Decomposition of 3-Azidopyridazine 2-Oxides. Ring Opening of the Pyridazine Ring

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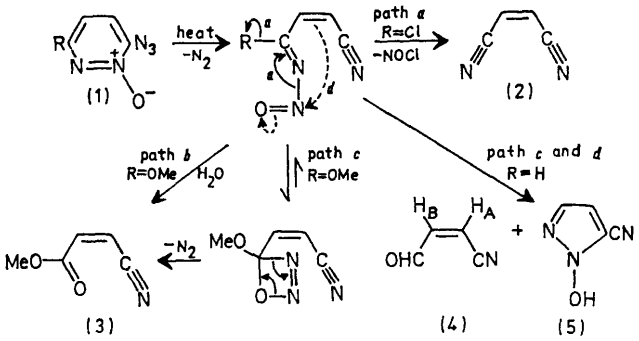
Summary Thermolysis of 6-chloro- and 6-methoxy-3-azidopyridazine 2-oxide in inert solvents gives maleonitrile and *cis*-β-cyanoacrylate, respectively; 3-azidopyridazine 2-oxide gives the unstable cyanoaldehyde and traces of 1-hydroxypyrazol-5-carbonitrile.

THE ring contraction of 2-azidopyridine-,[1] -quinoline,[2] -pyrazine,[1] and -quinoxaline 1-oxides[2] to give 2-cyano-1-hydroxypyrroles,[1] -indoles,[2] -imidazoles,[1] and -benzimidazoles[2] has been reported. A mechanism involving a concerted ring-opening nitrogen-elimination followed by recyclisation was proposed.[1] No ring-opened products could be isolated but they could be trapped in a nucleophilic solvent. An alternative mechanism involving ring-expansion to a diazepine followed by a sigmatropic ring-contraction was considered but rendered unlikely by the

trapping experiments. We now report the decomposition of 3-azidopyridazine 2-oxides (**1**) and the isolation of ring-opened products.



3-Azido-6-chloropyridazine 1-oxide (**1**; R = Cl), m.p. 100—102 °C (obtained in 64% yield from the 3-amino compound) in boiling toluene gave maleonitrile (**2**) (85%), m.p. 29—30 °C (lit.,[3] 32°), *m/e* 78 (M^+). In boiling benzene an 87% yield of (**2**) was obtained. A possible route to (**2**) involves loss of NOCl from the original ring-opened product. In the hope of avoiding this the chlorine substituent was replaced by methoxy. Thermolysis of the azide (**1**; R = OMe), m.p. 98—100 °C (decomp.) in dry benzene gave methyl *cis*-β-cyanoacrylate (**3**) (89%), b.p. 50—51 °C at 0·3 mm Hg, m.p. 29—31 °C, identical with an authentic sample.[4] No pyrazoles were isolated in either case.

Two possible routes to (**3**) are (i) hydrolysis of the intermediate *N*-nitrosoimine during work up, which is unlikely in view of the high yield of (**3**) and the precautions taken to avoid the intrusion of water, or (ii) intramolecular cycloaddition of the *N*-nitrosoimine followed by nitrogen elimination. There is precedent for such a cycloaddition in the first-order decomposition of *N*-nitrosoketimines.[5]

The azide (**1**; R = H)[6] underwent the same ring-opening to give the highly unstable cyano-aldehyde (**4**) as a yellow oil [ν_{max} 2240 (C≡N) and 1670 cm^{-1} (C=O); δ 9·1 (CHO), 7·3 (H_A), and 6·9 (H_B); *m/e* 81 (M^+), 53 (M − 28); 2,4-dinitrophenylhydrazone, m.p. 178—180 °C]. This was characterised by Ag^I oxidation to the acid followed by esterification with CH_2N_2 to (**3**), identical with the above sample. In addition to (**4**), small amounts of the cyclised product (**5**) were detected [ν_{max} 2800—3150 (br) (N–OH) and 2220 cm^{-1} (C≡N); δ 7·40 (d, J 2·6 Hz, H_B), 6·95 (s, OH), and 6·79 (d, H_A); *m/e* (10 eV) 109 (M^+)] but insufficient quantities were available for definitive characterisation.

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