

Dinitration of 1-Methylpyrazole: 1-Methyl-3,4-dinitropyrazole

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Abstract

Nitration in 80% sulphuric acid of 1-methylpyrazole gives 1-methyl-4-nitropyrazole and 1-methyl-3,4-dinitropyrazole in a 4 : 1 ratio. The dinitro compound is also formed by nitration of 1-methyl-3-nitropyrazole.

Introduction

Comparatively few examples are known of dinitropyrazoles in which both nitro groups are attached to ring carbon atoms,¹⁻⁵ and the majority of these examples are derived from the thermal rearrangement of *N*-nitropyrazoles. Among the few exceptions are the formation of 4-bromo-1-methyl-3,5-dinitropyrazole on nitration in sulphuric acid of 4-bromo-1-methylpyrazole,³ and the preparation of 3,4-dinitropyrazole under similar conditions from 3-nitropyrazole.¹

The synthesis of 1-methyl-4-nitropyrazole (2) by nitration of 1-methylpyrazole (1), at 5° in concentrated sulphuric acid, has been reported.⁶

Results and Discussion

Using a fivefold excess of fuming nitric acid in 80% sulphuric acid at room temperature, and monitoring the reaction by n.m.r. spectroscopy, we detected virtually no nitration of 1-methylpyrazole after two days. When the reaction mixture was heated at 100° the conversion was complete after 18 h. However, in addition to the expected product (2), a further major (20%) product was evident from the n.m.r. spectrum. This compound was isolated and identified as the previously undescribed 1-methyl-3,4-dinitropyrazole (4). That compound (4) cannot be prepared by further nitration of 1-methyl-4-nitropyrazole (2) parallels the reported resistance of 4-nitropyrazole to nitration.¹ An identical compound, however, could be prepared when

¹ Jansen, J. W. A. M., Koerners, H. J., Kruse, C. G., and Habraken, C. L., *J. Org. Chem.*, 1973, **38**, 1777.

² Lund, H., *J. Chem. Soc.*, 1935, 418.

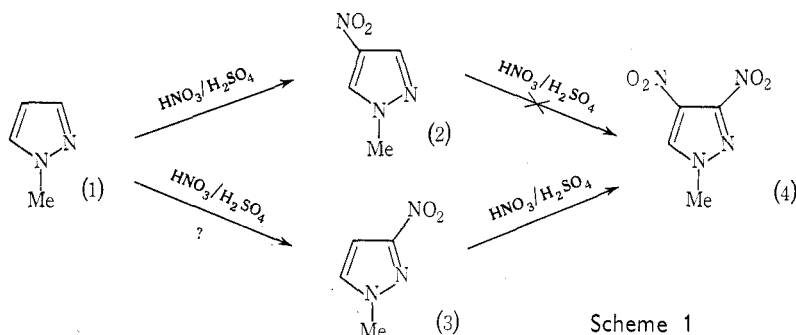
³ Coburn, M. D., *J. Heterocycl. Chem.*, 1970, **7**, 707.

⁴ Coburn, M. D., *J. Heterocycl. Chem.*, 1971, **8**, 153.

⁵ Ferguson, I. L., Grimmett, M. R., and Schofield, K., *Tetrahedron Lett.*, 1972, 2771.

⁶ U.S. Pat. 3,102,890 (1963) (*Chem. Abstr.*, 1964, **60**, 1762).

1-methyl-3-nitropyrazole (3) was nitrated in 80% sulphuric acid. Such a result implies that the mono- and di-nitro compounds formed on nitration of 1-methylpyrazole arise by different pathways, and that the formation of 1-methyl-3,4-dinitropyrazole may involve 1-methyl-3-nitropyrazole (3) as an intermediate (Scheme 1).



Although compound (3) was not isolated from the reaction mixture it could be detected on examination of n.m.r. spectra taken during the heating process. While the methyl signal is masked by the methyl peak for 1-methyl-4-nitropyrazole in 80% sulphuric acid solution, the ring proton signals can be detected downfield (184 and 238 Hz) from the methyl signal. Enhancement of both of these signals and of the methyl signal was noted on addition of an authentic sample of 1-methyl-3-nitropyrazole. Such a product could arise by the [1,5] sigmatropic rearrangement of a 1-methyl-2-nitropyrazolium species in a manner similar to that proposed⁷ to account for the abnormal nitration of 5-methyl-1-phenylpyrazole.

The dinitro compound (4) differed in physical properties from the previously described 1-methyl-3,5-dinitropyrazole,³ and its synthesis from 1-methyl-3-nitropyrazole shows that it cannot be the other possible isomer, 1-methyl-4,5-dinitropyrazole.

Experimental

Microanalyses were carried out by Professor A. D. Campbell and staff at the University of Otago. N.m.r. spectra were determined on Varian TA-60 and HA-100 instruments. Chemical shifts in CDCl_3 are in ppm relative to tetramethylsilane (δ 0.00) as internal reference standard, and spectra are reported in the order: chemical shift, multiplicity, proton count, assignment. Low-resolution mass spectra were determined on a Varian MAT CH-7 instrument. Infrared spectra were measured with a Beckman Acculab 4 instrument, while ultraviolet spectra in absolute ethanol or methanol were obtained with a Shimadzu UV-200 instrument.

Nitration of 1-Methylpyrazole

To 1-methylpyrazole (3.38 g; 0.40 mol) dissolved in 80% aqueous sulphuric acid (20 cm³) was added with cooling a solution of fuming nitric acid (15 g; 0.2 mol) in 80% sulphuric acid (10 cm³). After 2 days at room temperature (no reaction evident) the mixture was heated on a steam bath for 18 h. An n.m.r. spectrum indicated that no starting material remained, but at least two products were present. The solution was poured onto ice, neutralized with solid sodium carbonate and extracted with chloroform. The dried extracts were evaporated to yield an oily product (4.46 g; 64% of

⁷ Grimmett, M. R., Hartshorn, S. R., Schofield, K., and Weston, J. B., *J. Chem. Soc., Perkin Trans. 2*, 1972, 1654.

theoretical). N.m.r. δ (CDCl_3) 4.03, s, 3H, 1- CH_3 ; 4.15, s, 3H, 1- CH_3 ; 8.13, s, 1H, H5; 8.29, s, 1H, H5. Ratio of mono- to di-nitro products, 3.8 : 1. Mass spectrum: m/e 172, 142, 127, 126, 111, 97, 82, 74. Crystallization from ethanol gave 1-methyl-4-nitropyrazole (2.43 g), m.p. 92° (lit.⁶ 91–92°). λ_{max} (log ϵ) (ethanol) 272 (3.99), 223 (3.55) nm. N.m.r. δ (CDCl_3) 4.03, s, 3H, 1- CH_3 ; 8.13, s, 1H, H5; 8.29, s, 1H, H3. Mass spectrum: m/e 127, 111, 97, 82, 74. The oily residue (1.72 g) from the mother liquors separated from benzene–hexane as white crystals (0.80 g), m.p. c. 20° (Found: C, 27.9; H, 2.1; N, 32.3. $\text{C}_4\text{H}_4\text{N}_4\text{O}_4$ requires C, 27.9; H, 2.3; N, 32.5%). N.m.r. δ (CDCl_3) 4.15, s, 3H, 1- CH_3 ; 8.32, s, 1H, H5. N.m.r. δ [$(\text{CD}_3)_2\text{SO}$] 4.45, 8.53 (cf. 1-methyl-3,5-dinitropyrazole⁴ δ [$(\text{CD}_3)_2\text{SO}$] 4.33, 7.96; m.p. 60°). Mass spectrum: m/e 172, 156, 142, 126, 109, 79, 67, 65 (metastable ion $117.2 = 142^2/172$). ν_{max} (film) 1534 (C– NO_2), 1350 (C– NO_2) cm^{-1} . λ_{max} (log ϵ) (ethanol) 264 (4.01), 218 (4.28) nm. The residue (0.92 g) from the benzene–hexane mother liquors was shown by n.m.r. integration to consist of mononitro and dinitro products in the ratio 3 : 2.

Further nitration of this mixture in 80% sulphuric acid did not alter this ratio after 18 h heating at 100°. Further nitration of 1-methyl-4-nitropyrazole also did not take place.

In 80% sulphuric acid the n.m.r. proton signals for the mono- and di-nitropyrazoles moved down-field compared to spectra in deuteriochloroform. The signals for the mononitro species appear at lower field in acid medium than those for the dinitro compound; this perhaps reflects the relative ease of protonation.

1-Methyl-3-nitropyrazole

To a solution of 3-nitropyrazole (1.13 g; 0.01 mol) in sodium methoxide (sodium metal 0.26 g, methanol 15 cm^3) was added dimethyl sulphate (1.58 g; 0.0125 mol) and the mixture was refluxed (4 days). The excess methanol and dimethyl sulphate were removed under vacuum, water (50 cm^3) was added, and the aqueous solution was extracted with chloroform. An n.m.r. spectrum indicated that the ratio of 1-methyl-3-nitropyrazole to 1-methyl-5-nitropyrazole was 4 : 1. Column chromatography on alumina (Spence H) with ether–hexane (1 : 1) gave pure 1-methyl-3-nitropyrazole, m.p. 80–84° (after sublimation at 80°/0.3 mm) (0.42 g) (Found: C, 37.7; H, 4.1; N, 32.8. $\text{C}_4\text{H}_5\text{N}_3\text{O}_2$ requires C, 37.8; H, 3.9; N, 33.1%). N.m.r. δ (CDCl_3) 3.99, s, 3H, 1- CH_3 ; 6.87, d, 1H, H5; 7.42, d, 1H, H4. Mass spectrum: m/e 127, 111, 97, 80, 74, 59, 54, 52, 43, 42 (metastable ion $74.0 = 97^2/127$). λ_{max} (log ϵ) (methanol) 264 (3.90), 205 (3.67), 220sh nm.

Nitration of 1-Methyl-3-nitropyrazole

To 1-methyl-3-nitropyrazole (0.40 g; 0.003 mol) in 80% sulphuric acid (10 cm^3) was added fuming nitric acid (1.2 g; 0.015 mol) and the mixture was heated at 100° for 6 h. An n.m.r. spectrum showed only one product had been formed. The mixture was poured onto ice and worked up as before to give a yellow oil (0.47 g). N.m.r. δ (CDCl_3) 4.13, s, 3H, 1- CH_3 ; 8.32, s, 1H, H5. Mass spectrum: m/e 172, 156, 142. A sample of the oil sublimed at 100°/0.2 mm to give a pale yellow oil which crystallized from benzene–hexane, m.p. c. 20°. The infrared spectrum was identical with that of 1-methyl-3,4-dinitropyrazole. λ_{max} (log ϵ) (ethanol) 264 (4.01), 218 (4.28) nm.