THE CHLORINATION OF PYRIDINE

Investigations on pyridine and quinoline derivatives
41st. Communication 1)

BY

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On chlorinating pyridine in the gas phase at 270° a good yield of 2-chloropyridine is obtained together with a small quantity of 2:6-dichloropyridine. At 400° the main product is 2:6-dichloropyridine.

It is shown that among the products produced in the chlorination at 270°, a small amount of a pyridylpyridinium compound must be present, for 2-aminopyridine is obtained on hydrolysis of the reaction product.

Chlorination in the gas phase takes place very slowly at about 200°; at this temperature 3:5-dichloropyridine is obtained together with 3:4:5-trichloropyridine.

On chlorinating fused pyridine hydrochloride at about 170° a considerable yield of 3:5-dichloropyridine is produced along with a small amount of 3:4:5-trichloropyridine and pentachloropyridine.

Thus, in the chlorination of pyridine a specific temperature effect on the type of substitution is observed as in the bromination of pyridine. In the chlorination, the temperature limits for both types of substitution lie near together.

2-Aminopyridine is obtained on heating 2-chloropyridine with aqueous ammonia and copper sulphate. 2-Amino-6-chloropyridine is obtained on heating 2:6-dichloropyridine with aqueous ammonia.

Introduction.

Investigations on the chlorination of pyridine described in the literature have afforded rather unsatisfactory results. S e l l and D o o t s o n 2) allowed 10 times the amount of phosphorus pentachloride to react on pyridine at 210—220° for 15—20 hours. The

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1) In order to facilitate reference to following publications, on investigations on pyridine and quinoline, this publication is numbered; the forty previous communications of this series, which have appeared in the Rec. trav. chim. since 1925 are included in the enumeration.

2) W. J. S e l l and F. W. D o o t s o n. J. Chem. Soc. 73, 432 (1898).
product consisted mainly of higher chlorinated products and contained very little of the lower chlorinated pyridines. 2:6-Dichloropyridine 3), 2:3:5-trichloropyridine 4), 3:4:5-trichloropyridine 5) and a trichloropyridine of unknown structure were isolated from the reaction mixture; subsequently, three isomeric tetrachloropyridines, viz. 2:3:4:5-, 2:3:5:6- and 2:3:4:6-tetrachloropyridine 6), respectively, were identified and also pentachloropyridine. No reaction was observed at lower temperatures; less phosphorus pentachloride gave the same result but in smaller yield.

They also allowed pyridine and chlorine to react at temperatures varying from 0° to 117° 7); in some experiments chlorination was continued until free hydrogen chloride escaped. More tarry products were produced at higher temperatures than at lower temperatures. 3:4:5-Trichloropyridine was isolated from the reaction mixture. Finally, these investigators 8) saturated pyridine with hydrogen chloride and led chlorine at 110—120° into the liquid mass for several weeks. 3:5-Dichloropyridine, 2:3:4:5-tetrachloropyridine (the yield of which amounted to 70 % of the total reaction product) and pentachloropyridine were isolated from the reaction product along with some 3:4:5-trichloro-2-aminopyridine 9). The occurrence of this aminopyridine is very remarkable. Sell and Do n n o s o n 8) pointed out that a compound with two nitrogen atoms must be formed by the interaction of two molecules of pyridine and assumed that a compound containing two pyridine nuclei was formed primarily by the action of the chlorine. They succeeded in isolating a compound C_{10}H_{N_2}Cl_{11} from the reaction mixture, to which they ascribed the probable structure

![Diagram]

The trichloro-2-aminopyridine mentioned above is formed from this compound 10) during the working up, when the liquid is made alkaline, by the hydrolytic fission of the pyridine nucleus.

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3) Idem, Ibid. 77, 233 (1900).
4) Idem, Ibid. 93, 2001 (1908).
5) Idem, Ibid. 99, 1679 (1911).
6) Idem, Ibid. 77, 1 (1900).
7) Idem, Ibid. 73, 444 (1898).
8) Idem, Ibid. 75, 979 (1899).
9) Idem, Ibid. 77, 771 (1900).
10) Idem, Ibid. 79, 902 (1901).
Later, Koenigs and Greiner 11) prepared 4-pyridyl-pyridinium dichloride by the action of thionyl chloride on pyridine, from which 4-aminopyridine was obtained by the action of aqueous ammonia. Fundamental observations for an understanding of this reaction are to be found already in the communications of Sell and Dootsen, already mentioned, but this is not stated in the later literature.

A little 2-pyridyl-pyridinium chloride is formed, under the conditions of our experiments, in the chlorination of pyridine in the gas phase at 270°: on working up the reaction product we found a very small quantity of 2-aminopyridine, which must have been produced by the alkaline hydrolysis of 2-pyridyl-pyridinium chloride.

A similar observation is described by Koller and Ruppersberg 12). These authors heated a mixture of 2-chloropyridine and pyridine in a sealed tube to 200° and obtained 2-aminopyridine on working up the reaction products. Rodewald and Plazek 13) obtained 2-pyridyl-N-pyridinium iodide on heating pyridine hydrochloride with iodine monochloride for seven hours at 250°. They also obtained this compound by heating a mixture of 2-iodopyridine and pyridine after saturation with hydrogen chloride for 5 hours at 250°.

Since the method of Sell and Dootson led to a complicated mixture of reaction products, Wibaut and van der Ley 14) carried out the chlorination of pyridine in the vapour phase. From their preliminary experiments it appeared that a mixture of chlorination products was produced at about 250°, from which 2-chloropyridine, 3:5-dichloropyridine and pentachloropyridine could be isolated, while the presence of 2:6-dichloropyridine was shown to be highly probable. The total yield of chlorinated products amounted only to 4—6% of the pyridine used. These experiments led to an investigation of the bromination of pyridine in the gas phase. From these investigations 15) it appeared that the type of substitution occurring in the bromination of pyridine vapour in the presence of indifferent contact substances (pumice, asbestos, charcoal), is determined by the temperature, substitution occurring in positions 3 and 3 and 5 at about 300°, while at about 500° substitution takes place in the 2- and 2:6-positions. At about 400° a mixture of brominated pyridines is formed, in which pyridines, substituted both in the 3- and 3:5- and in the 2- and 2:6-positions are present.

11) E. Koenigs and H. Greiner, Ber. 54, 1049 (1931).
12) G. Koller and H. Ruppersberg, Monats. 50, 436 (1928).
We have now studied the chlorination of pyridine more closely and it appears that in the chlorination as in the bromination of pyridine in the vapour phase, there is a temperature range, viz. 170—220°, in which substitution occurs principally in the 3- and 3:5-positions and another range of temperatures viz. 260—420°, where substitution of the chlorine atoms takes place chiefly in the 2- and 2:6-positions. At 220° a very small amount of 3:5-dichloropyridine was formed along with 3:4:5-trichloropyridine; the rate of chlorination is very low. At 260° and above 2-chloro- and 2:6-dichloropyridine are formed in reasonable yield.

The production of 3:4:5-trichloropyridine is in agreement with the observation of Sell and Dootson and den Hertog and Wibaut, who found 3:4:5-tribromopyridine in the bromination product of pyridine at 300° and who also detected a very small quantity of 4-bromopyridine in this product.

We have an indication, that in the chlorination in the gas phase over a pumice mercuric chloride contact at about 220°, a small quantity of 4-chloropyridine is produced. A small quantity of yellow crystals, which dissolve easily in water, separated after some time from the fraction in which the presence of 4-chloropyridine was suspected. The aqueous solution contained chloride ions and became dark coloured when treated with alkali. This points to the formation of a pyridyl-pyridinium compound, which is readily formed from 4-chloropyridine. In this connection we would refer to the next communication (No. 42) by Wibaut and Broekman, in which we return to this observation.

The conditions, under which products containing substituents in the 2- and 2:6-positions are formed, need closer investigation. These investigations are made more difficult by the fact that 4-chloropyridine and to a much greater degree, 4-bromopyridine, are unstable compounds.

In the chlorination of pyridine, the temperature limit for 2- and 2:6-substitution lies much lower than for the bromination; the result is, that substitution in the 3- and 3:5-positions is only clearly apparent at temperatures where the velocity of the reaction is low. Thus the temperature limits of the two types of substitution lie much closer together for the chlorination than for the bromination of pyridine.

In the experiments of Wibaut and van der Ley the conditions of the experiments were not so closely defined as in the experiments now described. From the fact that these investigators found 3:5-dichloropyridine along with 2-chloropyridine in the reaction mixture, it must be concluded that they worked in a temperature
region, which lay between the limits of the temperature regions in which the substitution types mentioned above occur.

A confirmation of 3:5-substitution at 220° in the gas phase is found in the chlorination of pyridine hydrochloride. In consequence of a paper of Mayer Bode\textsuperscript{17}, in which it was stated, that in the bromination of fused pyridine hydrochloride at 212° with mercuric chloride as catalyst, a mixture of 3-bromo- and 3:5-dibromopyridine is produced, we have led chlorine gas at temperatures between 170—200° into molten pyridine hydrochloride either alone or in presence of mercuric chloride. 3:5-Dichloropyridine was obtained as the main product together with a small amount of 3-chloropyridine and a very small quantity of higher chlorinated products. We observed no effect from the mercuric chloride.

If we compare this result with the work of Sell and Doottson\textsuperscript{6}), it can be said that 3:5-substitution occurs in the chlorination of pyridine hydrochloride in the temperature range of 110° to 220°. In the experiments of Sell and Doottson, however, the course of the reaction is complicated since they found 2:3:4:5-tetrachloropyridine as the main product. The experimental conditions under which they worked, are not suitable for obtaining monochloropyridines, since they continued the action of chlorine for a very long time and, on account of the relatively low reaction temperatures, addition compounds could be formed, which could lead to further complications. At temperatures above 300° the chlorination of pyridine occurs with much greater violence than the bromination and charring occurs. This can be prevented to some extent by diluting the reacting gases with nitrogen.

In spite of this objection the method of chlorination we have worked out is the best for the preparation of 2-chloro- and 2:6-dichloropyridines. We found practically no charring at 250° so that chlorination of pyridine at 250° is a good method for preparing 2-chloropyridine. The significance of these compounds as starting materials for the preparation of other pyridines substituted in the 2- and 2:6-positions will be investigated further.

We have already found that the chlorine atoms in 2:6-dichloropyridine react much more slowly with ammonia than the bromine atoms in 2:6-dibromopyridine. 2-Amino-6-chloropyridine is produced on heating 2:6-dichloropyridine with ammonia at 190°. Under these conditions the second chlorine atom is not replaced by the amino

\textsuperscript{17} H. Mayer Bode, Ber. 69, 1535 (1936): cf. Swiss Pat. 174873, Chem. Zentr., 1935, II. 2283.
group. From 2:6-dibromopyridine, 2:6-diaminopyridine \(^{18}\) is obtained along with 2-amino-6-bromopyridine.

We did not succeed in converting 3:5-dichloropyridine into 3-amino-5-chloropyridine in this way.

2-Chloropyridine is converted into 2-aminopyridine in a yield of 50% by heating with concentrated ammonia and copper sulphate at 200°. The addition of copper sulphate is not necessary in the conversion of 2-bromopyridine into 2-aminopyridine \(^{19}\). Otto Fischer \(^{19}\) obtained 2-aminopyridine in good yield by heating 2-chloropyridine with anhydrous zinc chloride and anhydrous ammonia at 220°.

From the above it appears that the chlorine atoms in the 3- and 5-positions are more firmly bound than those in the 2- and 6-positions.

**EXPERIMENTAL PART.**

**A. Chlorination in the gas phase.**

The reaction tube \(A\) (see fig. 1), which is constructed of difficultly fusible glass (Sibor), is placed in an electric furnace in an inclined position; a thick walled copper tube, which surrounds the glass tube, is also placed in the electric furnace, so that a uniform temperature is reached. The greater part (43 cm) of \(A\) is filled with a contact substance such as granulated pumice. At \(E\), where the contact begins, end two laterally placed and diametrically opposed inlet tubes \(B\) and \(C\). Pyridine vapour, diluted with dry nitrogen, enters through \(B\) and dry gaseous chlorine through \(C\). The gases take the temperature of the furnace in tubes \(B\) and \(C\) and are then mixed in the reaction tube \(A\). The temperature is measured in the reaction tube by means of the thermo-element \(D\), which reaches to \(E\) in tube \(A\). In order to prevent \(D\) coming into direct contact with the reacting gases, \(D\) is surrounded by a tube, sealed on to the side of \(E\), which passes through the ground joint \(G\), closing tube \(A\). A wider glass tube is sealed on to \(F\), which it surrounds and holds in the reaction tube. In this way the gases are prevented from diffusing into the part of \(A\) where there is no contact substance and where the temperature is not yet constant.

The flow of pyridine through \(B\) is regulated by an automatic drop burette \(H\), which maintains a constant rate of flow and by which the pyridine (eventually mixed with nitrogen) can be accurately controlled. \(H\) is attached by a ground joint to the flask \(K\), which serves as a vaporizer for the pyridine and is placed in an oil bath at about 200°. The pyridine vapour leaves \(K\) by an exit tube consisting of a glass spring \(L\), which is surrounded with a heating spiral to prevent condensation of the pyridine vapour, and is connected with \(B\) through a ground joint. \(K\) also contains an inlet tube for nitrogen. The chlorine supply tube is via a glass spring \(M\), connected by a ground joint with \(C\). Both the chlorine and the nitrogen is dried with concentrated sulphuric acid and each passes through flow-meters filled with concentrated sulphuric acid and finally reach the furnace at \(C\) and the vaporizer \(K\), respectively. By this means the amounts of each gas can be regulated.


\(^{19}\) O. Fischer, Ber. 32, 1297 (1899).
The reaction mixture is collected in a receiver the neck of which is attached to A with a ground joint, and which is also furnished with an exit tube.

I. Chlorination at 290—300° (width of tube 20 mm).

A mixture composed of 2.4 mols. of gaseous pyridine, 2.4 mols. of nitrogen and 3.6 mols. of chlorine was passed through the tube in
9.5 hrs, which corresponds with a velocity of 0.88 mols. of gas mixture per hour. A small amount of charring occurred and a brown oil, which soon solidified to a crystalline mass, collected in the receiver. Water was added to this product when a vigorous evolution of chlorine occurred and a part remained undissolved from which no substitution products could be isolated. The contents of the receiver were then subjected to distillation in a current of steam, when a separation was effected between unchanged pyridine, which remained behind in the flask as the hydrochloride and the substituted pyridines, which are less basic and therefore pass over when the acid solution is distilled in steam. The distillate was saturated with potash and extracted with ether. After drying the ethereal layer over anhydrous sodium sulphate, the ether was removed by distillation and the residue fractionated through a Widmer apparatus.

The following fractions were thus obtained:

1. 50 g of liquid boiling between 166° and 175° and consisting mainly of 2-chloropyridine;
2. about 5 g, which passed over above 175°.

The 2-chloropyridine obtained from the first fraction was identified by heating 5 g in a sealed tube with 5.5 cm³ of methyl iodide for 10 hrs at 100°. The solid brown mass so obtained, was dissolved in alcohol, and after adding ether a pale yellow crystalline precipitate was formed, which melted with decomposition at 205—206° after recrystallisation from alcohol. This compound appeared to be identical with 2-iodopyridine methiodide melting at 207°, which is already known 19). A mixed melting point was 207°.

The isolation of pure 2-chloropyridine, b.p. 171°, is difficult because the small amount of 2:6-dichloropyridine is troublesome to remove. The refractive index of the fraction boiling at 166—175° was $n_\text{D}^\circ = 1.5337$, while $n_\text{D}^\circ = 1.5322$ was found for the refractive index of 2-chloropyridine prepared by diazotising 2-aminopyridine.

Chlorine determination: C₆H₄NCl requires Cl = 31.3 %.
   Found Cl = 32.59 %.
   Cl = 32.17 %.

Both the somewhat higher refractive index and the high chlorine content are an indication that a small amount of 2:6-dichloropyridine was present in this fraction.

The second fraction was distilled to 90° at 12 mm. A white crystalline mass was deposited in the condenser tube. This material melted at 84—85° after recrystallisation from light petroleum. A mixed melting point with 2:6-dichloropyridine, m.p. 87—88°, prepared by
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another method, was 84°, so that these products are identical. From this it may be concluded that this fraction consists of 2:6-dichloropyridine.

II. Chlorination at 270° (width of tube = 20 mm).

A mixture consisting of 1.9 mols. of gaseous pyridine, 0.36 mols. of nitrogen and 2.8 mols. of chlorine was passed through the tube in 71/4 hrs, which represents a speed of 0.73 mol. per hour.

The product was worked up as described in experiment I. There were obtained, a first fraction, boiling at 67°/17 mm and \( n_0^2 = 1.5330 \), wt. 67 g (0.59 mol.) consisting chiefly of 2-chloropyridine.

The refractive index is somewhat too high because 2:6-dichloropyridine is present as an impurity and it cannot be removed from the 2-chloropyridine by freezing.

A second fraction (b.p. 68—93° 12 mm) consisted of 5 g of crude product from which 0.5 g of 2:6-dichloropyridine was isolated.

A third fraction passed over at 93—107° at 12 mm and consisted of 3 g of crude product from which 1.5 g of 2:6-dichloropyridine were isolated.

After distilling for two hours, alkali was added to the liquid remaining in the flask and the alkaline mixture was distilled with steam. The distillate was extracted with ether; after removing the ether, an oil was obtained which consisted of 50 g of pyridine and a little residue from which no substitution products could be isolated.

The strongly alkaline liquid remaining in the flask was extracted with ether. From the extract a gram of a thick liquid oil was obtained, which gave a picrate, on treatment with a saturated alcoholic solution of picric acid, identical with the picrate of 2-aminopyridine, m.p. 216—217°.

The yield of 2-chloropyridine in experiment II amounted to 31% of theory calculated on the total quantity of pyridine and 46% calculated on the amount of pyridine consumed.

III. Chlorination at 320—330° (tube width 27 mm).

A mixture consisting of 2.65 mols. of gaseous pyridine, 1.3 mols. of nitrogen and 2.08 mols. of chlorine was passed through the tube in 8 hrs, corresponding with a velocity of 0.77 mols. of gas mixture per hour.

The product was worked up in the same way as described in experiment I. 98 g of a crude 2-dichloropyridine fraction boiling at 68—85° at 20—24 mm were obtained, of which 32 g boiled at 75—76° at 24 mm and showed \( n_0^2 = 1.5325 \). Thus this is pure 2-chloropyridine.
A small amount of 2:6-dichloropyridine was isolated by freezing from the second fraction (2 g) boiling at 85—100°/30 mm.

Twelve grams of crude 2:6-dichloropyridine were obtained from a third fraction by vacuum distillation at 100°/30 mm.

IV. Chlorination at 340—350° (width of tube 20 mm).

A mixture composed of 0.8 mol. of pyridine vapour, 0.8 mol. of nitrogen and 1.2 mols. of chlorine was led through the tube in 4 hrs. at a rate of 0.7 mol. of gas mixture per hour.

The method of working up was modified in this experiment. After adding water to the reaction mixture, the portion insoluble in water was separated and submitted to a steam distillation. In this way 39 g of impure 2:6-dichloropyridine, m.p. 79—81°, were obtained; recrystallisation from light petroleum gave a product melting at 85°.

After making the aqueous solution alkaline and extracting with ether, 49 g of oil were isolated, which distillation showed to consist of unchanged pyridine, 2-chloropyridine and 2:6-dichloropyridine.

The excess of chlorine apparently favours 2:6-substitution.

A fair amount of free carbon was deposited in the tube.

V. Chlorination at 420° (width of tube 20 mm).

A mixture of 0.1 mol. of pyridine vapour, 0.1 mol. of nitrogen and 0.16 mols. of chlorine was passed through the tube per hour. After 3½ hours the tube was blocked with carbon. The reaction mixture afforded 6 g. of crude 2-chloropyridine and 18 g of 2:6-dichloropyridine. Thus 2:6-substitution predominates.

VI. Chlorination at 220° (width of tube 20 mm).

a. In 12 hours a mixture of gases composed of 2 mols. of vaporized pyridine and 2.4 mols. of chlorine, was passed through the tube, which corresponds with a velocity of 0.37 mol. of gas mixture per hour. The product was worked up as described under experiment I. An oil was isolated, from which a solid was frozen out. The latter melted at 67° after recrystallisation from alcohol and was identical, according to a mixed melting point determination, with 3:5-dichloropyridine, the yield of which was very small.

b. A gas mixture composed of 1.4 mols. of pyridine vapour, 0.7 mol. of nitrogen and 2.1 mols. of chlorine, was passed through the tube in 7 hours, which agrees with a velocity of 0.6 mol. of gas mixture per hour.

The product was worked up as described in experiment I. After the product had been distilled in steam, a thick brown mass remained
behind and no definite product could be isolated from it. A mixture of 18 g of chlorinated pyridines was obtained from the steam distillate, and was separated by distillation into five fractions boiling between 60° and 135° at 15 mm. By cooling the first two fractions (60—70° and 70—80°) in a bath of solid carbon dioxide, a solid substance melting at 67° was obtained. This indicated 3:5-dichloropyridine.

From a fraction boiling at 100—117° a substance was isolated, which melted at 74—75° after repeated recrystallisation from alcohol and appeared to be identical with 3:4:5-trichloropyridine.

3-Chloropyridine could not be detected in experiments VIa or VIb.

VII. Chlorination at 220—240° (width of tube 20 mm).

The contact mass was composed of glass wool. A mixture composed of 1.25 mols. of pyridine, 0.31 mol. of nitrogen and 1.6 mols. of chlorine was passed through the tube in 5 hours at a rate of 0.63 mols. of gas mixture per hour.

A few grams were obtained of an oily liquid, from which needles crystallised after standing for some time; the crystalline material melted at 70° after recrystallisation from alcohol.

Analysis:

\[ C_3H_4NCl_3 \text{ requires } H = 1.11, \ C = 32.90\%. \]
found \( H = 1.19, \ C = 32.81\% \).

Thus this compound is a trichloropyridine and probably 3:4:5-trichloropyridine, which melts at 76—77° according to Dohrn and Diedrich 20).

B. Chlorination of fused pyridine hydrochloride.

Two and a half mols. of dry pyridine were saturated with hydrogen chloride at ordinary temperatures. Dry chlorine was then passed in through the tube \( A \) with rapid stirring at 165—175° for 12 hours. The flask was fitted with an upright tube \( B \) in which the stirrer was fixed. \( B \) also served as a condenser preventing loss by evaporation (see fig. 2).

The reaction product was distilled in steam after adding water and a solid substance passed over, which appeared to be 3:5-dichloropyridine, m.p. 67°, after recrystallisation from alcohol. The yield was 63 g (0.43 mol.).

The aqueous steam distillate was saturated with potash and extracted with ether. After distilling off the solvent from the dry

ethereal extract, 54 g of oil were obtained which boiled from 65° to 135° at 15 mm; small amounts of 3:5-dichloropyridine, 3:4:5-tri-chloropyridine and pentachloropyridine (mixed m.p. 125°) were isolated from this fraction.

The residue from the steam distillation was made alkaline and distilled in steam. After extraction with ether and redistillation, an oil was obtained which contained pyridine and a small amount of 3-chloropyridine. This was demonstrated by converting this compound into the picrate, which melts at 149—150° 21) and is identical with the picrate of a specimen of 3-chloropyridine prepared from 3-aminopyridine.

21) 135° is given as the literature melting point. A. H an t z s c h. Ber. 22, 2836 (1889); this is obviously a mistake.
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Chlorination of pyridine hydrochloride with the addition of mercuric chloride.

In this case the same products were obtained in about the same yields as in the previous experiment. No effect was observed on either the type of substitution or the yields of products obtained.

C. Conversion of 2:6-dichloropyridine into 6-chloro-2-aminopyridine.

Six grams of 2:6-dichloropyridine were heated with 30 cm³ of 20 % ammonia in a sealed tube for 40 hours at 180—190°. A white crystalline mass was produced in the tube; yield 2.6 g; the substance melted at 75° after recrystallisation from alcohol.

Analysis:
C₇H₆N₂Cl requires H = 3.93, C = 46.69 %.
found H = 3.88, C = 46.89 %.

Hence 2-amino-6-chloropyridine is produced.

Conversion of 2-chloropyridine into 2-aminopyridine.

Four grams of 2-chloropyridine were heated with 20 cm³ of 20 % ammonia, and 2 g of copper sulphate in a sealed tube to 180—190° for 20 hours. After saturating with potash the liquid was extracted with ether and 1 g of 2-aminopyridine was isolated from the ethereal solution.

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