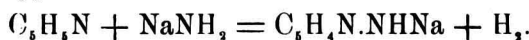


Chemistry. — “*The Action of Sodiumamide on Pyridine, and some Properties of α -aminopyridine*”. By J. P. WIBAUT and ELISABETH DINGEMANSE. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of December 30, 1922).

Through TSCHITSCHIBABIN'S¹⁾ beautiful researches α -aminopyridine has become easily accessible. This investigator found that sodium amide acts on pyridine as follows:



On decomposition of the reaction product with water, aminopyridine and sodium hydroxide is formed.

As we required this substance as starting material for synthetic investigations, we have applied the method of preparation found by TSCHITSCHIBABIN. Though also in our experiments α -aminopyridine was formed as chief product, we found other substances than the Russian investigator among the by-products.

We experienced that the action of sodium amide on pyridine can take place in different ways, dependent on the nature of the sodium amide preparation used. We have prepared sodium amide according to TITHERLEY'S indication by the action of carefully dried ammonia on melted sodium at 350—400° C. The preparation obtained was a pure white, showed a crystalline fracture, and contained no free sodium. This preparation did not react with pyridine. A preparation prepared at 300°, reacted very slowly with pyridine. In this experiment very little α -amino pyridine was however, formed; further a little γ - γ -dipyridyl, and some other products, which we did not examine.

A sodium amide preparation of KAHLBAUM, which was pretty impure, as it contained free sodium and also sodium hydroxide, acted vigorously on pyridine, as TSCHITSCHIBABIN states. Another preparation of KAHLBAUM, which was apparently much purer, acted in exactly the same way. A mol. of pyridine is diluted with toluene, and this mixture is heated with a mol. of finely powdered sodium amide at 120—125° for seven hours.

¹⁾ Journal de la Société Physico-Chimique Russe, **46**, 1216 (1914).
Chem. Zentral Blatt 1915. I. 1065.

We have decomposed the reaction product with water according to TSCHITSCHIBABIN's direction, dissolved it in ether, and distilled it at a pressure of 15 m.m. The bulk went over at 104—125°, and was almost pure aminopyridine in agreement with the records of the investigator mentioned. At 130—180° and 15 m.m. an oil distilled, which soon gets a dark colour when exposed to the air. After some time white crystals separated out of this oil. Recrystallized out of water these crystals became colourless, long needles melting at 73°. This substance is the hydrate of γ - γ -dipyridyl, which has already been described by ANDERSON. After drying in a vacuum exsiccator we obtained the γ - γ -pyridyl itself, which melts at 112°. We identified this substance by analysis and by oxidation with potassium permanganate. We obtained white crystals melting at 307°, which agrees with the melting-point of iso-nicotinic acid. On action of picric acid on γ - γ -dipyridyl, both dissolved in alcohol, we obtained a picrate crystallizing in fine yellow needles, and melting at 252°. As appears from analysis this picrate contains 1 mol. of picric acid to 1 mol. of γ - γ -dipyridyl. With anhydrous acetic acid and zinc dust the γ - γ -dipyridyl gave the intensive violet colour reaction, which was lately described by DIMROTH and HEENE.

There are still some more substances to be found in the oil that distilling at 130—180° and 15 m.m. pressure. After the bulk of the γ - γ -dipyridyl had been removed from this oil, we treated the liquid with hydrochloric acid. Two chlorides were then obtained, which both crystallized in white needles. After recrystallisation from diluted hydrochloric acid one melted at 115—116°; the second melted above 280°. The latter substance appeared to be the salt of γ - γ -dipyridyl.

We have liberated the base from the chloride of 115—116°, and obtained white crystals melting at 94—95°. This melting-point agrees with the α - α -dipyridyl-amine ($C_8H_8N_2$),NH, which was obtained by STEINHÄUSER and DIEPOLDER¹⁾ from α -chloro pyridine and α -amino pyridine by heating with barium oxide.

The nitrogen percentage of our crystals, which melt at 94—95°, agrees with the value calculated for dipyridyl amine.

TSCHITSCHIBABIN says that this dipyridyl amine is formed through the action of two molecules of pyridine on 1 mol. of sodium amide, but does not yet describe the experiments from which this appears. When speaking of the action of 1 mol. of pyridine on 1 mol of sodium amide (the same way as we performed the reaction) TSCHIT-

¹⁾ Journ. f. prakt. Chem. 93, 393 (1916).

SCHIBABIN does not mention the dipyridyl amine. He prepared the dipyridylamine from α -chloropyridine and α -aminopyridine by heating with zinc chloride, and gives as meltingpoint 86—87°.

We have prepared a picrate from the dipyridylamine, which melts at 227°.

Our observations on the melting-points of dipyridylamine itself, on the salt with hydrochloric acid, and on the picrate of this base are in perfect harmony with STEINHÄUSER and DIEPOLDER's records, so that we have no reason to doubt the identity of our preparation.

The investigation of the components of the oil that goes over at 130—180° and 15 m.m. pressure, was not yet completed then, for a large part of this oil remained liquid after treatment with hydrochloric acid. We removed the hydrochloric acid from this liquid part, and then distilled the oil at ordinary pressure. We collected three fractions, viz. of 293—295°, of 295—300° and above 300°. The first two fractions had a nitrogen percentage of 13.9%; the fraction above 300° had 16.4% of nitrogen. From this last fraction a little dipyridylamine was still deposited. The first two fractions were joined; this liquid appeared to be strongly unsaturated: it immediately decolours a solution of permanganate and soda at ordinary temperature. We have subjected part of this liquid to the oxidation with sodium permanganate in sulphuric acid solution. A white substance, which crystallized in white leaves and melted at 74°, could be isolated. The nitrogen percentage of it was 8.0%. This shows that it cannot be a dipyridylamine or a dipyridyl.

Besides these crystals, a viscid liquid was obtained from the oxidation product. The investigation of these substances is being continued.

It appears from all this that on action of sodium amide on pyridine there are formed, besides aminopyridine, several other pyridine derivatives, among which the γ - γ -dipyridyl seems to preponderate quantitatively. TSCHITSCHIBABIN likewise observed by-products in the reactionproduct which arises from sodium amide and pyridine. After the α -aminopyridine had been distilled off, he states that an oil went over which distilled at 120—180° and at 15—20 m.m., and besides a fraction that went over at 180—250° and 15—20 m.m.

From the fraction of 120—180° crystals are deposited which, after recrystallisation from benzene, melted at 158°. TSCHITSCHIBABIN supposed these crystals to be γ -aminopyridine, but he could not identify the substance for want of material. From the oil distilled at 180—250° this investigator isolated the α - α' diaminopyridine; there were also other substances present, which he did not identify.

In many experiments we prepared some hundreds of grammes of amino pyridine; the reaction always proceeded as we described above. We never observed a substance with a melting-point of 158° ; nor did we ever observe a diamino pyridine.

Accordingly the action of sodium amide on pyridine can evidently give rise to the formation of different substances. We have not been able to find out why with some sodium amide preparations amino pyridine was not formed. Addition of small quantities of water or free sodium had no influence on this. We also caused sodium to act on a mixture of pyridine and toluene, both at the ordinary temperature and at the temperature of boiling. In this case there was formed a tough amorphous mass, insoluble in water and in organic solvents, soluble in acids. By extraction with ether we could isolate only a small quantity of γ - γ -dipyridyl. This result is in accordance with the early experiments of ANDERSON.

The formation of the important quantities of γ - γ -dipyridyl in our amidisation seems, therefore, not to be in connection with a possible percentage of sodium in the sodium amide preparation used.

As amino pyridine seems comparable with aniline, we examined the action of oxidizers on this pyridine base. For so far as we know, nothing is known about this.

Bichromate and diluted sulphuric acid change a diluted solution of amino pyridine only slowly at ordinary temperature. When the mixture is left standing for some days, the liquid gets dark. From this solution an amorphous green substance is isolated, insoluble in water, alcohol, and ether, soluble with emerald green colour in diluted hydrochloric acid. On evaporation of the hydrochloric acid an amorphous blue substance was left behind. At 90° the action of sulphuric acid and bichromate on amino pyridine takes place more violently; and amorphous products are also formed. In these experiments part of the amino pyridine however remained unchanged.

The action of potassium bichromate in acid solution on this base takes place much less rapidly than in case of aniline.

The action of potassium permanganate proceeds in an entirely different way. Amino pyridine is rapidly changed by permanganate in acid solution; after a few minutes all the permanganate has disappeared. When a diluted solution of amino pyridine is added to a diluted permanganate solution containing soda, a slow action takes place. When, however, first a neutral permanganate solution is added to a diluted solution of amino pyridine, and then a few drops of 10% sodium hydroxide, a change of colour is immediately seen. When we start from a 0.1% solution of amino pyridine, the

liquid first becomes dark violet, then pure blue, after a few minutes the colour has become emerald green. This green colour does not change again, when there is no excess of permanganate present. If the solution of the amino pyridine is somewhat more concentrated, the green colour at once sets in after a transient dark colouring.

This reaction is characteristic of amino pyridine and very sensitive. In acetyl amino pyridine this colour reaction does not set in at the ordinary temperature until after some hours, soon however on boiling.

Whether the acetyl rest is split off primarily here, has not yet been examined.

A more detailed account of the observations discussed briefly here will be published in the *Recueil des Travaux chimiques*.
