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Nitration of amino- and diaminopyridines and -picolines led, in unexpected one-step reactions, to dinitrated derivatives. Dinitropicolines gave styrylpyridines, and 2-amino-6-hydroxy-3,5-dinitropyridine was transformed by the thermolysis of its azido derivative into 5-amino-6-nitro[1,2,5]oxadiazolo[3,4-*b*]pyridine. Using ^{1}H and ^{13}C nmr spectroscopy, azido-tetrazole tautomerism of 2-amino-6-azido-3,5-dinitropyridine and intramolecular hydrogen bonding at 20° for several 2-amino-3,5-dinitro-6-*R*-pyridines have been proved.

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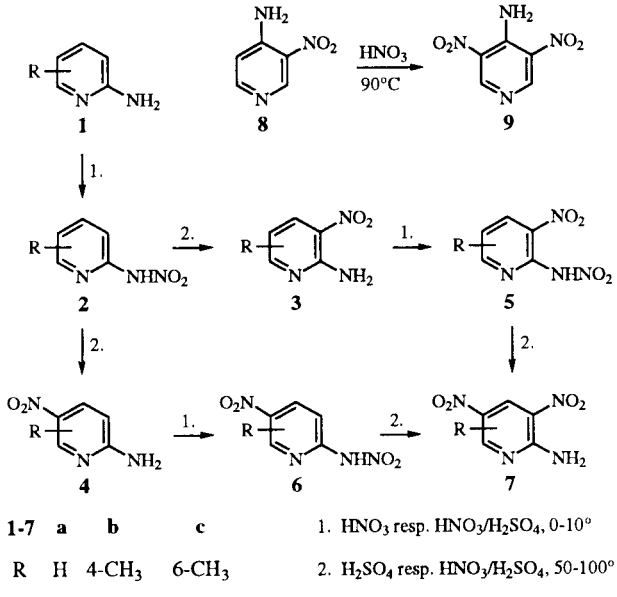
As part of our studies on nitrated hetarenes, we reported on the synthesis of 2,4,6-trinitropyridine and methylnitramino-substituted 3,5-dinitropyridines [1,2]. An investigation of the nitration of some amino derivatives of pyridine and picoline is now undertaken, since strongly activating substituents enable the introduction of more than one nitro group into the pyridine ring. Thus, monohydroxypyridines yield several dinitrated [3-5] and even a trinitrated [6] derivative.

During the nitration of aminopyridines **1a-c** with nitric acid at temperatures of 0-10°, the known nitraminopyridines **2** are first formed [7]; they can be isolated, but can also rearrange in acidic media at temperatures of 50-100° into aminonitropyridines **3a-c** and **4a-c** [7]. Compounds **3a-c** and **4a-c** give the dinitropyridines **7a-c** by a further nitration and subsequent rearrangement of the respective nitramines **5a-c** and **6a-c** [8,9]. In rare cases aminopyridines like **8** do not form nitramines; the activating amino group renders possible the direct *C*-nitration of **8**, leading to the dinitro derivative **9** [10,11] (Scheme 1).

Scheme 1



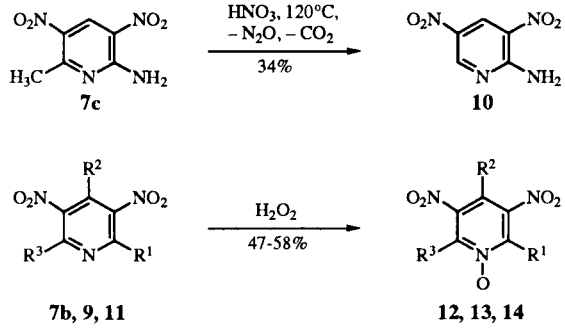
When 2-amino-6-methylpyridine **1c** was nitrated with 1.1 equivalents of nitric acid at 0°, we surprisingly isolated 2-nitramino-6-methyl-5-nitropyridine **6c** beside the nitramine **2c**. The nitration with three equivalents of nitric acid gave **6c** as the only product at 0°, whereas a final heating to 80° provided 2-amino-6-methyl-3,5-dinitropyridine **7c** in a one-pot-reaction; hitherto **7c** had been synthesized only in separate reaction steps [8]. From the fact that **3c**, the second rearrangement product of **2c**, was not isolated from reactions at 0°, we conclude that compound **6c** was not formed *via* aminonitropyridine **4c**, but by direct nitration of the pyridine carbon atom in position 5 of nitramine **2c**. Obviously, the 6-methyl group in **2c** activates the carbon atom in the *ortho*-position for this nitration. We found the same activation with 2-amino-3-nitro-6-methylpyridine **3c**. Its nitration directly yielded 2-amino-6-methyl-3,5-dinitropyridine **7c** instead of the expected nitramine **5c**, the nitro group entering position 5.

2-Amino-3-nitro-4-methylpyridine **3b** was unreactive, as it gave no nitramine on treatment with concentrated nitric acid. In contrast to the reported [7-11] rearrangement of nitramino precursors **2, 5** and **6** at higher temperatures, we obtained aminonitropyridines from the nitramines **2a, 2b, 6a** and **6b** at 20°. 2-Amino-5-nitropyridine **4a** was found in high yields from incomplete rearrangement reactions of 2-nitramino-5-nitropyridine **6a**, indicating the intermediate formation of nitronium ions, which were also observed during the rearrangement of other nitraminopyridines [12].

Compounds **7a** and **7b** were decomposed by nitric acid at elevated temperatures, while with 2-amino-6-methyl-3,5-dinitropyridine **7c** at 120° the methyl group was oxidized and decarboxylated and the amino group transformed into an hydroxy group by nitration and subsequent loss of dinitrogen oxide, giving 2-hydroxy-3,5-dinitropyridine **10**. By oxidation with hydrogen peroxide **7b** and **9** as well as 2,6-diamino-3,5-dinitropyridine **11** gave the corresponding *N*-oxides **12, 13** and **14**. The conversion of amino groups into nitro groups, well known from aminopolynitrobenzenes [13] and aminopyridines [14], was not observed here. Since the ^{1}H nmr spectrum of **12**

does not exhibit the expected pyridine H-6 signal, but a broad singlet at 10 ppm, tautomeric hydroxypyridine or pyridone forms are present (Scheme 2).

Scheme 2



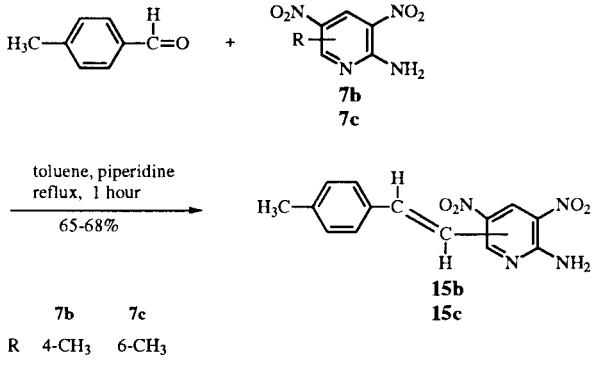
7c 10

7b, 9, 11 12, 13, 14

	7b, 12	9, 13	11, 14
R^1	NH_2	H	NH_2
R^2	CH_3	NH_2	H
R^3	H	H	NH_2

The pronounced activating effect of the two nitro groups on the methyl group of the aminomethyldinitropyridines **7b** and **7c** was demonstrated in the reaction with *p*-tolualdehyde. By analogy with reactions of di- and trinitrotoluenes [15] the represented stilbazoles **15b** and **15c** were obtained in the *trans* configuration, which was established by the coupling constant (J = 16 Hz) of the vinylic protons in the ^1H nmr spectra (Scheme 3).

Scheme 3



7b 7c

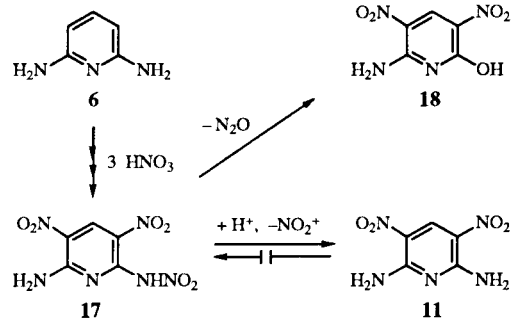
15b 15c

	7b	7c
R	4-CH_3	6-CH_3

2,6-Diamino-3,5-dinitropyridine **11** is the only reported nitration product of 2,6-diaminopyridine **16** [16,17]. Since we obtained 2-amino-6-hydroxy-3,5-dinitropyridine **18** as a second product besides compound **11**, we started a parametric study of this nitration. While reactions with only 2 equivalents of nitric gave undefinable products, prolonged heating after the addition of 3-5 equivalents of nitric acid favoured the formation of diaminodinitropyridine **11**. On the other hand, nitrations without any heating provided aminohydroxypyridine **18** as the only reaction product.

We first supposed that **18** was formed by nitration of one amino group of diaminodinitropyridine **11** and subsequent loss of dinitrogen oxide from the intermediate nitramino derivative **17**. As **11** was found to be inert against nitric acid, this reaction pathway had to be excluded. We suggest 2-amino-6-nitramino-3,5-dinitropyridine **17** to be an intermediate, formed by the step-wise reaction of 2,6-diaminopyridine with 3 equivalents of nitric acid. Compound **17** gives the hydroxypyridine **18** (with evolution of dinitrogen oxide from its nitramino group) as well as the diaminopyridine **11**. The formation of this latter compound by elimination of a nitronium ion from the protonated intermediate **17**, a process also known from other nitraminopyridines [12,18], is relatively slow at 0-20°; this explains the exclusive formation of aminohydroxypyridine **18** at low temperatures (Scheme 4).

Scheme 4



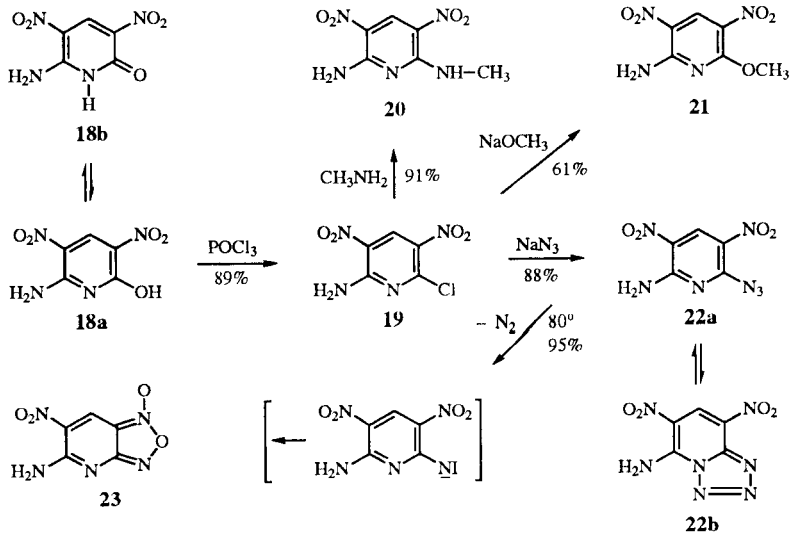
6 18

17 11

Chlorination of 2-amino-6-hydroxy-3,5-dinitropyridine **18** gave the chloropyridine **19**, which was converted into the substitution products **20, 21** and **22a** by methylamine, sodium methoxide and sodium azide, respectively. The azido-tetrazole tautomeric equilibrium between 2-azido-6-nitro-3,5-dinitropyridine **22a** and the tetrazolo form **22b** is shifted completely to **22b** in the solid state: no azido band was found in the ir spectrum. 5-Amino-6-nitro[1,2,5]oxadiazolo[3,4-*b*]pyridine **23** was obtained *via* an intermediate nitrene by elimination of nitrogen from the azido compound **22a** in apolar solvents like hexane or benzene. These solvents favour the azido form and accelerate its conversion, whereas polar solvants (ethanol or acetonitrile) shift the tautomeric equilibrium to the tetrazolo form **22b** (Scheme 5).

The ir spectrum of 2-amino-6-hydroxy-3,5-dinitropyridine **18** exhibited a carbonyl band at 1690 cm^{-1}, indicating the presence of the pyridone form **18b** in the solid state as in the case of 2-hydroxy-3,5-dinitropyridine **10** and other hydroxypyridines. Spectroscopy (uv) showed the predominance of the hydroxy form **18a** in the solvents

Scheme 5



acetonitrile, methanol and chloroform, since the 2-hydroxy compound **18a** and its 2-methoxy derivative **21** showed the same pronounced absorption maxima at 370 nm and 310 nm.

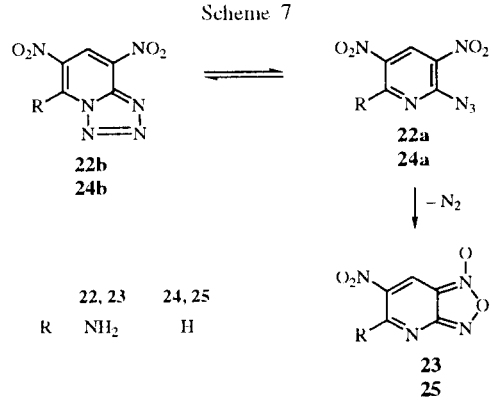
In the ^{1}H nmr spectrum of **18a** in dimethyl sulfoxide-d_6, the signal of the primary amino group did not exhibit the anticipated singlet shape, but was split into two broadened singlets at 7.0 and 8.0 ppm. Obviously, the amino group forms at room temperature a strong hydrogen bond to the adjacent nitro group. This hydrogen bonding was also observed for the 2-amino-3,5-dinitro-6-*R*-pyridines **7a, 7c, 11, 15c, 19, 20** and **21**. The coalescense temperature of the transition from hydrogen-bonded to non-bonded form is below 40° for compound **7c** in acetone-d_6, since at this temperature only one broad singlet was found as a signal of its amino group. The coplanarity of the amino and nitro groups in positions 2 and 3 of the pyridine ring, a precondition for the hydrogen-bonding, can be removed by a suitable substituent in position **4**. This was found for 2-amino-4-methyl-3,5-dinitropyridine **7b** and for stilbazole **15b** where the signal of the amino group was recorded only as one broad singlet (Scheme 6).

Scheme 6

	7a	7c	11	15
R	H	CH_3	NH_2	*p*-CH_3-C_6H_4-CH=CH-
	18	**19**	**20**	**21**
R	OH	Cl	OCH_3	$NH-CH_3$

Likewise, with tetrazolopyridine **22b** and [1,2,5]oxadiazolopyridine **23** the splitting of the amino signal is not observed. On the other hand, the part of the predominant tetrazolo form **22b** and of the azido form **22a** can be determined in different solvents by integration of the C-4 proton signal. In dimethyl sulfoxide-d_6, acetone-d_6 and acetonitrile-d_3 the relation of the tautomers **22a**:**22b** was found to be 1:99, 14:86 and 16:84, respectively. Lowe-Ma [19] determined the relation of the similar tautomeric dinitropyridines **24a**:**24b** in the same solvents to be 9:91, 40:60 and 38:62. A furoxane rearrangement of **23** - whereby the exocyclic oxygen atom of the furoxane ring changes its position from N1 to N3 - can be excluded when the ^{13}C nmr data of **23** and 6-nitro-[1,2,5]oxadiazolo[3,4-*b*]pyridine **25** are compared: The chemical shifts of the bridgehead carbon atoms of **23**, 107.5 and 158.3, are nearly identical to the corresponding values [19] of **25**, 108.8 and 159.9, and of 5-amino-[1,2,5]oxadiazolo[3,4-*b*]pyridine, 106.2 and 160.0 (Scheme 7).

Scheme 7



	22, 23	24, 25
R	NH_2	H

EXPERIMENTAL

Elemental analyses were performed by C.N.R.S. Service Central d'Analyses, Vernaison (France). All ir spectra were taken using potassium bromide discs on a Perkin Elmer 1240 IR spectrophotometer. The nmr spectra were recorded by C.N.R.S Service Central d'Analyse, Vernaison (France) on a Bruker AC 200 spectrometer, and by BICT, Swisttal-Heimerzheim (Germany) on a Bruker CXP/100 spectrometer; chemical shifts are in ppm relative to internal tetramethylsilane. Thermoanalytical measurements were made using a Setaram differential thermal analysis-thermogravimetry system DTA/TG 82.

2-Nitramino-6-methyl-5-nitropyridine **6c** and 2-Amino-6-methyl-3,5-dinitropyridine **7c**.

To a stirred solution of 2-amino-6-methylpyridine **1c** (10.8 g, 0.1 mole) in 100 ml of concentrated sulfuric acid was added dropwise a mixture of nitric acid (15 ml, d = 1.52, 0.36 mole) and 15 ml of concentrated sulfuric acid, the temperature being maintained by external cooling at 10°. The solution was slowly heated to 50° and maintained 4 hours at this temperature. After pouring on ice, the solid was filtered, washed with water and dried to give 15 g (75%) of yellow crystals of 2-amino-6-methyl-3,5-dinitropyridine **7c**, mp 174-175° (ref [8] mp 179°) after recrystallization from ethyl acetate. Without subsequent warming after the addition of nitric acid and sulfuric acid, 18.4 g (93%) of 2-nitramino-6-methyl-5-nitropyridine **6c**, dec 122° (ref [20] mp 116°) were obtained.

General Procedure for Rearrangement of Nitramines **2** and **6**.

The nitraminopyridine (0.01 mole) is slowly dissolved in concentrated sulfuric acid (25 ml) and the solution stirred at 20° during several hours. After pouring on ice and - if necessary - neutralization with aqueous ammonia (30 vol %) the rearrangement products are collected by filtration, washed with water and dried at 40°.

After a 1-24 hours stirring period. the following nitramines were completely rearranged: 2-nitraminopyridine **2a** and 2-nitramino-5-nitropyridine **6a** and their 4-methyl derivatives **2b** and **6b**. From incomplete reactions of **6a** yields up to 40% of 2-amino-5-nitropyridine **4a**, mp 189° (ref [7] mp 188°) are isolated.

2-Hydroxy-3,5-dinitropyridine **10**.

To a stirred solution of 2-amino-6-methyl-3,5-dinitropyridine **7c** (6.0 g, 0.03 mole) in concentrated sulfuric acid (40 ml) was added dropwise a mixture of nitric acid (d = 1.52, 25 ml, 0.3 mole) and concentrated sulfuric acid (15 ml); the temperature rose during the addition to 35°. The solution was slowly heated to 120°, maintained during 5 hours at this temperature and then poured on ice. Extraction with ethyl acetate and evaporation of the solvent yielded 0.95 g (17%) of 2-hydroxy-3,5-dinitropyridine **10**, yellow crystals with mp 168-170° (ref [3] mp 176-178°), identified by comparison of its ir spectrum with an authentic specimen.

2-Amino-4-methyl-3,5-dinitropyridine 1-Oxide **12**.

To a suspension of 2-amino-4-methyl-3,5-dinitropyridine **7b** (1.0 g, 0.05 mole) in glacial acetic acid (130 ml) was added hydrogen peroxide (30 vol %, 30 ml, 0.3 mole) at 20°. After stirring for 48 hours the clear solution was diluted with 600 ml water and the precipitate was filtered, washed with water and dried, yield 0.47 g (43%), red crystals, mp 193° dec; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 10.0 (v br s, 1H, O*H*), 6.88 (br s, 2H, NH_2), 2.23 (s, 3H, CH_3).

Anal. Calcd. for $C_6H_6N_4O_5$: C, 33.65; H, 2.82; N, 26.16. Found: C, 33.36; H, 2.80; N, 26.40.

4-Amino-3,5-dinitropyridine 1-Oxide **13**.

To a solution of 4-amino-3,5-dinitropyridine **9** (1.84 g, 0.01 mole) in glacial acetic acid (40 ml) was added hydrogen peroxide (30 vol %, 8 ml, 0.08 mole) at 20°. After stirring for 4 hours and cooling to 4°, the precipitate was filtered, washed with water and dried to give **13** (1.41 g, 70%) as fine yellow crystals, mp 210° dec; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.47 (s, 2H), 8.41 (br s, 2H, NH_2).

Anal. Calcd. for $C_5H_4N_4O_5$: C, 30.01; H, 2.01; N, 28.00. Found: C, 29.85; H, 2.01; N, 27.60.

2,6-Diamino-3,5-dinitropyridine 1-Oxide **14**.

To a solution of 2,6-amino-3,5-dinitropyridine **11** (4.0 g, 0.02 mole) in glacial acetic acid (80 ml) was added hydrogen peroxide (30 vol %, 16 ml, 0.16 mole) at 70°. After stirring for 6 hours at this temperature, **14** was obtained as a fine yellow powder by filtering the cooled solution, washing with water and drying, yield 3.7 g (86%), mp 340° dec; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 9.20 (br s, 1H, N*H*), 8.88 (br s, 1H, N*H*), 8.80 (s, 1H).

Anal. Calcd. for $C_5H_5N_5O_5$: C, 27.92; H, 2.34; N, 32.56. Found: C, 28.32; H, 2.39; N, 32.29.

2-Amino-3,5-dinitro-4-(*p*-methylstyryl)pyridine **15b**.

A solution of 2-amino-4-methyl-3,5-dinitropyridine (1.98 g, 0.01 mole), *p*-tolualdehyde (3.6 g, 0.03 mole) and piperidine (0.5 ml) in toluene (20 ml) was refluxed for 1 hour. The dark brown solution was cooled, the precipitate filtered after 2 hours and washed with dichloromethane (2 x 10 ml). The crude product was refluxed for 1 hour with dichloromethane (40 ml) and **15b** was filtered off after cooling, 2.03 g (68%) yellow needles, mp 225° after recrystallization from ethyl acetate; ^{1}H nmr (acetone-d_6): δ 8.97 (s, 1H), 7-8 (br s, 2H, NH_2), 7.45 (d, 2H, J = 8 Hz), 7.38 (d, 1H, J = 16 Hz), 7.23 (d, 2H, J = 8 Hz), 6.70 (d, 1H, J = 16 Hz), 2.34 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.75; H, 3.85; N, 18.59.

2-Amino-3,5-dinitro-6-(*p*-methylstyryl)pyridine **15c**.

Compound **15c** is prepared by a method analogous to that used for **15b**. Thus, from 2-amino-6-methyl-3,5-dinitropyridine (1.98 g, 0.01 mole) yellow needles of **15c** (1.94 g, 65%) were isolated, mp 235° dec, after recrystallization from ethyl acetate; ^{1}H nmr (acetone-d_6): δ 9.11 (s, 1H), 8.4 (br s, 1H, N*H*), 8.1 (br s, 1H, N*H*), 8.03 (d, 1H, J = 16 Hz), 7.94 (d, 1H, J = 16 Hz), 7.61 (d, 2H, J = 8 Hz), 7.30 (d, 2H, J = 8 Hz), 2.38 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03; N, 18.66; O, 21.31. Found: C, 56.30; H, 4.35; N, 18.68; O, 21.12.

2-Amino-6-hydroxy-3,5-dinitropyridine **18**.

To a stirred solution of 2,6-diaminopyridine **16** (5.45 g, 0.05 mole) in concentrated sulfuric acid (50 ml) was added nitric acid (6.8 ml, d = 1.49, 0.15 mole) at 15° during 2 hours. The solution was poured on ice (250 g) and filtered after 12 hours. The yellow-orange coloured precipitate was heated ten minutes at 80-90° in water (200 ml) adjusted at *p*H 10-11 with 10 *N* sodium

hydroxide solution and the hot solution was freed from some insoluble diaminodinitropyridine **11** by filtration. The filtrate was acidified and cooled; orange-brown crystals of 2-amino-6-hydroxy-3,5-dinitropyridine **18** were collected by filtration, washed with cold water and dried, yield 4.2 g (42%), mp 305° dec. When temperature was increased continously during a 60 minute period until 60° after addition of nitric acid and when the solution was cooled to rt before pouring on ice, the yield of **18** was 37%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 11.8 (v br s, 1H, O*H*), 9.04 (br s, 1H, N*H*), 9.01 (s, 1H), 7.98 (br s, 1H, N*H*).

Anal. Calcd. for $C_5H_4N_4O_5$: C, 30.01; H, 2.01; N, 28.00; Found: C, 29.87; H, 2.39; N, 26.34. We and others [13,21] have observed problems with low nitrogen analyses from polynitro compounds.

2-Amino-6-chloro-3,5-dinitropyridine **19**.

2-Amino-6-hydroxy-3,5-dinitropyridine **18** (5.0 g, 0.025 mole) was added to a well-stirred mixture of phosphoryl chloride (15 ml, 0.16 mole) and *N,N*-dimethylformamide (1.4 ml) at 20°. The cream-coloured suspension formed was heated to reflux for 45 minutes in an oil bath at 120-130°, rapidly chilled to 20° and poured on ice (50 g). The suspension was stirred until the end of the exothermic hydrolysis of residual phosphoryl chloride, then **19** was isolated by filtration, washed with cold water and dried. A second crop was obtained by addition of water to the filtrate, total yield 4.84 g (89%). Dissolving the product in benzene, filtering the hot solution and pouring the filtrate into petroleum ether afforded a pale yellow precipitate with mp 178-179°. Crystallization from ethyl acetate raised the melting point to 181-182°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 9.40 (br s, 1H, N*H*), 9.03 (s, 1H), 8.76 (br s, 1H, N*H*).

Anal. Calcd. for $C_5H_3N_4O_4Cl$: C, 27.48; H, 1.38; N, 25.64; Cl, 16.22. Found: C, 27.55; H, 1.43; N, 25.5; Cl, 16.3.

2-Amino-6-methylamino-3,5-dinitropyridine **20**.

To a suspension of 2-amino-6-chloro-3,5-dinitropyridine **19** (5.0 g, 0.023 mole) in methanol (50 ml) was added dropwise at 0-5° a mixture of an aqueous solution of methylamine (5.4 ml, 40 vol %, 0.07 mole) and methanol (20 ml). The yellow flocculent precipitate formed was removed by filtration, a second crop was obtained by diluting the filtrate with water. The crude yield was 4.44 g (91%), mp 202-203°. By crystallization from ethanol a fine yellow powder with mp 205-207° was obtained; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.99 (s, 1H), 8.90 (br s, 1H, N*H*), 8.64 (br s, 1H, N*H*), 8.38 (br s, 1H, N*H*), 3.03 (d, 3H, J = 4.8 Hz).

Anal. Calcd. for $C_6H_7N_5O_4$: C, 33.81; H, 3.31; N, 32.86. Found: C, 33.93; H, 3.13; N, 32.50.

2-Amino-6-methoxy-3,5-dinitropyridine **21**.

To a solution of 2-amino-6-chloro-3,5-dinitropyridine **19** (2.19 g, 0.01 mole) in methanol (30 ml) was added at 15° a methanolic solution of sodium methoxide (0.18 *M*, 72 ml, 0.013 mole). After stirring for 24 hours, the pale yellow precipitate was filtered, washed with cold methanol and dried to give 1.30 g (61%) **21**, mp 186° after recrystallization from methanol. The methoxy derivative **21** was also obtained by refluxing the chloropyridine **19** in methanol for a 48 hour period; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 9.11 (br s, 1H, N*H*), 9.01 (s, 1H), 8.70 (br s, 1H, N*H*), 4.04 (s, 3H, CH_3).

Anal. Calcd. for $C_6H_6N_4O_5$: C, 33.65; H, 2.82; N, 26.16; O, 37.36. Found: C, 33.54; H, 2.82; N, 26.09; O, 37.39.

5-Amino-6,8-dinitrotetrazolo[4,5-*a*]pyridine **22b**.

To a stirred solution of 2-amino-6-chloro-3,5-dinitropyridine **19** (3.7 g, 0.017 mole) in acetone (50 ml) was added at 20° a solution of sodium azide (1.7 g, 0.026 mole) in water (15 ml). A deep yellow precipitate was filtrated after 30 minutes, washed with water and dried. Addition of water to the filtrate gave a second crop: the total yield was 3.36 g (88%), mp 150° dec. By careful crystallization from ethanol/water 9:1 - prolonged heating caused transformation into furoxane **23** - fine yellow needles were obtained; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 10.7 (br s, 2H, NH_2), 9.25 (s, C*H* of tetrazole **22b**), 9.01 (s, C*H* of azidopyridine **22a**). The ratio of the isomers **22a:22b** is 1:99 in dimethyl sulfoxide-d_6, 14:86 in acetone-d_6 and 16:84 in acetonitrile-d_3, respectively.

Anal. Calcd. for $C_5H_3N_7O_4$: C, 26.68; H, 1.34; N, 43.55; O, 28.43. Found: C, 27.06; H, 1.47; N, 42.96; O, 28.45.

5-Amino-6-nitro[1,2,5]oxadiazolo[3,4-*b*]pyridine **23**.

A suspension of 5-amino-6,8-dinitrotetrazolo[4,5-*a*]pyridine **22b** (0.4 g, 0.0018 mole) in benzene (50 ml) was heated to reflux during 90 minutes to give a deep red solution. After cooling and addition of petroleum ether, **23** was collected by filtration, washed with petroleum ether and dried, yield 0.33 g (95%). Crystallization from benzene/petroleum ether provided a fine red powder, dec 172-174°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.90 (s, 1H), 8.34 (br s, 2H, NH_2); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 76.8, 107.5, 126.6, 138.0, 155.1, 158.3.

Anal. Calcd. for $C_5H_3N_5O_4$: C, 30.47; H, 1.53; N, 35.53; Found: C, 30.87; H, 1.70; N, 35.0.

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