mide was prepared by the method of Schmerling.[17] It contained 66% *endo* **4b**, 25% *exo* **4b**, and 9% of **5b**. The compositions of the halides were checked by infrared spectra and glpc. The use of a 20% silicone nitrile, XF-1155, on Chromosorb 60–80 mesh permitted the separation of the *exo*- and *endo*-norbornenyl and -nortricyclyl halides.

Characterization of Products.—The reactants were mixed together and sealed in glass ampoules under an atmosphere of prepurified nitrogen. The products were separated by preparative glpc. Their infrared spectra were found to be identical with those of the authentic substances.

Determination of Relative Reactivities.—The relative rate constants were determined by allowing the bromides to compete in pairs for an insufficient amount of tri-*n*-butyltin hydride. The competitors and internal standard were placed in the reaction flask followed by 5 ml of methylcyclohexane and tri-*n*-butyltin hydride. The flask was flushed with nitrogen, stoppered, and kept in a constant-temperature bath at 45° until all of the hydride was consumed as indicated by the disappearance of the Sn–H band at about 1815 cm^{-1}. Analysis for unreacted bromide was made by gas chromatography using a 6-ft column packed with 10% diethylene glycol succinate on Diatoport W (60–80). The method of analysis was the same used by Walling and Helmreich.[18] Results obtained by this method afforded the same relative rates when checked by the more commonly used internal standard method described by Keulemans.[19] The former method involves measuring peak heights of the competitors relative to the peak height of an internal standard before and after the reduction. Relative rate constants were computed by the method of Ingold and Shaw.[20] Relative reactivities of the chlorides were determined by irradiating the reactants in Pyrex tubes maintained at 45° in a constant temperature bath with a G.E. 100-w high-pressure mercury vapor lamp for about 10 hr. Analyses were carried out in the same way. Results are given in Table III.

These runs also served as control studies. It was found that the unreacted halides did not undergo interconversion under the reaction conditions. The hydrocarbons did not undergo interconversion under the reaction conditions, either.

Reduction of Nortricyclyl Bromide (5b) with Triphenyltin Hydride.—To 2 ml (7.69 mole) of triphenyltin hydride in 2 ml of *n*-pentane was added 0.245 ml of **5b** with stirring under a nitrogen atmosphere. The reaction mixture was allowed to stand for 2 days, and the hydrocarbon products were removed at reduced pressure into traps at −78 and −196° in tandem. The products were combined and analyzed by glpc yielding the results shown in Table I. The neat reaction was carried out in the same manner. It was observed to be slightly exothermic. Since triphenyltin hydride adds to norbornene the amount of nortricyclene was determined from the gas chromatogram, and the amount of norbornene was taken to be the difference between this value and the initial amount of hydride used.

(17) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2821 (1956).

(18) C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).

(19) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1957, p 32.

(20) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

The Preparation of Some Pyrido and Pyridyl Derivatives of Phenazine and Quinoxaline[1]

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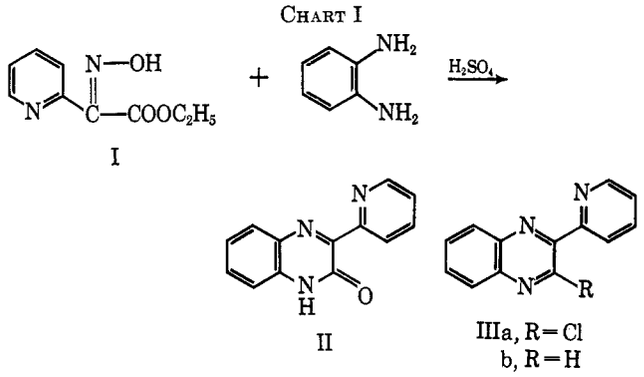
Received May 12, 1966

The Skraup reaction has been used to synthesize several phenazine and quinoxaline derivatives which are expected to form chelates with metal ions. Mono-, di-, tri-, and tetrapyridophenazines were prepared. 2-(2-Pyridyl)quinoxaline has been synthesized as well as some mono- and dipyrido-2- and 3-(2-pyridyl)-quinoxalines. The preparation of some new amino derivatives of phenazine and quinoxaline is described.

Various nitrogen heterocycles having substituent 2-pyridyl groups incorporated in "ferroin" groups[2] have been shown to be effective chelators of the transition elements.[3] In connection with further studies to determine sensitive and selective reagents for the detection of iron(II),[4] we required samples of quinoxaline derivatives that have in common a 2-pyridyl group. Also, pyridophenazines were desired in which the "ferroin" group remains rigid, as in 1,10-phenanthroline, in order to compare the chelating abilities of the pyridylquinoxalines and the pyridophenazines.

Pyridylquinoxalines.—For the synthesis of 2-(2-pyridyl)quinoxaline (IIIb), the three-step route shown in Chart I was employed. Ethyl 2-pyridylglyoxylate oxime (I) was condensed with *o*-phenylenediamine in dilute sulfuric acid at 75° to afford a 40% yield of 2-hydroxy-3-(2-pyridyl)quinoxaline (II). This compound exists almost exclusively in the lactam form.[5] Refluxing II with phosphorus oxychloride produced the 2-chloro derivative IIIa. Dehalogenation of IIIa with hydrogen over palladium gave IIIb in fair yield.

CHART I



The preparation of 2-(2-pyridyl)pyrido(3,2-*h*)quinoxaline (X) is indicated in Chart II. From the condensation of the anil[6] IV with 3-nitro-*o*-phenylenediamine (V) in acetic acid only one of the two possible quinox-

(1) This work was supported by a grant from the Committee on Research and Publications of Temple University.

(2) (a) F. H. Case, "A Review of Syntheses of Organic Compounds Containing the Ferroin Group," G. F. Smith Chemical Co., Columbus, Ohio (1960); (b) F. H. Case and W. A. Butte, *J. Org. Chem.*, **26**, 4415 (1961); (c) F. H. Case, *ibid.*, **27**, 640 (1962); (d) J. F. Geldard and F. Lions, *ibid.*, **30**, 318 (1965); (e) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **81**, 6415 (1959), and references cited therein.

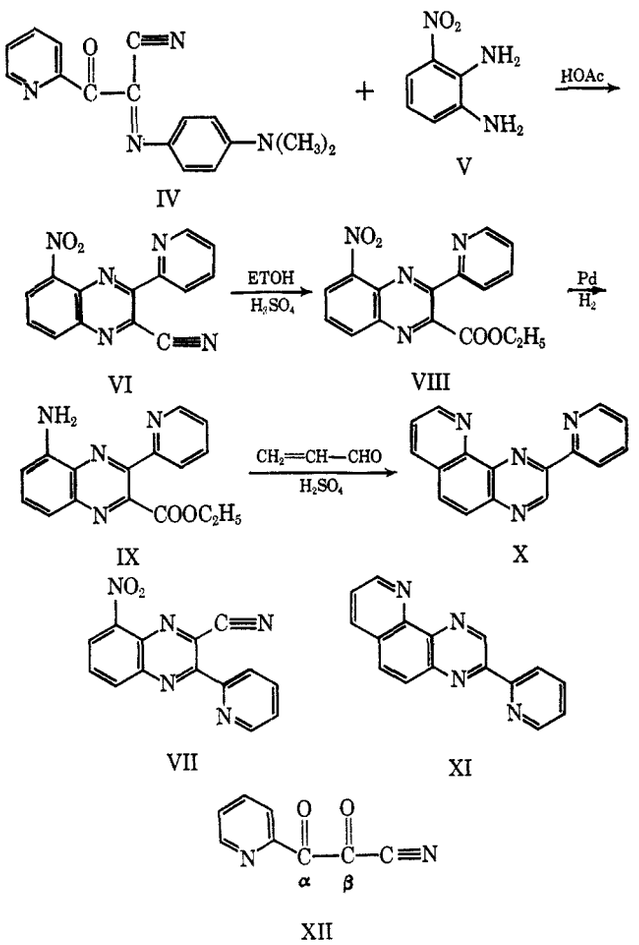
(3) W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

(4) F. H. Case, *J. Org. Chem.*, **30**, 931 (1965).

(5) A. Albert, "Heterocyclic Chemistry," Athlone Press, London, England, 1959, p 186.

(6) F. Krohnke and K. F. Gross, *Chem. Ber.*, **92**, 22 (1959).

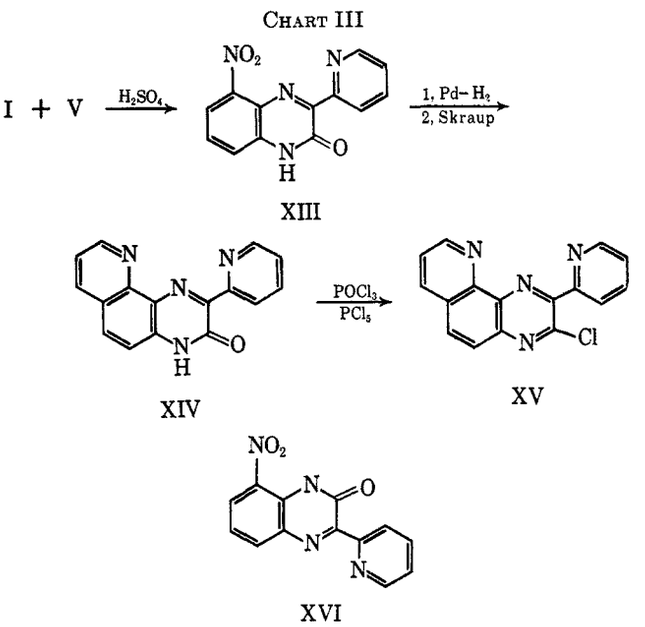
CHART II



alines (VI and VII) was isolated. The product was subsequently shown to be 2-cyano-5-nitro-3-(2-pyridyl)-quinoxaline (VI). Hydrolysis of VI with sulfuric acid in ethanol produced the ethyl ester VIII which was reduced with hydrogen over palladium to the amine IX. Under Skraup conditions IX was converted to X by concomitant cyclization of the amino group to a pyrido ring, hydrolysis of the ester, and decarboxylation of the resultant acid. A spectrophotometric titration[7] of X with ferrous iron solution (see Experimental Section) indicated the formation of a tridentate chelate,[8] which is compatible only with structure X, and not with the isomeric XI. Compound XI would have been produced from VII. Also, since the *meta* amino group of V has been shown to react preferentially with electrophiles[8] and since the β-carbonyl group of the intermediate XII, formed *in situ* from the acetic acid hydrolysis[9] of IV, should be the more electron-deficient carbonyl group,[10] then compound VI most likely results from the initial condensation of the *meta* amino group of V with the β-carbonyl group of XII with subsequent cyclization.

In an attempt to prepare 2-(2-pyridyl)pyrido(2,3-*f*)-quinoxaline (XI), the oxime I and the diamine V were warmed in 50% sulfuric acid, affording XIII as the major product. None of the isomeric XVI could be isolated from the reaction mixture. That XIII was, indeed, the major product from the ambiguous condensation was demonstrated by the reactions shown in Chart III. Compound XV was prepared as indicated with no difficulties. Using the procedure of Albert,[11] XV was condensed with *p*-toluenesulfonylhydrazide and the resulting adduct decomposed with dilute sodium hydroxide in dimethyl sulfoxide. The purified product was identical with X in all respects, *i.e.*, melting point, infrared, and comparison on a thin layer chromatogram. When XV was hydrogenated in tetrahydrofuran over palladium and sodium acetate in an attempt to remove the chlorine atom, thin layer chromatography indicated that at least five products were formed. A small amount of X was separated from the reaction mixture by column chromatography but the major product was a reddish, unstable oil which was not characterized.

CHART III

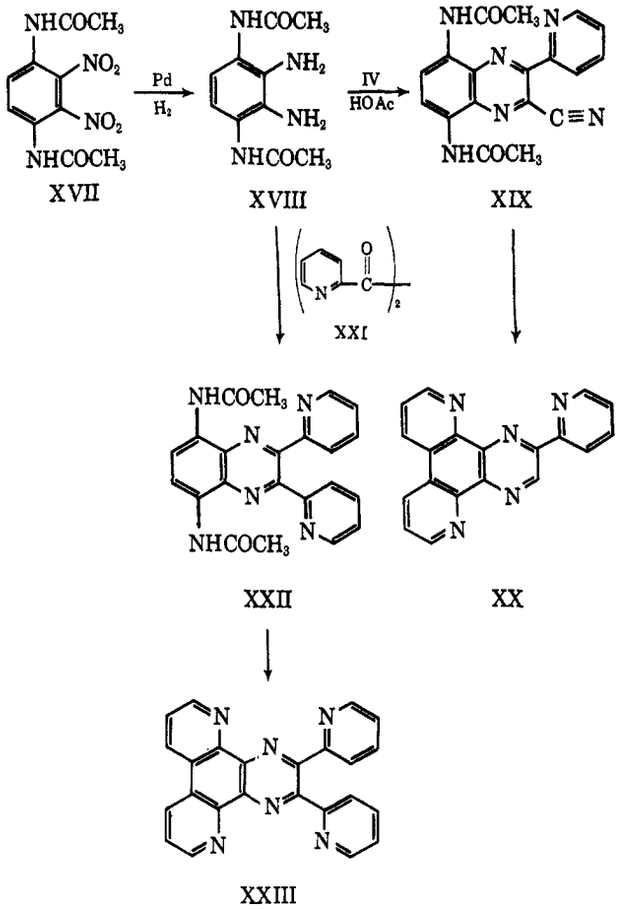


It has been shown[9] that anils, such as IV, are readily hydrolyzed with mineral acids to α-keto acids. As a final attempt at the preparation of the requisite intermediate XVI, the anil IV was heated in 2 *N* hydrochloric acid in the presence of V, but only XIII was obtained. Apparently, at low pH the *meta*-amino group of V is protonated. Then, the *ortho*-amino group of V should be the more nucleophilic center and react preferentially with the keto group of 2-pyridylglyoxylic acid (formed *in situ* from IV). This reasoning might be applied to the condensation of I and V mentioned above.

An improved procedure for the nitration of N,N′-diacetyl-*p*-phenylenediamine provided the key intermediate, N,N′-diacetyl-2,3-dinitro-1,4-phenylenediamine (XVII) in 51% yield. Catalytic reduction of XVII (see Chart IV) afforded the amine XVIII which was caused to react without isolation with IV to produce XIX in 83% yield. The infrared spectrum of XIX showed two distinct amide carbonyl bands at 5.94 and 6.05 μ. A double Skraup reaction on XIX

(7) P. F. Collins, H. Diehl and G. F. Smith, *Anal. Chem.*, **31**, 1862 (1959).
(8) J. Arient and J. Marhan, *Coll. Czech. Chem. Commun.*, **28**, 1292 (1963).
(9) (a) F. Krohnke, *Chem. Ber.*, **80**, 298 (1947); (b) F. Krohnke, *Angew. Chem.*, **65**, 605 (1953).
(10) Perhaps the combined influence of the two "electron sinks," the nitrile group on one side and the 2-pyridoyl group on the other side, accounts for the preferred reactivity of the β-carbonyl group of XII.
(11) A. Albert and R. Royer, *J. Chem. Soc.*, 1148 (1949).

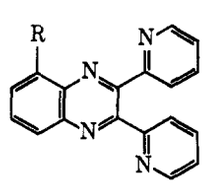
CHART IV



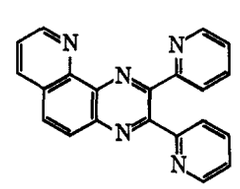
XVII XVIII XIX XXI XXII XX XXIII

(using sodium *m*-nitrobenzenesulfonate, glycerol and sulfuric acid) formed 2-(2-pyridyl)dipyrido(2,3-*f*:3′,2′-*h*)quinoxaline (XX) in 2% yield after chromatography over alumina. When 2,2′-pyridil (XXI) was treated with XVIII in refluxing methanol, there was obtained a 90% yield of XXII. A double ring closure on XXII afforded 2,3-bis(2-pyridyl)dipyrido(2,3-*f*:3′,2′-*h*)-quinoxaline (XXIII) in 60% yield.

Condensation of XXI with 3-nitro- and 3-acetamido-1,2-phenylenediamine in methanol gave XXIVa and XXIVc, respectively. With sulfuric acid and acrolein compound XXIVc was cyclized to 2,3-bis(2-pyridyl)-pyrido(2,3-*f*)quinoxaline (XXV). Catalytic reduction of XXIVa gave the amine XXIVb in quantitative yield.

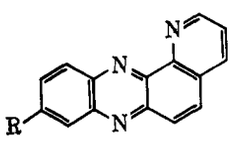


XXIVa, R = NO_2
b, R = NH_2
c, R = $NHCOCH_3$

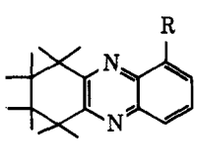


XXV

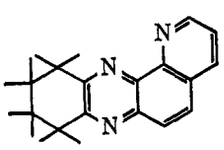
Pyridophenazines.—The preparation of 9-chloropyrido(2,3-*a*)phenazine (XXVIb) has been described.[12] The parent compound, pyrido(2,3-*a*)phenazine (XXVIa) was synthesized in this study by a Skraup reaction on 1-aminophenazine. Pyrido(2,3-*a*)-8,9,10,11-tetrahydrophenazine (XXVIII), the partially reduced derivative of XXVIa, was obtained by first condensing cyclohexane-1,2-dione with 3-acetamido-1,2-phenylenediamine affording XXVIIa in 60% yield. Then, a modified Skraup reaction[13] on XXVIIa with acrolein in 85% phosphoric acid at 100° gave XXVIII. When the ring closure was attempted with sulfuric acid and glycerol at 140°, compound XXVIII was isolated in less than 5% yield. Apparently, the cyclohexyl ring of XXVII is readily oxidized under these conditions.



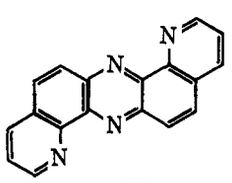
XXVIa, R = H
b, R = Cl



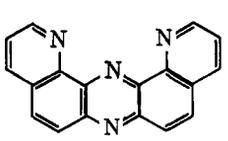
XXVIIa, R = $NHCOCH_3$
b, R = NH_2



XXVIII



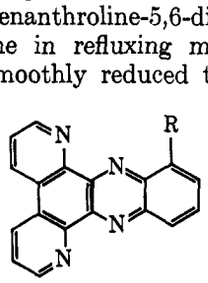
XXIX



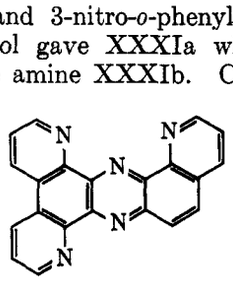
XXX

Nitration of phenazine[14] produces a mixture of 1,6- and 1,9-dinitrophenazine. These dinitro derivatives were reduced to 1,6- and 1,9-diaminophenazine and double Skraup reactions afforded the dipyridophenazines, XXIX and XXX, respectively.

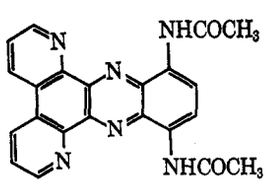
Tripyrido(2,3-*a*:3′,2′-*c*:3″,2″-*j*)phenazine (XXXII) was readily prepared in nearly quantitative yield by condensing 4,7-phenanthroline-5,6-dione[15] and 7,8-diaminoquinoline.[16] As an alternate route to XXXII, 4,7-phenanthroline-5,6-dione and 3-nitro-*o*-phenylenediamine in refluxing methanol gave XXXIa which was smoothly reduced to the amine XXXIb. Com-



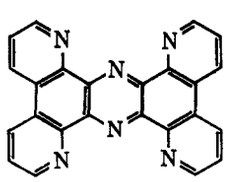
XXXIa, R = NO_2
b, R = NH_2



XXXII



XXXIII



XXXIV

(12) D. L. Vivian, J. L. Hartwell and H. C. Waterman, *J. Org. Chem.*, **19**, 1641 (1954).

(13) H. Yale and J. Bernstein, *J. Am. Chem. Soc.*, **70**, 254 (1928).

(14) (a) S. Maffei and M. Ayman, *Gazz. Chim. Ital.*, **84**, 667 (1954); (b) H. Otomasu, *Chem. and Pharm. Bull. (Japan)*, **6**, 77 (1958); *Chem. Abstr.*, **53**, 8146 (1959).

(15) J. Druey and P. Schmidt, *Helv. Chim. Acta*, **33**, 1080 (1950).

(16) F. Linsker and R. L. Evans, *J. Am. Chem. Soc.*, **68**, 149 (1946).

pound XXXII was obtained from XXXIb in 18% yield by a normal Skraup reaction at 140°.

Goodwin and Lions[2e] suggested that XXXIV, tetrapyrido(2,3-*a*:3′,2′-*c*:2″,3″-*h*:3‴,2‴-*j*)phenazine, if prepared, would be a planar ligand which might form polymeric coordination complexes with appropriate metal ions. The synthesis of XXXIV, a compound not melting below 500°, has been accomplished in the following manner. Warming the amine XVIII and 4,7-phenanthroline-5,6-dione in methanol for 15 min formed the bright red XXXIII in about 90% yield. Then, with sulfuric acid, glycerol and *m*-nitrobenzenesulfonic acid, the highly insoluble XXXIV was obtained in 60% yield after exhaustive extraction of the crude reaction product with chloroform. Both XXXIII and XXXIV form very stable hydrates; anhydrous XXXIII is a bright orange solid which immediately forms a bright red monohydrate on exposure to air, while XXXIV can be adequately dried only by prolonged heating at about 200°.

Experimental Section[17]

2-Hydroxy-3-(2-pyridyl)quinoxaline (II).—A solution of 1.84 g (0.01 mole) of ethyl 2-pyridylglyoxylate oxime (I) (Aldrich Chemical Co.), 1.08 g (0.01 mole) of *o*-phenylenediamine and 35 ml of 35% sulfuric acid was stirred at 70–75° for 3.5 hr. The mixture was poured into ice–water and adjusted to pH 8 with ammonium hydroxide solution. On cooling there was obtained 0.9 g (40%) of tan II, mp *ca.* 215°. Crystallization from aqueous ethanol (Darco) gave yellow feathers: mp 226–228°; λ_{max}^{EtOH} 224 mμ (ε 21,600), 305 (9,600), 364 (8,600); λ_{max}^{Nujol} 2.81 and 6.02 μ.

Anal. Calcd for $C_{13}H_9N_3O$: C, 69.94; H, 4.06; N, 18.82. Found: C, 69.89; H, 4.12; N, 18.88.

2-Chloro-3-(2-pyridyl)quinoxaline (IIIa).—A suspension of 3.8 g of II in 150 ml of phosphorus oxychloride was stirred and refluxed for 4 hr. The initial bright orange, flocculent suspension was transformed gradually into a pale yellow suspension. Excess phosphorus oxychloride was removed *in vacuo*, ice added to the residue and the product precipitated with 40% sodium hydroxide solution. The white solid, mp 113–115°, was recrystallized from aqueous ethanol (Darco) affording 2.1 g (51%) of pure IIIa, mp 115–117°. Sublimation at 90° (1 mm) gave the analytical sample: λ_{max}^{EtOH} 244 mμ (ε 47,200), 328 (12,800).

Anal. Calcd for $C_{13}H_8ClN_3$: C, 64.61; H, 3.34; N, 17.39. Found: C, 64.68; H, 3.43; N, 17.32.

2-(2-Pyridyl)quinoxaline (IIIb).—Using a Parr hydrogenator, a mixture of 1.0 g of IIIa, 1.0 g of 5% palladium on charcoal, 120 ml of tetrahydrofuran, and a solution of 0.75 g of potassium hydroxide in 15 ml of water was agitated at an initial pressure of 50 psi. The reduction was stopped after 1 hr, filtered through Supercel and the filtrate concentrated *in vacuo*. The residue was partitioned between benzene and water and the organic layer was separated, washed with water, dried (sodium sulfate) and evaporated to give an oily solid (0.9 g). This material was dissolved in 1:1 benzene–petroleum ether and added to a column of 17.5 g of alumina. Elution with 1:1 benzene–petroleum ether gave yellow, crystalline IIIb (0.2 g or 24%), which was recrystallized from hexane, mp 112–114°. The analytical sample was sublimed at 90° (1 mm) as a buff-colored solid: mp 116–118°; λ_{max}^{EtOH} 250 mμ (ε 26,700), 275 (14,300), 332 (12,400).

Anal. Calcd for $C_{13}H_9N_3$: C, 75.34; H, 4.38; N, 20.28. Found: C, 75.47; H, 4.32; N, 20.27.

2-Cyano-5-nitro-3-(2-pyridyl)quinoxaline (VI).—In 250 ml of 80% acetic acid were dissolved 9.6 g (0.064 mole) of 3-nitro-1,2-phenylenediamine[18] and 16.7 g (0.06 mole) of N-(2-pyridoylglyoxylonitrile)-*p*-dimethylaminoaniline[6] (IV) and the solution was stirred at room temperature for 2 hr, then warmed to 50° for 10 min. Addition of 750 ml of ice–water gave 12.6 g (76%) of maroon brown solid, mp 200–205°. Recrystallization from acetic acid, then from a large volume of methanol gave pure VI as tan crystals: mp 237–239°; λ_{max}^{EtOH} 244 mμ (ε 33,700), 283 (18,400), 350 (8,100); λ_{max}^{Nujol} 6.54 and 7.31 μ.

Anal. Calcd for $C_{14}H_7N_5O_2$: C, 60.65; H, 2.54; N, 25.26. Found: C, 60.54; H, 2.67; N, 25.21.

2-Carbethoxy-5-nitro-3-(2-pyridyl)quinoxaline (VIII).—A solution of 6.1 g of VI, 150 ml of absolute ethanol and 12 ml of sulfuric acid was heated on a steam bath for 6 hr, poured on 500 g of ice and basified with ammonium hydroxide solution. The brown solid was collected and crystallized from ethanol (Darco) to yield 3.7 g (52%) of VIII, mp 128–131°. Two more recrystallizations gave golden needles: mp 140–141°; λ_{max}^{Nujol} 5.80, 6.56, 7.31 and 8.68 μ.

Anal. Calcd for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.73, N, 17.28. Found: C, 59.65; H, 3.86; N, 16.95.

5-Amino-2-carbethoxy-3-(2-pyridyl)quinoxaline (IX).—A suspension of 500 mg of VIII, 300 mg of 10% Pd–C, and 100 ml of ethanol was reduced in the Parr hydrogenator at 50 psi. After 20 min the mixture was filtered and the filtrate evaporated under reduced pressure to a reddish syrup. Crystallization from absolute ethanol gave 350 mg (77%) of IX as orange crystals, mp 151–153°. The analytical sample was obtained after two additional recrystallizations from ethanol: mp 158–160°; λ_{max}^{EtOH} 229 mμ (ε 21,200), 299 (40,600); λ_{max}^{Nujol} 2.80, 2.89, 5.80 and 8.60 μ.

Anal. Calcd for $C_{16}H_{14}N_4O_2$: C, 65.29; H, 4.79; N, 19.04. Found: C, 65.28; H, 4.86; N, 18.72.

2-(2-Pyridyl)pyrido(3,2-*h*)quinoxaline (X). Method A.—5-Amino-2-carbethoxy-3-(2-pyridyl)quinoxaline (IX) (2.0 g), 30 ml of sulfuric acid, 2.0 g of sodium *m*-nitrobenzenesulfonate, 10 ml of water, and 10 ml of glycerol were heated at 135–140° for 3 hr. With cooling the dark reaction mixture was basified with 40% sodium hydroxide solution and the tarry precipitate was filtered and dried. Extraction of the crude product with chloroform (Soxhlet) provided 200 mg of tan solid which was chromatographed over 8 g of alumina, using chloroform as the eluent. The homogeneous fractions were crystallized from acetonitrile yielding 75 mg (4.3%) of buff X, mp 166–168°. A sublimation at 150° (1 mm) gave a white solid, mp 169–170°. A final crystallization from acetonitrile afforded white crystals: mp 170–171°; λ_{max}^{EtOH} 223 mμ (ε 36,000), 296 (31,000), 345 (10,000), 363 (8,960).

Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.69. Found: C, 74.19; H, 3.81; N, 21.49.

Method B.—2-Chloro-3-(2-pyridyl)pyrido(2,3-*f*)quinoxaline (XV) (200 mg), 150 mg of *p*-toluenesulfonylhydrazide[11] and 50 ml of benzene were refluxed for 2 hr. A reddish yellow precipitate forming during the reaction. Complete precipitation of the product was accomplished by the addition of an equal volume of petroleum ether and chilling. The crude hydrazide was warmed on the steam bath for 1.5 hr with 40 ml of dimethyl sulfoxide and 1 ml of 10% sodium hydroxide solution. After quenching the reaction with water, the aqueous layer was extracted with chloroform, and the extracts were washed with water, dried (sodium sulfate) and evaporated at reduced pressure to give 75 mg of crude X. Thin layer chromatography (tlc) on silica gel (eluting with 10:1 ethyl acetate–methanol) showed no XV to be present. A sublimation at 175° (1 mm), then a crystallization from acetonitrile gave 22 mg (12.5%) of X, mp 165–167°. A mixture melting point with the material prepared by method A showed no depression and the infrared spectra were superimposable. Also, tlc on alumina (using 6:1 ethyl acetate–methanol) exhibited identical R_f values for the compounds obtained from methods A and B.

Method C.—A mixture of 100 mg of XV, 100 mg of 10% palladium on carbon, 200 mg of sodium acetate and 80 ml of tetrahydrofuran was hydrogenated (50 psi) in the Parr apparatus for 1 hr. The crude product obtained after work-up contained three major and two minor components (tlc on alumina and silica gel with systems used above). By column chromatography were separated a red oil (eluted with petroleum ether–benzene mix-

(17) Melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord and ultraviolet spectra on a Cary Model 14 spectrophotometer. All column chromatographs were performed with Woelm neutral alumina, activity III. "Petroleum ether" refers to solvent of bp 30–60°. Microanalyses were performed by Miss Margaret Carroll and co-workers of the Analytical and Physical, Chemistry Section, Smith, Kline and French Laboratories, Philadelphia, Pa., and by Micro-Tech Laboratories, Skokie, Ill.

(18) (a) J. L. Rabinowitz and E. C. Wagner, *J. Am. Chem. Soc.*, **78**, 3030 (1951); (b) E. C. Fisher and M. M. Joullié, *J. Org. Chem.*, **23**, 1944 (1958).

tures) and a small amount of impure X (eluted with chloroform).

2-Hydroxy-5-nitro-3-(2-pyridyl)quinoxaline (XIII). Method A.—To a solution of 9.6 g (0.064 mole) of V in 300 ml of 50% sulfuric acid was added 11.1 g (0.06 mole) of the oxime I. The solution was stirred at 60–65° for 2 hr, poured on ice, and basified with ammonium hydroxide solution. The voluminous, reddish precipitate was filtered, washed with water, and dried yielding 9.1 g (57%), mp *ca.* 180°; tlc on silica gel (3:1 ethyl acetate–methanol) indicated one major and one small component. Several crystallizations from ethanol afforded pure XIII: mp 216–218°; λ_{max}^{EtOH} 237 mμ (ε 22,800), 300 (9,000), 363 (11,100); λ_{max}^{Nujol} 6.02, 6.60 and 7.35 μ.

Anal. Calcd for $C_{13}H_8N_4O_3$: C, 58.21; H, 3.01; N, 20.89. Found: C, 58.34; H, 3.25; N, 21.07.

Method B.—A solution of 0.93 g (3 mmoles) of the anil IV, 0.5 g (3 mmole) of 3-nitro-1,2-phenylenediamine and 125 ml of 2 *N* hydrochloric acid was heated at 95° for 1 hr and cooled and the product precipitated with ammonium hydroxide solution. The crude XIII (150 mg, 18.6%), mp 209–211°, was crystallized from aqueous methanol, then from methanol, mp 213–215°. A mixture melting point with the material prepared by method A showed no depression. The infrared spectra of both samples were identical.

2-Hydroxy-3-(2-pyridyl)pyrido(2,3-*f*)quinoxaline (XIV).—Finely ground XIII (6.0 g, 0.022 mole) was suspended in 500 ml of methanol (in two 500-ml Parr pressure bottles) and reduced over 1.5 g of 10% Pd–C (initial hydrogen pressure of 50 psi). The reductions were stopped after 1.5 hr, the liquid, was filtered through Supercel, and the filtrate was concentrated *in vacuo*. The crude amine was dissolved in a cold solution of 50 ml of sulfuric acid and 16 ml of water, added all at once to 5.7 g of sodium *m*-nitrobenzenesulfonate and 12 ml of glycerol and heated at 130–140° for 3 hr. Neutralization of the reaction mixture, then extraction of the basic solids with chloroform provided 2.0 g of syrup which was chromatographed over 60 g of alumina. The column was eluted with 1:1 benzene–chloroform to remove some oily material, then with 3% methanol in chloroform to afford a yellowish solid. Crystallization from aqueous methanol gave 380 mg (6.2%) of XIV as a pale yellow solid, mp 214–216°. The analytical sample had mp 215–217°; λ_{max}^{EtOH} 242 mμ (ε 41,000), 303 (18,500), 381 (16,000); λ_{max}^{Nujol} 2.99 and 6.03 μ.

Anal. Calcd for $C_{16}H_{10}N_4O$: C, 70.06; H, 3.67; N, 20.43. Found: C, 69.88; H, 3.61; N, 20.08.

2-Chloro-3-(2-pyridyl)pyrido(2,3-*f*)quinoxaline (XV).—A vigorously stirred suspension of 350 mg of XIV, 50 ml of phosphorus oxychloride and 0.5 g of phosphorus pentachloride was refluxed for 10 hr. Gradually, the solid dissolved and the clear, tan solution was concentrated on a rotary evaporator to a dark green syrup. Ice (100 g) was added and the product was precipitated by neutralization with ammonium hydroxide solution. The voluminous, white precipitate was filtered, washed well with water and dried. A crystallization from aqueous methanol (Darco) yielded 250 mg (64%) of XV as buff feathers, mp 223–225°. The pure product was obtained by a recrystallization from aqueous ethanol: mp 226–227°; λ_{max}^{EtOH} 228 mμ (ε 32,200), 274 (18,400), 301 (24,700), 355 (9000).

Anal. Calcd for $C_{16}H_9ClN_4$: C, 65.65; H, 3.10; N, 19.14. Found: C, 65.73; H, 3.20; N, 18.97.

N,N′-Diacetyl-2,3-dinitro-1,4-phenylenediamine (XVII).—Practical grade 1,4-phenylenediamine was acetylated by dissolving 108 g (1 mole) in 500 ml of pyridine and slowly adding 200 ml of acetic anhydride. The reaction is exothermic and no attempt was made to cool the mixture. After all the acetic anhydride had been added, the hot suspension (product precipitates) was allowed to stand for 0.5 hr, poured into 2.5 l. of ice–water and filtered. There was isolated 185 g (96.5%) of N,N′-diacetyl-1,4-phenylenediamine, mp 312–315° (lit.[19] mp 310–312°).

The following is an improved procedure[20] for the preparation of XVII. To a solution of 2 l. of glacial acetic acid and 300 ml of red fuming nitric acid (*d* 1.60) cooled to 20° was added in small portions 225 g of N,N′-diacetyl-1,4-phenylenediamine. Then the temperature of the stirred solution was slowly raised to 35–40° and held at that temperature for 3 hr. After about 1.5 hr a solid began to precipitate. The mixture was cooled to 0° overnight and the yellow solid filtered, washed with ice–water, and dried. The product weighed 127.6 g, mp 254–256°. The filtrate was diluted with an equal volume of water (total of 4.6 l. of filtrate) and cooled. Filtration gave an additional 38.7 g of XVII, mp 255–257°. The total yield was 166.3 g (50.5%). A crystallization from dimethylformamide–ether raised the melting point to 260–261° (lit.[20] mp 258°).

Anal. Calcd for $C_{10}H_{10}N_4O_6$: C, 42.56; H, 3.57; N, 19.85. Found: C, 42.69; H, 3.84; N, 19.71.

When N,N′-diacetyl-1,4-phenylenediamine was nitrated according to the reported procedure,[20] only the mononitro derivative could be isolated. Nitration of the mononitro derivative according to the procedure indicated above gave a good yield of XVII.

5,8-Diacetamido-2-cyano-3-(2-pyridyl)quinoxaline (XIX).—A mixture of 4.23 g (0.015 mole) of XVII, 1.0 g of 10% Pd–C, and 250 ml of methanol was reduced in the Parr apparatus at 50 psi of hydrogen pressure. After 15 min the theoretical amount of hydrogen had been absorbed and the mixture was filtered through Supercel. The filter cake was washed with about 150 ml of methanol. To the filtrate was added 3.45 g (0.0124 mole) of the anil IV and 100 ml of acetic acid. The solution was slowly concentrated on a rotary evaporator to one-third of the original volume. A yellow-red solid appeared after a short time. The suspension was diluted with two volumes of water and chilled, and the solid was collected by filtration. The russet brown compound (3.55 g, 83%) had mp 303–305°. Two crystallizations from dimethylformamide gave pure XIX as a yellowish solid: mp 316–318°; λ_{max}^{Nujol} 2.91, 5.94 and 6.05 μ.

Anal. Calcd for $C_{18}H_{14}N_6O_2$: C, 62.42; H, 4.07; N, 24.27. Found: C, 62.52; H, 4.31; N, 24.00.

2-(2-Pyridyl)dipyrido(2,3-*f*:3′,2′-*h*)quinoxaline (XX).—The procedure for this preparation was entirely similar to that for X (method A). From 11.75 g of XIX, 16 g of sodium *m*-nitrobenzenesulfonate, 45 ml of sulfuric acid, 15 ml of water, and 25 ml of glycerol, there was obtained 2.8 g of an orange syrup which was chromatographed over 100 g of alumina. Elution with benzene and increasing concentrations of chloroform in benzene removed some dark impurities. A tan solid (300 mg), which was eluted with chloroform, was crystallized from dimethylformamide giving 200 mg (1.9%) of XX, mp 275–278°. Another crystallization afforded buff crystals: mp 280–282°; λ_{max}^{EtOH} 228 mμ (ε 27,000), 258 (40,500), 314 (22,300). The analytical sample was dried at 140° (1 mm) for 24 hr.

Anal. Calcd for $C_{19}H_{11}N_5$: C, 73.77; H, 3.58; N, 22.64. Found: C, 73.42; H, 3.94; N, 22.26.

5,8-Diacetamido-2,3-bis(2-pyridyl)quinoxaline (XXII).—The reduction of 8.46 g (0.03 mole) of N,N′-diacetyl-2,3-dinitro-1,4-phenylenediamine (XVII) in 250 ml of methanol with 1.5 g of 5% Pd–C was entirely similar to the procedure used in the preparation of XIX. To the filtrate containing the crude XVIII was added 5.73 g (0.027 mole) of 2,2′-pyridil (XXI) in 200 ml of methanol. After refluxing for 2 hr, the mixture was concentrated to one-third of the original volume and the voluminous yellow precipitate was separated by filtration to provide nearly pure XXII (9.8 g, 90%), mp 289–291°. The analytical sample was obtained as yellow crystals from ethanol: mp 292–294°; λ_{max}^{Nujol} 2.92 and 5.97 μ.

Anal. Calcd for $C_{22}H_{18}N_6O_2$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.28; H, 4.64; N, 21.19.

2,3-Bis(2-pyridyl)dipyrido(2,3-*f*:3′,2′-*h*)quinoxaline (XXIII).—The usual Skraup conditions (see procedure for preparation of XX) on 5.0 g of XXII, 50 ml of sulfuric acid, 15 ml of water and 10 ml of glycerol, and subsequent work-up gave the crude product (3.2 g). Crystallization from dimethylformamide yielded 2.4 g (49.5%) of XXIII as golden needles, mp *ca.* 370°. An analytical sample, crystallized from the same solvent, melted at 374–376°: λ_{max}^{MeOH} 219 mμ (ε 31,100), 263 (45,400), 316 (26,500). The compound tenaciously retains water of hydration and was dried for analysis at 140° (1 mm) for 24 hr over phosphorus pentoxide.

Anal. Calcd for $C_{24}H_{14}N_6 \cdot 0.25\ H_2O$: C, 73.72; H, 3.61; N, 21.50. Found: C, 73.84; H, 3.97; N, 21.76.

5-Nitro-2,3-bis(2-pyridyl)quinoxaline (XXIVa).—A solution of 3.46 g (0.016 mole) of 2,2′-pyridil (XXI), 2.5 g of (0.016 mole) of 3-nitro-1,2-phenylenediamine and 150 ml of methanol was refluxed for 2 hr. The solvent was removed under reduced pressure and the residue crystallized from ethanol. There was obtained 4.6 g (85%) of XXIVa, mp 192–194°. The pure material is an orange solid (from ethanol), mp 198–200°.

(19) J. Burns, *et al.*, *J. Chem. Soc.*, 2928 (1928).
(20) R. Biedermann and H. Romer, *Ber.*, **7**, 1531 (1874).

Anal. Calcd for $C_{18}H_{11}N_5O_2$: C, 65.65; H, 3.37; N, 21.27. Found: C, 65.43; H, 3.50; N, 21.52.

5-Amino-2,3-bis(2-pyridyl)quinoxaline (XXIVb).—5-Nitro-2,3-bis(2-pyridyl)quinoxaline (XXIVa) (1.2 g) in methanol was reduced by hydrogen over Pd–C to yield the crude amine (0.9 g), mp *ca.* 150°. Crystallization from ethanol gave long, orange needles, mp 157–159°.

Anal. Calcd for $C_{18}H_{13}N_5$: C, 72.22; H, 4.38; N, 23.40. Found: C, 72.33; H, 4.43; N, 23.19.

5-Acetamido-2,3-bis(2-pyridyl)quinoxaline (XXIVc).—Reduction of 5.65 g (0.025 mole) of 2,3-dinitroacetanilide[21] by hydrogen over 1.0 g of 5% Pd–C in 250 ml of tetrahydrofuran in the Parr hydrogenator (at 50 psi) was complete in 0.5 hr. The suspension was filtered with the aid of additional tetrahydrofuran. To the filtrate was added a solution of 5.3 g (0.025 mole) of 2,2′-pyridil (XXI) in 80 ml of methanol. The solution was slowly concentrated on a rotary evaporator to about 75 ml over a period of one hour. On cooling pale yellow crystals separated (6.1 g, 72%), mp 184–186°. Two crystallizations from ethanol gave pure XXIVc as yellow feathers, mp 186–188°.

Anal. Calcd for $C_{20}H_{15}N_5O$: C, 70.37; H, 4.43; N, 20.52. Found: C, 70.17; H, 4.51; N, 20.44.

2,3-bis(2-Pyridyl)pyrido(2,3-*f*)quinoxaline (XXV).—Following the procedure used in the preparation of X (method A), from 3.41 g of XXIVc, 4.0 g of sodium *m*-nitrobenzenesulfonate, 15 ml of sulfuric acid, 5 ml of water, and 8.0 ml of glycerol there was obtained 900 mg (27%) of crude product. Crystallization from a small volume of acetone, mp *ca.* 175°, sublimation at 170° (1 mm) and a final crystallization from chloroform–petroleum ether yielded a cream-colored solid: mp 184–186°; λ_{max}^{EtOH} 242 mμ (ε 30,400), 292 (36,100), 346 (8,800), 363 (8,400).

Anal. Calcd for $C_{21}H_{13}N_5$: C, 75.21; H, 3.91; N, 20.88. Found: C, 75.05; H, 3.94; N, 20.92.

Pyrido(2,3-*a*)phenazine (XXVIa).—According to the procedure of Hegedus,[22] from 7.0 g of 2,6,2′-trinitrodiphenylamine, there was isolated 1.8 g (40%) of 1-aminophenazine, mp 177–179° (lit. mp 178–180°).

A mixture of 1.1 g of 1-aminophenazine, 0.9 g of sodium *m*-nitrobenzenesulfonate, 12 ml of sulfuric acid, 4 ml of water and 2 ml of glycerol was heated at 135–140° for 3 hr. The usual work-up and extraction of the basic solids with chloroform (Soxhlet) yielded 400 mg of crude product. Chromatography over 20 g of alumina (using chloroform as the eluent) gave 220 mg (17%), mp 159–162°, of pale yellow XXVIa. Sublimation at 150° (1 mm) followed by crystallization from acetone afforded the analytical sample: mp 172–174°; λ_{max}^{EtOH} 294 mμ (ε 34,000), 268 (27,000), 370 (7,900).

Anal. Calcd for $C_{15}H_9N_3$: C, 77.91; H, 3.92; N, 18.17. Found: C, 77.94; H, 3.91; N, 18.24.

1-Acetamido-6,7,8,9-tetrahydrophenazine (XXVIIa).—Reduction by hydrogen of 15.0 g (0.067 mole) of 2,3-dinitroacetanilide in 300 ml of tetrahydrofuran with 1.5 g of 5% Pd–C was performed according to the procedure used in the preparation of XXIVc. To the filtrate containing 3-acetamido-1,2-phenylenediamine was added a solution of 6.73 g (0.06 mole) of cyclohexane-1,2-dione (K and K Laboratories) in 30 ml of tetrahydrofuran and a solution of 6.0 g of sodium acetate, 30 ml of water, and 40 ml of acetic acid. The solution was boiled in an open flask on the steam bath. Most of the tetrahydrofuran had distilled out in 1 hr and the dark solution was diluted with 1 l. of water. Chilling and filtering gave a tan solid (8.3 g, 57.5%), mp 185–192°. Crystallization from ethanol yielded 6.6 g of pale yellow feathers, mp 194–196°. The analytical sample (from ethanol) had mp 196–198°, λ_{max}^{Nujol} 2.93 and 5.97 μ.

Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.99; H, 6.32; N, 17.44.

1-Amino-6,7,8,9-tetrahydrophenazine (XXVIIb).—A solution of 0.5 g of XXVIIa in 10 ml of acetic acid and 10 ml of concentrated hydrochloric acid was heated on the steam bath for 1 hr, poured on ice, and basified with ammonium hydroxide solution. The yellowish precipitate was filtered, washed with water, and dried, to provide 450 mg (91.5%) of XXVIIb, mp 175–185°. Several crystallizations from ethanol gave the analytical sample as yellow needles: mp 197–199°; λ_{max}^{EtOH} 238 mμ (ε 8,500), 272 (32,400), 326 (2,600); λ_{max}^{Nujol} 2.87, 2.99, 3.10 and 6.18 μ.

Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.58; N, 21.09. Found: C, 72.23; H, 6.84; N, 21.10.

8,9,10,11-Tetrahydropyrido(2,3-*a*)phenazine (XXVIII).—A mixture of 3.4 g (0.014 mole) of XXVIIa, 6.35 g (0.028 mole) of sodium *m*-nitrobenzenesulfonate, and 35 ml of 85% phosphoric acid was slowly heated to 100° for 45 min. Then 1.2 g (1.43 ml., 0.02 mole) of acrolein was added dropwise at 100° during 10 min. After 15 min an additional 0.8 ml of acrolein was added and the temperature was maintained at 100° for 0.5 hr longer. Ice–water was added, the mixture was made alkaline with ammonium hydroxide solution, and the solid was filtered, dried, pulverized and extracted in a Soxhlet apparatus with chloroform. Crystallization of the oily extracts from benzene–petroleum ether gave 300 mg (9.1%) of tan needles, mp 173–175°. A recrystallization from a small volume of 50% aqueous ethanol afforded pure XXVIII: mp 175–177°; λ_{max}^{EtOH} 225 mμ (ε 52,940), 279 (29,600), 336 (5,900), 352 (5,700).

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.33; H, 5.47; N, 17.69.

Dipyrido(2,3-*a*:2′,3′-*h*)phenazine (XXIX).—The method of Otomasu[14b] for the nitration of phenazine was followed. The resulting 1,6-dinitrophenazine had mp 338–339° (lit. mp 343°). In each of four 500-ml Parr pressure bottles were placed 3.1 g of 1,6-dinitrophenazine, 0.75 g of 10% Pd–C and 300 ml of tetrahydrofuran. The mixtures were reduced in a Parr apparatus at 50 psi of hydrogen. Reduction was complete in 10–15 min and the warmed mixtures were filtered through Supercel. The filter cake was washed with tetrahydrofuran until the filtrate was pale pink. Evaporation *in vacuo* of the combined filtrates gave crude 1,6-diaminophenazine (8.0 g, 83%), mp *ca.* 255° (lit.[14b] mp 265°). The crude diamine (8.0 g, 0.038 mole) was dissolved in 75 ml of sulfuric acid and added to a mixture of 12 g of arsenic pentoxide, 20 ml of water, and 19.5 ml (0.264 mole) of glycerol. The temperature was slowly raised to 140–145° and held there for 2.5 hr. The dark mixture was poured on ice and basified with 40% sodium hydroxide solution and the solids were collected, dried and extracted with chloroform (Soxhlet). The tan residue left after evaporation of the chloroform extracts was crystallized several times from chloroform–petroleum ether mixtures yielding 3.7 g (34.6%) of XXIX as pale yellow needles: mp 434–436°; λ_{max}^{EtOH} 234 mμ (ε 33,300), 301 (91,700), 380 (9,200), 402 (10,100).

Anal. Calcd for $C_{18}H_{10}N_4$: C, 76.58; H, 3.57; N, 19.85. Found: C, 76.66; H, 3.78; N, 19.79.

Dipyrido(2,3-*a*:3′,2′-*j*)phenazine (XXX).—A mixture of 3.25 g (0.012 mole) of 1,9-dinitrophenazine,[14b] mp 255° (lit. mp 260°), 1.0 g of 10% Pd–C and 250 ml of tetrahydrofuran was reduced according to the procedure used for 1,6-dinitrophenazine. There was obtained 3 g of red 1,9-diaminophenazine, mp *ca.* 230° (lit.[14b] mp 250°). The crude 1,9-diaminophenazine was cyclized according to the directions used in the synthesis of XXIX and using proportional amounts of reagents. The crude material (1.2 g) was isolated in the usual manner but the product failed to crystallize. Chromatography over 40 g of alumina (eluting first with benzene to remove some impurities, then with chloroform) provided 350 mg (10.3%) of buff solid, mp 283–285°. Several crystallizations from methanol gave the pure XXX as buff-to-lemon rosettes: mp 285–287°; λ_{max}^{EtOH} 219 mμ (ε 50,600), 249 (23,600), 305 (84,100), 372 (9,500), 392 (11,100). The analytical sample was dried at 140° (1 mm) for 7 hr.

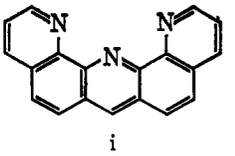
Anal. Calcd for $C_{18}H_{10}N_4 \cdot 1.5H_2O$:[23] C, 69.89; H, 4.24; N, 18.11. Found: C, 69.64; H, 4.48; N, 17.68.

Tripyrido(2,3-*a*:3′,2′-*c*:3″,2″-*j*)phenazine (XXXII). Method A.—Following the same procedure that was used in the preparation of XXIX, a Skraup reaction with 1.1 g of 10-amino-dipyrido(2,3-*a*:3′,2′-*c*)phenazine (XXXIb), 10 ml of sulfuric acid, 3 ml of water, 0.8 g of arsenic pentoxide, and 1 ml of glycerol gave 0.17 g of crude product from the basic solids and another 0.05 g from the chloroform extraction of the basified reaction

(21) (a) C. B. Kremer and A. Bendich, *J. Am. Chem. Soc.*, **61**, 2658 (1939); (b) D. L. Vivian, J. L. Hartwell and H. C. Waterman, *J. Org. Chem.*, **20**, 797 (1955).

(22) B. Hegedus, *Helv. Chim. Acta*, **33**, 766 (1950).

(23) XXX was isolated as the sesquihydrate which is consistent with the results observed by F. H. Case and E. Koft in the purification of the acridine i [*J. Org. Chem.*, **27**, 865 (1962)].



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filtrate (0.22 g, 18%), mp 392–395°. Several recrystallizations from acetonitrile provided the pure XXXII as buff feathers: mp 394–395°; λ_{max}^{EtOH} 231 mμ (ε 30,300), 244 (32,300), 266 (35,300), 307 (44,000), 314 (41,900), 370 (11,000), 390 (11,800). The analytical sample was dried at 132° (1 mm) for 18 hr.

Anal. Calcd for $C_{21}H_{11}N_5 \cdot 1.5H_2O$: C, 70.00; H, 3.92; N, 19.44. Found: C, 70.26; H, 3.89; N, 19.35.

When XXXII was dried at 160° (1 mm) for 24 hr, the following analyses were obtained.

Anal. Calcd for $C_{21}H_{11}N_5 \cdot 0.5H_2O$: C, 73.67; H, 3.54; N, 20.45. Found: C, 73.86; H, 3.72; N, 20.37.

Method B.—A solution of 0.8 g of 4,7-phenanthroline-5,6-dione,[15] 0.6 g of 7,8-diaminoquinoline,[16] and 70 ml of ethanol was refluxed for 1.5 hr. The ethanol was evaporated at reduced pressure and the residue crystallized from water yielding 1.1 g (88%), of buff feathers, mp 389–391°. This material was identical with the product prepared from method A when compared by the usual criteria.

10-Nitrodipyrido(2,3-*a*:3′,2′-*c*)phenazine (XXXIa).—To a warm solution of 0.92 g of 3-nitro-1,2-phenylenediamine in 40 ml of methanol was added a warm solution of 1.25 g of 4,7-phenanthroline-5,6-dione[15] in 100 ml of methanol. After refluxing for 1.5 hr, the solution was concentrated and diluted with water. The solid was filtered and crystallized from dimethylformamide–water yielding 1.7 g (87%), mp 318–320°. Another recrystallization from the same solvent system afforded pure XXXIa as yellow green crystals, mp 320–322°.

Anal. Calcd for $C_{18}H_9N_5O_2$: C, 66.05; H, 2.77; N, 21.40. Found: C, 65.95; H, 3.07; N, 21.66.

10-Aminodipyrido(2,3-*a*:3′,2′-*c*)phenazine (XXXIb).—A solution of 1.35 g of XXXIa in 80 ml of glacial acetic acid was reduced with 0.75 g of 10% Pd–C in a Parr shaker at three atmospheres pressure of hydrogen. After 15 min the blue suspension was filtered through Supercel and the acetic acid evaporated at reduced pressure. The residue was treated with a small amount of water and adjusted to pH 8 with ammonium hydroxide solution. Cooling and filtering provided a dark black solid. Crystallization from a large volume of methanol gave 1.1 g (89.5%) of XXXIb as short, purplish needles, mp *ca.* 340°. Further recrystallizations from methanol afforded maroon crystals, mp 345–347°. The compound is very hygroscopic and was dried for analysis at 132° (1 mm) for 24 hr.

Anal. Calcd for $C_{18}H_{11}N_5 \cdot 0.25H_2O$: C, 71.63; H, 3.84; N, 23.21. Found: C, 71.77; H, 3.98; N, 23.22.

10,13-Diacetamidodipyrido(2,3-*a*:3′,2′-*c*)phenazine (XXXIII).—To 1.5 g of moistened 5% Pd–C was added 7.4 g (0.0262 mole) of N,N′-diacetyl-2,3-dinitro-1,4-phenylenediamine (XVII) and 300 ml of methanol. The mixture was agitated in a Parr apparatus at three atmospheres pressure of hydrogen. The theoretical amount of hydrogen was absorbed in 10–15 min and the suspension filtered through Supercel with the aid of 200 ml of methanol. The filtrate was transferred to a 1-l. round-bottom flask containing 4.41 g (0.021 mole) of 4,7-phenanthroline-5,6-dione. This solution was concentrated on a rotary evaporator. Bright red feathers precipitated after 5 min and slow concentration of the suspension was continued for another 20 min. The product was filtered and washed well with diethyl ether yielding 7.35 g (88.5%), mp 390–392°. One recrystallization from dimethylformamide gave the analytical sample as red crystals, mp 392–394° which was dried at 138° (1 mm) for 18 hr to afford a bright orange solid. Equilibration of the dried sample with the atmosphere produced the bright red hydrate.

Anal. Calcd for $C_{22}H_{16}N_6O_2 \cdot H_2O$: C, 63.76; H, 4.38; N, 20.28. Found: C, 63.60; H, 4.58; N, 20.41.

Tetrapyrido(2,3-*a*:3′,2′-*c*:2″,3″-*h*:3‴,2‴-*j*)phenazine (XXXIV).—A mixture of 5.0 g (0.013 mole) of XXXIII, 6.1 g of sodium *m*-nitrobenzenesulfonate, 50 ml of sulfuric acid, 15 ml of water, and 10 ml of glycerol was heated at 135–340° for 3.5 hr with vigorous stirring. The dark mixture was poured on 300 g of ice and made alkaline with 40% sodium hydroxide solution. The brown solid was collected, dried and extracted with chloroform in a Soxhlet apparatus for 36 hr. Concentration of the chloroform extracts deposited russet crystals (3.0 g, 68%) which did not melt below 500°. Recrystallizations were achieved by dissolving 1.0 g of XXXIV in 600 ml of chloroform and concentrating to a small volume. A crystalline, russet product separated from the chloroform solution, which did not melt below 500°: $\lambda_{max}^{CHCl_3}$ 274 mμ (ε 52,300), 320 (30,400), 345 (12,900), 353 (12,500), 363 (13,900), 383 (13,500). XXXIV may also be crystallized by dissolving in methanol containing a small amount of water (it is insoluble in methanol alone), filtering, then adding more water to precipitate a buff, amorphous solid. Apparently, the degree of hydration accounts for the peculiar solubility characteristics and also the crystal structure. An analytical sample (from chloroform) was dried at 140° (1 mm) for 24 hr.

Anal. Calcd for $C_{24}H_{12}N_6 \cdot 1.5H_2O$: C, 70.06; H, 3.68; N, 20.43. Found: C, 70.23; H, 3.68; N, 20.57.

Reaction of Iron(II) with 2-(2-Pyridyl)pyrido(2,3-*h*)quinoxaline (X).—A 1×10^{-3} *M* iron(II) solution was prepared by dissolving the appropriate quantity of ferrous sulfate in 1 l. of distilled water.

A 10% solution of hydroxylammonium chloride [used to reduce any residual ferric ion in the standard iron(II) solution] was prepared from 10.0 g of hydroxylamine hydrochloride in 90 ml of water.

A spectrophotometric titration of X with iron(II) was carried out to determine the combining ratio of the reactants.[7] In a 25-ml volumetric flask was placed 10.801 mg of X. Dilution to the desired volume with 95% ethanol gave the stock ligand solution as 1.67×10^{-3} *M*. Titration solutions were prepared in 25-ml volumetric flasks containing 1.25 ml of the stock solution of X, 5 ml of 10% sodium acetate solution, 1 ml of 10% hydroxylammonium chloride solution and varying quantities of the standard ferrous iron solution (see Table I). The solutions were diluted to volume with distilled water which gave a concentration of 8.33×10^{-5} *M* in X in each flask. The chelate has maxima at 362 and 580 mμ. For this study the absorbancy values at 580 mμ were used for the titration curve. The absorbancy was at a maximum at the pH of the buffered solution. Each iron(II) atom was shown to chelate with two molecules of X.

The X and iron(II) chelate has extinction coefficients of 18,800 at 362 mμ and 7500 at 580 mμ.

TABLE I

ABSORBANCY OF X AS A FUNCTION OF IRON(II) CONCENTRATION

Flask no.	Ml of Fe (10^{-3} *M*)	Molarity of Fe ($\times 10^{-4}$)	Absorbancy
1	0.25	1	0.148
2	0.50	2	0.282
3	0.75	3	0.431
4	1.00	4	0.548
5	1.25	5	0.550
6	1.50	6	0.550
7	1.75	7	0.550

Acknowledgment.—The author (F.R.P) is indebted to Dr. James F. Kerwin for permitting him to use certain of the facilities available at Smith, Kline and French Laboratories.