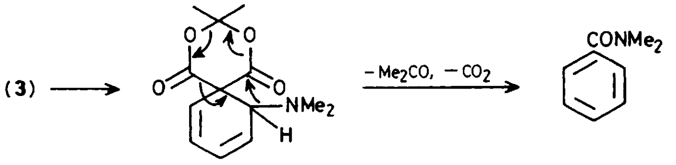
† All new compounds are characterised by spectra, and by elemental analysis (solids) or exact mass measurement (liquids).

‡ *E.g.* (**1a**), 64%, δ_H ($CDCl_3$) 6.88 (1H, dd), 6.75 (1H, d), 6.23 (1H, d), 5.21 (1H, dd), 3.57 (2H, s), and 3.20 (3H, s); δ_C 180.21 (C-3), 147.19 (C-7), 142.01 (C-5), 123.33 (C-6), 99.41 (C-4), 62.65 (C-2), and 44.04 (CH_3); *m/z* 123 (M^+, 61%).



Scheme 3

proposed by Klop and Brandsma.[10] This intermediate can either collapse to the azepinone by electrocyclisation (*cf.* pyrrolone formation[3]) or to the bicyclic intermediate (**7**) by cycloaddition across the carbonyl component of the ketene. Such cycloadditions are well known in the chemistry of azomethine ylides.[11] Further collapse of (**7**) gives cyclopentadienone [and hence (**5**)], and the imine (**8**); in agreement with this, benzylideneaniline (**8**; $R^1 = R^2 = Ph$) was identified in the pyrolysate from (**2d**).

Flash vacuum pyrolysis of (**3**) does not lead to the nine-membered azoninones. Instead, the exclusive formation of *N*,*N*-dimethylbenzamide (73%) can be explained by an alternative electrocyclisation followed by migration of the dimethylamino group. The amide can be detected under much milder conditions (350 °C) than is usual for Meldrum's acid pyrolyses in our apparatus, which suggests that it is either the triene segment of (**3**) itself (Scheme 3), or one of the early intermediates of Meldrum's acid cleavage,[4] which is involved in the cyclisation.

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