

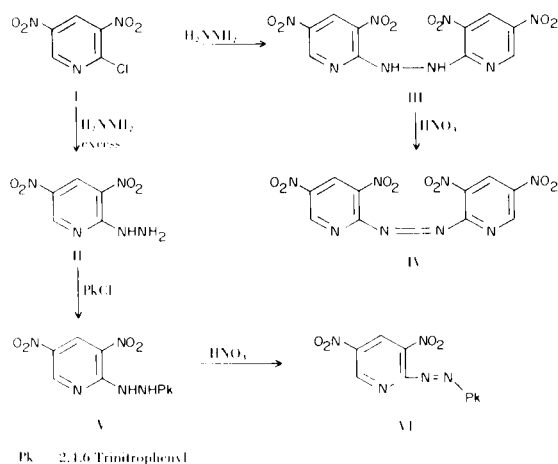
Synthesis of 3,3',5,5'-Tetranitro-2,2'-azopyridine and some
Picrylazo Derivatives of 3,5-Dinitropyridine (I)

Michael D. Coburn

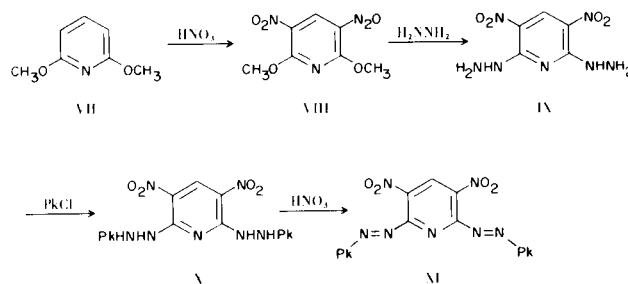
University of California, Los Alamos Scientific Laboratory, Los Alamos, NM 87544

Received June 24, 1974

It has been reported that 2-chloro-3,5-dinitropyridine (I) reacts with hydrazine to give, depending on conditions, either 3,5-dinitro-2-hydrazinopyridine (II) or 1,2-bis(3,5-dinitro-2-pyridyl)hydrazine (III), both of which are oxidized by silver acetate to 3,5-dinitropyridine (2). We have found that the oxidation of III with nitric acid gives a nearly quantitative yield of 3,3',5,5'-tetranitro-2,2'-azopyridine (IV). This discovery has led to the synthesis of some picrylazo derivatives of 3,5-dinitropyridine. Thus, picryl chloride reacted with II to give 1-(3,5-dinitro-2-pyridyl)-2-picrylhydrazine (V), which was oxidized with nitric acid to 3,5-dinitro-2-(picrylazo)pyridine (VI).



Nitration of 2,6-dimethoxyppyridine (VII) gave 2,6-dimethoxy-3,5-dinitropyridine (VIII) (3), which was treated with an excess of hydrazine to yield 2,6-dihydrazino-3,5-dinitropyridine (IX). Compound IX reacted with two equivalents of picryl chloride to form 2,6-bis(2-picrylhydrazino)-3,5-dinitropyridine (X). Oxidation of X with nitric acid produced 2,5-bis(picrylazo)-3,5-dinitropyridine (XI), which was obtained in two interconvertible polymorphic forms.



The structures of the new compounds described in this communication were confirmed by their elemental analyses (Table I) and nmr spectra (Table II). No attempt was made to determine whether the azo compounds are in the *syn* or *anti* configurations. The bulk of the picryl and 3,5-dinitropyridyl groups would seem to favor the *anti* configuration.

TABLE I

Elemental Analyses

Compound	Molecular Formula	Calculated, %			Found, %		
		C	H	N	C	H	N
IV	C ₁₀ H ₄ N ₈ O ₈	32.99	1.11	30.77	32.76	1.15	30.78
V	C ₁₁ H ₆ N ₈ O ₁₀	32.21	1.47	27.32	31.98	1.48	27.23
VI	C ₁₁ H ₄ N ₈ O ₁₀	32.37	0.99	27.45	32.00	0.74	27.77
IX	C ₅ H ₇ N ₇ O ₄	26.21	3.08	42.79	26.31	3.44	42.96
X	C ₁₇ H ₉ N ₁₂ O ₁₆	31.35	1.39	27.96	31.53	1.49	27.77
XI	C ₁₇ H ₅ N ₁₂ O ₁₆	31.54	0.78	28.13	31.38	0.41	28.11

TABLE II
NMR Spectra (a)

Compound	δ_{C-H} (ppm)			Picryl Protons
	C-4	Pyridine Protons C-6	J (cps)	
IV	9.78 (d)	9.50 (d)	2.3	
V	9.28 (d)	9.03 (d)	2.2	8.97 (s)
VI	9.82 (d)	9.52 (d)	2.2	9.35 (s)
IX	8.90 (s)			
X	8.93 (s)			8.85 (s)
XI	9.86 (s)			9.38 (s)

(a) Determined with a Varian A-60A spectrometer as DMSO- d_6 solutions using TMS as an internal standard.

EXPERIMENTAL (4)

Caution! Most of the compounds prepared in this study are explosives with impact sensitivities comparable to that of RDX. 3,3',5,5'-Tetranitro-2,2'-azopyridine (IV).

1,2-Bis(3,5-dinitro-2-pyridyl)hydrazine (III) (2) (1.0 g., 0.0027 mole) was added to concentrated nitric acid (70% nitric acid) (15 ml.), and the resulting mixture was stirred at 25° for 1 hour. The mixture was poured over ice, and the solid was collected by filtration, washed with water, and dried to yield 0.96 g. (96%) of IV, m.p. 253° dec.

1-(3,5-Dinitro-2-pyridyl)-2-picrylhydrazine (V).

A solution of 2-hydrazino-3,5-dinitropyridine (II) (2) (1.5 g., 0.0073 mole), picryl chloride (1.82 g., 0.0073 mole), and sodium acetate (0.60 g., 0.0073 mole) in ethanol (50 ml.) was refluxed for 45 minutes and cooled. A solution of 2.5 ml. of concentrated hydrochloric acid in 20 ml. of water was added. The solid was removed by filtration and recrystallized from acetic acid to give 0.96 g. (32%) of V, m.p. 220°.

3,5-Dinitro-2-(picrylazo)pyridine (VI).

Compound V (0.60 g., 0.0015 mole) was added to concentrated nitric acid (70% nitric acid) (10 ml.) at 25°. The mixture was stirred at 25° for 1 hour, then it was poured over ice. The solid was collected by filtration, washed with water, and dried to yield 0.54 g. (91%) of VI, m.p. 168-170°. An analytical sample, m.p. 171-172°, was obtained by recrystallization from aqueous acetic acid.

2,6-Dimethoxy-3,5-dinitropyridine (VIII).

2,6-Dimethoxypyridine (VII) (25.0 g., 0.18 mole) was added dropwise to fuming nitric acid (90% nitric acid) (250 ml.) with the

temperature controlled at 10-15° by cooling with an ice bath. The resulting solution was allowed to stir at room temperature for 2 hours, then it was gradually heated to 50°, held at 50° for 20 minutes, and poured over ice (1.5 kg.). The precipitated product was collected by filtration, washed with water, and dried to provide 28.2 g. (68%) of VIII, m.p. 133° [lit (3) m.p. 131-133°].

2,6-Dihydrazino-3,5-dinitropyridine (IX).

Compound VIII (2.29 g., 0.01 mole) was added to a stirred solution of hydrazine (1.0 ml., 0.03 mole) in ethanol (25 ml.), and the mixture was heated under reflux for 1 hour. The cooled mixture was filtered to remove the product, which was washed with ethanol and dried. The yield of pure IX, m.p. 243° dec., was 2.27 g. (99%).

2,6-Bis(2-picrylhydrazino)-3,5-dinitropyridine (X).

Picryl chloride (4.96 g., 0.02 mole) was added to a solution of IX (2.29 g., 0.01 mole), and sodium acetate (1.64 g., 0.02 mole) in *N,N*-dimethylformamide (50 ml.), and the mixture was allowed to stir at 25° for 16 hours. Acetic acid (200 ml.) was added to the stirred solution, then it was diluted with water (100 ml.) to cause precipitation of the product, which was removed by filtration, washed with water, and dried at 120° to yield 6.1 g. (94%) of X, m.p. 253° dec. The product was used without further purification for the preparation of XI. An analytically pure sample, m.p. 266° dec., was obtained by recrystallizing a portion of the material from acetone-acetic acid.

2,6-Bis(picrylazo)-3,5-dinitropyridine (XI).

A solution of X (5.4 g., 0.0085 mole) in fuming nitric acid (90% nitric acid) (50 ml.) was stirred at 25° for 1 hour, heated under reflux for 15 minutes, and treated dropwise with water until it became turbid. The product crystallized as dark red needles, which were collected by filtration, washed first with concentrated nitric acid (70% nitric acid) and then with water, and dried at 150° to give 5.2 g. (97%) of XI, m.p. 215°. Recrystallization from acetone converts the red crystals to very fine, fluffy yellow needles, m.p. 192°, which can be converted back to the higher melting form by recrystallization from nitric acid.

Acknowledgement.

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

REFERENCES

- (1) This work was performed under the auspices of the U. S. Atomic Energy Commission.
- (2) E. Plazek, *Rec. Trav. Chim.*, **72**, 569 (1953).
- (3) C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, and M. Viney, *J. Chem. Soc. (B)*, 1204 (1967).
- (4) Microanalyses by M. J. Naranjo. All melting points are corrected.