[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE]

The Preparation of Substituted Hydrazines. II.[1] 3-Pyridylhydrazine *via* the Phototropic N-(3-Pyridyl)-sydnone[2]

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RECEIVED JUNE 7, 1955

The successful conversion of 3-aminopyridine *via* N-(3-pyridyl)-sydnone to 3-pyridylhydrazine has further demonstrated the generality of this method of converting a primary amine (RNH_2) to a monosubstituted hydrazine ($RNHNH_2$). Up to the present this method has been applied successfully to compounds in which R is alkyl, cycloalkyl, aralkyl, aryl and heteroaryl. N-(3-Pyridyl)-glycine hydrochloride has been prepared by hydrogenation of a mixture of ethyl glyoxylate and 3-aminopyridine in hydrochloric acid, a method presumably general for other N-substituted glycines. Dehydration of N-nitroso-N-(3-pyridyl)-glycine afforded N-(3-pyridyl)-sydnone, which was hydrolyzed to 3-pyridylhydrazine. All reactions proceeded quickly and gave excellent yields of pure products. N-(3-Pyridyl)-sydnone, the first uncondensed heterocyclic derivative of a sydnone, unexpectedly proved to be phototropic. Infrared spectra of the sydnone and its precursors are discussed.

Work done in England and Australia has shown that N-cycloalkyl-, N-aralkyl- and N-arylsydnones all are stable compounds which on acid hydrolysis yield the corresponding monosubstituted hydrazines. Paper I[1] of the present series, which contains references to earlier work, reported the synthesis of the first N-alkylsydnones and emphasized that virtually any amine can be converted *via* the N-substituted glycine and N-substituted sydnone to the corresponding monosubstituted hydrazine in highly satisfactory over-all yields. Since the intermediates need not be isolated, this synthesis obviously affords an attractive method for preparing hydrazines from amines, especially when the amine cannot be diazotized. Furthermore, even if the amine can be diazotized, the stable sydnone offers the chemist a most convenient source from which a hydrazine may be generated for use in synthesis.

A recent Communication[4] briefly reported the synthesis of the first uncondensed heterocyclic derivative of a sydnone, namely, N-(3-pyridyl)-sydnone, and from it the known 3-pyridylhydrazine. The entirely unexpected colorless-to-blue phototropy exhibited by N-(3-pyridyl)-sydnone also was mentioned. The present paper will extend and elaborate these observations. The successful preparation of N-(3-pyridyl)-sydnone and from it of 3-pyridylhydrazine shows that heterocyclic hydrazines as well as alkyl-, aryl- and aralkylhydrazines can be prepared by the same general process.

The preparation of N-(3-pyridyl)-sydnone (I) required N-(3-pyridyl)-glycine as starting material. Much to our surprise we were unable to prepare this glycine by reaction of 3-aminopyridine with either iodoacetic acid, chloroacetic acid or ethyl bromoacetate.[5] However, the desired glycine hydrochloride (II) finally was obtained in excellent yield by a process which may prove to be as general a method for preparing N-substituted amino acids as the Knoop process is for preparing unsubstituted amino acids. Thus, equimolar amounts of ethyl glyoxylate and 3-aminopyridine were mixed in water and immediately hydrogenated in approximately 6*N* hydrochloric acid over a palladium catalyst in a Parr apparatus. The hydrogenation proceeded very quickly at room temperature to produce a high yield of II. It is interesting to note that the ester was hydrolyzed during the hydrogenation. This procedure, the generality of which will be the subject of a forthcoming paper,[6] is much more convenient than the conventional preparation of an N-substituted glycine from the amine and a halogenated acetic acid derivative.

During an investigation of optimum conditions for this reaction it was discovered that 2 moles of aminopyridine and 1 mole of ethyl glyoxylate condense readily at room temperature on standing in an aqueous medium. The crystalline product thus obtained, ethyl bis-(3-pyridylamino)-acetate (III), can be hydrogenated to yield N-(3-pyridyl)-glycine and 3-aminopyridine. However, when equimolar amounts of glyoxylate and aminopyridine are mixed, nothing separates on standing. Hydrogenation of this mixture yields N-(3-pyridyl)-glycine (as stated above) but no 3-aminopyridine. These facts indicate that either the Schiff base or the hydroxyester is the intermediate formed by condensation of equimolar amounts of glyoxylate and amine. Further investigation of this point was not attempted.

Nitrosation of N-(3-pyridyl)-glycine was successful only when colorless or slightly colored glycine hydrochloride was used. Like other sydnones, N-(3-pyridyl)-sydnone (I) readily was obtained by heating the N-nitroso-N-(3-pyridyl)-glycine (IV) with acetic anhydride. Much to our surprise, however, this sydnone proved to be phototropic (*cf.* Experimental part for details). The compound was obtained as colorless crystals which almost instantly turned blue on brief exposure to direct sunlight. The blue modification became colorless rapidly on heating to about 80° and much more

(1) Paper I, J. Fugger, J. M. Tien and I. M. Hunsberger, THIS JOURNAL, **77**, 1843 (1955).

(2) This work was sponsored by the Air Force under Contract No. AF 33(038)-22909, Supplemental Agreement Nos. S2(53-1063) and 5(54-1875).

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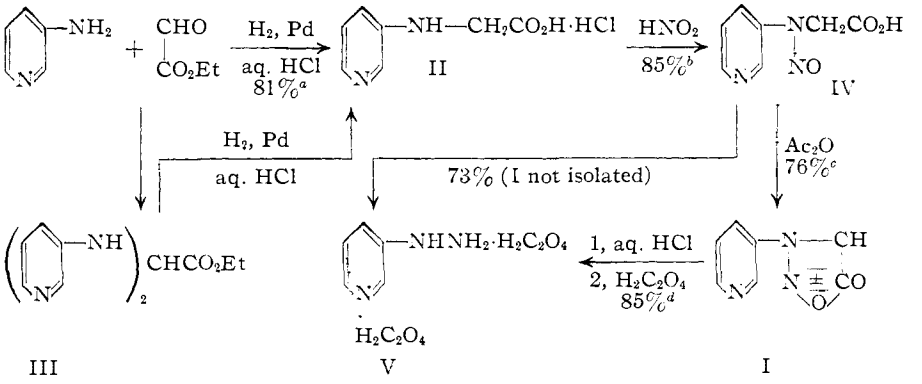
(4) J. M. Tien and I. M. Hunsberger, *Chemistry & Industry*, 119 (1955).

(5) Limited attempts to prepare analogous glycines from iodoacetic acid and 2-aminothiazole and from ethyl chloro- or bromoacetate and 2-aminopyrimidine or 2-amino-3-methylpyridine were unsuccessful. In this connection it is interesting to note that the product F. Reindel [*Ber.*, **57**, 1381 (1924)] obtained from condensation of 2-aminopyridine and sodium chloroacetate was shown by F. Reindel and H. Rauch [*ibid.*, **58**, 393 (1925)] to be 1,2-dihydro-2-iminopyridine-1-acetic acid rather than N-(2-pyridyl)-glycine.

(6) A. Skita and C. Wulff [*Ann.*, **453**, 190 (1927)] prepared N-ethylglycine by hydrogenating a mixture of ethylamine and glyoxylic acid, but apparently this type of reaction has not been investigated further.



[a] Average yield from five preparations. [b] Average yield from thirty preparations. [c] Representative of the yield from seventeen preparations. [d] Average yield from three preparations.

slowly on standing in the dark. This loss of color on heating made it impossible to determine the m.p. of the blue modification.

Work is in progress to determine whether other heterocyclic derivatives of the sydnone ring also are phototropic. Prolonged irradiation of N-benzylsydnone with ultraviolet light has produced no detectable change.

Whether the above color change is limited to the surface layer of molecules has not yet been determined. Nevertheless, it is interesting to note that the infrared spectra of the colorless and of the blue modifications are identical (*cf.* Fig. 1) and that both contain a band ascribable to the sydnone carbonyl group.[7]

temperature in a few minutes by treatment with concentrated hydrochloric acid. Careful ether extraction produces a high yield of 3-pyridylhydrazine, which is most easily isolated as its stable dioxalate V. The sydnone need not be isolated or purified before conversion to the hydrazine.

The yields in each step of the conversion of 3-aminopyridine *via* N-(3-pyridyl)-sydnone to 3-pyridylhydrazine are unusually high (*cf.* reaction sequence). All reactions have been duplicated many times. Furthermore, each step can be executed very quickly with simple laboratory apparatus. These factors combine to make the entire synthesis most attractive. Thus, the over-all yield of 3-pyridylhydrazine dioxalate (V) from 3-aminopyridine was 45% when the sydnone was isolated and 50% when the sydnone was not isolated.

The infrared spectra of N-(3-pyridyl)-glycine hydrochloride (II), its methyl ester, N-nitroso-N-(3-pyridyl)-glycine (IV) and the colorless and blue modifications of N-(3-pyridyl)-sydnone (I) have been determined. Figure 1 shows the spectrum of the blue modification of the sydnone. This was

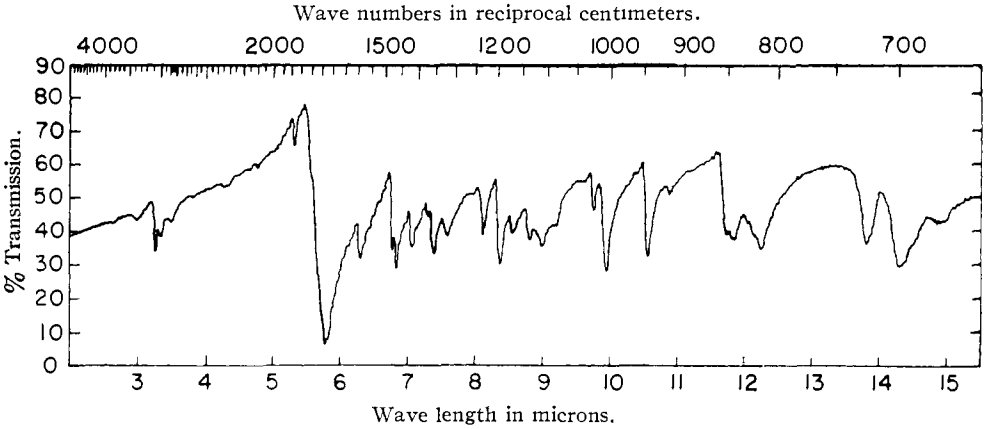


Fig. 1.—Infrared spectrum of N-(3-pyridyl)-sydnone (in KBr disc).

Since N-(3-pyridyl)-sydnone (I) is the only sydnone thus far reported to be phototropic, a rigorous proof of its structure was desirable. The given structure is established conclusively by virtue of the combustion analyses, infrared spectra and acid hydrolysis to 3-pyridylhydrazine, identified by conversion to the known acetophenone 3-pyridylhydrazone and by direct comparison, as the dioxalate, with an authentic sample of 3-pyridylhydrazine dioxalate (V).

N-(3-Pyridyl)-sydnone (I) is hydrolyzed at room

(7) The referee has suggested that, although the reversible appearance of a blue color might imply the presence of a C-nitroso function, this interpretation seems to be inconsistent with the hydrolysis to a hydrazine (barring rearrangement).

identical with the spectrum of the colorless modification. The paucity of published spectra on similar compounds prevents a detailed analysis of these spectra, but certain features merit comment.

The strong bands at 3344 and 3356 cm.$^{-1}$ exhibited, respectively, by II and its methyl ester are attributed to NH stretching vibrations, while the bands at 1635 and 1634 cm.$^{-1}$ undoubtedly are produced by NH deformation vibrations. It is significant that neither the nitroso compound IV nor the sydnone I exhibited these bands. Only IV showed a band at 1404 cm.$^{-1}$, which is believed to be characteristic of the nitroso group.[8] The

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 254.

carboxyl absorption of II and IV appeared at 1713 and 1734 cm.$^{-1}$, respectively, while the methyl ester of II showed ester carbonyl absorption at 1748 cm.$^{-1}$.

Since all of the above compounds exhibited a band near 3065 cm.$^{-1}$,[9] this absorption presumably must be attributed to the pyridine CH rather than to the CH of the sydnone ring. All three earlier-reported[1] sydnones exhibited a strong band at 3140–3194 cm.$^{-1}$, which had tentatively been assigned to the unique CH of the sydnone ring. What must be the carbonyl absorption of the sydnone I appeared as a broad band with peaks at 1732 and 1721 cm.$^{-1}$. The carbonyl absorption of earlier-reported[1] sydnones varied from 1752 to 1768 cm.$^{-1}$. Although the carbonyl band of N-benzylsydnone was reported[1] at 1761 cm.$^{-1}$, actually that band also was broad, having peaks at 1723 and 1761 cm.$^{-1}$. Thus, the exact position and nature of the sydnone carbonyl absorption appear to vary considerably with the structure of the sydnone.

Experimental[10]

Starting Materials.—Some of the **3-aminopyridine** used in this investigation was prepared from nicotinamide according to Allen and Wolf.[11] Recrystallization from ligroin–benzene (1:4) afforded very pale yellow thin plates, m.p. 63–64°. Some 3-aminopyridine was purchased[12] and used after one recrystallization. The **ethyl glyoxylate**, b.p. 65–70° at 20 mm., was prepared from diethyl tartrate (Eastman Kodak Co., White Label Grade) essentially according to Vargha and Reményi[13] and characterized as its known[13] phenylhydrazone, m.p. 128°, lit.[13] m.p. 130°. The ethyl glyoxylate thus obtained always was about 60% pure (determined by assay with phenylhydrazine). Further information on the preparation of this compound will be given in a forthcoming paper.

Ethyl Bis-(3-pyridylamino)-acetate (III).—To 1.0 g. (0.011 mole) of 3-aminopyridine in 5 ml. of water 1.0 g. of ethyl glyoxylate (60% pure), *i.e.*, 0.0059 mole of pure glyoxylate, was added with shaking. The turbid mixture became clear in a few minutes and in about 2 hours deposited 0.34 g. (23%,[14] based on aminopyridine) of white needles, m.p. 129–129.5°, which were very soluble in ethanol and methanol, slightly soluble in isopropyl alcohol, and insoluble in ether, petroleum ether, chloroform and ethyl acetate. By diluting the colorless filtered solution of 122 mg. of this product in 1.2 ml. of 95% ethanol with 10 ml. of water, 32 mg. of pure product separated at once as white needles, m.p. 130–131°.

Anal. Calcd. for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.93; H, 6.21; N, 20.67.

This material turned quite yellow on standing and gave off an odor like pyridine or aminopyridine.

Hydrogenation of Ethyl Bis-(3-pyridylamino)-acetate.—A solution of 0.30 g. (0.0011 mole) of pure ester in 10 ml. of 6 *N* hydrochloric acid was hydrogenated using 0.1 g. of 4% palladium–charcoal catalyst. The filtered reaction mixture was treated with 20% sodium hydroxide solution up to *p*H 9 and then was extracted with three 20-ml. portions of ether. Evaporation of the dried ether extracts at reduced pressure afforded 0.066 g. (64%) of 3-aminopyridine as a nearly white solid, m.p. 60–61°. The sodium salt of the N-(3-pyridyl)-glycine remained in the above alkaline layer.

N-(3-Pyridyl)-glycine Hydrochloride (II).—3-Aminopyridine (0.940 g., 0.010 mole) in 5 ml. of water was mixed with 1.72 g. of ethyl glyoxylate (60% pure), *i.e.*, 0.010 mole of pure glyoxylate, and 6 ml. of concentrated hydrochloric acid and hydrogenated at once over 0.15 g. of 4% palladium–charcoal catalyst. In one hour at 29° the pressure dropped from 24.3 to 23.5 lb./in.^{2}. If crystallization occurred in the hydrogenation bottle (as was usually the case), the crystals were dissolved by heating prior to removal of the catalyst. The filtered catalyst was washed with a little water and the combined filtrate and washings evaporated to dryness at reduced pressure. The residue was dissolved in 10 ml. of concentrated hydrochloric acid by warming on a steam-bath. On standing at room temperature this solution deposited 1.44 g. of tan crystal rosettes, m.p. 223–225°. Concentration of the mother liquor afforded another 0.25 g. of crystals, m.p. 221–223°, the total yield being 1.69 g. (90%).

Anal. Calcd. for $C_7H_9O_2N_2Cl$: C, 44.60; H, 4.81; N, 14.85; Cl, 18.85; neut. equiv., 94.3. Found: C,[15] 44.58; H,[15] 5.22; N,[15] 14.93; Cl,[16] 19.15, 18.85; neut. equiv., 93.5, 91.5.

Some pure samples of this compound were colorless instead of tan.

If the hydrogenation was conducted in 95% ethyl alcohol, water or acetic acid and the product dissolved in warm concentrated hydrochloric acid, the same glycine hydrochloride separated on cooling. From five hydrogenations, performed in water or in hydrochloric acid using 1–23 g. of glyoxylate, the average yield was 81%. The time of the hydrogenation varied from 15 minutes to several hours and the interval between mixing the reagents and starting the hydrogenation varied from 0–1 hour. As long as equimolar amounts of aminopyridine and glyoxylate were used, no 3-aminopyridine was noticeable after hydrogenation.

Methyl Ester of N-(3-Pyridyl)-glycine Hydrochloride.—(a) The glycine hydrochloride (0.189 g., 0.001 mole) in methanol was saturated with dry hydrogen chloride. The hot solution was allowed to cool to room temperature, diluted with ether and refrigerated. In this way 0.183 g. (90%) of methyl ester was obtained as slender opaque needles, m.p. 147–148°. Further recrystallization from methanol did not alter the m.p.

Anal. Calcd. for $C_8H_{11}O_2N_2Cl$: C, 47.40; H, 5.43; N, 13.83; Cl, 16.50; neut. equiv., 203. Found: C,[15] 47.37; H,[15] 5.22; N,[15] 13.62; Cl,[16] 16.10; neut. equiv., 202.

(b) The filtrate from a hydrogenation of ethyl glyoxylate and 3-aminopyridine performed in concentrated hydrochloric acid was evaporated to dryness under reduced pressure and the residue dissolved in hot methanol. On diluting to the cloud point with ether and then cooling, the glycine methyl ester separated.

This ester cannot be prepared merely by dissolving pure N-(3-pyridyl)-glycine hydrochloride in warm methanol. In this case the unchanged glycine hydrochloride separates upon cooling. Hence, in the above preparation the residue after evaporation must have contained some excess hydrogen chloride. If the methyl ester is dissolved in warm concentrated hydrochloric acid, the glycine hydrochloride II, m.p. 220–221°, separates on cooling.

N-Nitroso-N-(3-pyridyl)-glycine (IV).—To a solution of 7.28 g. (0.0386 mole) of the glycine hydrochloride in 58 ml. of water held below 0° 2.90 g. (0.0420 mole) of solid sodium nitrite was added portionwise over several minutes. In a few minutes the solution deposited 5.34 g. (76%) of brownish granular crystals, m.p. 158–159° dec. Although this nitroso compound can be recrystallized from hot water, recrystallization was not necessary in order to obtain an analytical sample. In fact, the recrystallized material had more of a yellow color than the original even though the m.p. of the two samples was identical. The nitroso compound gave a positive Liebermann test and a negative test for chlorine.

The yield of nitroso compound could be increased (over that given above) by overnight refrigeration prior to filtration and by further cooling of the mother liquor to obtain a second crop of less pure, yellowish material. Furthermore, the first fraction was obtained directly as colorless needles

(9) The specific locations were 3063 (II), 3062 (methyl ester of II), 3078 (IV), and 3065 cm.$^{-1}$ (I).

(10) All m.p.'s are uncorrected unless designated otherwise. All neutral equivalent determinations were performed in water or aqueous alcohol using cresol red-thymol blue mixed indicator (Chicago Apparatus Co.), whose *pH* range is 7.5–9.5 on the alkaline side. All elemental analyses, unless designated otherwise, were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(11) C. F. H. Allen and C. N. Wolf, *Org. Syntheses*, **30**, 3 (1950).

(12) Aldrich Chemical Co., Milwaukee, Wisconsin.

(13) L. Vargha and M. Reményi, *J. Chem. Soc.*, 1068 (1951).

(14) No attempt was made to increase this yield.

(15) Analysis performed by Clark Microanalytical Laboratory, Urbana, Ill.

(16) Analysis performed gravimetrically in our laboratories.

of analytical purity if 2 ml. of water was used to dissolve each millimole of glycine hydrochloride and if the solution was allowed to crystallize undisturbed.

Anal. Calcd. for $C_7H_7O_3N_3$: C, 46.42; H, 3.90; N, 23.21; neut. equiv., 181. Found: C, 46.32; H, 4.32; N, 22.89; neut. equiv., 179.

Using the above modifications in 30 separate nitrosations of 1-millimole quantities of glycine hydrochloride, yields of 70–94% were obtained, the average yield being 85%.

Nitrosation of impure glycine hydrochloride gave either unsatisfactory results or no nitroso compound at all. It is interesting to note that the nitrosoglycine was obtained as the free base even when the crystals separated from a solution of *p*H 2. As was the case with N-nitroso-N-alkylglycines,[1] this nitrosoglycine soon developed a yellowish color on standing.

N-(3-Pyridyl)-sydnone (I).—In a typical preparation 9.14 g. (0.0505 mole) of the pure nitrosoglycine and 110 ml. of acetic anhydride were heated in an open flask for 30 minutes at 95–105°. Reduced pressure concentration (under nitrogen) of the hot, light yellow solution left a solid brownish residue,[17] which was cooled (ice-bath) and stirred with 10–12 ml. of ethanol–water (1:3). Filtration followed by two washings with aqueous ethanol afforded 5.88 g. of pale white plates, m.p. 119–121° dec. The filtrate was treated with Norit and concentrated[18] to yield another 0.33 g. of crystalline sydnone, the total yield being 6.21 g. (76%).

From 17 preparations performed under a variety of conditions the highest yield was 79%, and the reproducible yield was above 70%. Higher temperatures, longer reaction periods, and larger amounts of acetic anhydride definitely are not necessary. The entire preparation as given above requires only about one hour.

Two recrystallizations (Norit) from hot water afforded the analytical sample as colorless needles, m.p. 120.3–121.9° (cor.) with vigorous evolution of gas to a dark brown melt.

Anal. Calcd. for $C_7H_5N_3O_2$: C, 51.55; H, 3.09; N, 25.77. Found: C, 51.45; H, 3.28; N, 25.63.

The colorless sydnone could be prepared in ordinary daylight without any special precautions, which means that it is quite stable in solution in acetic anhydride. However, on exposure of the solid sydnone to direct sunlight, the *colorless* analytical sample changed almost *instantly* to a beautiful *deep blue*. The m.p. of the blue modification could not be determined because at about 80° it quickly turned virtually colorless and then melted at 119.5–120.5° (cor.) with slight evolution of gas to a dark brown melt. Even at room temperature the blue form became virtually colorless on standing overnight in the dark. These color changes have been repeated several times without any noticeable fatigue, but it is not known whether fatigue ultimately would occur. Also, no experiments were performed to determine the relation between the speed of the color change and the wave length of the illumination.

The colorless modification has kept unchanged for a period of several months.

Acetophenone 3-Pyridylhydrazone.—A solution of 0.489 g. (0.0030 mole) of N-(3-pyridyl)-sydnone in 3 ml. of concentrated hydrochloric acid and 6 ml. of water was heated on a steam-bath until no more gas was evolved. The cooled yellow solution was made alkaline (red color) with 20% sodium hydroxide and extracted with three 25-ml. portions of ether. The combined extracts were dried over potassium carbonate and evaporated. The viscous yellowish residue solidified on overnight refrigeration in an evacuated vessel to yield 0.058 g. (18%) of crude **3-pyridylhydrazine**, m.p. 52.5–54.5°, lit.[19] m.p. 53–55°.

This hydrazine was heated for five hours with 0.075 g. of acetophenone in *ca.* 4 ml. of refluxing alcohol. The residue obtained on removing the alcohol was washed with a little ether to yield the crude hydrazone as oily crystals. One recrystallization from 70% alcohol produced yellowish crystals, m.p. 155.5–159°. Two more recrystallizations afforded nearly colorless crystals of the pure **hydrazone**, m.p. 151–152.5° (cor.), lit.[19] m.p. 156°.

Anal. Calcd. for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.90. Found: C, 73.72; H, 6.16; N, 19.91.

Even though recrystallization lowered the m.p., the recrystallization obviously accomplished a purification.

An authentic sample of the same hydrazone was prepared[19] from hydrazine obtained by reduction of diazotized 3-aminopyridine. Two recrystallizations from aqueous alcohol afforded yellowish hair-like needles, m.p. 153–154°.

Both of the above hydrazine preparations proceeded in low yield only because of incomplete extraction of the hydrazine from the aqueous reaction mixtures. A more efficient extraction of this hydrazine is described below.

3-Pyridylhydrazine Dioxalate (V). (a) **From Purified N-(3-Pyridyl)-sydnone.**—On treating 0.489 g. (0.0030 mole) of N-(3-pyridyl)-sydnone at room temperature with *ca.* 3 ml. of concentrated hydrochloric acid, carbon dioxide evolution began immediately and ceased in a few minutes. The pale yellow frozen mixture (ice–salt-bath) slowly was made alkaline (red color) with 20% sodium hydroxide, saturated with solid potassium carbonate, and repeatedly extracted[20] with 25-ml. portions of ether. The combined extracts on treatment with *ca.* 30 ml. of a 10% solution of oxalic acid in ethanol precipitated 0.774 g. (89%) of pale yellow dioxalate, m.p. 220–222°. One recrystallization from 50% ethanol (Norit A) produced the pure dioxalate as long hair-like white needles, m.p. 226–227.5°; a mixture m.p. with authentic 3-pyridylhydrazine dioxalate (part c below) showed no depression.

Two similar preparations, using 0.489 g. and 8.15 g. of sydnone, proceeded in yields of 82 and 83%, respectively.

As stated above, the sydnone loses carbon dioxide in a few minutes at room temperature with concentrated or with 1:1 hydrochloric acid. However, when 1:2 concentrated hydrochloric acid–water is used, heat is required to cause loss of carbon dioxide. If heat is used to hydrolyze the sydnone or if the ether solution of the hydrazine is evaporated completely before making the oxalate, the resulting oxalate has a brown color and a lower m.p. If the sydnone is hydrolyzed at room temperature and if the ether solution of the hydrazine is only partly evaporated, the oxalate separates immediately on mixing the reagents. Furthermore, this oxalate will dissolve on gentle heating of the reaction mixture. Cooling then produces the colorless oxalate as well-formed needles, which are pure without further recrystallization.

(b) **From N-Nitroso-N-(3-pyridyl)-glycine without Isolation of the Sydnone.**—The sydnone residue obtained from 0.543 g. (0.0030 mole) of nitrosoglycine was hydrolyzed as above to yield 0.630 g. (73%, based on nitrosoglycine) of hydrazine dioxalate, m.p. 225–226°. If the reaction mixture obtained by hydrolysis of the sydnone is rendered alkaline at room temperature instead of at ice-bath temperature, the yield of hydrazine is greatly reduced.

(c) **By Reduction of Diazotized 3-Aminopyridine.**—3-Aminopyridine was diazotized and reduced essentially according to Räth.[19] An ether extract of the resulting hydrazine was dried over potassium carbonate and evaporated. The yellowish semi-solid residue was dissolved in alcohol and treated with a 10% solution of oxalic acid in ethanol. Two recrystallizations (Norit A)[21] of the crude product from 50% alcohol yielded the pure 3-pyridylhydrazine dioxalate as hair-like needles, m.p. 226–227.5°.

Anal. Calcd. for $C_9H_{11}N_3O_8$: C, 37.38; H, 3.83; N, 14.53; neut. equiv., 72.3. Found: C, 37.47; H, 4.01; N, 14.58; neut. equiv., 74.5.

Acknowledgments.—The authors take pleasure in thanking Dr. H. V. Knorr of the Kettering Foundation, Yellow Springs, Ohio, for determining the infrared spectra with a double-beam Perkin-Elmer instrument. Mr. Elwood R. Shaw assisted with some of the preparative work.

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(17) If the solution is concentrated only to the point at which crystallization begins, cooling then produces the sydnone as well-formed tan plates.

(18) If too much Norit is used, all remaining sydnone is adsorbed. If the filtrate is concentrated without decolorization, a gum is obtained.

(19) C. Räth, *Ann.*, **486**, 95 (1931).

(20) The extraction was discontinued when a portion of the dried extract on treatment with oxalic acid in ethanol produced no precipitate.

(21) Too much Norit will adsorb most of the oxalate salt from the solution.