Synthesis of Pyrazolinones from β-*N*,*N*-Dimethylhydrazinopropenoates: an Example of a Thermally Induced [1,4] Alkyl Shift

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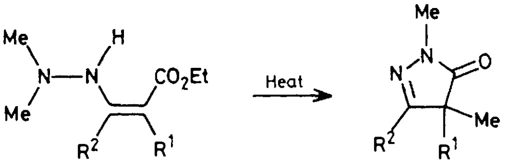
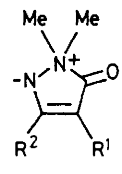
Gas phase thermolysis of β-*N*,*N*-dimethylhydrazinopropenoates (**1**) provides a new route to pyrazolinones (**2**) involving a [1,4] methyl shift from nitrogen to carbon in the pyrazolinium ylide intermediates (**3**); the mechanism is supported by the isolation of ylides (**3a,b,e**), the structures of (**3a**) and (**3e**) being confirmed by *X*-ray crystallography.

The synthesis of pyrazolinones from β-hydrazinopropenoates, since it requires a hydrogen atom on the terminal nitrogen atom of the hydrazine group,[1] cannot be carried out with *N*,*N*-dialkyl derivatives such as (**1**). We are currently studying the thermal behaviour of β-enaminoesters and we now report that flow pyrolysis of compounds (**1**), in toluene, gives facile access to pyrazolinones (**2**) through the intermediacy of pyrazolinium ylides (**3**). We believe that the last step of the reaction is the first known example of a [1,4] alkyl shift from nitrogen to carbon in an ylide of type (**3**).†

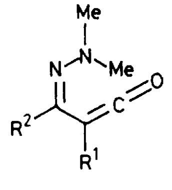
Flow pyrolysis (440 °C; 15 Torr) of compounds (**1**) in toluene, prepared by condensation of *N*,*N*-dimethylhydrazine with ethoxy propenoate derivatives for (**1a, b**) or with β-ketoesters for (**1c, d**), led to the pyrazolinones (**2a**—**d**) in 37—48% yields following flash column chromatography. The reaction is accompanied by loss of ethanol. Structural assignment was achieved spectroscopically, in particular by detailed n.m.r. studies which showed a consistent pattern for the series.‡



(1a-d) (2a-d)



(3)



(4)

a; R^1 = CN, R^2 = H
b; R^1 = CO_2Et, R^2 = H
c; R^1,R^2 = $-[CH_2]_4-$
d; R^1,R^2 = $-[CH_2]_3-$
e; R^1 = CO_2Me, R^2 = H

Moreover, when the pyrolysis was conducted at a lower temperature (380 °C) with (**1a**) and (**1b**), crystalline products (**3a**) (60%, m.p. 175 °C) and (**3b**) (65%, m.p. 102 °C) respectively were isolated. Two mechanistic pathways may be invoked to account for the formation of these compounds: (i) intramolecular nucleophilic attack by the hydrazine NMe_2-group on the ester carbonyl substituent, (ii) a concerted [1,4] elimination of ethanol and then electrocyclisation of the 6π-electron intermediate ketene (**4**) formed. By analogy with previous results[3] we believe that mechanism (ii) is favoured and this is supported by the following experiments. The flow pyrolysis of (**1b**) (380 °C) conducted in methanol gave the methyl ester ylide (**3e**), m.p. 127 °C, (63%) instead of (**3b**) and moreover, a dimethyl ester resulting from the transesterification of the starting diethyl ester was also isolated (15%). Apparently these results imply the intermediate formation of ketene (**4**) [during the transesterification of (**1**) if not during the ring closure step] since compound (**3b**) in methanol could not be converted into (**3e**) under the same reaction conditions.

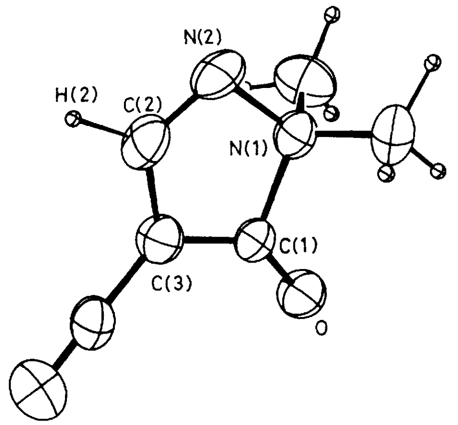


Figure 1. Crystal structure of compound (**3a**): C(1)–C(3) 1.385(3); C(1)–N(1) 1.553(2); N(1)–N(2) 1.467(3); N(2)–C(2) 1.283(3); C(2)–C(3) 1.413(3); C(2)–H(2) 1.08(2) Å.

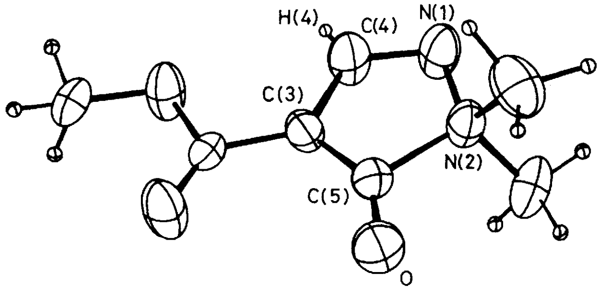


Figure 2. Crystal structure of compound (**3e**): C(5)–C(3) 1.379(3); C(5)–N(2) 1.571(3); N(2)–N(1) 1.456(3); N(1)–C(4) 1.307(3); C(4)–C(3) 1.419(3); C(4)–H(4) 0.98(2) Å.

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† Examples of [1,4] alkyl shifts in cyclic sulphur–nitrogen ylides have been recently reported (ref. 2).

‡All new compounds have ^1H and ^{13}C n.m.r., i.r., and mass spectra, together with elemental analysis in accord with the assigned structures. Selected spectral data: (**2a**), ^1H n.m.r. $\delta(CDCl_3)$ 1.70 (s, 3H, 4-Me), 3.35 (s, 3H, 1-Me), and 7.3 (s, 1H, 3-CH); ^{13}C n.m.r. $\delta(CDCl_3)$ 19.5 (q, 4-Me), 32.1 (q, 1-Me), 44.0 (s, C-4), 113.8 (s, C≡N), 146.0 (d, C-3), and 168.5 p.p.m. (s, C-5); i.r. $\nu(CHCl_3)$ 2210 (CN) and 1720 cm^{-1} (C=O); M^+, m/z 137 (26%).

Little information was available from the spectroscopic data in order to establish the structure of compounds (**3a**) and (**3b**).[4] Only two typical signals appear in the ^{1}H n.m.r. spectra: δ ($CDCl_3$) 3.0 (s, 6H), 8.2 or 8.4 (s, 1H), while i.r. spectroscopy reveals conjugated nitrile (ν_{max} 2220 cm^{-1}) and ester (1675 cm^{-1}) groups respectively. *X*-Ray measurements were carried out to settle unambiguously the pyrazolinium ylide structure of these compounds§ (Figures 1 and 2). It appears that the five ring atoms are located in the same plane and that the ring hydrogen atom (H-3) is 0.298 Å out of the plane, indicating a hybridisation between sp^2 and sp^3 for the C-(3) atom.

Finally, ylides (**3a,b**) were thermolysed at 440 °C and afforded (**2a,b**) in almost quantitative yields. It must be noted that none of the products expected from the typical reactions of vinylogous aminimides (N–N bond cleavage,[6] [1,2] alkyl shifts to nitrogen,[7] or migrations to oxygen[8]) have been detected.

This last result supports the intermediacy of ylides (**3**) in the thermal syntheses of pyrazolinones (**2**) from β-*N*,*N*-dimethylhydrazinopropenoates (**1**) and the [1,4] migration of a methyl substituent from nitrogen to carbon in the rearrangement (**3**) → (**2**).

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§ *Crystal data.* Compound (**3a**): $C_6H_7N_3O$, M = 137.14, monoclinic, space group *Cm*, a = 16.381(4), b = 6.632(2), c = 6.523(2) Å, β = 104.1(3)°, Z = 2. Compound (**3e**): $C_7H_{10}N_2O_3$, M = 170.17, monoclinic, space group $P2_1$, a = 6.644(2), b = 7.609(3), c = 8.388(3) Å, β = 93.8(3)°, Z = 2. The intensities of 648 independent reflections [$I > \sigma(I)$] for compound (**3a**) and 757 independent reflections [$I > \sigma(I)$] for compound (**3e**) were measured (Mo-K_α, scan $\omega/2\theta$) with an automatic Enraf–Nonius CAD-4 diffractometer at the 'Centre de Diffractométrie,' University of Rennes. The two structures were solved by direct methods with the SDP Enraf–Nonius package (ref. 5). All the hydrogen atoms were located by a difference Fourier [between 0.522 and 0.233 e Å^{-3} for (**3a**) and between 0.497 and 0.285 e Å^{-3} for (**3e**)]. The best least-square calculation gives a final *R*-value of 0.044 for (**3a**) and 0.054 for (**3e**). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23729 (10 pp.) from the British Library Lending Division. For details, see Instructions for Authors, *J. Chem. Soc., Perkin Trans.* 1, 1983, issue 1, p. xvii.

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