

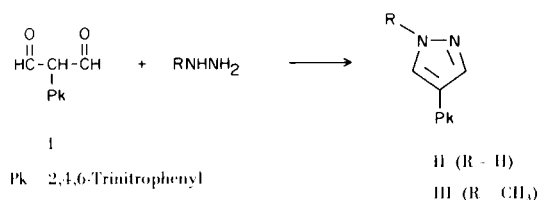
## The Nitration of 1-Methyl-4-(polynitrophenyl)pyrazoles (I)

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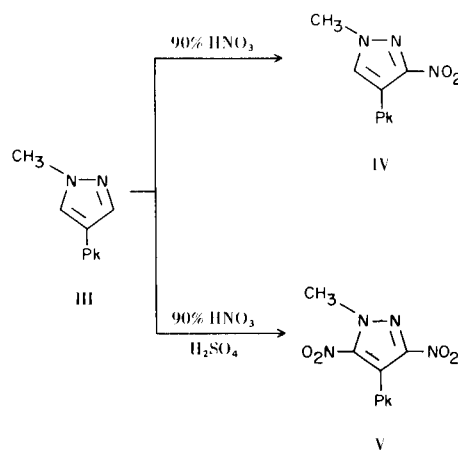
The synthesis of 2-picrylmalonaldehyde (I) and its subsequent reaction with hydrazine to form 4-picrylpyrazole (II) was reported recently (2). It has been shown that certain 4-substituted pyrazoles can be nitrated to their 3- or 5-nitro derivatives (3,4,5). However, various attempts to nitrate II gave either water-soluble products or small amounts of unreacted II, depending upon the condition employed.

1-Methyl-4-picrylpyrazole (III) was obtained when I was treated with methylhydrazine. Nitration of III with 90% nitric acid at reflux gave 1-methyl-3-nitro-4-picryl-

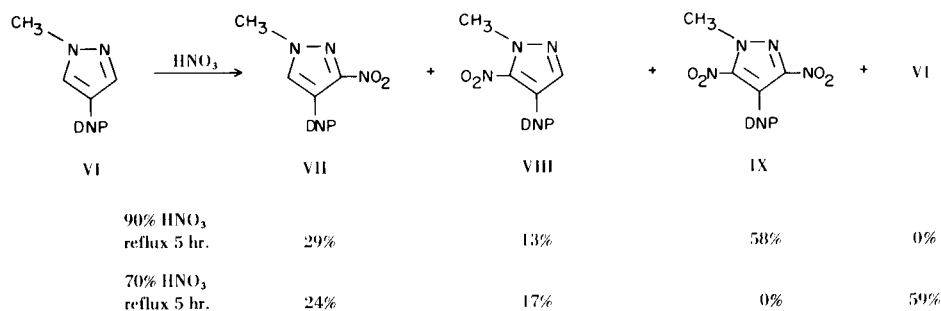


pyrazole (IV). The assignment of structure IV was based upon the observation of an intramolecular nuclear Overhauser effect (6). When the methyl protons were saturated, the ratio of the nmr signal of the pyrazole proton to that of the picryl protons increased by 22%.

When III was refluxed with a mixture of nitric and sulfuric acids, 3,5-dinitro-1-methyl-4-picrylpyrazole (V) was obtained. Compound V is believed to be the first example of a 3,5-dinitropyrazole.



4-(2,4-Dinitrophenyl)-1-methylpyrazole (VI) (3) was nitrated with refluxing 90% nitric acid to a mixture of 4-(2,4-dinitrophenyl)-1-methyl-3-nitropyrazole (VII), 4-(2,4-dinitrophenyl)-1-methyl-5-nitropyrazole (VIII), and 3,5-dinitro-4-(2,4-dinitrophenyl)-1-methylpyrazole (IX) in the proportions shown below. The ratio of VII to VIII was altered considerably when VI was nitrated with refluxing 70% nitric acid. Both product mixtures were converted to pure IX with mixed nitric and sulfuric acids at reflux.



DNP = 2,4-Dinitrophenyl

TABLE I  
NMR Spectra (a)

Pyrazole	$\delta$ (C-H) (p.p.m.)			
	Pyrazole C-3	Pyrazole C-5	Picryl	Methyl
4-Picryl- (b)	7.83	7.83	9.15	
1,4-Dipicryl- (c)	8.08	8.64	9.20, 9.29	
1-Methyl-4-picryl-	8.02	7.55	9.13	3.95
1-Methyl-3-nitro-4-picryl-		8.28	9.26	4.10
3,5-Dinitro-1-methyl-4-picryl-			9.31	4.42
4-(2,4-Dinitrophenyl)-1-methyl-	(d)	(d)		3.95
4-(2,4-Dinitrophenyl)-1-methyl-3-nitro-		(d)		4.12
4-(2,4-Dinitrophenyl)-1-methyl-5-nitro-	(d)			4.29
3,5-Dinitro-4-(2,4-dinitrophenyl)-1-methyl-				4.43

(a) Determined as DMSO- $d_6$  solutions with a Varian A-60A spectrometer using tetramethylsilane as an internal standard. (b) V. L. Zbarskii, G. M. Shutov, V. F. Zhilin, and E. Yu. Orlava, *Zh. Org. Khim.*, **4**, 1973 (1968). (c) M. D. Coburn, *J. Heterocyclic Chem.*, in press. (d) It was impossible to distinguish these protons from the 2,4-dinitrophenyl multiplets with absolute certainty.

Although pure samples of VII and VIII were not isolated, their identities were established by the nmr chemical shifts of their methyl protons (see Table I). The chemical shifts of the methyl protons of III and V are nearly identical with those of VI and IX, respectively. Thus, the chemical shift of the methyl protons of VII may be expected to be about the same as that of IV. Furthermore, the 5-nitro group in VIII will deshield the protons of the adjacent methyl group to a greater extent than the 3-nitro group will deshield those of the nonadjacent methyl group in VII; therefore, the chemical shift of the methyl protons of VIII will be greater than that of VII.

The fact that the mononitration of VI occurs at positions 3 and 5 while that of III occurs exclusively at position 3 may reflect an increased steric hindrance at position 5 in III.

#### EXPERIMENTAL (7)

##### 1-Methyl-4-picrylpyrazole (III).

A solution of methylhydrazine (3.4 g., 0.074 mole) and concentrated hydrochloric acid (6.0 ml., 0.074 mole) in 50 ml. of water was added to a solution of 2-picrylmalonaldehyde monohydrate (7.5 g., 0.025 mole) (2) in 500 ml. of water at 90°. The mixture was refluxed for 3 hours and cooled. The black, tar-like material was removed by filtration and dissolved in 70% nitric acid (100 ml.). The solution was boiled gently until the evolution of nitrogen oxides ceased and the color of the solution became light yellow; it was then poured over crushed ice (1 l.). The solid was collected by filtration and recrystallized from methanol-water to yield 1.84 g. (25%) of 1-methyl-4-picrylpyrazole, m.p. 156°.

*Anal.* Calcd. for  $C_{10}H_7N_5O_6$ : C, 40.96; H, 2.39; N, 23.89. Found: C, 41.17; H, 2.26; N, 23.81.

##### 1-Methyl-3-nitro-4-picrylpyrazole (IV).

1-Methyl-4-picrylpyrazole (0.77 g., 0.0026 mole) was dissolved in 10 ml. of fuming nitric acid (90% nitric acid) and the resulting solution was refluxed gently for 5 hours. The cooled solution was poured over crushed ice, and the precipitated solid was collected by filtration, washed with water, and recrystallized from ethanol to give 0.48 g. (55%) of 1-methyl-3-nitro-4-picrylpyrazole, m.p. 197°, crystal density 1.71 g./ml.

*Anal.* Calcd. for  $C_{10}H_6N_6O_8$ : C, 35.51; H, 1.80; N, 24.85. Found: C, 35.47; H, 1.91; N, 24.93.

The crude product was shown to be 90% IV with 10% unreacted III by nmr analysis. No other product was observed.

##### 3,5-Dinitro-1-methyl-4-picrylpyrazole (V).

1-Methyl-4-picrylpyrazole (0.50 g., 0.0017 mole) was added to a mixture of 5 ml. of fuming nitric acid (90% nitric acid) and 10 ml. of concentrated sulfuric acid. The solution was heated under reflux for 2 hours and poured over crushed ice. The product was collected by filtration, washed with water, and recrystallized from acetone-ethanol to provide 0.36 g. (55%) of 3,5-dinitro-1-methyl-4-picrylpyrazole, m.p. 215°, crystal density 1.72 g./ml., impact sensitivity 118 cm (7).

*Anal.* Calcd. for  $C_{10}H_5N_7O_{10}$ : C, 31.34; H, 1.32; N, 25.59. Found: C, 31.12; H, 1.22; N, 25.35.

##### Nitration of 4-(2,4-dinitrophenyl)-1-methylpyrazole (VI).

(a) 4-(2,4-Dinitrophenyl)-1-methylpyrazole (3) (0.50 g., 0.002 mole) was dissolved in 35 ml. of fuming nitric acid (90% nitric acid) and the resulting mixture was refluxed for 5 hours. The solution was poured over ice and the product was extracted with chloroform. The chloroform extracts were dried (magnesium sulfate) and the solvent was removed under reduced pressure to leave the product mixture, which was analyzed by nmr spectroscopy. The methyl protons of the products were integrated to give the product distribution reported.

(b) The preceding procedure was followed except that concentrated nitric acid (70% nitric acid) was used instead of fuming

nitric acid.

3,5-Dinitro-4-(2,4-dinitrophenyl)-1-methylpyrazole (IX).

The product mixtures obtained from (a) and (b) of the preceding experiments were nitrated separately as follows. The product was dissolved in a mixture of 5 ml. of fuming nitric acid (90% nitric acid) and 10 ml. of concentrated sulfuric acid. The solution was heated at reflux for 2 hours, then poured over ice. The precipitated product was collected by filtration, washed with water, and recrystallized from ethanol-water to provide pure 3,5-dinitro-4-(2,4-dinitrophenyl)-1-methylpyrazole, m.p. 183°, crystal density 1.71 g./ml. The yield from (a) was 0.57 g. (85%) and that from (b) was 0.52 g. (78%), based on VI.

*Anal.* Calcd. for C<sub>10</sub>H<sub>6</sub>N<sub>6</sub>O<sub>8</sub>: C, 35.51; H, 1.80; N, 24.85. Found: C, 35.51; H, 1.52; N, 24.55.

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- (7) Microanalyses by M. J. Naranjo. Crystal densities by Marion L. Clancy. All melting points are corrected.
- (8) Drop-weight impact sensitivity determined by F. M. Muse with the LASL Type 12 machine (2.5 kg. weight, sample on sandpaper). The 50% points of several common explosives are: PETN, 11 cm.; RDX, 23 cm.; TNT, 160 cm.

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