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THE NITRATION OF 1-METHYLPYRAZOLE 2-OXIDE

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The nitration of pyridine 1-oxide to give 4-nitropyridine 1-oxide is a reaction of great practical and theoretical interest.[1] Carried out in sulphuric acid, the reaction involves the free base. The availability of 1-methylpyrazole 2-oxide[2] made it of interest to examine the orientation of nitration of this compound and to study the mechanism of the reaction.

Preparative nitration of the oxide in 65.8% sulphuric acid [typically a solution of the oxide (590 mg) in 65.8% sulphuric acid (2 ml) was cooled in ice and treated with a solution of fuming nitric acid (1 ml) in 65.8% sulphuric acid (5 ml). The mixture was kept for 12 h at room temperature and then poured on ice; the product was extracted with dichloromethane] gave 90% of 1-methyl-5-nitropyrazole 2-oxide* (yellow powder, m.p. 109 °C, from heptane. Literature[3] m.p. 109 °C).

The kinetics of mono-nitration were studied in the acidity range 65.8 - 75.48% sulphuric acid at 25 °C when good first order reactions were observed (k_2 = 3.92×10^{-3}, 1.19×10^{-2}, 2.80×10^{-2}, 1.58×10^{-1}, and 4.61×10^{-1} l mol^{-1} s^{-1} for 65.8, 68.44, 70.1, 73.26, and 75.48% sulphuric acid, respectively). The value of $d(\log k_2)/d(\% H_2O_4)$ was 0.22, which we take to indicate that mono-nitration involved the free base,[1] a conclusion consonant with the orientation observed; if the cation were involved nitration would be expected to occur at C-4 as it does in the pyrazolium cation.[1]

Attempts to extend the kinetic studies to higher acidities were unsatisfactory; "infinity" readings were not stable. This may have been a consequence of dinitration, though we have not established this point, and are studying the reaction further.

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*For this and the dinitro-compound satisfactory analytical and spectroscopic data were obtained.

In preparative experiments we were able to prepare a dinitro-compound in high yield [typically a solution of 1-methylpyrazole 2-oxide (250 mg) in 87% sulphuric acid (1.5 ml) was cooled in ice and treated with a solution of fuming nitric acid (0.5 ml) in 87% sulphuric acid (2.5 ml). After 75 min. at room temp. the solution was poured on ice giving the product (295 mg)]. Crystallised from methanol it gave a yellow powder, m.p. 186-188 °C. It seems probable that this is 1-methyl-3,5-dinitropyrazole 1-oxide, but we have not yet been able to prove this.

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