EXPERIMENTAL

The reactions, details of which are given in Table I, were carried out in 400-ml. stainless steel shaker tubes for 14–16 hr. unless otherwise noted. The amount of catalyst used was 1–5% of the weight of the sulfur compound. The products were isolated and purified by conventional methods.

CONTRIBUTION NO. 609 FROM
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Pyrrolopyridines. III. The Madelung Cyclization of 3-Acylamino-4-picolines[1,2]

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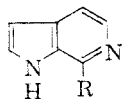
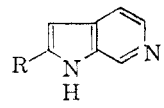
Received April 8, 1960

Literature methods for the synthesis of pyrrolo-(2,3-c)-pyridine (6-azaindole, I, R = H) are not very satisfactory. Koenigs and Fulde[4] reported the preparation of 2-methylpyrrolo(2,3-c)pyridine (II, R = CH_3) in 23% yield by a Madelung cyclization of 3-acetamido-4-picoline, the later in turn being made by a tedious route. Clemo and Holt[5]



I

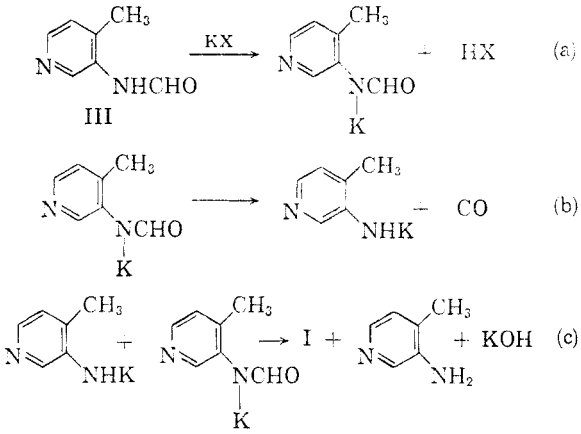


II

were unable to apply the Fischer indole ring closure to 2-methyl-3-pyridylhydrazone. Süs and Möller[6] obtained I (R = H) from the photochemical decomposition of 3-diazo-1,7-naphthyridin-4-(3H)-one and decomposition of the resulting 3-carboxypyrrolo(2,3-c)pyridine, but the multistep synthesis of the required diazo derivative interferes with the utilization of this method for preparative purposes. Somewhat earlier, Herz and Tocker[2] had succeeded in synthesizing I (R = H and CH_3) by the Pomeranz-Fritsch method from readily available starting materials, but the yields were very low.

Recent improvements in the Madelung cyclization of 2-formamidotoluene,[7] the successful preparation of 7-azaindole[8] by an adaptation of this method and the availability of 3-amino-4-picoline[9] suggested that the Madelung cyclization of 3-formamido-4-picoline might give I (R = H) in better yields. The results of such a study are presented here.

3-Amino-4-picoline, prepared by a slightly improved method, was converted to the formamido derivative (III) in 86% yield, but the cyclization, under a variety of conditions, resulted in the isolation of 3-amino-4-picoline only. Tyson's mechanism[7] for the Madelung cyclization as applied to the case at hand (see scheme below) requires the



formation of equivalent amounts of 3-amino-4-picoline and pyrrolo(2,3-c)pyridine by decomposition of the potassium salt of the former; hence it was hoped to direct the reaction toward the formation of I by heating a mixture of the potassium salt of the amine and III in the presence of sodium formate, the latter to repress step *b*. However, the resulting product consisted entirely of 3-amino-4-picoline. It was therefore concluded that the decomposition of the potassium salt of III has a much lower activation energy than the formation of I. In this connection it may be pointed out that while the sodium salt of III, prepared from sodium hydride and III, decomposed below 200°, III itself was stable up to 250°.

It was hoped that cyclization of a diacyl derivative of 3-amino-4-picoline, which cannot form a salt of the amino function and would therefore not undergo decomposition by step *b*, might occur more readily. The diformamido derivative could not be obtained, but diacetyl-3-amino-4-picoline (IV) was prepared by refluxing the amine in acetic anhydride for four hours. Madelung cyclization of IV with potassium ethoxide gave II-(R = CH_3) in 40% yield. Under the same conditions the monoacetyl derivative gave only a 5% yield although Koenigs and Fulde[4] claimed 23%. The fact that the diacetyl compound gave higher yields could, however, be partly accounted for on a statistical basis.

(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 S. Tocker, *J. Am. Chem. Soc.*, **77**, 6355 (1955).

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

(4) E. Koenigs and A. Fulde, *Ber.*, **60**, 2106 (1927).

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

(6) O. Süs and K. Möller, *Ann.*, **599**, 233 (1956).

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

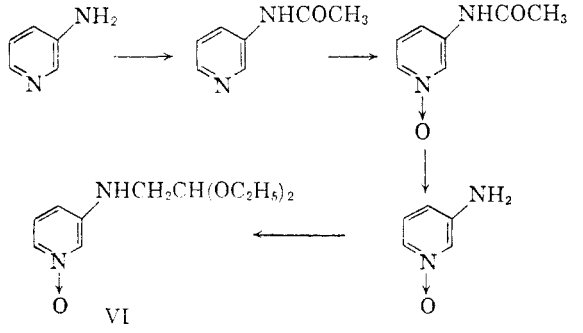
(8) M. M. Robison and B. L. Robison, *J. Am. Chem. Soc.*, **77**, 457 (1955).

(9) H. F. Baumgarten, H. C. Su, and A. L. Krieger, *J. Am. Chem. Soc.*, **76**, 596 (1954).

Since the function of the base in the Madelung cyclization involves the abstraction of a proton from the methyl group, it was hoped that an increase in the acidity of the methyl hydrogens would result in a successful cyclization. There are several examples which demonstrate that the γ-methyl group in pyridine-*N*-oxides is more active than the γ-methyl group in pyridine itself. Hence the cyclization of 3-acetamido- and 3-formamido-4-picoline-1-oxide was studied.

The oxides were made from III and its acetamido analog by the action of peracetic acid. When treated with potassium ethoxide at 300°, they not only decomposed to the free amine, but also lost the *N*-oxide function. 3-Acetamido-4-picoline-1-oxide, when refluxed in dimethylformamide solution with lithium amide, gave a mixture on catalytic reduction and fractional crystallization afforded II (R = CH_3) in about 5% yield. Refluxing 3-formamido-4-picoline-1-oxide (V) with lithium amide in dimethyl formamide yielded a compound which was identical with 3-amino-4-picoline-1-oxide, obtained by the acid hydrolysis of V.

Tilak and co-workers[10] developed a successful method for the synthesis of benzothiophenes by cyclizing arylthioacetals with polyphosphoric acid. By analogy, the precursor for a 6-azaindole synthesis would be *N*-(3-pyridyl)aminoacetal which was prepared by the condensation of 3-aminopyridine and chloroacetal in the presence of lithium amide. Reaction with polyphosphoric acid gave an intractable tar. This was not surprising in view of the known difficulty of electrophilic substitution at the 2- and 4-positions of the pyridine ring. Since such substitutions are greatly favored in pyridine-*N*-oxides, the synthesis of VI was carried out as shown below. However, the cyclization step failed. Decomposition resulted immediately upon addition of VI to polyphosphoric acid. Similar failures have been recorded recently[11] when attempts were made to subject appropriate derivatives of pyridine and pyridine-*N*-oxide to the Pictet-Spengler, Bischler-Napieralski, Pictet-Gams, and Pomeranz-Fritsch reactions.



(10) L. J. Pandya and B. D. Tilak, *Chem. & Ind. (London)*, 981 (1958); B. D. Tilak, *Proc. Indian Acad. Sci.*, 32A, 390 (1950).

(11) K. W. Merz and H. Stolte, *Arch. Pharm.*, 293, 92 (1960).

EXPERIMENTAL[12]

3-Amino-4-picoline. Commercially available 2-amino-4-picoline was converted to a mixture of 2-chloro-3-nitro-4-picoline and 2-chloro-5-nitro-4-picoline according to the method of Baumgarten, Su, and Krieger.[9] Ten grams of the mixture was dissolved in 200 ml. of ethanol and hydrogenated with 2 g. of 5% palladium-charcoal at 3 atm. The solution was filtered, concentrated to 50 ml., and rendered basic with dilute sodium hydroxide solution. The mixture was extracted with chloroform, the extracts dried, and the chloroform removed *in vacuo*. The solid residue was recrystallized from benzene, m.p. 105–107° (lit.[4] m.p. 106°), m.p. of picrate 179–180° (lit.[4] m.p. 179°). The yields in several experiments were about 90%.

3-Formamido-4-picoline. A mixture of 1 ml. of formic acid (98–100%) and 2.4 ml. of acetic anhydride was heated to 50° for 2 hr., cooled, and added to a suspension of 2.5 g. of finely powdered 3-amino-4-picoline in 50 ml. of anhydrous ether. An oil separated which gradually dissolved on shaking. After 4 days the ether was evaporated and volatile components removed by distillation *in vacuo*. The residue was dissolved in acetone and purified by passing over a column of activated alumina. Subsequent recrystallization afforded pure 3-formamido-4-picoline, m.p. 104°, yield 2.6 g.

Anal. Calcd. for $C_7H_8N_2O$: C, 61.75; H, 5.92. Found: C, 61.48; H, 6.04.

The *picrate* melted at 196–198°.

Anal. Calcd. for $C_{13}H_{11}N_5O_8$: C, 42.77; H, 3.01. Found: C, 42.62; H, 3.00.

Cyclization studies. Method A. Compound III and excess of freshly prepared sodium or potassium ethoxide were mixed thoroughly under a stream of nitrogen in a round bottom flask to the neck of which was connected a delivery tube which in turn was joined to a receiving flask, the latter being immersed in a Dry Ice–acetone bath. The system was protected from the atmosphere by a drying tube attached to the receiving flask. The reaction flask was immersed in a woods metal bath and heated gradually. When the bath temperature reached 160° decomposition began, but heating was continued until the bath attained a temperature of 300° and maintained thereat for 10–15 min. During this period a clear colorless liquid collected in the delivery tube and the receiving flask. The reaction flask was allowed to cool in a nitrogen atmosphere and the dark solid mass triturated with a little water and thoroughly extracted with chloroform. The extracts were dried, concentrated, and the residue recrystallized from benzene. It was identical with 3-amino-4-picoline by mixed melting point. The liquid collected in the receiving flask and delivery tube was mainly ethanol; evaporation gave pure 3-amino-4-picoline. In some experiments dry sodium formate was added to the reaction mixture at 150° but the results were unaltered.

Method B. Sodium anilide was prepared by heating and stirring 48 g. of aniline and 10.8 g. of sodium hydride under nitrogen in a three-necked flask fitted with stirrer and nitrogen inlet. When the temperature of the contents reached 160°, 13 g. of dry potassium formate, followed by 10.2 g. of III, was added. Heating and stirring was continued until the temperature of the contents reached 290–300°. Occasionally, the nitrogen stream and stirring were interrupted to permit removal of the aniline formed in the course of the reaction under reduced pressure. The temperature was maintained at 300° for 40 min., the mixture was cooled, decomposed with water, extracted thoroughly with ether, the ether extracts dried and concentrated. Aniline was removed from the residue at reduced pressure and the remaining material dissolved in ether and chromatographed over alumina. The residual solid was recrystallized from benzene and found to be identical with 3-amino-4-picoline, the recovery being 25–40%.

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

Method C. A mixture of 5 g. of 3-amino-4-picoline and 1.25 g. of sodium hydride in a 50-ml. three-necked flask fitted with stirrer, reflux condenser, and nitrogen inlet was heated gradually to 150° with stirring under nitrogen; 6 g. of III was added and the temperature raised to 300°. After 20 min. at 300°, the mixture was cooled and worked up in the usual manner. The residual solid upon recrystallization from benzene gave pure 3-amino-4-picoline.

In order to test the stability of the sodium salt of III, a mixture of 1 g. of III and 0.3 g. of sodium hydride was heated to 200° with stirring under nitrogen. Working up in the usual manner and recrystallization from benzene gave 0.7 g. of 3-amino-4-picoline. In the absence of sodium hydride, III was recovered quantitatively.

Diacetyl-3-amino-4-picoline. A mixture of 4 g. of 3-amino-4-picoline and 9 ml. of acetic anhydride was refluxed for 4 hr. and then fractionated at reduced pressure. The fraction, b.p. 139–145° (1.2 mm.), was redistilled, b.p. 139–140° (1 mm.), and solidified on standing, m.p. approximately 80°. Because the material was extremely soluble and hygroscopic, it was analyzed as the picrate, m.p. 137.5°.

Anal. Calcd. for $C_{16}H_{15}N_5O_9$: C, 45.61; H, 3.59; N, 16.62. Found: C, 45.77; H, 3.39; N, 17.10.

2-Methylpyrrolo(2,3-c)pyridine. Cyclization of the preceding compound with sodium ethoxide by method A gave 2-methylpyrrolo(2,3-c)pyridine in 30–40% yields, m.p. 182–183° (lit.[4] m.p. 183°). Under these conditions 3-acetamido-4-picoline[4] gave a yield of 5%.

3-Acetamido-4-picoline-1-oxide. A mixture of 18 g. of 3-amino-4-picoline and 35 ml. of acetic anhydride was refluxed for 30 min. Excess anhydride was removed at reduced pressure and the residue was added to 50 ml. of 40% peracetic acid. The mixture was gently warmed on a steam bath; when the exothermic reaction began, heating was stopped and the flask cooled intermittently. The mixture was allowed to stand overnight, excess reagents were removed at reduced pressure, and the residual solid dissolved in ethanol and passed through an alumina column. Evaporation of the eluate gave 20.4 g. of product, m.p. 189–194°. The analytical sample, m.p. 194–196°, was prepared by recrystallization from acetone-ethanol.

Anal. Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.81; H, 5.78; N, 17.28.

The *picrate* melted at 157.5–158.5°.

Anal. Calcd. for $C_{14}H_{13}N_5O_9$: C, 42.50; H, 3.31. Found: C, 42.00; H, 3.28.

3-Formamido-4-picoline-1-oxide. Three grams of III were treated with 10 ml. of peracetic acid in the manner described above. The usual workup yielded 1.5 g. of product, m.p. 150–155°. The analytical sample, m.p. 155–156° (sinters at 110°) was recrystallized from water-acetone.

Anal. Calcd. for $C_7H_8N_2O_2.H_2O$: C, 49.40; H, 5.92; N, 16.46. Found: C, 49.72; H, 5.88; N, 16.74.

The *picrate* melted at 141–143°.

Anal. Calcd. for $C_{13}H_{11}N_5O_9$: C, 40.95; H, 2.91; N, 18.38. Found: C, 40.61; H, 2.92; N, 18.57.

Cyclization studies. Method A, when applied to both oxides, gave 40% of 3-amino-4-picoline.

A solution of 0.5 g. of 3-acetamido-4-picoline-1-oxide and 0.3 g. of freshly prepared lithium amide in 20 ml. of dimethylformamide was refluxed under nitrogen for 8 hr. The solvent was removed *in vacuo* and the residue decomposed with water, extracted with chloroform, and dried. Removal of chloroform gave solid material which was dissolved in ethanol and hydrogenated with palladium-charcoal. Fractional crystallization of the reduction product gave 20 mg. of 2-methylpyrrolo(2,3-c)pyridine and 50 mg. of 3-amino-4-picoline.

Treatment of 1 g. of 3-formamido-4-picoline-1-oxide with 0.6 g. of lithium amide in 25 ml. of dimethylformamide gave, upon removal of solvent, a solid residue which was extracted with 50 ml. of absolute ethanol. The extract was concentrated and the solid residue, 0.33 g., identified with authentic 3-amino-4-picoline-1-oxide.

3-Amino-4-picoline-1-oxide. A solution of 3 g. of 3-acetamido-4-picoline-1-oxide in 35 ml. of 20% sulfuric acid was refluxed overnight. The contents were cooled, neutralized with dilute sodium hydroxide solution and the mixture evaporated to dryness *in vacuo*. The residue was extracted with acetone, the extracts were dried, and the acetone removed. The solid product, 1.3 g., was recrystallized from acetone, m.p. 195–196°.

Anal. Calcd. for $C_6H_8N_2O$: C, 58.00; H, 6.50; N, 22.57. Found: C, 57.80; H, 6.45; N, 22.76.

Diethyl N-(3-pyridyl)aminoacetal. A mixture of 11.2 g. of 3-aminopyridine, 3.2 g. of lithium amide, and 50 ml. of toluene was refluxed in a flask protected from the atmosphere. After 3 hr., 19.2 g. of chloroacetal was added dropwise to the hot solution and refluxing was continued for an additional 8 hr. The solution was filtered and the solid residue washed several times with ether. The filtrate and washings were concentrated to 40 ml. at reduced pressure and fractionated *in vacuo*. There was obtained 10 g. of a colorless oil, b.p. 140–150° (6 mm.), which on redistillation boiled at 118–120° (1.2 mm.).

Anal. Calcd. for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.52; H, 8.69; N, 13.50.

The *picrate* melted at 137–139°.

Anal. Calcd. for $C_{17}H_{21}N_5O_9$: C, 46.47; H, 4.82; N, 15.94. Found: C, 46.23; H, 4.69; N, 15.96.

3-Acetamidopyridine. A mixture of 15 g. of 3-aminopyridine and 30 ml. of acetic anhydride was refluxed for 1 hr. Excess anhydride was removed at reduced pressure. The remaining material solidified on trituration with benzene, 16.2. Two recrystallizations from acetone afforded the analytical sample, m.p. 134–136° (lit.[13] m.p. 133°).

Anal. Calcd. for $C_7H_8N_2O$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.73; H, 5.67; N, 20.51.

The *picrate* melted at 249–250°.

Anal. Calcd. for $C_{13}H_{11}N_5O_8$: C, 42.74; H, 3.03. Found: C, 42.64; H, 2.93.

3-Acetamidopyridine-1-oxide. Oxidation of 5 g. of 3-acetamidopyridine with 12 ml. of peracetic acid in the usual fashion gave 5.3 g. of oxide, m.p. 209–210.5° after recrystallization from acetone-ethanol.

Anal. Calcd. for $C_7H_8N_2O_2$: C, 55.25; H, 5.30. Found: C, 55.61; H, 5.39.

The *picrate* melted at 135–137°.

Anal. Calcd. for $C_{13}H_{11}N_5O_9$: C, 40.95; H, 2.91; N, 18.38. Found: C, 41.50; H, 2.64; N, 18.22.

3-Aminopyridine-1-oxide. A mixture of 3.3 g. of the preceding compound and 30 ml. of 20% sulfuric acid was refluxed overnight. The cold solution was neutralized, concentrated to 50 ml., refrigerated, filtered from sodium sulfate, and evaporated to dryness *in vacuo*. The solid residue was extracted with chloroform in a Soxhlet apparatus. Evaporation of the chloroform gave 1.4 g. of crude product which was purified by chromatography over alumina (solvent and eluent ethanol) and recrystallization from chloroform-alcohol, m.p. 124–125° (lit.[14] m.p. 125°), mixed melting point with a sample prepared by heating 3-bromopyridine-1-oxide and ammonia in a sealed tube undepressed.

In a large scale run, 140 g. of 3-aminopyridine was refluxed with 300 ml. of acetic anhydride for 1 hr., the residue obtained after removal of excess anhydride oxidized with 400 ml. of peracetic acid, excess acetic acid was removed, and the residue obtained after removal of excess anhydride oxidized with 400 ml. of peracetic acid, excess acetic acid was removed and the residue hydrolyzed directly with 1500 ml. of dilute sulfuric acid. Working up the product as described gave 60 g. of 3-aminopyridine-1-oxide. This is more convenient than the literature method.[14]

Diethyl N-(3-1-oxypyridyl)aminoacetal. The procedure was similar to that used for the preparation of VI except

(13) R. Camps, *Arch. Pharm.*, **240**, 345 (1902).

(14) J. G. Murray and C. R. Hauser, *J. Org. Chem.*, **19**, 2013 (1954).

for the substitution of ethanol as a washing agent, yield from 13 g. of 3-aminopyridine-1-oxide 2.3 g. of light yellow oil, b.p. 95–100° (2 mm.) which solidified on standing, m.p. 53°. It was unstable in air.

Anal. Calcd. for $C_{11}H_{18}N_2O_3$: N, 12.38. Found: N, 12.29.

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Reaction of Phenyl Isocyanate with *N,N*-Dimethylformamide

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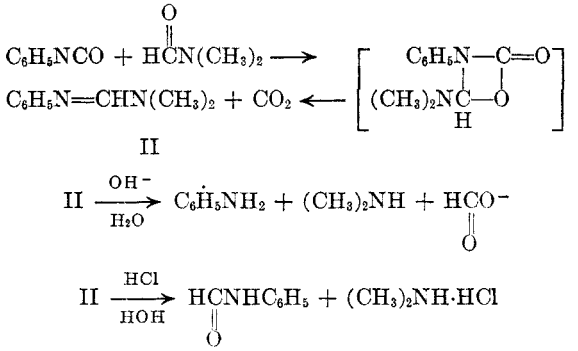
Received April 28, 1960

The reactions of phenyl isocyanate with *p*-dimethylaminobenzaldehyde to form *p*-dimethylaminobenzalaniline, and with nitrosobenzene to form azobenzene have been earlier reported.[2] In both reactions, the authors have postulated the intermediate formation of an unstable four-membered ring which loses carbon dioxide to form the final product.

In the present work, phenyl isocyanate was found to react readily with *N,N*-dimethylformamide (I) in excess I as solvent at 150°. The reaction proceeded analogously to the earlier reported reactions[2] with the evolution of nearly one mole of carbon dioxide per mole of isocyanate and led to the formation of *N,N*-dimethyl-*N'*-phenylformamidine (II) in 80% yield. A parallel instance of this amidine-forming reaction, one which involves the reaction of *p*-toluenesulfonyl isocyanate with *N,N*-dimethylformamide, has recently been reported.[3]

Alkaline hydrolysis of II led to the isolation of aniline, dimethylamine, and formic acid. Mild acidic hydrolysis of II permitted the isolation of the intermediate hydrolysis product, formanilide.



The reaction of an excess of phenyl isocyanate with I at 150° resulted in a reduced yield (25%) of the formamidine II and the concomitant recovery of a considerable quantity of a mixture of solid products. Fractional recrystallization of these solids led to the isolation of 1,1-dimethyl-3-phenylurea and a second material (III) that was not fully characterized.

EXPERIMENTAL[4]

N,N-Dimethyl-N'-phenylformamidine (II). A mixture of of 40 g. (0.336 mole) of phenyl isocyanate and 161 g. (2.21 moles) of redistilled *N,N*-dimethylformamide (I) was refluxed for 4 hr. with provision made for the absorption of any evolved carbon dioxide in aqueous potassium hydroxide solution. At the end of the reflux period, 0.312 mole of carbon dioxide was found to have been liberated. The major portion of the unchanged I was removed by distillation. The residue was then distilled to provide 41 g. (80%) of impure *N,N*-dimethyl-*N'*-phenylformamidine (II), b.p. 68–71° (0.05 mm.), n_D^{25} 1.5913, λ_{max} 6.12 and 9.05 μ.

Anal. Calcd. for $C_9H_{12}N_2$: C, 72.97; H, 8.11; N, 18.92. Found: C, 72.14; H, 7.82; N, 20.13.

Basic hydrolysis of the formamidine II. A mixture of 19.3 g. (0.132 mole) of II, 8.6 g. (0.131 mole) of potassium hydroxide, 30 ml. of water, and 100 ml. of methanol was refluxed for 16 hr. with provision made for the absorption of any evolved dimethylamine in dilute aqueous hydrochloric acid. The reaction mixture was distilled free of methanol the distillate being collected in another portion of dilute acid. The two acid solutions were combined, concentrated, and adjusted to a *p*H of 11 by the addition of 20% aqueous potassium hydroxide solution at 5°. The addition of 20 g. of phenyl isothiocyanate to the basic solution, with agitation, caused almost immediate solidification of the mixture. After standing at room temperature for several hours, the solids were filtered to provide 16.9 g. (0.093 mole) of crude 1,1-dimethyl-3-phenylthiourea, m.p. 116–126°. Repeated recrystallization from benzene raised the melting point to 133–136.5° (lit.[5] m.p. 135°), undepressed on admixture with an authentic sample prepared from dimethylamine and phenylisothiocyanate.

The basic residue from the distillation of the hydrolysis reaction mixture was steam distilled and the distillate was extracted with benzene. Addition of 20 g. of phenylisothiocyanate to the concentrated benzene extract resulted in the isolation of a 68% yield of aniline as thiocarbanilide, m.p. 151–152.5° (lit.[5] m.p. 154°), undepressed on admixture with an authentic sample.

The residue from the steam distillation of the reaction mixture was brought to *p*H 8 and, after dilution with an equal volume of ethanol, was refluxed with 16 g. of *p*-bromophenacyl bromide for 1 hr. The hot reaction mixture was filtered and the solids obtained were recrystallized from toluene to provide 7.9 g. (0.032 mole; 24%) of crude *p*-bromophenacyl formate, m.p. 128–133°. Repeated recrystallization from 95% ethanol raised the melting point to 138–141° (lit.[6] m.p. 140°), undepressed on admixture with an authentic sample.

Acid hydrolysis of the formamidine II. A mixture of 5 g. (0.038 mole) of II and 100 ml. of 0.38*N* aqueous hydrochloric acid was allowed to stand for 16 hr. and was then heated at 50° for 45 min. The cooled solution was saturated with sodium chloride and extracted with benzene. The benzene was evaporated at room temperature to leave an oil which subsequently solidified on standing in the freezer. The solidified oil was recrystallized from a mixture of toluene and ligroin to give 2.65 g. (65%) of formanilide, m.p.

(1) Kordite Company, Macedon, N. Y.
(2) H. Staudinger and R. Endle, *Ber.*, **50**, 1042 (1917).
(3) C. King, *J. Org. Chem.*, **25**, 352 (1960).
(4) All melting and boiling points are uncorrected.
(5) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 3rd Ed., 1948, p. 234.
(6) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 3rd Ed., 1948, p. 222.