Tetrahedron Letters No. 13, pp. 1049-1052, 1970. Pergamon Press. Printed in Great Britain.

THE THERMAL DECOMPOSITION OF ν-TRIAZOLO[1,5-a]pyridines. A NEW RE-ARRANGEMENT

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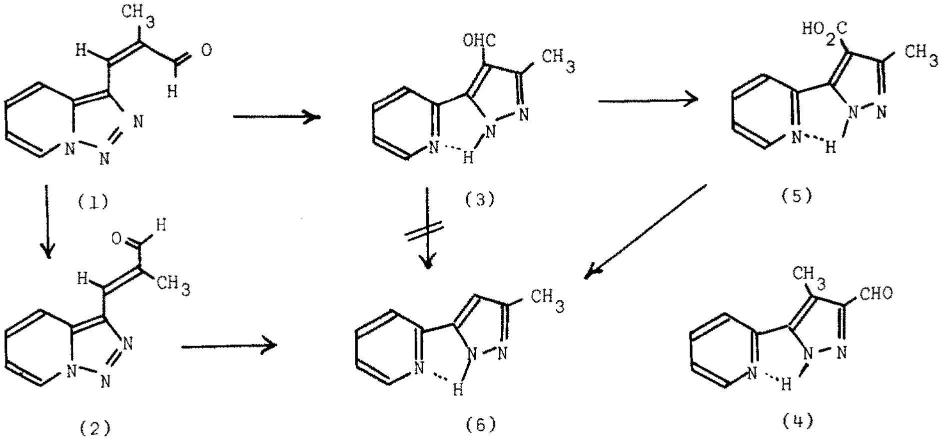
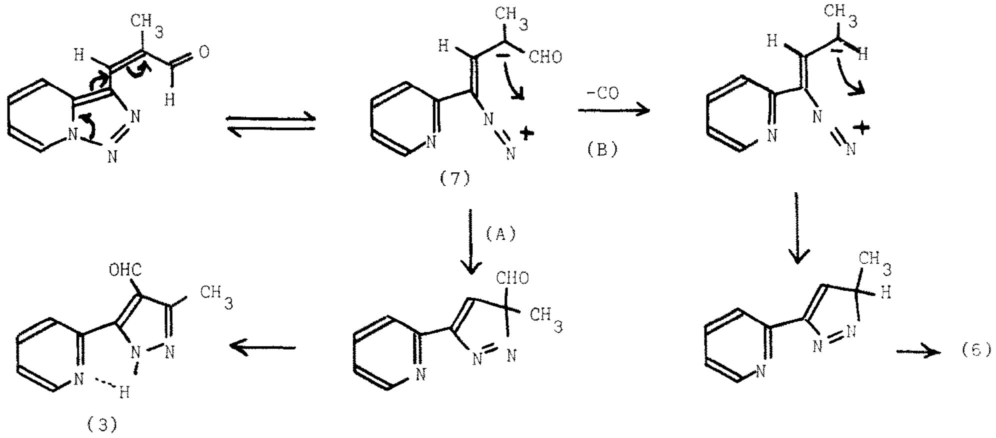
(Received in UK 4 February 1970; accepted for publication 12 February 1970)

We have reported[1,2] that a number of quinolizinium-1-diazonium salts re-arrange at room temperature in aqueous media to give ν-triazolo[1,5-a]pyridines such as (1); these first-formed cis aldehydes re-arrange easily to the more stable trans forms (e.g. 2). The mass spectra of compounds (1) and (2) were found to be identical; to discover if this was due to a thermal re-arrangement of (1) to (2) in the heated inlet, we heated the cis aldehyde briefly above its melting point (180-185°). Some gas evolution was noted and proved by evacuation directly into a mass spectrometer to be a mixture of nitrogen and carbon monoxide. On cooling the heated mixture three compounds could be isolated; a trace of the trans aldehyde (2) (6%), a minor product (35%) which was an isomer of compounds (1) and (2), and a major product (56%) of formula $C_9H_9N_3$ in which loss of CO has occurred. A higher temperature (205-208°) was required to decompose the trans aldehyde (2) and the only product was the de-carbonylated material (40%). At lower temperatures the cis aldehyde (1) gave as major product the trans aldehyde (2).



The minor product from heating cis aldehyde (1), m.p. 167-168°, shown below to be the pyridylpyrazole (3), had an identical mass spectrum to that obtained[2] from compounds (1) and (2) and it seems clear that it is the breakdown of compound (3) which is seen in all three cases. Loss of N_2H and CO (with an alternative pathway of loss of HCO followed by N_2) led us to consider only structures containing these fragments. An aldehyde proton (singlet at δ 10.5 p.p.m.), confirmed by an absorption at 1675 cm^{-1}, and a singlet methyl absorption at δ 2.45 p.p.m. (presumably for a methyl group still attached to an unsaturated or aromatic system), narrowed the possibilities still further. A notable feature of the ultraviolet spectrum was a large bathochromic shift in the band of longest wavelength (277 nm. to 306 nm.) on acidification; such a shift has been reported[3] between the neutral and quaternary forms of some 3-(4-pyridyl) pyrazoles.[3] To confirm the structure (3) for the thermally produced isomer and in particular to distinguish between the isomers (3) and (4), we oxidized the aldehyde (3) with $KMnO_4$ at room temperature, obtaining the acid (5) (76%) m.p. 229°-236°, $\nu_{max}^{CHCl_3}$ 3420, 1668 cm^{-1}, λ_{max}^{EtOH} 250, 286 nm. ($\log_{10}\varepsilon$ 3.0, 3.04), λ_{max}^{HCl} 250, 294 ($\log_{10}\varepsilon$ 2.88, 3.03). The acid (5) was with difficulty decarboxylated to give 3-methyl-5-(2-pyridyl)pyrazole (6) (33%) m.p. 115-116°, which was identical with the major thermal product from the cis-aldehyde (1). The n.m.r. spectrum of the pyrazole (6) showed a singlet (1H) at δ 6.56 p.p.m. in good agreement with that expected for a pyrazole H-4[4]; this, and the difficulty of decarboxylation of the acid (5)[5] lead to the formula (6), confirmed by a synthesis by a standard route.



We have shown that the formyl pyrazole (3) is stable to temperatures well above those at which the re-arrangement occurs, so that decarbonylation to give compound (6) must proceed at some intermediate stage. We suggest that the reaction probably proceeds through the monocyclic diazo-aldehyde (7) (at which point cis-trans isomerisation can occur to produce, by recyclisation, aldehyde (2)); the diazo-aldehyde (7) can then cyclise as shown in path A, to give the pyridyl pyrazole (3), or it can lose carbon monoxide and cyclise as in path B. It is well known that 3H-pyrazoles re-arrange thermally to 1-H-pyrazoles[6]; what is surprising in our case is that the formyl group migrates to position 4 in preference to the methyl group and we have no evidence of the presence of any isomer (4). The only suggested mechanism for the 3H-to 1-H-pyrazole re-arrangement involves a carbonium ion mechanism and the above observation throws some doubt on the extension of such a mechanism to the thermal re-arrangement. We are investigating the thermal 3H-to 1-H-pyrazole re-arrangement in more detail.

One of us (L.S. Davies) thanks the Science Research Council for a Studentship; we thank Professor A.H. Jackson for the original mass spectra, and Dr. J.D. Baty and Mr. P. Holbrook for further mass spectral work.

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