

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

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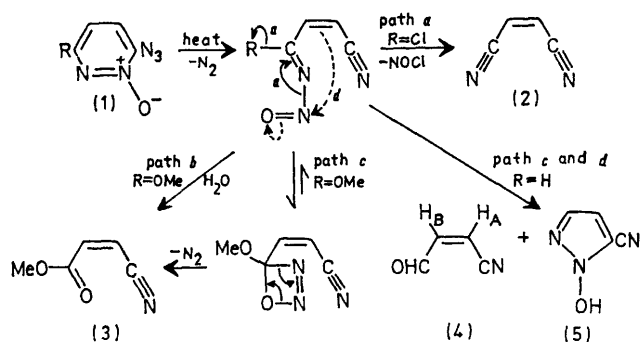
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**Summary** Thermolysis of 6-chloro- and 6-methoxy-3-azidopyridazine 2-oxide in inert solvents gives maleonitrile and *cis*- $\beta$ -cyanoacrylate, respectively; 3-azidopyridazine 2-oxide gives the unstable cyanoaldehyde and traces of 1-hydroxypyrazol-5-carbonitrile.

THE ring contraction of 2-azidopyridine,<sup>1</sup> -quinoline,<sup>2</sup> -pyrazine,<sup>1</sup> and -quinoxaline 1-oxides<sup>2</sup> to give 2-cyano-1-

hydroxypyrroles,<sup>1</sup> -indoles,<sup>2</sup> -imidazoles,<sup>1</sup> and -benzimidazoles<sup>2</sup> has been reported. A mechanism involving a concerted ring-opening nitrogen-elimination followed by recyclisation was proposed.<sup>1</sup> 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.,<sup>3</sup> 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*- $\beta$ -cyanoacrylate (3) (89%), b.p. 50–51 °C at 0.3 mm Hg, m.p. 29–31 °C, identical with an authentic sample.<sup>4</sup> 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.<sup>5</sup>

The azide (1; R = H)<sup>6</sup> underwent the same ring-opening to give the highly unstable cyano-aldehyde (4) as a yellow oil [ $\nu_{\max}$  2240 (C $\equiv$ N) and 1670  $\text{cm}^{-1}$  (C=O);  $\delta$  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  $\text{Ag}^I$  oxidation to the acid followed by esterification with  $\text{CH}_3\text{N}_2$  to (3), identical with the above sample. In addition to (4), small amounts of the cyclised product (5) were detected [ $\nu_{\max}$  2800–3150 (br) (N–OH) and 2220  $\text{cm}^{-1}$  (C $\equiv$ N);  $\delta$  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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