

A Novel Entry to the Imidoylketene–Oxoketenimine Energy Surface

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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.

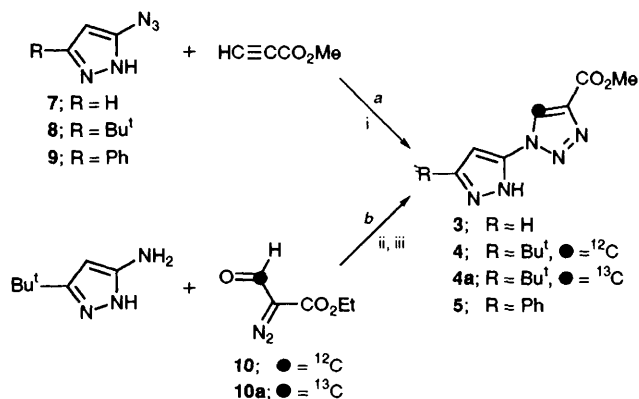
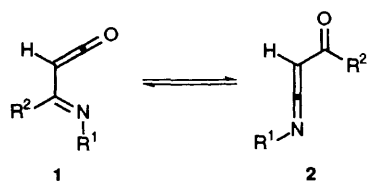
There is current interest in the gas-phase formation and equilibration of imidoylketene **1** and oxoketenimine **2** intermediates.^{1–3} We have discovered an unprecedented means of generating ketenimine carboxylic esters (**2**: R² = OMe or OEt) by pyrolysis of 1,2,3-triazole derivatives, and report their intramolecular trapping *via* the rearranged imidoylketene (**1**: R² = 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

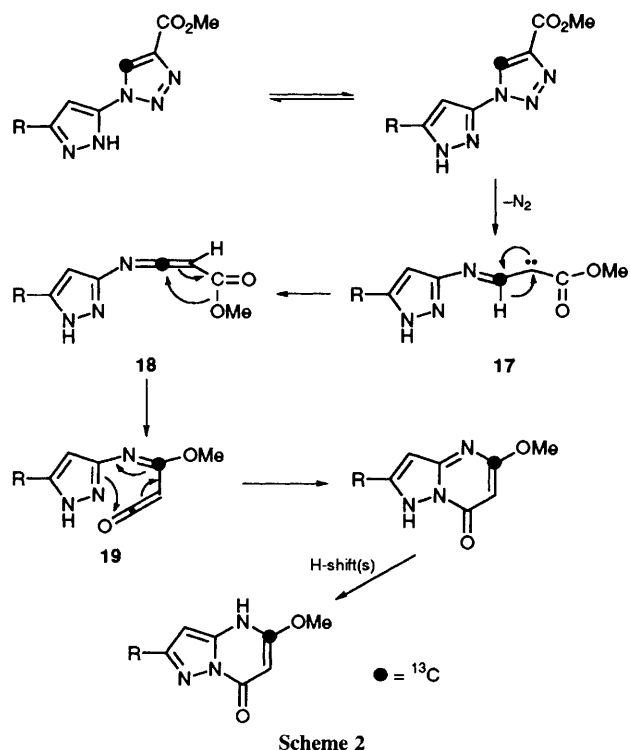
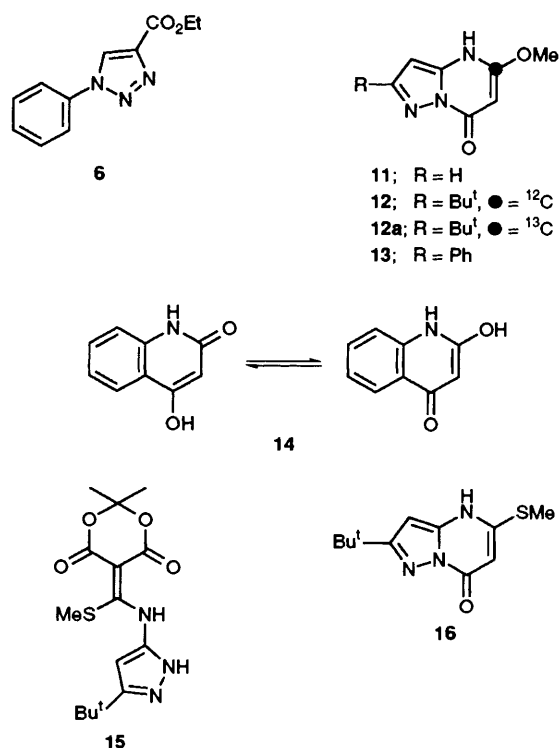
[10⁻² to 10⁻³ Torr (1 Torr = 133.3 Pa)]. Instead, the pyrazolopyrimidinones **11–13** and the quinolinone **14** respectively were obtained in 40–50% yield as the only significant crystalline products. The identity of **14** was confirmed by comparison with an authentic sample, and the structures of **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 ¹³C-labelled triazole **4a** leads exclusively to the [¹³C]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



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

Scheme 1 Reagents: i, toluene or acetonitrile, heat; ii, EtOH; iii, MeO⁻/MeOH



sequence are (i) well-precedented α -insertion⁹ 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 imidoalkene **19**. Facile 1,3-shifts of thioalkoxy groups on this energy surface have been reported.^{1,3} Finally, electrocyclic ring closure 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-imidoalkene energy surface. The triazole precursors (e.g. **3-6**) are readily available, and the method allows scope for wide variation of substituents.

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