XLVI.—*Note on the Action of Chlorine on Pyridine.*

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IN the preceding communication, the authors described a trichloropyridine fusing between 71° and 72° . The coincidence between this melting point and that assigned by Keiser (*Am. Chem. J.*, 1886, 8, 310) to a compound which he describes as the hydrochloride of dichloropyridine,* together with the great similarity in properties of the two compounds, suggested that they might be identical. With the object of investigating this point, Keiser's work was in part repeated.

At the outset, it was not intended to prosecute the search in this direction further than the isolation of sufficient of the substituted product for comparison, since the results which had been obtained by Keiser did not seem to hold out much prospect that the method would prove a serviceable one for the object with which the authors were concerned, namely, the preparation of the chloropyridines. However, in the course of the work, conclusions were arrived at differing so materially from those of Keiser, that the action of dry chlorine on dry pyridine was studied at somewhat greater length.

The general plan of Keiser's investigation was to pass dry chlorine into dry pyridine, and separate the products by fractional distillation. The substances thus obtained were (1) the excess of pyridine used, coming over at 116° ; (2) the so-called hydrochloride of dichloropyridine, partly mixed with pyridine, and partly condensing in the neck of the retort, distilling at 130° ; (3) a substance distilling at $218\text{--}219^{\circ}$ and condensing to a waxy solid, regarded by Keiser as an additive compound, having the formula C_5H_5NCl ; (4) a tarry residue of unknown composition.

No mention is made of the temperature at which the chlorination was effected, or of the relative amounts of material used, although, from the results obtained, the chlorine could not have been in excess.

In repeating the work, therefore, experiments were made at temperatures varying from 0° to the boiling point of pyridine, whilst the stream of chlorine was sometimes continued until hydrogen chloride was freely evolved. It was not found that the yield of the substance sought was materially affected by this variation of treat-

* The authors desire to point out that the melting point of this "hydrochlorate of dichloropyridine" is erroneously given in Muir and Morley's edition of Watts' dictionary of chemistry as the melting point of dichloropyridine itself, which latter, as is stated in the memoir, was never obtained.

ment, although the amount of residual tarry matter increased with rise of temperature.

In all cases where heat was employed, a light, feathery sublimate settled in the colder parts of the flask, which was in most cases removed before proceeding to the separation of the other products. This compound has a faint odour resembling that of bleaching powder and is partly soluble in water. Its hot alcoholic solution deposits an oil on cooling, and, later, needle-like crystals appear; its aqueous solution gives a heavy, white precipitate with silver nitrate, insoluble in nitric acid. In general properties and appearance, it recalls the compound obtained by Anderson (*Trans. Roy. Soc. Edin.*, 1857). It was not further examined, but the authors hope shortly to have an opportunity of more fully investigating this substance.

In some cases, the separation of the remaining products was effected as in Keiser's experiments, but in consequence of the violent frothing of the contents of the flask as the temperature rose, this method was abandoned in favour of distillation in a current of steam, by which means separation was more easily obtained. The oil which separated from the first portions of the steam distillate solidified on cooling, and when drained by the aid of the filter pump and recrystallised several times from alcohol, was obtained in long, colourless needles melting between 71° and 72° , and identical with the product obtained by fractional distillation. Later portions of the distillate contained an oil which did not solidify on cooling, and, in appearance and properties, resembled the oil obtained by the action of phosphorus pentachloride on pyridine (p. 434), which has been shown to be a mixture of chlorine substitution products of pyridine, for the greater part at least. The yield of this oil was, however, too small to render the method an advantageous one for its preparation.

The amount of black tarry mass remaining in the flask after the steam distillation was complete was considerable; it was carefully dried, and an attempt made to distil it under diminished pressure, but although the temperature was cautiously and slowly raised to 250° (15 mm.), practically nothing distilled over, whilst the contents of the flask frothed violently, giving off pungent smelling gases. It was not further examined.

That the crystalline compound melting at 72° is not the hydrochloride of a base, is shown by the fact that its solution in alcohol or strong nitric acid gives no precipitate with silver nitrate.

The only evidence adduced by Keiser that it has the constitution expressed by the formula $C_5H_3Cl_2N.HCl$, lies in a chlorine determination, and an estimation of the residual platinum obtained by heating the double compound of this substance with platinic chloride. No carbon and hydrogen determination was made. It is plain that

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the hydrogen determination is crucial, and analyses made on the compound separated by fractional distillation in the manner described by Keiser, and which melted between 71° and 72° , give the following numbers.

- I. 0.1775 gave 0.2132 CO_2 and 0.0166 H_2O .
 II. 0.2299 „ 0.2776 CO_2 „ 0.0250 H_2O .
 III. 0.1343 „ 0.3131 AgCl .
 IV. 0.2051 „ 13.6 c.c. nitrogen at 14° and 767 mm.

Calculated for	Calculated for	Found.			
$\text{C}_5\text{H}_3\text{Cl}_2\text{N}, \text{HCl}$.	$\text{C}_5\text{Cl}_3\text{H}_2\text{N}$.	I.	II.	III.	IV.
C = 32.57	32.87	32.75	32.93	—	—
H = 2.17	1.09	1.04	1.20	—	—
Cl = 57.65	58.35	—	—	57.68	—
N = 7.60	7.69	—	—	—	7.95

The double compound, which crystallises out from the alcoholic solution of this substance on adding platonic chloride, gave 27.60 per cent. of platinum (Keiser). This agrees very nearly with the corresponding salt of trichloropyridine described by the authors, who found 28.12 per cent. of platinum.

This double compound, therefore, should have the constitution expressed by the formula $(\text{C}_5\text{H}_2\text{Cl}_3\text{N})_2\text{PtCl}_4$ (calculated, Pt = 27.66 per cent.), analogous to that obtained from pyridine by long continued boiling with platonic chloride. The formula $(\text{C}_5\text{Cl}_3\text{H}_2\text{N})_2\text{H}_2\text{PtCl}_6$ requires Pt = 25.13 per cent.

If an alcoholic solution of mercuric chloride is added to the alcoholic solution of the chloropyridine, crystals are obtained which, after purification, melt without decomposition at 168 — 170° , and are identical with the compound shown by the authors (*loc. cit.*) to have the composition expressed by the formula $(\text{C}_5\text{Cl}_3\text{H}_2\text{N})_2\text{HgCl}_2$.

There can, therefore, be no doubt that the compound obtained by Keiser is not a hydrochloride of dichloropyridine, but a trichloropyridine identical with that obtained by the action of phosphorus pentachloride on pyridine.

It should here be further pointed out that the reasons adduced for assigning the formula $\text{C}_5\text{H}_5\text{NCl}$ to the third fraction of the distillate, which constitutes the "yellow waxy solid," boiling between 218 — 219° , are inadequate. This product agrees, so far as its properties have been described in Keiser's memoir, with hydrochloride of pyridine. On searching the literature on the subject, no record could be found of the boiling point of hydrochloride of pyridine, but an experiment showed that it distilled unchanged at 218 — 219° (uncorr.).

Since, in Keiser's experiments, unchanged pyridine was recovered by distillation and a substitution of chlorine for hydrogen had

undoubtedly taken place, hydrochloride of pyridine must have been present; on the other hand, it is extremely unlikely that an additive product, having the constitution given, would distil unchanged at exactly the same temperature as hydrochloride of pyridine.

Further, by an error in the calculation of the analysis quoted in support of this contention, Keiser gives the percentage of hydrogen, which ought to be 5.05 per cent., as 4.68 per cent. With this correction, the analyses obtained agree more nearly with the numbers required for hydrochloride of pyridine than with those required by the formula C_5H_5NCl , as is seen below.

Calculated for $C_5H_5N \cdot Cl$.	Calculated for $C_5H_5N \cdot HCl$.	Found (Keiser).
C = 52.39	51.94	52.00
H = 4.37	5.20	5.05* (4.68)
Cl = 30.96	30.70	30.89

The double compound obtained by the addition of platonic chloride to an aqueous solution of this substance is admittedly pyridine platinum chloride.

The conclusions arrived at therefore are.

1. There is, without doubt, an additive product of pyridine and chlorine formed, as to the constitution of which there is, as yet, no conclusive evidence.
2. The so-called hydrochloride of dichloropyridine is a trichloropyridine.
3. Other chloropyridines are formed in small amount.
4. The compound described as an additive product of chlorine and pyridine, to which the formula C_5H_5NCl has been assigned, is really hydrochloride of pyridine.

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