A Novel Entry to the Imidoylketene–Oxoketenimine Energy Surface

David Clarke,[a] **Richard W. Mares**[b] **and Hamish McNab***[b]

[a] *Research Division, Kodak Ltd, Headstone Drive, Harrow, Middlesex, UK HA1 4TY*
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

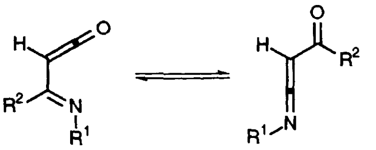
Gas-phase pyrolysis of the 1,2,3-triazoles **3–6** gives the pyrazolopyrimidinones **11–13** and the quinolinone **14** respectively: the mechanism involves an oxoketenimine–imidoylketene rearrangement.

There is current interest in the gas-phase formation and equilibration of imidoylketene **1** and oxoketenimine **2** intermediates.[1–3] We have discovered an unprecedented means of generating ketenimine carboxylic esters (**2**: R^2 = OMe or OEt) by pyrolysis of 1,2,3-triazole derivatives, and report their intramolecular trapping *via* the rearranged imidoylketene (**1**: R^2 = OMe or OEt).

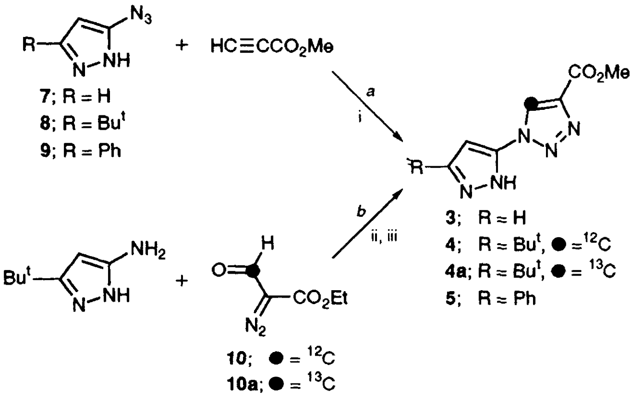
Our starting materials† **3–6** were made by two complementary routes (Scheme 1). Dipolar cycloaddition of the azides **7–9**[4] to methyl propiolate (toluene, or acetonitrile, reflux 2–4 h) (route *a*) gave generally a 5 : 1 mixture of regioisomers in up to 86% yield, from which the major isomers **3–5** could be obtained by recrystallisation. The regiochemistry was confirmed by direct synthesis of **4** using Arnold's formyl diazoacetic ester **10**[5] as the key starting material (route *b*). The *N*-phenyl compound **6** was made by a known method.[5]

The formation of indoles by photolysis or pyrolysis of 1-aryl-1,2,3-triazoles is well known,[6,7] and we were therefore surprised to discover that no new five-membered rings were generated by flash vacuum pyrolysis (FVP) of **3–6** at 600 °C [10^{-2} to 10^{-3} Torr (1 Torr = 133.3 Pa)]. Instead, the pyrazolopyrimidinones **11–13** and the quinolinone **14** respectively were obtained in 40–50% yield as the only significant crystalline products. The identity of **14** was confirmed by comparison with an authentic sample, and the structures of **11–13** follow both by analogy, and by comparison with a sample of the thiomethoxy compound **16**, made by FVP of the Meldrum's acid derivative **15** (*cf.* ref. 8).

Pyrolysis of the ^{13}C-labelled triazole **4a** leads exclusively to the [^{13}C]pyrazolopyrimidinone **12a**, and so the carbon skeleton of the precursors is not involved in the double-rearrangement leading to products. The mechanism shown in Scheme 2 is consistent with these observations. The key steps in the



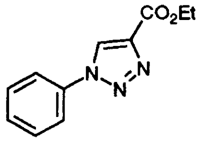
1 **2**



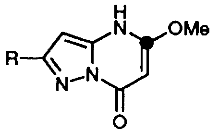
Scheme 1 *Reagents*: i, toluene or acetonitrile, heat; ii, EtOH; iii, MeO$^-$/MeOH

---

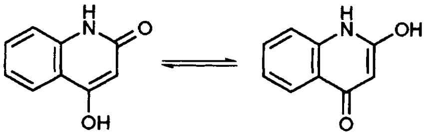
† All new compounds were characterised by their spectra and by elemental analysis or accurate mass measurement.



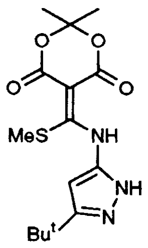
6



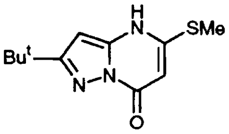
11; R = H
12; R = $\mathrm{Bu^t}$, ● = $^{12}\mathrm{C}$
12a; R = $\mathrm{Bu^t}$, ● = $^{13}\mathrm{C}$
13; R = Ph



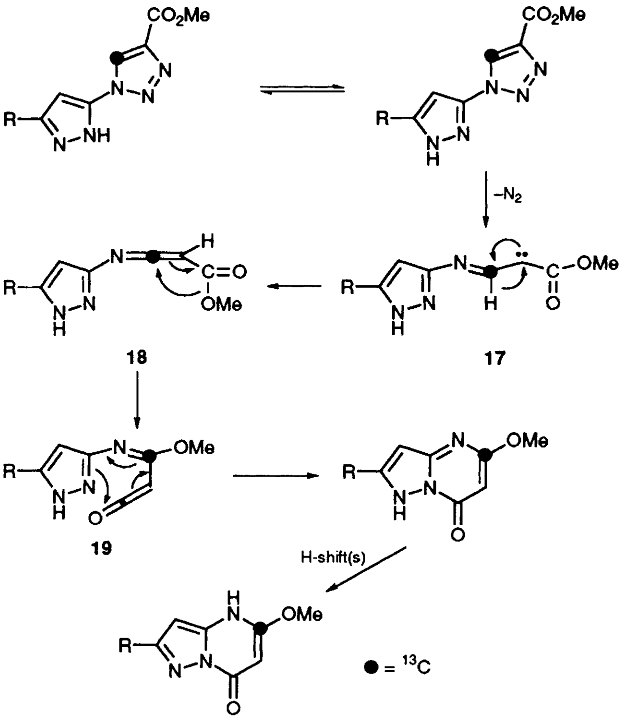
14



15



16



Scheme 2

sequence are (*i*) well-precedented α-insertion[9] of the initial carbene[6,7] **17**, to generate the oxoketenimine **18** and (*ii*) rearrangement of **18** by 1,3-migration of the alkoxy group to give the imidoylketene **19**. Facile 1,3-shifts of thioalkoxy groups on this energy surface have been reported.[1,3] Finally, electrocyclisation of **19** generates the ring system of the final products.

In conclusion, our route provides a simple and flexible entry to the oxoketenimine side of the oxoketenimine–imidoylketene energy surface. The triazole precursors (*e.g.* **3–6**) are readily available, and the method allows scope for wide variation of substituents.

We are grateful to the SERC and Kodak Ltd for a CASE award (to R. W. M.).

Received, 14th April 1993; Com. 3/02148C

References

1 C. O. Kappe, G. Kollenz, R. Leung-Toung and C. Wentrup, *J. Chem. Soc., Chem. Commun.*, 1992, 487.
2 C. O. Kappe, G. Kollenz, G.-P. Netsch, R. Leung-Toung and C. Wentrup, *J. Chem. Soc., Chem. Commun.*, 1992, 488.
3 A. Ben Cheikh, J. Chuche, N. Manisse, J. C. Pommelet, K.-P. Netsch, P. Lorenčak and C. Wentrup, *J. Org. Chem.*, 1991, **56**, 970.
4 E. Alcalde, J. de Mendoza and J. Elguero, *J. Heterocycl. Chem.*, 1974, **11**, 921.
5 F. M. Stojanovič and Z. Arnold, *Collect. Czech. Chem. Commun.*, 1967, **32**, 2155.
6 T. L. Gilchrist, G. E. Gymer and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1.
7 G. Mitchell and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 413.
8 B. Chen, X. Huang and J. Wang, *Synthesis*, 1987, 482.
9 For example, W. D. Crow and H. McNab, *Aust. J. Chem.*, 1979, **32**, 89.