

## Picrylamino-substituted Heterocycles. IV. Pyrazoles (1,2)

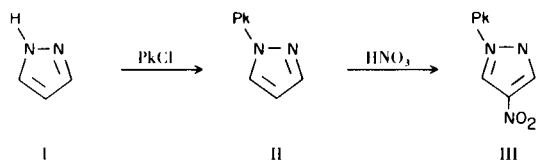
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This paper describes the synthesis of various picryl- and picrylamino-substituted pyrazoles. These compounds were prepared by condensing the appropriate pyrazole or aminopyrazole with a picryl halide or picrylpyrazole. Some of these materials could be nitrated under carefully controlled conditions to the corresponding nitropyrazole derivatives. The products were identified by n.m.r. spectroscopy, and their crystal densities and thermal stabilities were determined. Drop-weight impact sensitivities were measured for some of the more interesting compounds.

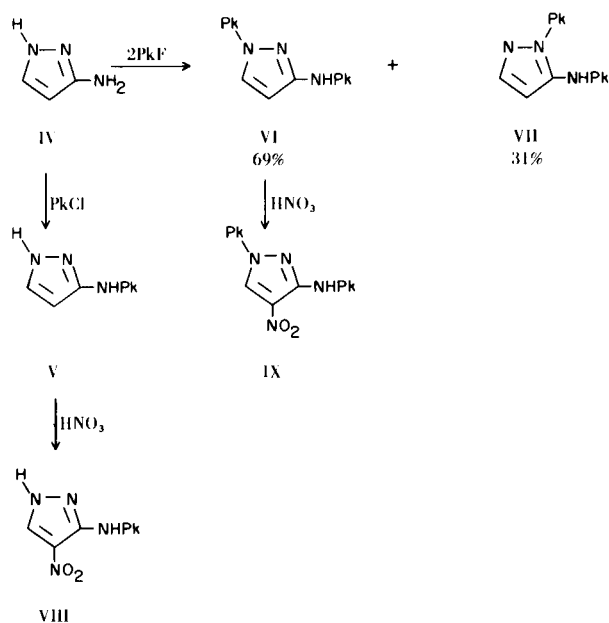
Various picryl-, picrylamino-, and nitro-substituted pyrazoles have been prepared and evaluated as potential high explosives as part of our continuing effort in the field of picrylamino-substituted heterocycles.

The condensation of pyrazole (I) with picryl chloride to form 1-picrylpyrazole (II) has been reported (3). We found that III could be nitrated to 4-nitro-1-picrylpyrazole (III). The n.m.r. chemical shifts of the pyrazole protons of



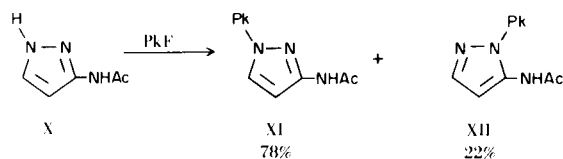
II and III were used as models for the identification of most of the other compounds prepared in this work. The 1-picryl group deshields the adjacent C-5 pyrazole proton to a much greater extent than the nonadjacent C-3 proton in both II and III (Table I).

3-Aminopyrazole (IV) reacted with one molecule of picryl chloride to form 3-picrylamino-5-pyrazole (V) and with two molecules of picryl fluoride to give a mixture of 1-picryl-3-picrylamino-5-pyrazole (VI) and 1-picryl-5-picrylamino-3-pyrazole (VII). The structural assignments of VI and VII were based upon the chemical shifts of the C-3(5) protons of the products as compared with those of II (see Table I). The n.m.r. spectrum of the crude product was determined and the C-3(5) protons of VI and VII were integrated to give the product distribution shown. The nitration of V to 4-nitro-3-picrylamino-5-pyrazole (VIII) and of VI to 4-nitro-1-picryl-3-picrylamino-5-pyrazole (IX) was accomplished.

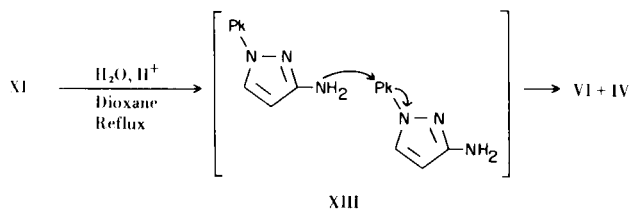


Since no 1(or 2)-picryl-3-aminopyrazole was formed in the reaction of IV with picryl chloride, the amino group is therefore much more nucleophilic than the ring nitrogens. The distribution of products VI and VII indicates that position 1 of V is somewhat more nucleophilic than position 2, which may be the result of the close proximity of position 2 to the bulky, electron-withdrawing picryl group.

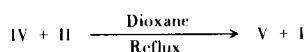
Treatment of 3-acetylamino-5-pyrazole (X) with picryl fluoride produced a mixture of 3-acetylamino-1-picrylpyrazole (XI) and 5-acetylamino-1-picrylpyrazole (XII) in the proportions indicated. The products were identified in essentially the same manner as the mixture of VI and VII. Compound XI was subjected to acid catalyzed hydrolysis in an attempted preparation of 3-amino-1-picrylpyrazole (XIII). However, the product isolated was identi-



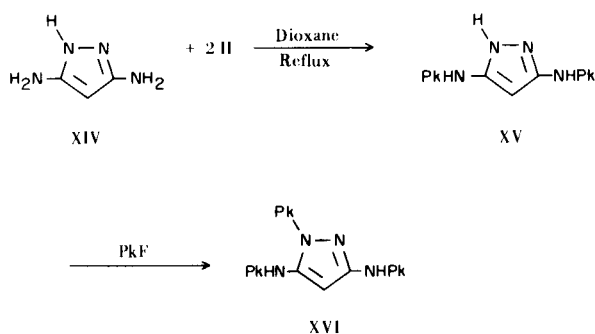
fied as VI. Apparently XI was hydrolyzed to XIII, which then underwent an intermolecular displacement reaction with itself to form VI and IV as illustrated below.



In order to test the validity of this hypothesis, IV was treated with II in refluxing dioxane. The yield of V obtained in this manner was higher than that obtained from the reaction of IV with picryl chloride.

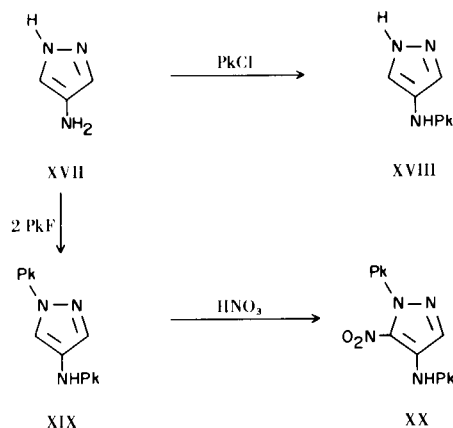


3,5-Diaminopyrazole (XIV) failed to produce 3,5-bis(picrylamino)pyrazole (XV) when treated with either picryl chloride or picryl fluoride; however, the desired XV was obtained from the reaction of XIV with II. Picryl fluoride condensed with XV to form 3,5-bis(picrylamino)-1-picrylpyrazole (XVI). Both XV and XVI were degraded when subjected to various nitration conditions.

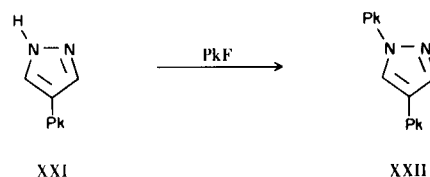


4-Aminopyrazole (XVII), which was obtained in quantitative yield by the catalytic hydrogenation of 4-nitropyrzazole, condensed with one equivalent of picryl chloride to give 4-picrylamino-pyrazole (XVIII) and with two equivalents of picryl fluoride to produce 1-picryl-4-picrylamino-

pyrazole (XIX). Nitration of XVIII to the corresponding 3-nitro derivative has been unsuccessful thus far; however, XIX has been nitrated to 5-nitro-1-picryl-4-picrylamino-pyrazole (XX).



The most interesting explosive in this series was obtained from the reaction of 4-picrylpyrazole (XXI) with picryl fluoride. The product, 1,4-dipicrylpyrazole (XXII), is extremely resistant to both heat and chemical attack. It has been recovered unchanged after treatment with potassium nitrate in 30% oleum at 150° for several hours.



The n.m.r. chemical shifts of the various protons of the compounds prepared in this work are given in Table I. Table II contains the physical and explosive properties determined for these materials.

#### EXPERIMENTAL (4)

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

1-Picrylpyrazole (2.79 g., 0.01 mole) (3) was dissolved in 15 ml. of concentrated sulfuric acid, then absolute nitric acid (15 ml.) was added slowly. The mixture was heated at 95° for one hour, cooled, and poured over crushed ice. The solid was collected by filtration, washed with water, and crystallized from acetone-ethanol to yield 2.26 g. (70%) of III, m.p. 219°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>4</sub>N<sub>6</sub>O<sub>8</sub>: C, 33.35; H, 1.24; N, 25.93  
Found: C, 33.28; H, 1.41; N, 25.90.

##### 3-Picrylamino-pyrazole (V).

(a) A solution of 3-aminopyrazole (0.91 g., 0.011 mole) and picryl chloride (1.24 g., 0.005 mole) in 15 ml. of dimethylsulf-

TABLE I  
N.M.R. SPECTRA (a)

Pyrazole	$\delta_{C-H}$ (p.p.m.)				
	C-3	Pyrazole C-4	C-5	Picryl	Aryl Picrylamino
1-Picryl-	7.88	6.65	8.21	9.24	
3-Picrylamino-		6.18	7.66		8.93
3,5-bis(Picrylamino)-		5.91			8.96
4-Picrylamino-	7.57		7.57		8.92
1-Picryl-3-picrylamino-		6.57	8.17	9.22	8.94
1-Picryl-5-picrylamino-	7.69	5.78		9.28	8.86
3,5-bis(Picrylamino)-1-picryl-		5.70		9.23	8.87, 8.91
1-Picryl-4-picrylamino-	7.86		8.27	9.24	8.97
3-Acetylamino-1-picryl-		6.95	8.08	9.23	
5-Acetylamino-1-picryl-	7.74	6.45		9.24	
4-Nitro-1-picryl-	8.73		9.64	9.36	
4-Nitro-3-picrylamino-			8.87		9.07
4-Nitro-1-picryl-3-picrylamino-			9.60	9.31	9.03
5-Nitro-1-picryl-4-picrylamino-	8.14			9.37	9.14
1,4-Dipicryl-	8.08		8.64	9.20, 9.29	

(a) Determined with a Varian A-60A spectrometer as dimethylsulfoxide solutions using tetramethylsilane as an internal standard.

TABLE II  
Physical and Explosive Properties

Pyrazole	m.p. (°C)	Thermal (a) Stability (°C)	Impact (b) Sensitivity (cm.)	Crystal Density (g./ml.)
1-Picryl-	157	285		1.60
4-Nitro-1-picryl-	219	305	112	1.70
3-Picrylamino-	190	230		1.70
4-Nitro-3-picrylamino-	267 (dec)	260	> 320	1.77
1-Picryl-3-picrylamino	284 (dec)	275		1.67
1-Picryl-5-picrylamino-	253 (dec)	250		1.67
4-Nitro-1-picryl-3-picrylamino-	340 (dec)	310	149	1.72
3,5-bis(Picrylamino)-	251 (dec)	240		1.70
3,5-bis(Picrylamino)-1-picryl-	210 (dec)	175		1.67
4-Picrylamino-	249 (dec)	150		1.70
1-Picryl-4-picrylamino-	206 (dec)	200		1.73
5-Nitro-1-picryl-4-picrylamino-	243 (dec)	240	> 320	1.72
1,4-Dipicryl-	352 (dec)	350 (c)	314	1.71

(a) Temperature of the beginning of the first exotherm in differential thermal analysis at 10°/minutes.

(b) Determined 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.

(c) Vacuum Stability: 3.6 ml./g./48 hours @ 200°.

oxide was heated at 65° for 4 hours, then poured over ice. The solid was collected by filtration, washed with water, and crystallized from methanol-water to give 1.20 g. (82%) of V, m.p. 190°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>6</sub>N<sub>6</sub>O<sub>6</sub>: C, 36.74; H, 2.06; N, 28.57. Found: C, 36.52; H, 2.47; N, 28.27.

(b) A solution of 3-aminopyrazole (0.83 g., 0.01 mole) and 1-picrylpyrazole (2.79 g., 0.01 mole) in 30 ml. of dioxane was refluxed for one hour, then diluted to 500 ml. with ice water. The solid was collected by filtration, washed with water, and crystallized from methanol-water to give 2.63 g. (89%) of product, identical in all respects with that obtained in (a).

1-Picryl-3-picrylamino-pyrazole (VI) and 1-Picryl-5-picrylamino-pyrazole (VII).

3-Aminopyrazole (0.41 g., 0.005 mole) and picryl fluoride (2.50 g., 0.011 mole) were dissolved in 20 ml. of *N,N*-dimethylformamide and the resulting solution was stirred for 6 hours at 25°. The solution was diluted with ice water and the precipitated solid was collected by filtration, washed with water, and dried to give a crude product containing a 69/31 mixture of VI to VII, according to n.m.r. analysis. Crystallization of the product from acetone-methanol gave a first crop of 0.56 g. of VI, m.p. 284° dec., which contained no VII according to n.m.r. analysis.

*Anal.* Calcd. for C<sub>15</sub>H<sub>7</sub>N<sub>9</sub>O<sub>12</sub>: C, 35.66; H, 1.40; N, 24.95. Found: C, 35.90; H, 1.75; N, 24.83.

The filtrate was concentrated and chilled in the freezer to provide a second crop of 0.82 g. of a mixture VI (25%) and VII (75%). Two more fractional crystallizations from acetone-methanol produced a 0.31 g. sample of VII, m.p. 253° dec., containing no VI.

*Anal.* Calcd. for C<sub>15</sub>H<sub>7</sub>N<sub>9</sub>O<sub>12</sub>: C, 35.66; H, 1.40; N, 24.95. Found: C, 35.76; H, 1.21; N, 25.08.

4-Nitro-3-picrylamino-pyrazole (VIII).

3-Picrylamino-pyrazole (1.30 g., 0.0044 mole) was added to 20 ml. of 70% nitric acid at 25° and the resulting solution was gradually heated to 75°. The temperature was maintained at 75° for 20 minutes while the product crystallized from the solution. The mixture was chilled to 0° and the product was collected by filtration. The crystals were washed with water until the washings were neutral and dried to give 1.14 g. (76%) of VIII, m.p. 267° dec.

*Anal.* Calcd. for C<sub>9</sub>H<sub>5</sub>N<sub>7</sub>O<sub>8</sub>: C, 31.87; H, 1.49; N, 28.91. Found: C, 31.74; H, 1.76; N, 28.70.

4-Nitro-1-picryl-3-picrylamino-pyrazole (IX).

1-Picryl-3-picrylamino-pyrazole (0.33 g., 0.00065 mole) was added to 10 ml. of 70% nitric acid at 25°. The slurry was gradually heated to 65°. At 60-65° a clear solution was obtained and at 65° the product began to crystallize from the solution. The reaction mixture was controlled at 65° for 15 minutes, then cooled to 0°. The product was collected by filtration, washed with water, and dried to yield 0.35 g. (97%) of IX, m.p. 340° dec.

*Anal.* Calcd. for C<sub>15</sub>H<sub>5</sub>N<sub>10</sub>O<sub>14</sub>: C, 32.74; H, 1.10; N, 25.46. Found: C, 32.83; H, 1.23; N, 25.12.

3-Acetylamino-1-picrylpyrazole (XI) and 5-Acetylamino-1-picrylpyrazole (XII).

A solution of 3-acetylamino-pyrazole (1.25 g., 0.01 mole) (5) and picryl fluoride (2.50 g., 0.011 mole) in 25 ml. of dimethylsulfide was stirred at 25° for 16 hours. The product was precipitated by diluting the solution with ice water. After the precipitate had been collected by filtration, washed with water, and dried, it was analyzed by n.m.r. spectroscopy and found to contain a mixture of XI (78%) and XII (22%). The product was crystallized from

ethanol to give a first crop of 1.65 g. of pure XI, m.p. 226°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>N<sub>6</sub>O<sub>7</sub>: C, 39.29; H, 2.40; N, 25.00. Found: C, 39.31; H, 2.47; N, 25.39.

The filtrate was concentrated until crystallization began to occur and chilled in the freezer. A second crop of 0.30 g. which was discovered to be pure XII, m.p. 217°, was obtained.

*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>N<sub>6</sub>O<sub>7</sub>: C, 39.29; H, 2.40; N, 25.00. Found: C, 39.21; H, 2.29; N, 24.96.

Hydrolysis of 3-Acetylamino-1-picrylpyrazole (XI).

3-Acetylamino-1-picrylpyrazole (1.0 g., 0.003 mole) was refluxed with a mixture of 5 ml. of concentrated hydrochloric acid, 5 ml. of water, and 10 ml. of dioxane for one hour. The resulting solution was diluted with water and the precipitated solid was collected by filtration. The product was crystallized from acetone-ethanol to give 0.21 g. (14%) of pure 1-picryl-3-picrylamino-pyrazole (VI), which was identified by infrared and n.m.r. spectroscopy.

3,5-bis(picrylamino)pyrazole (XV).

3,5-Diaminopyrazole (0.49 g., 0.005 mole) (6) and 1-picrylpyrazole (2.79 g., 0.01 mole) were dissolved in 50 ml. of dioxane, and the resulting solution was refluxed for 7 hours. Concentrated hydrochloric acid (5 ml.) was added to the cooled solution, which was subsequently poured into 500 ml. of ice water. The tar-like material which separated was dissolved in boiling acetone, treated with Norite, filtered, and poured slowly into 500 ml. of ice water. Concentrated hydrochloric acid (5 ml.) was added to coagulate the precipitate, which was collected by filtration and crystallized from acetone-methanol to yield 1.55 g. (60%) of XV, m.p. 251° dec.

*Anal.* Calcd. for C<sub>15</sub>H<sub>8</sub>N<sub>10</sub>O<sub>12</sub>: C, 34.63; H, 1.55; N, 26.92. Found: C, 34.69; H, 1.61; N, 26.80.

3,5-bis(Picrylamino)-1-picrylpyrazole (XVI).

3,5-bis(picrylamino)pyrazole (2.60 g., 0.005 mole) was dissolved in 25 ml. of *N,N*-dimethylformamide along with 1.15 g. (0.005 mole) of picryl fluoride. The resulting solution was allowed to stir at 25° for 16 hours, then diluted with ice water. The precipitate was collected by filtration and crystallized twice from acetone-ethanol. The yield of XVI was 2.34 g. (64%), m.p. 210° dec.

*Anal.* Calcd. for C<sub>21</sub>H<sub>9</sub>N<sub>13</sub>O<sub>18</sub>: C, 34.49; H, 1.24; N, 24.90. Found: C, 34.54; H, 1.13; N, 24.39.

4-Picrylamino-pyrazole (XVIII).

4-Nitropyrazole (2.26 g., 0.02 mole) (7) was hydrogenated over 5% palladium on charcoal in ethanol under 50 p.s.i. of hydrogen in a Parr low pressure hydrogenation apparatus at 25° for one hour. The catalyst was removed by filtration and the solvent was removed under reduced pressure to leave 4-aminopyrazole, which was used without further purification because it darkens rapidly when exposed to oxygen. The 4-aminopyrazole (0.02 mole) obtained above was dissolved in 50 ml. of ethanol, and picryl chloride (2.47 g., 0.01 mole) was added to the solution. The mixture was stirred at 25° for 16 hours, then it was diluted with water. The precipitated solid was collected by filtration, washed with water, and crystallized from acetone-ethanol to provide 2.54 g. (86%) of XVIII, m.p. 249° dec.

*Anal.* Calcd. for C<sub>9</sub>H<sub>6</sub>N<sub>6</sub>O<sub>6</sub>: C, 36.74; H, 2.06; N, 28.57. Found: C, 36.79; H, 2.21; N, 28.74.

1-Picryl-4-picrylamino-pyrazole (XIX).

4-Aminopyrazole (0.01 mole), obtained from the hydrogenation of 4-nitropyrazole (1.13 g., 0.01 mole) as described previously,

was dissolved in 50 ml. of *N,N*-dimethylformamide and the solution was treated with picryl fluoride (5.77 g., 0.025 mole). After the solution had stirred at 25° for 16 hours, it was diluted with water in order to precipitate the product, which was collected by filtration and recrystallized from acetone-ethanol. After the product (XIX) had been dried overnight in an oven at 100° it weighed 4.27 g. (85%), m.p. 206° dec.

*Anal.* Calcd. for  $C_{15}H_7N_9O_{12}$ : C, 35.66; H, 1.40; N, 24.95. Found: C, 35.84; H, 1.74; N, 24.96.

#### 5-Nitro-1-picryl-4-picrylamino-pyrazole (XX).

1-Picryl-4-picrylamino-pyrazole (3.0 g., 0.006 mole) was dissolved in 50 ml. of 70% nitric acid at 25°. After a clear solution was obtained the temperature was gradually raised to 40° and held there for 15 minutes. During this period the product began to crystallize from the solution. After the mixture was cooled to 0° the solid was collected by filtration, washed with water, and crystallized from acetone-ethanol. The yield of XX was 1.87 g. (57%), m.p. 243° dec.

*Anal.* Calcd. for  $C_{15}H_6N_{10}O_{14}$ : C, 32.74; H, 1.10; N, 25.46. Found: C, 32.75; H, 1.16; N, 25.50.

#### 1,4-Dipicrylpyrazole (XXII).

4-Picrylpyrazole (1.0 g., 0.0036 mole) (8) and picryl fluoride (1.0 g., 0.0043 mole) were dissolved in *N,N*-dimethylformamide (15 ml.) and the solution was stirred at 25° for 16 hours. After the solution was diluted with water, 5 ml. of concentrated hydrochloric acid was added to coagulate the precipitate, which was collected by filtration and crystallized from acetone-ethanol. The

product (XXII) weighed 1.33 g. (76%), m.p. 352° dec.

*Anal.* Calcd. for  $C_{15}H_6N_8O_{12}$ : C, 36.75; H, 1.23; N, 22.86. Found: C, 36.71; H, 1.11; N, 22.81.

#### Acknowledgment.

The author is grateful to Dr. L. C. Smith for helpful criticism of the manuscript.

#### REFERENCES

- (1) This work was performed under the auspices of the U. S. Atomic Energy Commission.
- (2) Part III, *J. Heterocyclic Chem.*, **5**, 199 (1968). This paper was presented in part before the Second International Congress of Heterocyclic Chemistry, Montpellier, France, July 7-11, 1969.
- (3) J. Elguero and R. Jacquier, *Bull. Soc. Chim. France*, 2832 (1966).
- (4) Microanalyses by M. J. Naranjo. Crystal densities by Marion Clancy. Drop-weight impact sensitivities by C. E. Hannaford and F. M. Muse. All melting points are corrected.
- (5) E. I. du Pont de Nemours & Co., Netherlands Application 6.406,077. *Chem. Abstr.*, **63**, 11570c (1965).
- (6) J. A. Settepani and J. B. Stokes, *J. Org. Chem.*, **33**, 2606 (1968).
- (7) R. Hüttel and F. Büchele, *Chem. Ber.*, **88**, 1586 (1955).
- (8) V. L. Zbarskii, G. M. Shutov, V. F. Zhilin, and E. Yu. Orlava, *Zh. Org. Khim.*, **4**, 1973 (1968).

Received November 3, 1969

Los Alamos, N. M. 87544