

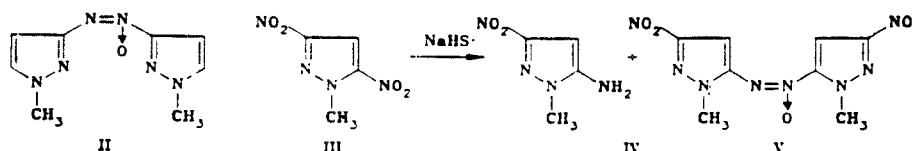
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REDUCTIVE BEHAVIOR OF NITRO- AND DINITRO-1-METHYLPYRAZOLES

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The position of the nitro groups in the heterocycle determines the different reactivities of nitropyrazoles and the structures of the reaction products. We have shown that 1-methyl-4- and -5-nitropyrazoles are reduced by hydrazine hydrate on Raney nickel only to the amines. However, under analogous conditions, 1-methyl-3-nitropyrazole (I) forms 1,1'-dimethyl-3-azoxypyrazole (II) as the principal product. Reaction of 1-methyl-3,5-dinitropyrazole (III) with NaHS selectively reduces the 5-nitro group to form 5-amino-1-methyl-3-nitropyrazole (IV) and 1,1'-dimethyl-3,3'-dinitro-5-azoxypyrazole (V) in the ratio 3:1 (according to PMR spectral data). The presence of the nitro group at position 3 is confirmed by mass spectral data in which the peak for the ion with m/z ($M - 17$), characteristic of 1-methyl-5-nitropyrazole [1], is absent.



To a refluxing solution of I (19.0 g, 150 mmoles) in ethanol (100 ml) there was added portionwise hydrazine hydrate (8.7 ml) and Raney nickel until disappearance of the starting material (by TLC). The catalyst was filtered off and the solution cooled to give azoxypyrazole II (7.2 g, 54%) with mp 171-172°C. PMR spectrum (DMSO- D_6): 3.47 (s, 1- CH_3); 3.53 (s, 1'- CH_3); 6.17 (d, 4-H); 6.75 (d, 4'-H); 7.86 (d, 5-H); 7.42 ppm (d, 5'-H). M^+ 178. After removal of II the solvent was distilled from the filtrate and the residue distilled in vacuo to give 3-amino-1-methylpyrazole (7.1 g) with bp 85-89°C (1 mm Hg) (according to [2], bp 61°C at 0.02 mm Hg). M^+ 97. According to TLC, reduction of the 4- and 5-nitro isomers under analogous conditions gives only the starting material and the amine.

Reduction of dinitropyrazole III [3] (0.86 g, 5 mmoles) in aqueous ethanol (2:3, 10 ml) with a solution of sodium hydrosulfide in the presence of magnesium sulfate (0.1 g) for 4 h at 80°C gave a mixture of IV and V (3:1, 0.54 g). Column chromatography (silica gel 100/250, chloroform-acetone 20:1) gave azoxypyrazole (V, 0.12 g) with mp 245-247°C and R_f 0.47. PMR spectrum: 4.16 (s, 1- CH_3); 4.34 (s, 1'- CH_3); 7.82 (s, 4-H); 8.02 ppm (s, 4'-H), M^+ 296. Also obtained was the aminopyrazole IV (0.36 g) with mp 216-217°C and R_f 0.10. PMR spectrum: 3.62 (s, 1- CH_3); 5.73 (s, NH_2); 5.90 ppm (s, 4-H), M^+ 142.

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