JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*The Chlorine Derivatives of Pyridine. Part. IV.* *Constitution of the Tetrachloropyridines.*

By W. J. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

IN accordance with the generally accepted view of the constitution of pyridine, there are three theoretically possible derivatives in which four hydrogen atoms may be replaced by the same element or radicle ; and these, in the case of chlorine, may be represented thus :

These compounds have all been isolated from the products formed by the action of phosphorus pentachloride on pyridine (Trans., 1898, 72, 432), but in only one case, that of the compound represented by formula I, has the constitution been proved. This substance, which melts at 90—91°, was first obtained by the distillation of tetrachloroisonicotinic acid with glycerol, thus :

Of the two remaining compounds, it was suggested (*loc. cit.*) that the one melting at 21—22° has the chlorine atoms adjacent, that is, the compound is represented by formula III, whilst the compound melting at

74—75° is represented by II. This surmise was founded upon the distinctly greater basic character of the former (m. p. 21—22°), which alone forms a well-defined additive product with mercuric chloride. Direct evidence of the constitution of these compounds was, however, wanting, and it was with the object of supplying this that the present work was undertaken.

In a communication on the synthesis of pyridine derivatives (*Amer. Chem. J.*, 1886, **6**, 377; *Ber.*, 1887, **20**, 2655), Stokes and Pechmann described, among other compounds, two chlorinated derivatives of glutazine to which they gave the alternative formulæ :

Subsequently (*Trans.*, 1898, **72**, 777), the existence of the amino-group in these compounds was demonstrated, from which it follows that the formulæ (a) and (c) correctly represent the facts.

Now the tetrachloropyridine melting at 21—22° must have the constitution represented by either formula II or III, and if the view already expressed as to its constitution is correct, then it seemed probable, from a consideration of the behaviour of pentachloropyridine and its derivatives towards ammonia, that, on treatment with this agent, the 4- [or γ -] position relatively to the nitrogen would be the one attacked. This was found to be the case, and was shown as follows :

The tetrachloropyridine was treated with ammonia, and the resulting aminotrichloropyridine purified. The latter compound was thereupon further chlorinated by means of phosphorus pentachloride, and an aminotetrachloropyridine obtained identical with (c) above.

It follows therefore, as the only alternatives consistent with the accepted theory, that this aminotrichloropyridine must have one or other of the two formulæ :

A compound represented by formula IV has already been described by Stokes and Pechmann. The new compound, however, differs widely from the description given by them. Although obtained in a state of undoubted purity, it fuses at a lower temperature, gives a

well-defined platinichloride containing $3\text{H}_2\text{O}$, forms a beautifully crystalline additive product with mercuric chloride, and can under no conditions be made to yield with bromine water a precipitate which is insoluble in acids (compare *Amer. Chem. J.*, 1886, **6**, 377).

In the alternative, therefore, this aminotrichloropyridine must be held to have the constitution represented by the formula V, and as a consequence must have been derived from a tetrachloropyridine of the constitution given by formula III, thus confirming the view previously held.

An attempt to confirm this still further by obtaining the aminotrichloropyridine of formula IV from the tetrachloropyridine melting at $74-75^\circ$, which must, of course, have the constitution given by formula II, was unsuccessful. Whilst it was very unlikely that in a compound of this orientation the 4-position would be as reactive as in the other isomerides, it was hoped that the reaction might occur to an extent sufficient to allow of the identification of the compound sought. Want of material prevented further investigation in this direction, as the tetrachloropyridine melting at $74-75^\circ$ was only isolated in small amount from the product by the action of phosphorus pentachloride or pyridine in sealed tubes, and not at all by the other methods described.

EXPERIMENTAL.

Tetrachloropyridine (m. p. $21-22^\circ$) does not appear to be acted on in the cold by aqueous or alcoholic ammonia of any strength. At a temperature of $130-140^\circ$, one atom of chlorine is attacked and aminotrichloropyridine, $\text{C}_5\text{HNCl}_3\cdot\text{NH}_2$, formed. The operation was carried out in sealed tubes and the heating continued for three hours. At the end of that time, practically no unchanged tetrachloropyridine remained in those cases in which an alcoholic solution containing 16 per cent. of ammonia was employed. When aqueous ammonia was used, it was found necessary to continue the heating for a longer time but the same product was obtained. The contents of the tubes were diluted and filtered, and the product purified by crystallisation from dilute alcohol, from which it separates in slender needles. These crystals melted at $153-153.5^\circ$ (uncorr.), and this melting point was not changed by further recrystallisation. The following numbers were obtained on analysis:

0.1865 gave 0.2075 CO_2 and 0.0265 H_2O . C = 30.34; H = 1.58.

0.1950 „ 24.0 c.c. of nitrogen at 20° and 770 mm. N = 14.27.

$\text{C}_5\text{H}_3\text{N}_3\text{Cl}_3$ requires C = 30.44; H = 1.52; N = 14.20 per cent.

The compound is moderately soluble in boiling, and practically

4 THE CHLORINE DERIVATIVES OF PYRIDINE. PART IV.

insoluble in cold water, but is freely soluble in the usual organic solvents, and in moderately dilute mineral acids, from which it is precipitated on neutralisation. It sublimes unchanged on heating and is volatile in steam. Its solution in alcohol or hydrochloric acid gives no precipitate with bromine. If a saturated solution of mercuric chloride is added to a solution of the substance in alcohol, an additive compound is formed which crystallises from dilute alcohol in long, silky needles and melts at $213\text{--}214^\circ$ (uncorr.). A platinichloride is formed on addition of platinic chloride to a solution of the substance in hydrochloric acid or in alcohol. This separates out in thick, golden needles, which are decomposed by boiling water, but can be crystallised apparently unchanged from a dilute solution of platinic chloride in hydrochloric acid. The following numbers were obtained on analysis:

0.3865 lost 0.0243 H_2O at 100° and gave 0.0859 Pt. $\text{H}_2\text{O} = 6.28$;
Pt = 22.22.

$(\text{C}_5\text{HNC}_3\text{Cl}_3 \cdot \text{NH}_2)_2 \cdot \text{H}_2\text{PtCl}_6 + 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.29$; Pt = 22.69
per cent.

4-Aminotetrachloropyridine.—This substance was obtained from the preceding compound by the action of an excess of phosphorus pentachloride in sealed tubes at a temperature of $220\text{--}230^\circ$ maintained for four hours. On cooling, the contents of the tubes were thrown into water, the precipitate collected and crystallised from alcohol, when colourless plates, or, if deposited slowly, cubes, were obtained. These crystals melted at $214\text{--}215^\circ$ (uncorr.), a temperature somewhat higher than that previously given, and gave the following numbers on analysis:

0.2150 gave 0.5333 AgCl. Cl = 61.33.

0.2605 „ 26.73 c.c. nitrogen at 20.5° and 760 mm. N = 11.71.

$\text{C}_5\text{H}_2\text{N}_2\text{Cl}_4$ requires Cl = 61.14; N = 12.06 per cent.

The properties of this compound agree with those of the aminotetrachloropyridine described by Stokes and Pechmann (*loc. cit.*), and shown by them and by the authors to have the constitutional formula (c) given above. When boiled for two hours with excess of a solution of sodium ethoxide in absolute alcohol, 2-ethoxy-4-aminotrichloropyridine, melting at 83° (uncorr.), was obtained (*Amer. Chem. J.*, 1886, 6, 393), a reaction which affords further confirmation of the identity of the compound.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.