[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Pyrrolopyridines. IV. Synthesis of Possible Intermediates[1,2]

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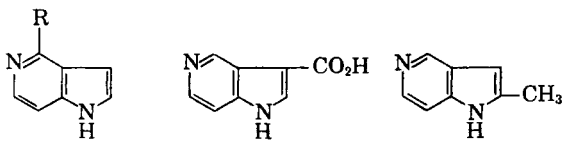
Possible routes to pyrrolo(3,2-c)pyridines from pyridine intermediates were studied. Efficient syntheses were developed for a number of pyridine derivatives, but none of them could be used for the desired purpose. 4-Nitro-3-nicotinic acid 1-oxide undergoes nucleophilic displacement by aniline.

A general synthesis of pyrrolo(3,2-c)pyridines (I,5-azaindoles) through the Bischler-Napieralski reaction of acyl derivatives of 2-(2-pyrrole)ethylamine was described in an earlier paper.[4] However, the method failed when attempts were made to prepare the parent compound (I, R = H). More recently Möller and Süs[5] obtained I (R = H) from 3-diazo-1,6-naphthyridin-4-(3H)-one by a photochemical ring contraction followed by decarboxylation of the resulting 3-carboxypyrrolo(3,2-c)pyridine (II), but in view of the large number of steps their method seemed unattractive for the synthesis of I in quantity. This paper describes our efforts to develop more convenient routes to pyrrolo(3,2-c)-pyridine.



I II III

Although Clemo and Swan[6] were unsuccessful in their attempts to prepare I (R = H) by the Madelung cyclization of 4-formamido-3-picoline (IV) and obtained only a 1% yield of 6-methylpyrrolo(3,2-c)-pyridine (III) from 4-acetamido-3-picoline, a reinvestigation of the Madelung reaction was considered advisable on two counts. First, the requisite starting material—4-amino-3-picoline (V)—is now readily available.[7] Secondly, the work of Tyson[8] on the Madelung cyclization leading to indole resulted in greatly enhanced yields due to the introduction of new bases such as sodium *t*-butoxide and sodium anilide and the use of dry sodium formate to repress an undesirable side reaction. Robison and Robison[9] utilized these findings and obtained a 51% yield of 7-azaindole, a substance which had been prepared in only 3% yield by the older technique.[10] Thus, it was reasonable to expect a similar improvement in the cyclization of IV, especially since the samples of IV prepared in the course of this work were of greater purity than the material used by the English workers.[6]

Unfortunately these expectations were not realized. In spite of many attempts under different reaction conditions, the only substance isolated in all experiments was the decomposition product 4-amino-3-picoline.[11]

Alternate methods for the synthesis of I were therefore sought. Adaptations of other standard indole syntheses[12] were considered, although the most generally useful method, the Fischer indole ring closure, was ruled out because of the report[13] that the cyclization of pyridylhydrazones proceeds only with the greatest of difficulties. This had recently been confirmed by other workers.[14]

Most of the proposed syntheses required an adequate supply of 4-nitro-3-picoline (VI). Herz and Tsai[7] reported the small-scale preparation of VI

(1) Supported in part by research grant CY-3034 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service.

(2) Previous paper, W. Herz and D. R. K. Murty, *J. Org. Chem.*, **25**, 2242 (1960).

(3) Abstracted from a thesis submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy, June 1960.

(4) W. Herz and S. Tocker, *J. Am. Chem. Soc.*, **77**, 6353 (1955).

(5) K. Möller and O. Süs, *Ann.*, **612**, 153 (1958).

(6) G. R. Clemo and G. A. Swan, *J. Chem. Soc.*, 198 (1948).

(7) W. Herz and L. Tsai, *J. Am. Chem. Soc.*, **76**, 4184 (1954).

(8) F. T. Tyson, *J. Am. Chem. Soc.*, **72**, 2801 (1950).

(9) M. M. Robison and B. L. Robison, *J. Am. Chem. Soc.*, **77**, 457 (1955).

(10) G. R. Clemo and G. A. Swan, *J. Chem. Soc.*, 603 (1945).

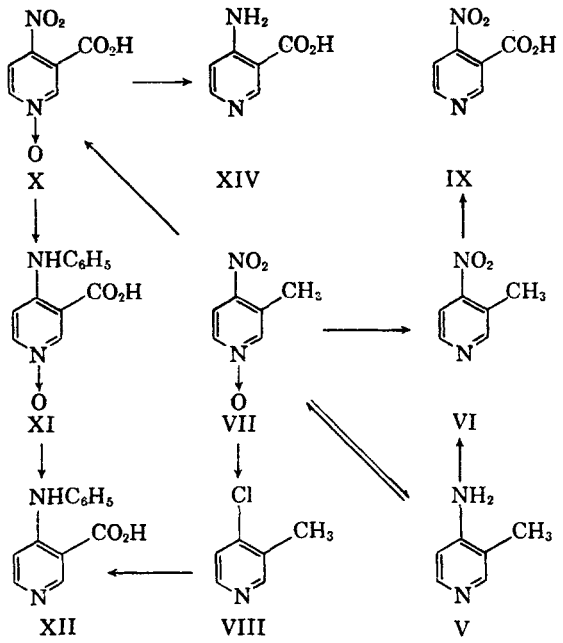
(11) After all experiments described in this paper were completed, we were informed by Dr. M. M. Robison that work in his laboratory had led to the successful preparation of I (R = H) from 4-formamido-3-picoline. This has since been published, S. Okuda and M. M. Robison, *J. Org. Chem.*, **24**, 1003 (1959). We are very grateful to Dr. Robison for communicating details of this work prior to publication. Several attempts to duplicate the cyclization under the exact conditions recommended by Okuda resulted in failure. The only substance isolated was 4-amino-3-picoline (20–25% yield). Although the melting points of 4-amino-3-picoline and pyrrolo(3,2-c)pyridine are very close, Okuda and Robison were able to establish the nature of their product by comparison with an authentic sample. We are unable to account for the discrepancy in their results and ours.

(12) P. L. Julian, E. W. Meyer, and H. C. Printy in R. C. Elderfield, *Heterocyclic Compounds*, Vol. III, Chap. 1 (1952).

(13) G. R. Clemo and R. J. W. Holt, *J. Chem. Soc.*, 1313 (1953).

(14) S. Okuda and M. M. Robison, *J. Am. Chem. Soc.*, **81**, 740 (1959). F. G. Mann, A. F. Prior, and T. J. Wilcox, *J. Chem. Soc.*, 3830 (1959).

from the corresponding *N*-oxide (VII) by the action of phosphorus trichloride, but it has now been found that the reduction is accompanied by the formation of 4-chloro-3-picoline (VIII) through nucleophilic displacement at C_4. Since the formation of VIII is favored at higher temperatures and proceeds in excellent yield at steam bath temperature, this is probably the best method for the preparation of 4-chloro-3-picoline. Large-scale runs at lower temperatures resulted in extensive recovery of VII and little VI.



Attempts were then made to obtain VI by persulfuric acid oxidation of 4-amino-3-picoline (V). The reaction was found to be very exothermic. Carefully controlled experiments gave rise to a mixture of VI and 4-nitro-3-picoline-1-oxide (VII), the latter predominating in large scale runs.

Several attempts were made to oxidize 4-nitro-3-picoline to 4-nitro-3-nicotinaldehyde which was envisioned as an intermediate in several of the proposed syntheses. Oxidations with selenium dioxide, chromic acid, and chromyl chloride failed. Potassium permanganate oxidation gave a 40% yield of 4-nitronicotinic acid (IX), but no further work was done with this substance in view of the low over-all yield from VII. Photobromination or treatment with *N*-bromosuccinimide resulted in the formation of unstable tarry products which could not be utilized. Base-catalyzed condensation of VI with ethyl oxalate, intended as the first step in a synthesis modeled on the Reissert method, was also unsuccessful. This is rather surprising since *o*-nitrotoluene easily undergoes this reaction.[15]

Attention was then focused on the use of 4-nitro-3-picoline-1-oxide (VII), whose methyl group was expected to be somewhat more reactive.[16] However, the condensation with ethyl oxalate was again a failure nor was it possible to convert it to the corresponding aldehyde. Reaction with chromyl chloride and *p*-nitroso-*N*,*N*-dimethylaniline gave intractable resinous material. No reaction took place when VII was heated with selenium dioxide in various solvents. Chromic acid oxidation gave an improved yield (80%) of X.[18] Attempts to convert this to an acid chloride failed because of conversion to 4-chloro-3-nicotinic acid-1-oxide which is very unstable.[18] Direct esterification of X was also unsuccessful. Although the methyl ester was finally prepared by the action of methyl iodide on the silver salt of X, further work directed toward a synthesis of 4-nitro-3-nicotinaldehyde or its *N*-oxide from X was abandoned because of the poor yields and the sparing solubility of the ester in common organic solvents. Ozonolysis of 4-nitro-3-styrylpyridine-1-oxide[17] followed by reductive work-up gave benzoic acid, but no aldehyde.

It has already been mentioned that further work with 4-nitronicotinic acid (IX) was not undertaken because of the poor yields encountered in the synthesis of its precursor (VI). An alternate route to the acid (IX) seemed to be deoxygenation of the corresponding *N*-oxide (X). Phosphorus trichloride, which is commonly employed for this purpose, could not be used because of the insolubility of X in suitable organic solvents. Triphenyl phosphite[19] and triphenylphosphine[20] are not suitable for the deoxygenation of nitro-pyridine-1-oxides and Meisenheimer's method[21] also seemed inapplicable. Pachter and Kloetzel[22] accidentally observed deoxygenation of a phenazine-*N*-oxide by means of aniline, but we are not aware of any systematic study of the use of this reagent.

On heating X with aniline on the steam bath, there was obtained not the expected 4-nitronicotinic acid, but a substance of formula $C_{12}H_{10}N_2O_3$ (A) which could be reduced catalytically to another substance $C_{12}H_{10}N_2O_2$ (B). Infrared spectra and chemical behavior revealed the presence of the carboxyl and the absence of a nitro group in both compounds. A logical explanation for these observations is that the reaction of X with aniline involves nucleophilic displacement of the nitro group by aniline to yield 4-anilino-3-nicotinic acid-1-oxide (XI) which is deoxygenated to XII upon catalytic reduction. This

(15) F. Mayer and G. Balle, *Ann.*, **403**, 167 (1914).

(16) The facile condensation of VII with benzaldehyde[17] is an example of this activation due to the presence of the *N*-oxide function.

(17) D. Jerchel and H. E. Heck, *Ann.*, **613**, 171 (1958).

(18) E. C. Taylor, Jr., and A. J. Crovetti, *J. Am. Chem. Soc.*, **78**, 214 (1956).

(19) M. Hamana, *J. Pharm. Soc. Japan*, **75**, 139 (1953).

(20) F. Schmitz, *Ber.*, **91**, 1488 (1958); L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).

(21) J. Meisenheimer, *Ann.*, **397**, 273 (1913); A. R. Katritzky, *J. Chem. Soc.*, 2404 (1956).

(22) I. J. Pachter and M. C. Kloetzel, *J. Am. Chem. Soc.*, **74**, 971 (1952).

conclusion finds its support in the general behavior of 4-nitropyridine-1-oxides,[23] the nitro group being susceptible to displacement by strong nucleophiles such as alkoxides, phenoxides, and thiophenoxides.

Because, to our knowledge, this is the first instance of a displacement by as weak a nucleophile as aniline, because it is known that nucleophilic substitution can occur at the 2- as well as at the 4-position and because there are examples of the elimination of a nitro group on the pyridine ring,[23] it was deemed desirable to establish the structure of B more securely by comparison with authentic samples of 4-anilino-(XII) and 6-anilinonicotinic acid (XIII). The properties of the third possible isomer, 2-anilinonicotinic acid, were already recorded and differed from those of B,[24]

The synthesis of XII was accomplished as follows. 4-Chloro-3-picoline, prepared as described earlier, was oxidized with potassium permanganate to 4-chloronicotinic acid[25] which in turn on heating with aniline gave a 60% yield of XII.

XIII was prepared as shown below. 2-Amino-5-methylpyridine was converted to 2-hydroxy-5-methylpyridine. Treatment of the latter with phosphorus pentachloride gave 2-chloro-5-methylpyridine. This was oxidized with potassium permanganate to the known 6-chloronicotinic acid[26] which on heating with aniline gave XIII. Compound B was identical with XII by mixed melting point and comparison of the infrared spectra.

The facile displacement of the nitro group in X by the weak nucleophile aniline is undoubtedly due to the combined effect of the *N*-oxide function and the carboxylic acid group. In order to test this assumption, 4-nitropyridine-1-oxide and 4-nitronicotinic acid were separately treated with aniline. As anticipated, no reaction took place and the starting materials were recovered.

Miescher and Kägi[27] reported that a diazoketone prepared from 2-amino-3-nicotinoyl chloride could be cyclized to 7-azaindoxyl. It was hoped that a similar reaction sequence starting with 4-aminonicotinic acid (XIV) would lead to 5-azaindoxyl. Known methods for the preparation of XIV are laborious and proceed in low yields,[25] but the route VII → X → XIV, the last step involving a catalytic reduction in ammoniacal solution, proved to be convenient and economical. Treatment of XIV with thionyl chloride produced a highly unstable acid chloride whose formation was indicated by conversion to the methyl ester. However, the action of diazomethane produced only intractable resinous material.

Another possible route to 5-azaindoxyl involved the cyclization of 4-amino-3-acetic acid. Attempts to prepare the latter by nitration of 3-carboxymethylpyridine-1-oxide or 3-cyanomethylpyridine-1-oxide resulted in extensive decomposition whereas nitration of 3-hydroxymethylpyridine-1-oxide was accompanied by oxidation to X.

EXPERIMENTAL[28]

4-Formamido-3-picoline (IV). 4-Amino-3-picoline was prepared by catalytic reduction of 4-nitro-3-picoline-1-oxide,[7] formylated by the procedure of Clemo and Swan[6] and distilled at reduced pressure. The distillate solidified, but melted over a wide range. Prior to cyclization it was recrystallized twice from acetone, m.p. 141°. The picrate melted at 198° (lit.[6] m.p. 199–200°).

The methods used for the attempted cyclization were the same as those described previously.[2] Method A, with or without addition of dry sodium formate, gave 4-amino-3-picoline. Method B gave 4-amino-3-picoline in 25–40% yield. No other substance was isolated.

4-Nitro-3-picoline and 4-chloro-3-picoline. A solution of 25 g. of 4-nitro-3-picoline-1-oxide in 500 ml. of dry chloroform was cooled in an ice bath to 3°. Phosphorus trichloride, 100 ml., was added dropwise at such a rate that the temperature of the mixture did not rise above 10°. Stirring was continued at 5° for 40 min., and the mixture was poured over crushed ice and cautiously made basic with dilute sodium hydroxide solution. The aqueous layer was separated and extracted several times with chloroform. The combined chloroform extracts were dried, and distilled. The first fraction, 11 g., b.p. 54–64° (1.5 mm.), was colorless. Redistillation at 36° (0.5 mm.) gave an oil which was unstable at room temperature and was converted to a picrate, m.p. 151–152°. The picrate of 4-chloro-3-picoline, prepared recently by a more circuitous route, melts at 152–153°.[29]

Anal. Calcd. for $C_{12}H_8N_4O_7Cl$: C, 40.40; H, 2.54; N, 15.71. Found: C, 40.75; H, 2.16; N, 15.74.

Catalytic reduction of 4-chloro-3-picoline with palladium charcoal gave a colorless oil which was identified as 3-picoline through its picrate.

Fraction 2, b.p. 64–74° (1.5 mm.), 10 g., was redistilled. The yellow oil, b.p. 67–69° (1.5 mm.), solidified on cooling, m.p. 30°, picrate m.p. 127–128° [lit.[7] for 4-nitro-3-picoline, b.p. 57–59° (0.5 mm.), m.p. 27–29°, picrate m.p. 128–129°].

The yields of 4-chloro-3-picoline increased when the temperature of the reaction mixture was raised after the addition of phosphorus trichloride. When the mixture was refluxed for a few minutes, 4-chloro-3-picoline was isolated in 65% yield and no 4-nitro-3-picoline was obtained.

4-Nitro-3-picoline from 4-amino-3-picoline. A solution of 30 g. of 4-amino-3-picoline in 150 ml. of concd. sulfuric acid was added at 10–20° to a cold solution consisting of 525 ml. of 15% fuming sulfuric acid and 263 ml. of 30% hydrogen peroxide. Stirring was continued at 10–20° for 1 hr. A few minutes after cooling was discontinued a vigorous reaction ensued which was difficult to control. After the reaction subsided, the mixture was allowed to cool, poured over crushed ice, neutralized with dilute sodium hydroxide solution, and extracted thoroughly with chloroform. Removal of the dried chloroform at reduced pressure gave a yellow solid mixed with some oil which was filtered and recrystallized from acetone, yield 15 g. of 4-nitro-3-picoline-1-oxide. Distillation of the oily filtrate afforded a pale yellow

(23) E. Ochiai, *J. Org. Chem.*, 18, 534 (1953); A. R. Katritzky, *Quart. Revs.*, 10, 395 (1956).

(24) W. O. Kermack and A. P. Weatherhead, *J. Chem. Soc.*, 726 (1942).

(25) E. C. Taylor, Jr., and A. J. Crovetti, *J. Org. Chem.*, 19, 1633 (1954).

(26) H. V. Pechmann and W. Welsch, *Ber.*, 17, 2384 (1884).

(27) K. Miescher and H. Kägi, *Helv. Chim. Acta*, 24, 1471 (1941).

(28) Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford, England.

(29) Y. Suzuki, *Pharm. Bull.* (*Tokyo*), 5, 78 (1957).

oil, 4.3 g., b.p. 70° (1 mm.), picrate m.p. 128°, undepressed on admixture of the picrate of authentic 4-nitro-3-picoline.

When the reaction mixture was stirred below 20° for an extended period and the product worked up without allowing to warm up to room temperature, no reaction took place and starting material was discovered. Brown[30] reported an 80% yield of crude 4-nitro-3-picoline from this reaction.

4-Nitronicotinic acid. Potassium permanganate oxidation of 7 g. of 4-nitro-3-picoline in 100 ml. of water at steam bath temperature followed by extraction with benzene gave 4 g. of starting material. The aqueous layer was concentrated and acidified, yield 1.5 g. of 4-nitronicotinic acid, m.p. 120° (lit.[30] m.p. 120°).

4-Nitronicotinic acid-1-oxide. A solution of 7.5 g. of 4-nitro-3-picoline-1-oxide in 60 ml. of concd. sulfuric acid was oxidized with 27 g. of sodium dichromate at 45–55°. After 4 hr., the viscous mixture was poured over crushed ice, filtered, and washed; yield 6.1 g. The green color[18] was removed by solution in dilute base, filtration, and reprecipitation. Two crystallizations from ethanol water gave an analytical sample, m.p. 171°.

Anal. Calcd. for $C_6H_4N_2O_5$: C, 39.14; H, 2.19; N, 15.22. Found: C, 39.50; H, 2.12; N, 15.30.

Methyl-4-nitronicotinate-1-oxide. 4-Nitronicotinic acid-1-oxide, 4 g., was dissolved in the calculated amount of dilute ammonium hydroxide solution and mixed with an equivalent quantity of silver nitrate solution. The yellow silver salt was filtered, washed, and dried, 6 g., suspended in 300 ml. of absolute methanol and refluxed with excess methyl iodide under an efficient reflux condenser with stirring overnight. Excess methyl iodide was distilled and the unchanged silver salt filtered and washed with hot methanol. The combined filtrate and washings were combined and concentrated at reduced pressure. The yellow product was recrystallized from water–dimethyl formamide, yield 0.9 g., m.p. 158–159° dec.

Anal. Calcd. for $C_7H_6N_2O_5$: C, 42.43; H, 3.05; N, 14.14. Found: C, 42.80; H, 3.20; N, 13.60.

4-Anilinonicotinic acid-1-oxide. A mixture of 25 ml. of aniline and 4 g. of 4-nitronicotinic acid-1-oxide was heated on a steam bath for 4 hr., cooled, and mixed with dilute sodium hydroxide solution. The aqueous layer was washed and acidified. The pale yellow precipitate was filtered and washed with cold water, yield 2.5 g., m.p. 242–244°. It was almost insoluble in most organic solvents and only slightly soluble in hot water and dimethyl formamide. One reprecipitation and recrystallization from water–dimethyl formamide gave the analytical sample, m.p. 244–245°.

Anal. Calcd. for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.46; H, 4.14; N, 11.90.

4-Anilinonicotinic acid. (A) A solution of 0.45 g. of the *N*-oxide in 200 ml. of hot methanol was hydrogenated with 0.2 g. of 10% palladium charcoal. The catalyst was filtered and washed with hot methanol. The combined filtrate and washings were concentrated to small volume, yield 0.2 g. of a colorless solid, which was recrystallized from methanol, m.p. 267–269° dec.

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.04; H, 4.81; N, 12.80.

(B) A mixture of 6.3 g. of 4-chloro-3-picoline, 18.6 g. of potassium permanganate, and 200 ml. of water was refluxed for 6 hr. with stirring. The apparatus was adjusted for steam distillation and the mixture steam distilled until 100 ml. of distillate had been collected. Extraction of the distillate gave 1.1 g. of starting material. The hot reaction mixture was filtered through Filtercel and the manganese dioxide washed with hot water. The combined filtrate and washings were concentrated to 60 ml. and acidified. The pale yellow precipitate was filtered, washed with a little cold water, and dried, 4.1 g. (64%, based on 4-chloro-3-picoline actually consumed). Vacuum sublimation gave a colorless solid, m.p. 162–163°. This substance has previously been synthesized in 5% yield from nicotinic acid-1-oxide.[25]

A mixture of 1 g. of the above and 2 g. of aniline was heated at 150° for 1.5 hr., poured into a small flask while still hot, and mixed with a few milliliters of acetone. A colorless solid separated on standing and scratching. It was filtered, washed with a little acetone, and recrystallized from water-dimethylformamide, m.p. 268–269°, mixed melting point with material prepared by method A undepressed.

2-Hydroxy-5-methylpyridine. A solution of 125 g. of 2-amino-5-methylpyridine in 3 l. of 5% sulfuric acid was cooled to 5° and a solution of 150 g. of sodium nitrite in 400 ml. of water was added with stirring during a period of 40 min. The ice bath was removed, stirring continued for 1 hr., and the mixture was heated to 60°, cooled, neutralized with dilute sodium hydroxide solution, concentrated to 1.5 l., and allowed to stand overnight. The solid was filtered and washed with a small amount of acetone which removed a yellow coloration, yield 95 g. (75%). Two recrystallizations from methanol raised the m.p. to 185–187°. This compound has since been reported elsewhere,[29] m.p. 181–182°.

Anal. Calcd. for C_6H_7NO: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.81; H, 6.41; N, 12.71.

2-Chloro-5-methylpyridine. A mixture of 28 g. of 2-hydroxy-5-methylpyridine, 100 ml. of phosphorus oxychloride, and 20 g. of phosphorus pentachloride was heated for 2 hr. at 115°, cooled, poured over crushed ice, neutralized with dilute sodium hydroxide, and extracted with ether. The ether extracts were dried, concentrated, and the residue was distilled, b.p. 56° (2.5 mm.).

Anal. Calcd. for C_6H_6NCl: C, 56.46; H, 4.74; N, 11.00. Found: C, 55.90; H, 4.95; N, 11.50.

6-Chloronicotinic acid. Oxidation of 9.4 g. of 2-chloro-5-methylpyridine with potassium permanganate in a manner similar to that described for 2-chloro-3-picoline described earlier gave 1.7 g. of starting material and 6.8 g. of 6-chloronicotinic acid (71%), m.p. 198–199° (lit.[26] m.p. 199°).

6-Anilinonicotinic acid. Treatment of 1 g. of 6-chloronicotinic acid with aniline in the manner described earlier gave a quantitative yield of XIII which was recrystallized from acetone, m.p. 260–262°.

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.30; H, 4.73; N, 12.80.

4-Aminonicotinic acid. A solution of 1 g. of 4-nitronicotinic acid-1-oxide in the calculated amount of ammonium hydroxide was diluted with 40 ml. of water and hydrogenated with palladium charcoal. The catalyst was filtered and washed with dilute ammonium hydroxide solution. The combined filtrate and washings were concentrated to 15 ml. and neutralized. The precipitate was washed with cold water and recrystallized from ethanol water, yield 2.2 g., m.p. 330°, undepressed on admixture of a sample prepared by heating 4-chloronicotinic acid and ammonia in a sealed tube.[25]

4-Aminonicotinoyl chloride. A mixture of 0.7 g. of 4-aminonicotinic acid and 6 ml. of thionyl chloride was warmed gently and stirred for 1 hr. in an apparatus protected from the atmosphere. Excess thionyl chloride was removed *in vacuo*. The residue was very unstable. Treatment with diazomethane in methylene chloride and working up in the usual fashion gave intractable resinous material. The acid chloride was converted to the methyl ester as follows. Excess methanol was added to the residue obtained from a similar run. The mixture was heated to reflux, cooled, treated with ice, and made basic with sodium carbonate solution. Extraction with ether, drying of the ether extracts, and evaporation gave a yellow residue which solidified on cooling and was washed with a small amount of acetone, yield 0.5 g. (46%). Crystallization from acetone gave yellow plates, m.p. 170°.

Anal. Calcd. for $C_7H_8N_2O_2$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.13; H, 5.16; N, 18.36.

(30) E. V. Brown, *J. Am. Chem. Soc.*, **76**, 3167 (1954).

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