

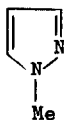
1-METHYLPYRAZOLE-2-OXIDE

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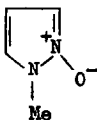
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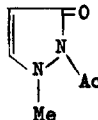
The recent recording of the incidental formation of 1-methyl-5-nitropyrazole-2-oxide by direct oxidation of 5-amino-1-methylpyrazole,¹ prompted this publication of the preparation of 1-methylpyrazole-2-oxide and of some of its properties. When 1-methylpyrazole (I) is treated with hydrogen peroxide in acetic acid either at room temperature or at 60°, it is converted into an oxide which may be isolated by distillation as a liquid b.p. 105-107°/0.3 mm which solidifies to a hygroscopic solid, m.p. 65-69° (picrate m.p. 105-107°). The ultra-violet spectrum of the reaction mixture (I, λ_{\max} 218 nm, ϵ_{\max} 4100; II, λ_{\max} 251 nm, ϵ_{\max} 4200) indicated that at least 20% of the product was formed if successive additions of a large excess of reagent were used and if heating were prolonged, but because of the difficulties of isolation, only a 10% yield of the product was obtained.



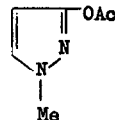
(I)



(II)



(III)



(IV)

The formulation of the oxidation product as 1-methylpyrazole-2-oxide (II) is supported by the NMR spectrum at 60MHz in deuteriochloroform and its chemical properties, δ 3.71 δ singlet, N-Me; 6.08 δ doublet x doublet $J = 3$ c/s and 2.5 c/s, ring proton 4; 7.08 δ doublet x doublet $J = 4$ c/s and 1 c/s, ring proton 5 (or 3); 7.16 doublet x doublet $J = 1$ c/s and 2.5 c/s, ring proton 3 (or 5); water impurity 4.35 δ .

Catalytic reduction (Pd/C) of (II) or treatment with phosphorus trichloride removed the oxygen, regenerating the base (I), isolated as its picrate (m.p. and mixed m.p.). Treatment of (II) with acetic anhydride gave a mixture of two products $C_6H_8N_2O_2$, a solid (III) m.p. 147-148° and a liquid (IV) b.p. 70°/0.3 mm. (bath temp.) (picrate m.p. 99-100°), the formulations of which are supported by the infra-red spectra: (III), two C=O bands 1680 cm^{-1} and 1700 cm^{-1} ; (IV) 1 C=O band 1775 cm^{-1}). My thanks are due to Mr. T.L. Threlfall for recording and interpreting the spectra.

* Satisfactory analyses were obtained on all compounds prepared, with the exception of the N-oxide which gave poor results due to the absorption of water (Found, C, 48.3; H, 6.5; N, 27.8. $C_4H_6N_2O$ requires C, 49.0; H, 6.1, N, 28.6%).

¹Coburn, M.D. J.Het.Chem., 1970, 7, 455