XCIII.—*The Chlorine Derivatives of Pyridine.* *Part VII. Some Condensation Products.*

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IN Part III of this series of papers (Trans., 1899, 75, 979) a number of compounds were described as resulting from the action of dry chlorine on pyridine hydrochloride. Among these was a substance to which the empirical formula $C_{10}HN_2Cl_{11}$ was assigned, but no structural formula was offered. The present communication deals with some of the reactions of this compound, and the bearing which the results have on the constitution which should be assigned to it.

(1) In the communication referred to above, it was stated that the substance interacts with water, forming hydrogen chloride, and a new compound, also insoluble in water, having the molecular formula $C_{10}HON_2Cl_9$. In order, if possible, to gain a clearer insight into the relationship between the two compounds, a quantitative examination of the interaction was made. In the result, there remained no doubt that the reaction takes place according to the equation :

With water at a higher temperature ($120-130^\circ$), the substance darkens in colour, evidently decomposing, and in the liquid there is found 2-amino-3 : 4 : 5-trichloropyridine (Trans., 1900, 77, 771), held in solution by the hydrogen chloride also formed.

When the substance $C_{10}HN_2Cl_{11}$ is crystallised from ethyl alcohol, a similar interaction takes place, and the compound $C_{10}HON_2Cl_9$ is deposited.

The ready interaction with water and with ethyl alcohol, with the formation of an oxy-derivative, accompanied by hydrogen chloride in one case and alkyl chloride in the other, suggested the possibility that organic acids, for example, acetic or benzoic acid, might interact with formation of the acid chloride. This was found to be the case, a theoretical yield of benzoyl chloride being produced from benzoic acid. In the case of acetic acid, acetyl chloride was recognised as one of the products formed.

The crystalline residual product of these interactions was identical in properties and composition with that left by treatment of the parent substance $C_{10}HN_2Cl_{11}$ with water. Hence the change may be thus represented :

This behaviour is remarkable, and, so far as we are aware, is the first recorded instance in which the acid chloride has been formed by the interaction of an acid with a purely organic substance.

It may here be pointed out that, in the cases cited, the oxygen is in the OH condition. Ketonic oxygen does not appear to react under these conditions, inasmuch as the compound may be recrystallised unchanged from acetone.

(2) When the substance $C_{10}HON_2Cl_9$ is treated with a solution of sodium hydroxide and the resulting magma distilled in steam, a bulky crop of filamentous needles separates out from the distillate. This was found to be 2-amino-3:4:5-trichloropyridine (compare Part III, Trans., 1899, 75, 981 ; also Trans., 1900, 77, 771).

(3) Interesting results were obtained by treating the substance with sulphuric acid containing approximately 80 per cent. of the acid. The experiments were made under varying conditions of time and temperature. When the compound was merely dissolved in the acid at a temperature not exceeding 150° , and the whole poured into water as soon as solution had been effected, a white precipitate was obtained which on purification from acetic acid proved to have the composition $C_{10}HO_2N_2Cl_7$. The filtrate from this precipitate, on addition of ammonia in excess, yielded 2-amino-3:4:5-trichloropyridine.

It was, moreover, found that as the heating was continued for a greater length of time the yield of the substance $C_{10}HO_2N_2Cl_7$ diminished and that of the 2-amino-3:4:5-trichloropyridine increased until, in the maximum, a theoretical yield of the latter was obtained. When the substance, after being brought into solution, was rapidly raised to the boiling point and boiled, the products obtained were pentachloropyridine, hydrogen chloride, and carbon dioxide. At the same time, the liquid remained perfectly colourless, and contained 2-amino-3:4:5-trichloropyridine in solution.

(4) When the compound $C_{10}HN_2Cl_{11}$ is heated alone under diminished pressure, it melts, and at a higher temperature decomposes, yielding chlorine and pentachloropyridine. Nothing of a crystalline character has so far been recovered from the residue.

(5) A similar experiment was carried out with the substance $C_{10}HON_2Cl_9$, obtained from the parent compound by recrystallisation from acetic acid. In this case also, free chlorine was given off and pentachloropyridine distilled over. The experiment was stopped at an earlier stage than in the preceding one, and before complete decomposition had been effected. The residue, dissolved in acetic acid, on cooling yielded crystals melting at 225° and having the composition $C_{10}HON_2Cl_7$.

(6) The same substance, $C_{10}HON_2Cl_7$, was also obtained by reduction of the compound $C_{10}HN_2Cl_{11}$ by means of anhydrous stannous

chloride in acetone solution, and subsequent recrystallisation of the reduced product from acetic acid.

From these facts, the following appear to be legitimate deductions.

I. That the compound $C_{10}H_2N_2Cl_{11}$ consists of two pyridine nuclei linked by the 2-position of the one (which for reference may be called the *a* ring) to the nitrogen atom of the other (*b* ring) (compare 2 and 3, above).

II. That the hydrogen atom of the compound $C_{10}H_2N_2Cl_{11}$ occupies the 6-position in the *a* ring.

III. That the *b* ring, since it is capable of yielding pentachloropyridine, must contain at least six chlorine atoms, as shown by the formula,

The two additional atoms of chlorine contained in the molecule which are still unaccounted for in this formula are regarded as being united to the *b* ring for the following reasons.

1. The oxy-derivative of the formula $C_{10}HON_2Cl_9$ yields, on heating either pentachloropyridine, or a compound, $C_{10}HON_2Cl_7$, according to the conditions of the experiment. The latter, with sulphuric acid, yields 2-amino-3:4:5-trichloropyridine, but cannot be made to yield pentachloropyridine by any of the reactions mentioned above.

2. The compound $C_{10}HO_2N_2Cl_7$, obtained by the action of sulphuric acid on the parent substance $C_{10}H_2N_2Cl_{11}$, may be made to yield 2-amino-3:4:5-trichloropyridine, but no pentachloropyridine.

It may be observed that when decomposition takes place it has only hitherto been possible, in the same change, to isolate derivatives from *one* ring which throw any light on the constitution of the compounds, (the cleavage of the molecule following the line α or β),

as is shown in the quantitative experiments described later. The chief derivative of the *a* ring is 2-amino-3:4:5-trichloropyridine; of the *b* ring, pentachloropyridine. It is possible, and even probable, that there are tautomeric forms of the compound. With this reservation, the changes and formulæ described above may be represented in the following way (p. 902):

EXPERIMENTAL.

Interaction with Water.—A quantity of the substance, $\text{C}_{10}\text{HN}_2\text{Cl}_{11}$, weighing 0.7925 gram was heated on the water-bath with 50 c.c. of water for 3 hours and then filtered. The filtrate, after neutralisation with pure chalk, was found to require 29 c.c. of $N/10$ silver nitrate for complete precipitation. This indicates that, by interaction with water, 100 grams of the compound give 13.35 grams of hydrogen chloride. The equation

requires the production of 13.53 grams of hydrogen chloride from 100 grams of the compound.

Interaction with Alcohol.—The parent substance, $\text{C}_{10}\text{HN}_2\text{Cl}_{11}$, dissolved in boiling alcohol, on cooling deposited crystals melting at $171\text{--}172^\circ$ (uncorr.) which were analysed with the following results:

0.5790 gave 0.5250 CO_2 and 0.0127 H_2O . $\text{C} = 24.73$; $\text{H} = 0.24$.

0.2200 „ 0.5870 AgCl . $\text{Cl} = 65.99$.

$\text{C}_{10}\text{HON}_2\text{Cl}_9$ requires $\text{C} = 24.82$; $\text{H} = 0.21$; $\text{Cl} = 65.86$ per cent.

Interaction with Benzoic and Acetic Acids.—In the case of benzoic acid 2 grams of the acid were mixed with 10 grams, or rather more than the theoretical quantity, of the chlorinated derivative, and the mixture distilled from a metal-bath. The distillate, which weighed 2.3 grams,

was almost pure benzoyl chloride, as shown by its boiling point and general properties, and was gradually resolved by interaction with water into a solid mass of crystals of benzoic acid. The residue left in the distillation flask was recrystallised from acetic acid and was found, by its melting point and general character, to be identical with the product formed by interaction of the substance $C_{10}HN_2Cl_{11}$ with water or alcohol. The equation

requires that 2 grams of benzoic acid should produce 2.3 grams of benzoyl chloride, so that the yield obtained is seen to be quantitative.

When acetic acid was substituted for benzoic acid in the above experiment, a distillate was obtained from which acetyl chloride was isolated by fractionation.

Interaction with Sodium Hydroxide.—Since the parent substance $C_{10}HN_2Cl_{11}$ invariably yields the monooxy-derivative, $C_{10}HON_2Cl_9$, on treatment with water as shown above, the latter substance was used in this experiment. Ten grams of this material were treated with an excess of dilute sodium hydroxide (1 in 10) and distilled with steam until nothing further was carried over. The aqueous distillate on cooling deposited the calculated quantity of 2-amino-3:4:5-trichloro pyridine, recognised by its melting point (159—160° uncorr.), and a nitrogen determination.

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

$C_5H_3N_2Cl_3$ requires $N = 14.20$ per cent.

So far, nothing crystalline has been isolated from the contents of the distillation flask.

Interaction with Sulphuric Acid containing 80 per cent. of H_2SO_4 .—The first product of the interaction of sulphuric acid on the parent substance under the conditions tried is the compound $C_{10}HON_2Cl_9$ in all cases. Ten grams of the latter were heated to incipient boiling with 100 c.c. of acid, but not boiled. Hydrogen chloride was freely evolved, and on cooling the mass was poured into several times its volume of water. The precipitate was collected, washed, and dried, and was found to weigh 1.6 grams. On recrystallisation from glacial acetic acid, this compound was obtained in large, lustrous cubes which melted at 146—147° (uncorr.), and furnished the following numbers on analysis:

0.3149 gave 0.3195 CO_2 and 0.0067 H_2O . $C = 27.73$; $H = 0.23$.

0.2905 „ 17.4 c.c. nitrogen at 17° and 759 mm. $N = 6.95$.

0.1546 „ 0.3603 $AgCl$. $Cl = 57.66$.

$C_{10}HO_2N_2Cl_7$ requires $C = 27.90$; $H = 0.23$; $N = 6.51$; $Cl = 57.85$ per cent.

The filtrate from the above, on being made alkaline with ammonia,

deposited a bulky crop of filamentous needles, weighing 3·2 grams after washing and drying. These, on recrystallisation and subsequent analysis, proved to be 2-amino-3:4:5-trichloropyridine, melting at 159—160° (uncorr.). A nitrogen determination was made, with the following result :

0·2192 gave 27·5 c.c. nitrogen at 22° and 762 mm. $N = 14·25$.

$C_5H_3N_2Cl_3$ requires $N = 14·20$ per cent.

On calculating the weight of the precipitate above into the corresponding weight of the material which was originally taken (1·6 grams corresponds to 1·8 grams), and subtracting this from the 10 grams used, it will be seen that 8·2 grams of the compound $C_{10}HON_2Cl_9$ underwent the more complete decomposition. This amount should yield theoretically 3·3 grams of aminotrichloropyridine, as against 3·2 grams actually found.

In a second experiment, 10 grams of the compound were heated with 170 c.c. of 80 per cent. sulphuric acid in a distillation flask immersed in a metal-bath, the temperature being gradually raised to 160° and maintained there for 45 minutes. On cooling, the contents of the flask were distilled with steam until practically nothing further was carried over. From the aqueous distillate, 1·3 grams of pentachloropyridine were obtained by filtration. The contents of the distilling flask deposited nothing on standing for 24 hours, but on addition of ammonia yielded a crop of crystals of 2-amino-3:4:5-trichloropyridine, which, after washing and drying, weighed 2·8 grams. The latter weight is the theoretical yield of aminotrichloropyridine from 6·8 grams of the substance $C_{10}HON_2Cl_9$ taken. The material not thus accounted for, 3·2 grams, should theoretically yield 1·6 grams of pentachloropyridine, as against 1·3 grams actually obtained.

A further experiment, in which the interaction of sulphuric acid with the compound $C_{10}HON_2Cl_7$ was studied, showed by its yielding 2-amino-3:4:5-trichloropyridine that the former is essentially a derivative of the parent substance $C_{10}HN_2Cl_{11}$, from which it has been obtained by reduction with stannous chloride and subsequent recrystallisation from acetic acid, as also by partial decomposition by heat of the hydrolysed product, $C_{10}HON_2Cl_9$.

Influence of Heat.—The parent substance, $C_{10}HN_2Cl_{11}$, was heated in a distillation flask with a wide delivery tube immersed in a metal-bath and under a pressure of 15—20 mm. Beyond melting, no change was observed to take place until the temperature of the bath reached 230—240°, when an oil distilled over which solidified in the delivery tube. As the temperature of the bath approached 260°, the amount of the distillate increased, and the apparatus was full of chlorine. On every occasion at this stage a slight explosion was noticed, which was

succeeded by an increased flow of liquid in the delivery tube. The temperature of the bath was slowly raised to 300° , when the experiment was stopped.

The residue, which was light brown in colour and showed no traces of charring, was completely soluble in glacial acetic acid, imparting to it an intense greenish-yellow fluorescence, but nothing crystalline could be obtained from it. The distillate gave a very pure specimen of pentachloropyridine, identified by its melting point ($124\text{--}125^{\circ}$ uncorr.) and by a chlorine determination.

0.1296 gave 0.3700 AgCl. $\text{Cl} = 70.66$.

C_5NCl_5 requires $\text{Cl} = 70.51$ per cent.

A repetition of the above experiment in which the temperature of the bath was not allowed to exceed 270° led to precisely similar results.

In view of the foregoing, it became of interest to examine the effect of heat on the oxy-derivative of the original substance. With this object, 20 grams of the compound $\text{C}_{10}\text{HON}_2\text{Cl}_9$ were heated in a similar way, the condenser in this case containing crystals of potassium iodide moistened with water. The volatile products were the same, namely, chlorine (which, of course, reacted in part with the potassium iodide) and pentachloropyridine. The reaction was in this case stopped when the temperature of the bath reached 270° and the pentachloropyridine was still coming over. The residue was recrystallised from acetic acid, and the first crop of crystals, melting at $225\text{--}226^{\circ}$ (uncorr.), was analysed, with the following results:

0.5815 gave 0.6317 CO_2 and 0.0111 H_2O . $\text{C} = 29.62$; $\text{H} = 0.21$.

0.3405 „ 0.8246 AgCl. $\text{Cl} = 59.82$.

$\text{C}_{10}\text{HON}_2\text{Cl}_7$ requires $\text{C} = 29.07$; $\text{H} = 0.25$; $\text{Cl} = 60.00$ per cent.

It is thus seen that the compound $\text{C}_{10}\text{HON}_2\text{Cl}_7$, obtained by incomplete chlorination of pyridine hydrochloride (Trans., 1899, 75, 980) and by the reduction of the parent substance, $\text{C}_{10}\text{HN}_2\text{Cl}_{11}$, by stannous chloride and subsequent crystallisation from acetic acid, may also be obtained by heating the oxy-derivative, $\text{C}_{10}\text{HON}_2\text{Cl}_9$.

Reduction by means of Stannous Chloride.—The compound $\text{C}_{10}\text{HN}_2\text{Cl}_{11}$ was dissolved in acetone containing an equal weight of anhydrous stannous chloride. The mixture, when heated on the water-bath in a reflux apparatus, reacted energetically. The product obtained on dilution was recrystallised from acetic acid, from which it separated in rectangular prisms melting at $223\text{--}224^{\circ}$ (uncorr.). A chlorine determination furnished the following numbers:

0.2098 gave 0.5050 AgCl. $\text{Cl} = 59.75$.

$\text{C}_{10}\text{HON}_2\text{Cl}_7$ requires $\text{Cl} = 60.00$ per cent.

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