Picrylamino-substituted Heterocycles. V. Pyridines (1,2)

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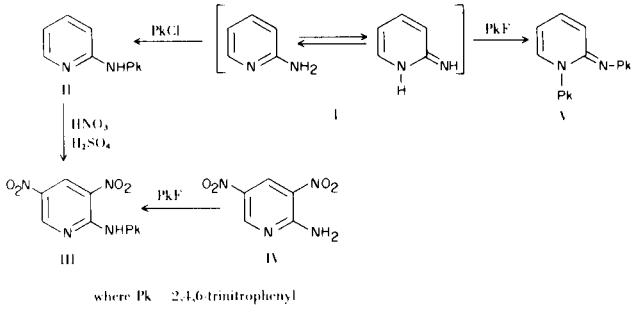
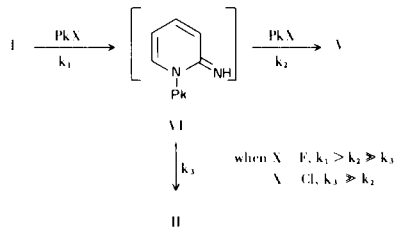
The condensation of various aminopyridines with picryl chloride and picryl fluoride has been investigated as part of our continuing effort in the field of picrylamino-substituted heterocycles. In addition to the expected picrylamino derivatives we obtained the 1-picryl derivatives of the imino forms of some of the amines.

The condensation of 2-aminopyridine (I) with picryl chloride in ethanol gave the known 2-picrylaminopyridine (II) (3), which was nitrated to 3,5-dinitro-2-picrylaminopyridine (III). Compound III was also obtained when 2-amino-3,5-dinitropyridine (IV) (4) was heated with picryl fluoride in DMF. However, I reacted with two molecules of picryl fluoride to give 1-picryl-2-picrylimino-1,2-dihydropyridine (V) as the only product.



The reaction of II with picryl fluoride in DMF also produced V, but this reaction is much slower than the formation of V from I and picryl fluoride. The conversion of II to V with picryl fluoride is only 40% after 24 hours, while that of I to V is complete after 1 hour under the same conditions. We have therefore concluded that II is not an intermediate in the conversion of I to V with picryl fluoride. When picryl fluoride was treated with two molar equivalents to I in DMF, we obtained a mixture of II (60%) and V (40%); with equimolar quantities the product comprised 44% II and 56% V. The possibility that the II obtained in these last two reactions was formed in a reaction of V with the excess I was eliminated when we found that pure V will not react with I under these conditions.

A mechanism consistent with all of these results is that picryl fluoride reacts preferentially with the imino form of I to give 2-imino-1-picryl-1,2-dihydropyridine (VI) as an intermediate. If sufficient picryl fluoride is present, it will react with VI to form V with a rate constant (k_2) slightly less than that of its reaction with I (k_1). If insufficient picryl fluoride is present to convert all the VI to V, then the excess VI may rearrange to II with a rate constant (k_3) much smaller than that of its reaction with picryl fluoride. In the reaction of I with picryl chloride, which is much less reactive than picryl fluoride toward nucleophilic substitution, the same mechanism may be operating except that in this case k_2 is much smaller than k_3 so that II is the only product isolated.



The postulation of VI as an intermediate is supported by the fact that 4-aminopyridine (VII) reacts with picryl chloride in ethanol to give 4-imino-1-picryl-1,4-dihydropyridine hydrochloride (VIII), which is stable because it does not possess the correct geometry for intramolecular rearrangement. Treatment of VII with two molar equivalents of picryl fluoride in DMF produced 1-picryl-4-picrylimino-1,4-dihydropyridine (IX). 4-Amino-3,5-dinitropyridine (X) (5) reacted with two molecules of picryl fluoride in DMF to form 3,5-dinitro-1-picryl-4-picrylimino-1,4-dihydropyridine (XI).

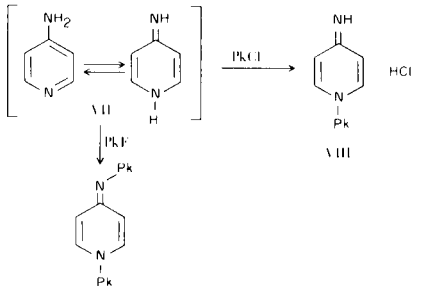
The nature of the rearrangement of VI to II is not presently clear. One possibility is an intramolecular migration of the picryl group from the ring nitrogen to the exocyclic nitrogen through a four-centered transition state. Another possibility is that VI undergoes the Dimroth rearrangement. Studies to determine the mechanism of the rearrangement are in progress.

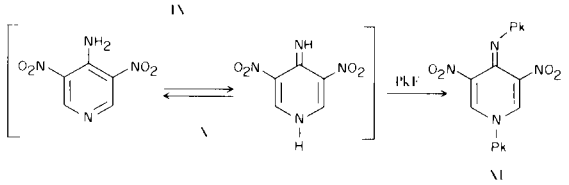
TABLE I

NMR Spectra (a)

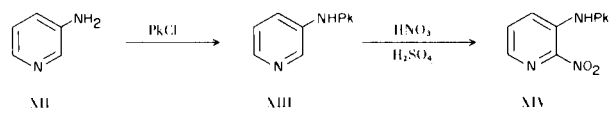
Pyridine	δ C-H (ppm)							
	Picryl Protons			Pyridine Protons				
	1-Picryl	Picrylamino	Picrylimino	C-2	C-3	C-4	C-5	C-6
2-Picrylamino-		9.01			7.28	7.75	7.03	8.05
3-Picrylamino-		9.03		8.43		7.63	7.34	8.43
2,3-bis(Picrylamino)-		9.08, 9.12				7.64	7.03	7.97
2,5-bis(Picrylamino)-		8.97, 9.01			7.27	7.67		7.92
2,6-bis(Picrylamino)-		8.60			6.92	7.71	6.92	
3,5-bis(Picrylamino)-		9.02		8.17		7.47		8.17
1-Picryl-2-picrylimino-1,2-dihydro-	9.37		8.90		6.52	7.67	6.75	7.98
1-Picryl-4-picrylimino-1,4-dihydro-	9.38		9.00	7.86	6.46		6.46	7.86
4-Imino-1-picryl-1,4-dihydro-	9.43			8.52	7.23		7.23	8.52
1-Picryl-3-picrylamino-2-picrylimino-1,2-dihydro-	9.47	8.87	8.85			7.49	6.70	8.00
1-Picryl-3-picrylamino-4-picrylimino-1,4-dihydro-	9.39	8.99	8.99	7.96			6.01	8.14
2-Nitro-3-picrylamino-		9.12				7.83	7.83	8.40
2-Nitro-5-picrylamino-		9.13			8.30	7.78		8.45
3,5-Dinitro-2-picrylamino-		9.17				9.20		9.22
3,5-Dinitro-1-picryl 4-picrylimino-1,4-dihydro-	9.55		9.13	9.42				9.42
2,6-bis(Picrylamino)-4-nitro-		8.87			7.58		7.58	
2,5-bis(Picrylamino)-3,6-dinitro-		9.12, 9.18				8.93		
2,6-bis(Picrylamino)-3,5-dinitro-		8.93				9.23		
3,5-bis(Picrylamino)-2,6-dinitro-		9.07				8.46		

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





3-Aminopyridine (XII), which cannot tautomerize to an imino form, condensed with picryl chloride in DMF to yield 3-picrylaminopyridine (XIII). Nitration of XIII provided a mononitro derivative that is believed to be 2-nitro-3-picrylaminopyridine (XIV) because of the complex splitting of the pyridine protons in its nmr spectrum. In addition to the singlet of the picryl protons at 9.12 δ (2H), the nmr spectrum contained a quartet at 8.40 δ (1H) and a complex multiplet centered at 7.83 δ (2H). Condensation of 5-amino-2-nitropyridine (XV) (6) with picryl fluoride in DMF gave 2-nitro-5-picrylaminopyridine (XVI), which is different from the nitro derivative of XIII.



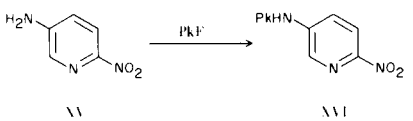


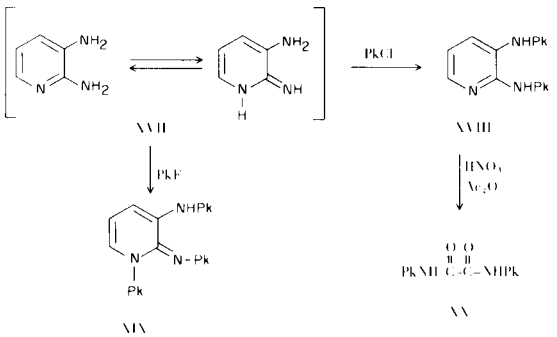
TABLE II

Condensation of the Aminopyridines with Picryl Halides

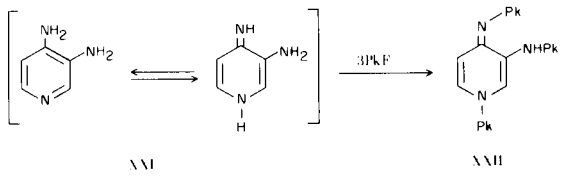
Reactants (moles)	Reaction Solvent (ml.)	Reaction Temp. (°C)	Reaction Time (hours)	Recrystallization Solvent	Product(s) (% yield)	M.p. (°C)
I (0.02), PkCl (0.01)	Ethanol (50)	Reflux	5	Ethanol-water	II (87)	135 (a)
I (0.005), PkF (0.01)	DMF (10)	25	1	Acetone-ethanol	V (94)	223 dec.
I (0.005), PkF (0.005)	DMF (10)	25	1		II (44), V (56)	
I (0.01), PkF (0.005)	DMF (10)	25	1		II (60), V (40)	
II (0.005), PkF (0.01)	DMF (10)	25	24		II (60), V (40)	
VII (0.02), PkCl (0.02)	Ethanol (50)	Reflux	1	None (b)	VIII (83)	220 dec.
VII (0.005), PkF (0.01)	DMF (15)	25	16	Acetone-ethanol	IX (77)	294 dec.
X (0.0025), PkF (0.0054)	DMF (20)	90	24	Acetone-ethanol	XI (80)	267 dec.
XII (0.02), PkCl (0.01)	DMF (20)	25	16	Acetone-ethanol	XIII (80)	173
XV (0.02), PkF (0.02)	DMF (20)	25	16	Acetone-ethanol	XVI (88)	248
XVII (0.01), PkCl (0.022), NaOAc (0.022)	DMF (50)	25	96	Acetone-ethanol	XVIII (60)	218
XVII (0.002), PkF (0.01)	DMF (20)	25	96	Acetone-ethanol	XIX (77)	240 dec.
XXI (0.002), PkF (0.01)	DMF (20)	25	96	Acetone-ethanol	XXII (96)	245 dec.
XXIII (0.01), PkF (0.02)	DMF (20)	25	5	None (c)	XXIV (97)	305 dec.
XXVI (0.01), PkF (0.02)	DMF (50)	25	16	Acetone-ethanol	XXVII (79)	232 dec.
XXX (0.01), PkF (0.02)	DMF (20)	25	16	Acetone-ethanol	XXXI (90)	271 dec.
XXXIV (0.01), PkF (0.02)	DMF (20)	25	16	Acetone-ethanol	XXXV (59)	295 dec.
XXXIX (0.01, PkF (0.03)	DMF (20)	25	16	Acetone-ethanol	XXXX (59)	306 dec.

(a) Lit. (3) m.p. 135°. (b) The product was removed from the reaction mixture by filtration, washed with ethanol and acetone respectively, and dried to give analytically pure material. (c) The solid obtained by diluting the reaction mixture with water was digested in boiling methanol, removed by filtration, and dried to yield analytically pure product.

Treatment of 2,3-diaminopyridine (XVII) with two molar equivalents of picryl chloride in DMF produced 2,3-bis(picrylamino)pyridine (XVIII), while 1-picryl-3-picrylamino-2-picrylimino-1,2-dihydropyridine (XIX) was obtained from the reaction of XVII with three molar equivalents of picryl fluoride in DMF. Compound XVIII was oxidized to *N,N'*-dipicryloxamide (XX) when it was treated with a mixture of nitric acid in acetic anhydride. Attempted nitration of XVIII with mixed acids gave only water soluble products.



3,4-Diaminopyridine (XXI) failed to give a picrylamino derivative when it was treated with picryl chloride in DMF or ethanol; however, it reacted with three molecules of picryl fluoride in DMF to give 1-picryl-3-picrylamino-4-picrylimino-1,4-dihydropyridine (XXII).



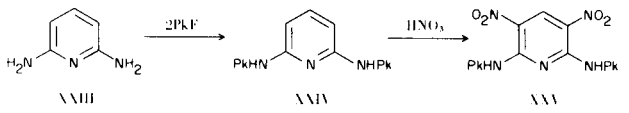
2,6-Diaminopyridine (XXIII) condensed with two molecules of picryl fluoride in DMF to yield 2,6-bis(picrylamino)pyridine (XXIV). When a large excess of picryl fluoride was used we were unable to detect any derivative of the imino form of XXIII in the product. Nitration of XXIV produced 2,6-bis(picrylamino)-3,5-dinitropyridine (XXV).

TABLE III

Elemental Analyses

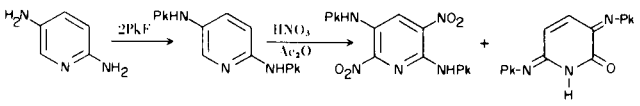
Compound	Molecular Formula	Calculated, % C	H	N	Found, % C	H	N
III	$C_{11}H_5N_7O_{10}$	33.43	1.28	24.81	33.51	1.29	24.95
V	$C_{17}H_8N_8O_{12}$	39.55	1.56	21.70	39.45	1.47	21.81
VIII	$C_{11}H_8ClN_5O_6$	38.66	2.36	20.50	38.76	2.27	20.45
IX	$C_{17}H_8N_8O_{12}$	39.55	1.56	21.70	39.76	1.79	21.26
XI	$C_{17}H_6N_{10}O_{16}$	33.68	0.99	23.09	34.02	0.96	22.53 (a)
XIII	$C_{11}H_7N_5O_6$	43.29	2.31	22.95	43.32	2.18	23.09
XIV	$C_{11}H_6N_6O_8$	37.73	1.73	24.00	37.70	1.66	24.20
XVI	$C_{11}H_6N_6O_8$	37.73	1.73	24.00	37.95	1.60	24.00
XVIII	$C_{17}H_9N_9O_{12}$	38.43	1.71	23.73	38.25	1.53	23.89
XIX	$C_{23}H_{10}N_{12}O_{18}$	37.21	1.36	22.64	36.81	0.98	22.50
XXII	$C_{23}H_{10}N_{12}O_{18}$	37.21	1.36	22.64	37.42	1.61	22.44
XXIV	$C_{17}H_9N_9O_{12}$	38.43	1.71	23.73	38.07	1.96	23.77
XXV	$C_{17}H_7N_{11}O_{16}$	32.86	1.14	24.80	32.60	1.13	25.02
XXVII	$C_{17}H_9N_9O_{12}$	38.43	1.71	23.73	38.36	1.70	23.56
XXVIII	$C_{17}H_7N_{11}O_{16}$	32.86	1.14	24.80	33.11	0.94	24.72
XXIX	$C_{17}H_7N_9O_{13}$	37.45	1.29	23.12	37.15	0.91	23.86
XXXI	$C_{17}H_9N_9O_{12}$	38.43	1.71	23.73	38.54	1.97	23.61
XXXII	$C_{17}H_7N_{11}O_{16}$	32.86	1.14	24.80	32.59	1.41	24.55
XXXV	$C_{17}H_8N_{10}O_{14}$	35.43	1.40	24.30	35.41	1.35	24.18
XXXVII	$C_5H_2Br_2N_4O_4$	17.56	0.59	16.39	17.33	0.78	15.84 (a)
XXXVIII	$C_5H_6N_6O_4$	28.04	2.82	39.25	27.78	3.08	39.67
XXXX	$C_{23}H_{11}N_{13}O_{18}$	36.47	1.46	24.04	36.78	1.53	24.13
XXXXI	$C_{23}H_9N_{15}O_{22}$	32.60	1.07	24.79	32.56	1.03	24.53

(a) Upon reanalysis better analytical data was not obtainable.



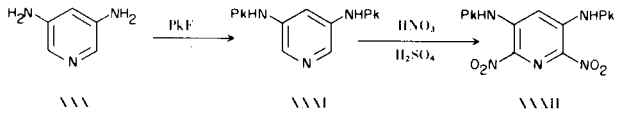
XXIII XXIV XXV

Similar results were obtained with 2,5-diaminopyridine (XXVI) (6). The only product isolated from the reaction of XXVI and an excess of picryl fluoride in DMF was 2,5-bis(picrylamino)pyridine (XXVII). Attempted nitration of XXVII with mixed acids or nitric acid alone gave water-soluble products or unreacted XXVII, depending upon the conditions employed. However, nitration of XXVII with a mixture of nitric acid in acetic anhydride gave a mixture of 2,5-bis(picrylamino)-3,6-dinitropyridine (XXVIII) and an oxidation proudct that we believe is 3,6-bis(picrylimino)-3,6-dihydro-2-pyridone (XXIX). Structure XXIX is consistent with the elemental analysis of the product and its nmr spectrum, which contains a singlet at 9.21 δ (4H) and doublets at 7.70 δ (1H) and 7.35 δ (1H) with J = 10 cps. The infrared spectrum of XXIX contains a carbonyl band at 1725 cm^{-1}.



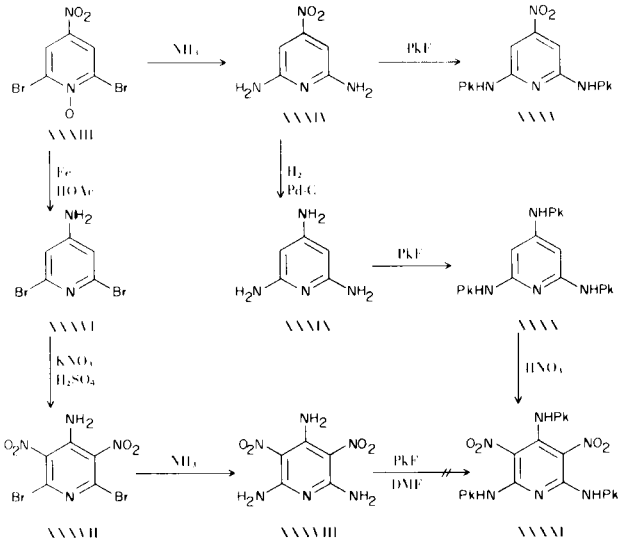
XXVI XXVII XXVIII XXIX

Condensation of 3,5-diaminopyridine (XXX) (7) with picryl fluoride in DMF produced 3,5-bis(picrylamino)-pyridine (XXXI), which was nitrated to 3,5-bis(picrylamino)-2,6-dinitropyridine (XXXII).



XXX XXXI XXXII

2,6-Dibromo-4-nitropyridine-1-oxide (XXXIII) (8) was heated with ethanolic ammonia to give 2,6-diamino-4-nitropyridine (XXIV), which reacted with picryl fluoride in DMF to provide 2,6-bis(picrylamino)-4-nitropyridine (XXXV). 4-Amino-2,6-dibromopyridine (XXXVI), obtained from the reduction of XXXIII (8), was nitrated to 4-amino-2,6-dibromo-3,5-dinitropyridine (XXXVII), which was aminated to 3,5-dinitro-2,4,6-triaminopyridine (XXXVIII); the latter would not react with picryl fluoride in DMF. Hydrogenation of XXIV produced 2,4,6-triaminopyridine (XXXIX), which was treated with picryl fluoride in DMF to yield 2,4,6-tris(picrylamino)-pyridine (XXXX). 3,5-Dinitro-2,4,6-tris(picrylamino)-pyridine (XXXXI) was obtained from the nitration of XXXX.



The structures proposed for the condensation products of the various aminopyridines with picryl chloride and picryl fluoride are based upon the elemental analyses and the nmr spectra of the products (see Table I). The chemical shifts of the aryl protons of the picrylamino and picrylimino groups are generally in the vicinity of 9.0 δ, while those of the 1-picryl groups are around 9.4 δ. Introduction of nitro groups in the pyridine ring generally leads to greater chemical shifts for these protons.

EXPERIMENTAL (9)

Condensation of the Aminopyridines with Picryl Halides.

The appropriate quantities of the reactants and solvent indicated in Table II were mixed and allowed to react under the conditions given in the table. The resulting mixtures were diluted with ten times their volumes of water to precipitate the products, which were collected by filtration, washed with water, dried, and recrystallized from the appropriate solvents. In some instances the precipitates were colloidal, but the addition of a saturated sodium chloride solution caused the precipitates to coagulate. When the product contained more than one compound, the crude material was analyzed by nmr spectroscopy to give the distribution reported. The yields and melting points of the recrystallized products are given in Table II and the elemental analyses of the new compounds prepared in this study are given in Table III.

3,5-Dinitro-2-picrylaminopyridine (III).

(a) 2-Picrylaminopyridine (II) (5.0 g., 0.016 mole) was added to fuming nitric acid (90% nitric acid) (50 ml.) at -20°. The mixture was stirred at 25° for one hour, then it was heated under reflux for two hours. The cooled solution was poured over ice (500 g.) and the precipitated solid was collected by filtration, washed with water, and recrystallized from acetone-ethanol to give 4.3 g. (66%) of III, m.p. 205-206°.

(b) 2-Amino-3,5-dinitropyridine (IV) (0.92 g., 0.005 mole) and picryl fluoride (2.31 g., 0.01 mole) were dissolved in anhydrous DMF (15 ml.). The solution was heated at 90-100° for 6 hours; it was then diluted with water (150 ml.). The solid was removed by filtration, washed with water, and dried to yield 1.5 g., which was found to be a mixture of III (60%) and unreacted IV (40%) by nmr analysis. No attempt was made to resolve the mixture since analytically pure III was obtained by procedure (a).

2-Nitro-3-picrylaminopyridine (XIV).

3-Picrylaminopyridine (XIII) (2.0 g., 0.0065 mole) was added to an ice-cold mixture of fuming nitric acid (90% nitric acid) (20 ml.) and concentrated sulfuric acid (20 ml.). The solution was stirred at 25° for 4 hours, then it was poured over ice (500 g.). The product was collected by filtration, washed with water, and recrystallized from acetone-ethanol to provide 1.36 g. (59%) of XIV, m.p. 184-185°.

Nitration of 2,3-bis(picrylamino)pyridine (XVIII).

To an ice-cold solution of fuming nitric acid (90% nitric acid) (5 ml.) in acetic anhydride (20 ml.) was added XVIII (1.0 g., 0.0019 mole). The solution was stirred at 25° for 24 hours; it was then poured over ice (200 g.) and the resulting mixture was stirred until the acetic anhydride was hydrolyzed. The solid was removed by filtration, washed with water and dried to give 0.82 g. (84%). Recrystallization of the product from acetone-ethanol provided a sample, m.p. 310° dec., that had an infrared spectrum identical with that of authentic *N,N'*-dipicryloxamide (XX) obtained from the nitration of oxanilide (11).

2,6-bis(Picrylamino)-3,5-dinitropyridine (XXV).

2,6-bis(Picrylamino)pyridine (XXIV) (5.3 g., 0.01 mole) was added to fuming nitric acid (90% nitric acid) (50 ml.) at 0-5°. The mixture was stirred at 25° for one hour, heated under reflux for 3 hours, then diluted with concentrated nitric acid (100 ml.) and chilled. The product was collected by filtration, washed respectively with concentrated nitric acid, water, and methanol, then dried at 140°. The yield of pure XXV, which begins to decompose without melting at 350°, was 5.4 g. (87%).

2,5-bis(Picrylamino)-3,6-dinitropyridine (XXVIII) and 3,6-bis-(Picrylimino)-3,6-dihydro-2-pyridone (XXIX).

2,5-bis(Picrylamino)pyridine (XXVII) (2.0 g., 0.0038 mole) was added to an ice-cold solution of fuming nitric acid (90% nitric acid) (10 ml.) in acetic anhydride (40 ml.), and the resulting mixture was stirred at 25-30° for one hour. After the mixture had been chilled to 5°, the solid was removed by filtration, washed with ethanol, and recrystallized from acetone-ethanol to provide 0.27 g. (11.5%) of XXVIII, m.p. 301° dec.

The filtrate was poured over ice (200 g.) and the resulting mixture was stirred until the acetic anhydride had hydrolyzed. The solid was collected by filtration, washed with water, and dried. Recrystallization of the crude material from 1,2-dichloroethane-ethyl acetate provided 1.07 g. (52%) of XXIX, m.p. 266° dec.

3,5-bis(Picrylamino)-2,6-dinitropyridine (XXXII).

To a mixture of fuming nitric acid (90% nitric acid) (20 ml.) and concentrated sulfuric acid (20 ml.) was added 3,5-bis(picrylamino)pyridine (XXXI) (2.0 g., 0.0038 mole) at 0-5°; the solution was allowed to stir at 25° for two hours; it was then poured over ice (400 g.). After the product had been collected by filtration and washed with water, it was recrystallized from acetone-ethanol to yield 0.96 g. (41%) of XXXII, m.p. 311° dec.

2,6-Diamino-4-nitropyridine (XXXIV).

2,6-Dibromo-4-nitropyridine 1-oxide (XXXIII) (3.0 g., 0.01 mole) and a saturated solution of ammonia in ethanol (75 ml.) were heated in an autoclave under nitrogen (2500 psi) at 150° for 16 hours. The dark solution was treated with Norite, filtered, and evaporated to dryness under reduced pressure. The residue was extracted with boiling toluene (150 ml.) and the extract was chilled to -30°. The product that crystallized from the solution was removed by filtration and dried to provide 0.25 g. (16%) of XXXIV, m.p. 185°.

2,4,6-Triaminopyridine (XXXIX).

2,6-Diamino-4-nitropyridine (XXXIV) (2.0 g., 0.013 mole) was hydrogenated in ethanol (50 ml.) over 5% palladium on charcoal under 50 psi of hydrogen for one hour at 25°. The catalyst was removed by filtration and the solution was evaporated to dryness under reduced pressure. The residue was extracted with boiling toluene in a Soxhlet apparatus and the extract chilled to yield 0.80 g. (50%) of XXXIX, m.p. 182-183° [lit. (11) m.p. 185°], after it was collected by filtration and dried.

4-Amino-2,6-dibromo-3,5-dinitropyridine (XXXVII).

4-Amino-2,6-dibromopyridine (XXXVI) (1.26 g., 0.005 mole) was dissolved in concentrated sulfuric acid (5 ml.), and a solution of potassium nitrate (0.50 g., 0.005 mole) in concentrated sulfuric acid (5 ml.) was added at 0-5°. The resulting solution was gradually heated to 85°, and an additional 0.50 g. of potassium nitrate in sulfuric acid (5 ml.) was added. The solution was heated at 85-90° for 0.5 hour, cooled, and poured over ice (200 g.). The precipitate was removed by filtration, washed with water, and dried to give 1.54 g. (90%) of XXVII, m.p. 176-178°.

3,5-Dinitro-2,4,6-triaminopyridine (XXXVIII).

4-Amino-2,6-dibromo-3,5-dinitropyridine (XXXVII) (1.3 g., 0.0038 mole) was heated with a saturated solution of ammonia in ethanol in an autoclave at 80-90° for one hour. The solid that crystallized from the solution was collected by filtration, washed with water, and recrystallized from DMF to yield 0.72 g. (88%) of XXXVIII, m.p. 342° dec.

3,5-Dinitro-2,4,6-tris(picrylamino)pyridine (XXXXI).

2,4,6-tris(Picrylamino)pyridine (XXXX) (1.6 g., 0.0021 mole) was added to fuming nitric acid (90% nitric acid) (20 ml.) at 0-5°. The mixture was gradually heated to reflux and was refluxed for one hour, then poured over ice (200 g.). The precipitate was removed by filtration, washed with water, and recrystallized from acetone-ethanol to give 0.50 g. (28%) of XXXXI, m.p. 276° dec.

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