

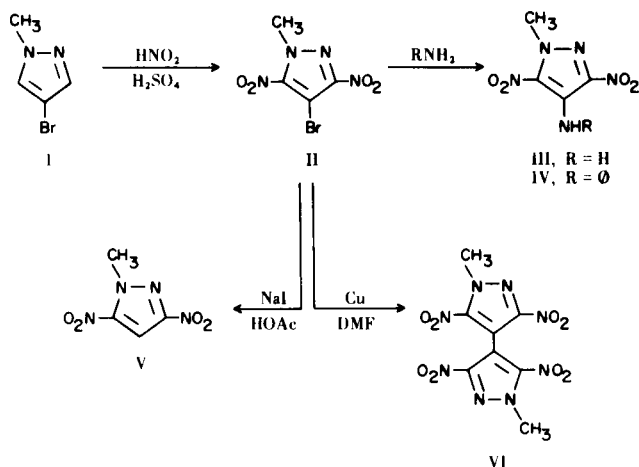
## 3,5-Dinitropyrazoles (1)

Michael D. Coburn

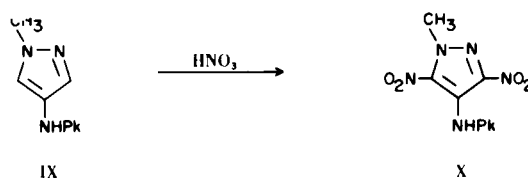
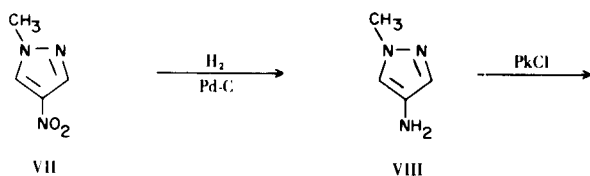
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

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The nitration of 1-methyl-4-picrylpyrazole and 4-(2,4-dinitrophenyl)-1-methylpyrazole to their corresponding 3,5-dinitropyrazole derivatives was reported in a recent communication from this laboratory (2). Subsequently, it was discovered that 4-bromo-1-methylpyrazole (I) could be nitrated to its dinitro derivative, 4-bromo-3,5-dinitro-1-methylpyrazole (II), which is a useful intermediate in the preparation of various 3,5-dinitropyrazoles. Thus, II reacted with ammonia to give 4-amino-3,5-dinitro-1-methylpyrazole (III) and with aniline to provide 4-anilino-3,5-dinitro-1-methylpyrazole (IV). Treatment of II with sodium iodide in acetic acid produced 3,5-dinitro-1-methylpyrazole (V), the first example of a 3,5-dinitropyrazole that is unsubstituted at position 4. Compound II also underwent the Ullmann reaction in DMF to yield 1,1'-dimethyl-3,3',5,5'-tetranitro-4,4'-bipyrazolyl (VI).



1-Methyl-4-nitropyrazole (VII) was hydrogenated to 4-amino-1-methylpyrazole (VIII), which reacted with picryl chloride to form 1-methyl-4-picrylamino-1-pyrazole (IX). Nitration of IX under mild conditions provided 3,5-dinitro-1-methyl-4-picrylamino-1-pyrazole (X).



## EXPERIMENTAL (3)

## 4-Bromo-3,5-dinitro-1-methylpyrazole (II).

4-Bromo-1-methylpyrazole (4) (10.0 g., 0.062 mole) was added in one portion with stirring to a mixture of 50 ml. of fuming nitric acid (90% nitric acid) and 50 ml. of concentrated sulfuric acid at 25°. After the initial exothermic reaction had subsided, the solution was refluxed for 2 hours, then it was poured over crushed ice (1 kg.). The precipitated solid was collected by filtration, washed repeatedly with water, and dried to yield 4.0 g. (26%) of II, m.p. 110°; nmr (DMSO-d<sub>6</sub>) 4.33 δ.

*Anal.* Calcd. for C<sub>4</sub>H<sub>3</sub>BrN<sub>4</sub>O<sub>4</sub>: C, 19.14; H, 1.20; N, 22.32. Found: C, 18.87; H, 1.27; N, 22.37.

## 4-Amino-3,5-dinitro-1-methylpyrazole (III).

A solution of 4-bromo-3,5-dinitro-1-methylpyrazole (3.0 g., 0.012 mole) in ethanol (100 ml.) was saturated with ammonia and heated under pressure at 120° for 16 hours. The solvent was removed under reduced pressure and the residue was slurried with water. The insoluble solid was collected by filtration and recrystallized from ethanol to give 1.4 g. (62%) of III, m.p. 162°; nmr (DMSO-d<sub>6</sub>) 4.23 δ.

*Anal.* Calcd. for C<sub>4</sub>H<sub>5</sub>N<sub>5</sub>O<sub>4</sub>: C, 25.67; H, 2.69; N, 37.43. Found: C, 25.54; H, 2.41; N, 37.68.

## 4-Anilino-3,5-dinitro-1-methylpyrazole (IV).

4-Bromo-3,5-dinitro-1-methylpyrazole (1.25 g., 0.005 mole) and aniline (1.0 g., 0.01 mole) were refluxed in 15 ml. of DMF for 20 hours. The solution was diluted with water (200 ml.) and the precipitated solid was collected by filtration. Recrystallization of the product from ethanol provided 0.55 g. (42%) of IV, m.p. 158-159°; nmr (DMSO-d<sub>6</sub>) 4.27 δ (s, 3H), 7.07 δ (m, 5H).

*Anal.* Calcd. for C<sub>10</sub>H<sub>9</sub>N<sub>5</sub>O<sub>4</sub>: C, 45.63; H, 3.45; N, 26.61. Found: C, 45.53; H, 3.47; N, 26.46.

## 3,5-Dinitro-1-methylpyrazole (V).

A mixture of 4-bromo-3,5-dinitro-1-methylpyrazole (10.0 g., 0.04 mole) and sodium iodide (20 g., 0.13 mole) in glacial acetic acid (100 ml.) was heated under pressure at 155° for 20 hours. The solution was poured into a solution of sodium bisulfite (10 g.) in water (500 ml.) and the resulting solution was extracted with dichloromethane (5 x 50 ml.). The combined extracts were washed with water, dried (magnesium sulfate), and evaporated to dryness under reduced pressure. The residue was recrystallized

from ethanol to yield 1.80 g. (27%) of V, m.p. 60-61°; nmr (DMSO-d<sub>6</sub>) 4.33 δ (3H), 7.96 δ (1H).

*Anal.* Calcd. for C<sub>4</sub>H<sub>4</sub>N<sub>4</sub>O<sub>4</sub>: C, 27.92; H, 2.34; N, 32.55. Found: C, 27.91; H, 2.72; N, 32.55.

1,1'-Dimethyl-3,3',5,5'-tetranitro-4,4'-bipyrazolyl (VI).

A solution of 4-bromo-3,5-dinitro-1-methylpyrazole (6.0 g., 0.024 mole) in DMF (40 ml.) was heated to reflux and activated copper powder (5) (5.0 g.) was added with stirring. The mixture was refluxed 4 hours, an additional 5.0 g. of copper was added, and the resulting mixture was refluxed another 4 hours. After the cooled reaction mixture was diluted to 1 l. with water, the solids were removed by filtration, washed with water, and dried. The filter cake was digested in 300 ml. of boiling acetone, the insoluble material was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized twice from acetone-ethanol to provide 1.4 g. (34%) of VI, m.p. 193-194°; nmr (DMSO-d<sub>6</sub>) 4.43 δ.

*Anal.* Calcd. for C<sub>8</sub>H<sub>6</sub>N<sub>8</sub>O<sub>8</sub>: C, 28.08; H, 1.77; N, 32.75. Found: C, 27.90; H, 1.78; N, 32.93.

1-Methyl-4-picrylamino-pyrazole (IX).

1-Methyl-4-nitropyrazole (6) (2.54 g., 0.02 mole) was hydrogenated in 50 ml. of ethanol over 5% palladium on charcoal under 50 psi of hydrogen for 1 hour. The catalyst was removed by filtration and picryl chloride (5.0 g., 0.02 mole) was added to the filtrate. The mixture was refluxed for 1 hour, then diluted with water (200 ml.). The solid was collected by filtration and recrystallized from acetone-ethanol to give 4.5 g. of IX, m.p. 196°; nmr (DMSO-d<sub>6</sub>) 3.79 δ (3H), 7.30 δ (1H), 7.70 δ (1H), 8.90 δ

(2H).

*Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>N<sub>6</sub>O<sub>6</sub>: C, 38.97; H, 2.62; N, 27.27. Found: C, 39.17; H, 2.64; N, 27.47.

The mother liquor was concentrated and chilled to yield a second crop of 0.6 g., m.p. 195°. The combined yield of IX was 5.1 g. (83%).

3,5-Dinitro-1-methyl-4-picrylamino-pyrazole (X).

1-Methyl-4-picrylamino-pyrazole (3.0 g., 0.01 mole) was added in small portions to 30 ml. of fuming nitric acid (90% nitric acid) at 0°. The solution was stirred at 25° for 5 hours, then it was poured over crushed ice. The solid was collected by filtration, washed with water, and recrystallized from acetone-ethanol to provide 2.35 g. (59%) of X, m.p. 164°; nmr (DMSO-d<sub>6</sub>) 4.35 δ (3H), 9.03 δ (2H).

*Anal.* Calcd. for C<sub>10</sub>H<sub>6</sub>N<sub>8</sub>O<sub>10</sub>: C, 30.16; H, 1.52; N, 28.14. Found: C, 29.95; H, 1.30; N, 28.42.

#### REFERENCES

- (1) This work was performed under the auspices of the U. S. Atomic Energy Commission.
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- (6) D. E. Wright, U. S. Patent 3,102,890.