XCV.—*The Chlorine Derivatives of Pyridine. Part III.
The Interaction of Chlorine and Pyridine Hydrochloride.*

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IN a former communication (Trans., 1898, 73, 432), the authors described a method of obtaining a considerable number of the chlorinated derivatives of pyridine by the direct action of phosphorus pentachloride on this substance. The experimental difficulties, however, were considerable, and it was of importance that some readier method should, if possible, be found for bringing about the desired substitution, since, in order to study the properties and reactions of the chloropyridines in any degree satisfactorily, considerable quantities of these substances would be required. With this object in view, the authors have studied the direct action of chlorine on pyridine hydrochloride. The action of chlorine on the base itself has already been described (Trans., 1898, 73, 442), and has been shown to be of little utility for the preparation of chloropyridines.

In this series of experiments, pyridine was saturated with hydrogen chloride, the amount of gas absorbed being usually about 50 per cent. in excess of that required for the formation of pyridine hydrochloride. The substance thus obtained fuses at a much lower temperature than the normal compound, and was thus more suitable for the purpose in view. Chlorine was led through this product, a temperature of 115–120° being maintained by means of a thermostat. The materials were all carefully dried, for reasons which will appear later. The operation is a long one, requiring several weeks for completion; but as the yield is comparatively good and large quantities of material can be operated on at one time, the method is regarded as a very satisfactory one for the preparation of such of the chloropyridines as are described below.

In the course of these experiments, the action of various so-called catalytic agents as chlorine carriers was tried, such as sulphur chloride, phosphorus pentachloride, aluminium chloride, and iodine,* but no material advantage resulted from their use.

* In those experiments in which iodine had been used as a chlorine carrier (to the extent of 1 per cent. of the weight of pyridine hydrochloride taken), the clear liquid left in the flask after the steam distillation (p. 982) deposited golden yellow crystals in long, flat plates, sometimes 5 cm. long and 1 cm. broad. This substance melted at 180° (uncorr.) and was identified as the hydrochloride of an additive compound of pyridine, chlorine, and iodine, C_5H_5N, ICl, HCl , described

After the chlorination had proceeded for a few days, the contents of the flask were seen to separate into two layers, the lower of which increased from day to day, and when it was stopped on the disappearance of the upper layer, the flask, on cooling, contained a solid or semi-solid mass of nearly colourless products, carbonaceous matter being entirely absent.

In the first experiments, the chlorination was stopped at an earlier stage, and the upper layer removed for examination. It was found to consist, for the greater part, of unchanged pyridine hydrochloride, but contained a certain amount of chloropyridines, and a substance to be described later. The following compounds were isolated:

1. A light, colourless, feathery sublimate, which settled in the neck and colder portions of the flask. This is probably the compound described by Anderson (*Trans. Roy. Soc. Edin.*, 1857) and mentioned by the authors (*Trans.*, 1898, 73, 443).

2. A trichloraminopyridine, m. p. 159—160°.

3. A compound, $C_{10}Cl_{11}HN_2$, which, by the action of moisture, is converted into a second compound, $C_{10}Cl_9OHN_2$.

4. A compound, $C_{10}Cl_7OHN_2$.

5. A dichloropyridine, identical with that described by Königs and Geigy (*Ber.*, 1884, 17, 1833).

6. A tetrachloropyridine, m. p. 21—22°.

7. Pentachloropyridine.

Of the ten theoretically possible isomerides of the formula $C_5NHCl_3 \cdot NH_2$, the following have been described:

1. A trichloro-*a*-aminopyridine, in which the position of the chlorine atoms is unknown. This compound was obtained by the action of phosphorus pentachloride on β -oxyglutaramide (Anschütz, Richter's *Organische Chemie*, 2, 573), and melts at 143—144°.

2. A trichloraminopyridine, obtained by the action of phosphorus pentachloride on glutazine by Stokes and Pechmann (*Amer. Chem. J.*, 1886, 6, 377), which melts at 157·5°, and has been shown to have formula I.

3. A trichloraminopyridine, obtained by the authors from tetrachlorisonicotinic acid by the action of ammonia. This compound

by Pictet and Krafft (*Bull. Soc. Chim.*, 1892, [iii], 7, 72). This was confirmed by recrystallising it from dilute alcohol, when colourless crystals were obtained which, like Pictet and Krafft's compound, C_5H_5N, ICl , melted at 132—133°.

melts at 158–160°, and has the remaining hydrogen atom in the γ -position relatively to the nitrogen. The position of the amino-group is not known with certainty, but the formula is probably represented by II (Trans., 1897, 71, 1083).

It will be noticed that the fusing points of these isomerides very closely approach each other. The compound now described melts at almost exactly the temperature given for (3), whilst (2) melts at a temperature only very slightly lower. The authors, however, have satisfied themselves that these substances are not identical. The new aminotrichloropyridine yields a well-defined platinum salt, and (3) does not. Again, the new compound differs from (2), in that it does not yield a precipitate with bromine water in the manner described by Stokes and Pechmann (*loc. cit.*), and further, it is very unlikely that if (2) had been capable of forming a platinum salt, the fact would have been overlooked.

Although (2) and (3) are so similar in properties, both melting practically at the same temperature and neither forming a compound with platinic chloride, their identity is out of the question, since it has been shown by Stokes and Pechmann (*loc. cit.*), and by the authors (Trans., 1898, 73, 777) that the parent substance of (2), glutazine, has an amino-group in the γ -position relatively to the nitrogen, whilst (3) was derived from $\alpha\alpha'\beta\beta'$ -tetrachloropyridine, in which the γ -position is undoubtedly occupied by a hydrogen atom.

The method of formation of the new aminotrichloropyridine is of considerable interest. The only possible source of the nitrogen of the amino-group must have been a pyridine nucleus, since pyridine was the only substance containing nitrogen which had been introduced into the flask at any stage. It is noteworthy that the presence of the compound could not be detected in the strongly acid liquor (p. 982), and was recognised only after steam distillation from a strong solution of sodium carbonate. Further, it has been shown by many reactions (Trans., 1898, 73, 777) that the substitution of chlorine by the amino-group, in the class of compounds under consideration, does not take place with any great readiness, except at temperatures considerably above 100°, and it is therefore impossible that the production of this aminotrichloropyridine can be due to the liberation of ammonia in a current of steam, by the action of sodium carbonate, from any possible ammonium compound formed by the breaking down of the pyridine ring, and the subsequent action of the ammonia so formed on a tetrachloropyridine. From these considerations, the only possible conclusion that can be drawn is that the antecedent of this substance is a compound in which one pyridine nucleus is united through the nitrogen atom with a carbon atom of a second—a compound which, waiving for

the moment the question as to which of the carbon atoms is concerned, would be represented thus :

If this explanation is correct—and in its support the authors believe they have further evidence, which, however, cannot well be offered here—this is the first recorded instance of the existence of a complex of this type.

EXPERIMENTAL.

Dry chlorine was passed into fused, dry pyridine hydrochloride (containing an excess of hydrogen chloride as described in the introduction) at 115–120° during several weeks, until the upper layer disappeared. On cooling, a crystalline mass was obtained. Two methods were adopted in the examination of the products. In the first, the whole was distilled in steam, whilst in the second the crystalline material was separated by means of dry chloroform before steam distillation of the liquid portion was undertaken.

I. The contents of the flask, after chlorination, were distilled in a current of steam without any previous separation, and an oil passed over precisely as in the manner described in Part I. (*loc. cit.*), the process requiring some days for its completion. The greater part of the contents of the chlorination flask formed an emulsion, gradually darkening in colour to a deep chocolate brown, which, on cooling, settled down as a guttapercha-like cake. The strongly acid mother liquor, on being made alkaline with ammonia, deposited a small crop of colourless crystals, which, on purification from dilute alcohol, melted at 66–67° (uncorr.). The same product was found in much larger quantity in the volatile oil, and is described below (p. 985).

The brown cake was again distilled in a current of steam from a saturated solution of sodium carbonate, when feathery, colourless needles were obtained from the aqueous distillate on cooling. These crystals are readily soluble in acids, and are reprecipitated by alkalis ; they dissolve in the usual organic solvents, but are only sparingly soluble in hot, and almost insoluble in cold water. After recrystallisation several times from dilute alcohol, the substance melted at 159–160° (uncorr.), and, on analysis, proved to be a trichloraminopyridine.

0.3224 gave 0.3568 CO₂ and 0.0448 H₂O. C = 30.18 ; H = 1.54.

0.3827 „ 46.7 c.c. nitrogen at 19° and 764 mm. N = 14.11.

0.2887 „ 0.6463 AgCl. Cl = 54.54.

C₆NHCl₃·NH₂ requires C = 30.44 ; H = 1.52 ; N = 14.20 ; Cl = 53.83 per cent.

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When dissolved in hydrochloric acid and treated with platonic chloride, the platinochloride was obtained in short, thick, golden-yellow needles.

0.4137 gave 0.1005 Pt. Pt = 24.29.

$(C_5NHCl_3 \cdot NH_2)_2 \cdot H_2PtCl_6$ requires Pt = 24.30 per cent.

The contents of the flask, which were strongly alkaline from the excess of sodium carbonate, after filtration and neutralisation with hydrochloric acid, yielded a precipitate of brown, crystalline matter, very soluble in alkalis, reprecipitated by acids, and moderately soluble in the usual organic solvents. This substance is still under examination, as is also the residue of the steam distillation.

II. In order to avoid the rather considerable amount of decomposition which takes place when the separation is carried out as above described, a modification of this plan was adopted in the later experiments. The solid or semi-solid product of the chlorination was warmed, drained by the aid of the filter pump and washed with chloroform, when a considerable quantity of colourless crystals was left behind. This crystalline separation was purified by several recrystallisations from dry chloroform, dried in a vacuum, and kept in a well stoppered bottle.

It was found that when these crystals were dried in the air they gave off hydrogen chloride for some time after removal to a desiccator. This was doubtless due to interaction with the small amount of moisture absorbed from the air during the process of drying, and does not occur when the substance is dried in a desiccator over sulphuric acid, the crystals in the latter case decreasing in weight by an insignificant amount when left for some days in a vacuum over potash. The compound melted sharply at 187—188° (uncorr.), and gave the following numbers on analysis:

0.7575 gave 0.6050 CO_2 and 0.0155 H_2O . C = 21.72; H = 0.22.

0.2830 „ 0.8340 AgCl. Cl = 72.86.

$C_{10}Cl_{11}HN_2$ requires C = 22.22; H = 0.18; Cl = 72.22 per cent.

It is freely soluble in hot, but only sparingly in cold chloroform, carbon tetrachloride, benzene, or pyridine. On treatment with boiling spirit, an interaction takes place, and very beautiful, highly refractive, colourless crystals are obtained which melt at 171—172° (uncorr.), whilst the mother liquor becomes strongly acid, owing to the production of hydrogen chloride. The same change is brought about on contact with water, but the solid is not taken into solution. Glacial acetic acid dissolves it readily on boiling, with copious evolution of hydrogen chloride, and on cooling deposits the crystals melting at

171—172°. These have the composition expressed by the formula $C_{10}N_2Cl_9HO$.

The presence of hydrogen in the parent substance (m. p. 187—188°) was first attributed to the latter being the hydrochloride of a base, but its occurrence with oxygen in the compound now described was so unexpected, considering the methods of preparation, that numerous analyses were made of specimens from different experiments, and in some cases of relatively large amounts of material, before its existence in the molecule was regarded as placed beyond doubt. The following are typical of the numbers obtained :

0.3639 gave 0.3303 CO_2 and 0.0078 H_2O . C = 24.75 ; H = 0.23.

0.5790 „ 0.5250 CO_2 „ 0.0127 H_2O . C = 24.73 ; H = 0.24.

0.8110 „ 0.7400 CO_2 „ 0.0163 H_2O . C = 24.89 ; H = 0.22.

0.2360 „ 0.6310 AgCl. Cl = 66.14.

0.2200 „ 0.5870 AgCl. Cl = 65.99.

0.3098 „ 15.5 c.c. nitrogen at 18° and 765 mm. N = 5.84.

$C_{10}N_2Cl_9HO$ requires C = 24.82 ; H = 0.21 ; Cl = 65.86 ; N = 5.79 percent.

A determination of the freezing point of a solution in benzene gave the following numbers :

0.2320 gram lowered the freezing point of 19.59 grams of benzene 0.130° ; Mol. wt. = 445 ; calculated for $C_{10}N_2Cl_9HO$ = 484.

This substance is readily soluble in chloroform, carbon tetrachloride, benzene, or glacial acetic acid, but only sparingly so in alcohol, and is insoluble in water, dilute acids, or alkalis. Strong sulphuric or nitric acid, on warming, dissolves it with decomposition, and in the former case with liberation of hydrogen chloride. From its solution in chloroform, if deposited slowly, it is obtained in lustrous, highly refractive crystals of large size. It can be crystallised from pyridine without decomposition, and therefore is not the hydrochloride of a base. It is not affected by long-continued boiling with water. The evidence at present is insufficient to decide whether the hydrogen and oxygen in the compound are present as hydroxyl. Its behaviour with phosphorus pentachloride has only partly been examined, but it may be stated that pyridine pentachloride was one of the products, thus showing that the pyridine nucleus still remains. The ease with which the parent substance interacts with liquids containing the OH-group points to the presence of this radicle in the new compound, yet, on the other hand, it may be crystallised unchanged from benzoyl chloride or acetyl chloride.

If the crude cake obtained by draining the contents of the chlorination flask is at once crystallised from alcohol, the first crop of

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crystals contains another and somewhat similar compound, which, after purification by several recrystallisations from alcohol, glacial acetic acid, or chloroform, melts unchanged at 228° (uncorr.). This substance gave the following numbers on analysis :

0.4115 gave 0.4350 CO_2 and 0.110 H_2O . C = 28.82 ; H = 0.29.

0.2010 required 0.5814 AgNO_3 . Cl = 60.22.

0.1922 gave 0.4635 AgCl . Cl = 59.68.

0.2885 „ 17.3 c.c. nitrogen at 14° and 754 mm. N = 6.99.

$\text{C}_6\text{N}_2\text{Cl}_7\text{HO}$ requires C = 29.07 ; H = 0.25 ; Cl = 60.00 ; N = 6.78 per cent.

This product is isolated in very much smaller quantity than the preceding one. It is dissolved by the same solvents, but to a less extent. It is probably formed by the interaction of water with a substance of the formula $\text{C}_{10}\text{N}_2\text{Cl}_5\text{H}$, which has not been isolated.

The authors are not at present prepared to put forward any constitutional formulæ for these compounds, but the investigation is being pursued, and several interesting derivatives have been obtained. This branch of the subject, however, is reserved for a future communication.

The oily filtrate separated from the crystalline products of the chlorination was freed from chloroform and distilled in a current of steam until nothing further was carried over. The residue, which varied between 5 and 10 per cent. of the total weight of material obtained, was in the form of a light, reddish-brown resin very soluble in chloroform or glacial acetic acid, but only sparingly so in alcohol, and insoluble in water. It is very rich in chlorine, but so far no crystalline products have been obtained from it.

The oil volatile in steam, which was obtained from all the experiments in only slightly varying quantities, was treated in the manner described in Part I. (*loc. cit.*) for the separation of the chloropyridines. It differs very considerably in composition from the product of the action of phosphorus pentachloride on pyridine, as might be expected in view of the difference in the material employed and the conditions under which the chlorination was carried out. The constituents which do not form compounds with mercuric chloride are present in insignificant proportion, whereas in the former case they reached approximately 50 per cent. of the total weight of oil obtained. From this oil, the only crystalline product is pentachloropyridine.

On fractionating the dried oil, separated from the compound with mercuric chloride (*loc. cit.*), the first portion of the distillate was found to consist of a dichloropyridine not obtained in the previous work. This compound, which is formed in fair amount, was purified by dissolving in hydrochloric acid, pouring off from any undissolved oil, reprecipitating with ammonia, and subsequent recrystallisation from

dilute alcohol, when it was obtained in lustrous, flexible flat needles which melted at $66-67^{\circ}$ (uncorr.). This fusing point agrees with that of the dichloropyridine described by Königs and Geigy (*Ber.*, 1884, 17, 1833) and the identity of the substance was established by the preparation of the mercurichloride (m. p. = 183° , uncorr.) and the platinochloride, the latter of which gave the following numbers on analysis :

0.36 lost, at 100° , 0.019 H_2O and gave 0.0945 Pt. $H_2O = 5.27$;
Pt = 26.26.

$(C_5NH_3Cl_2)_2 \cdot H_2PtCl_6 + 2H_2O$ requires $H_2O = 4.84$; Pt = 26.48 per cent.

The second fraction of the distillate, which was small in amount, consisted of an oil which remained liquid in a freezing mixture of ice and salt. The third fraction, constituting 90 per cent. of the weight of the oil, was redistilled, and the portion boiling between $135-137^{\circ}$ under 24 mm. pressure was collected separately. This consisted of the tetrachloropyridine melting at $21-22^{\circ}$, and amounted to upwards of 70 per cent. of the total yield of chloropyridines. Large quantities of this substance have now been obtained and the authors hope to be able to work out its constitution.

As in the former series of experiments (Part I.), the yield of pentachloropyridine is a good one. This substance is chiefly found in the last portions of the steam distillate, which were always collected separately, but is invariably present in the oil separated by treatment with mercuric chloride, and was obtained from it as described in the former paper.

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