CXCVIII.—*The Chlorine Derivatives of Pyridine.*
Part IX. Preparation and Orientation of 3:5-Dichloropyridine.

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THE substance which forms the subject of this communication has long been known, and was first described by Königs and Geigy, who obtained it together with a trichloropyridine by the interaction of phosphorus pentachloride and barium pyridinedisulphonate (*Ber.*, 1884, 17, 589, 1833). The dichloropyridine has since been obtained by Dootson and the author (*Trans.*, 1899, 79, 979), and, more recently, the author has found the yield of this substance much improved by modifying the apparatus previously used (*loc. cit.*) so as to encourage the sublimation of the dichloropyridine hydrochloride as the chlorination proceeds. The same compound was also found to result from the distillation with glycerol of the dichloropicolinic acid prepared by the action of 80 per cent. sulphuric acid on one of the products of the chlorination of α -picoline (this vol., 1993).

The well-marked basic characters of the substance, together with its great stability, as indicated especially by its unalterability by ammonia at any temperature below 300°, suggested that the chlorine atoms in the compound occupied the 3:5-positions. This conclusion was strengthened by the analogy in general properties and stability under similar conditions to the dibromopyridine, m. p. 110—111°, in which the bromine atoms are known to occupy the 3:5 positions. The latter substance was discovered by Hofmann (*Ber.*, 1879, 12, 988), and the orientation conclusively proved by, among others, G. Pfeiffer (*Ber.*, 1887, 20, 1343).

With the object of testing the above conjecture, it was determined to prepare a quantity of Hofmann's 3:5-dibromopyridine, m. p. 110—111°, according to the directions of that investigator (*loc. cit.*). It was then converted into the diethoxypyridine by heating in sealed tubes with excess of sodium ethoxide.

Similarly, a quantity of diethoxide was made from the dichloropyridine in question. The examination of the two specimens of diethoxypyridine showed that they were similar to each other, and corresponded with the description given by Weidel and Blau (*Monatsh.*, 1885, 6, 669), who prepared their specimen from 3:5-dibromopyridine. It was then determined to institute experiments in the hope of obtaining some sparingly soluble, definite, crystalline compound of marked individuality, by which a comparison could be made of the

identity of the diethoxide from the two sources. The result was the discovery that the diethoxide from both sources reacts with bromine and chlorine to form identical compounds. When bromine water is added to an aqueous solution of the diethoxide in dilute hydrochloric acid, a bulky, white precipitate is produced, consisting of delicate needles almost insoluble in water, but fairly soluble in dilute alcohol, from which the substance crystallises in somewhat flattened needles with a satiny sheen, melting at $141\text{--}142^\circ$ (uncorr.). As will be seen below, the diethoxypyridine absorbs two atoms of bromine, and, in view of the fact that by heating the compound to 150° with concentrated hydrochloric acid it is converted into dibromodihydroxypyridine, the new compound is represented by one of the subjoined formulæ, of which (I) is regarded as the more probable, but further experiments are necessary to justify it.

An analogous compound containing two atoms of chlorine is obtained from the diethoxide from both sources by the use of chlorine water in place of bromine water. The compound forms beautiful needles from dilute alcohol, melting at $123\text{--}124^\circ$. This substance, when heated with concentrated hydrochloric acid to 150° , is converted into dichlorodihydroxypyridine, crystallising from water in colourless needles containing 3 molecules of water of crystallisation, which are lost in a vacuum over sulphuric acid, the substance becoming opaque. The compound is represented by one of the following formulæ, but the question as to which is the correct one must be the subject of further study.

EXPERIMENTAL.

The dichloropyridine (2 grams) was heated in sealed tubes for five hours with a solution of sodium (1.5 grams) in absolute alcohol (20 c.c.) to a temperature of $190\text{--}200^\circ$. After cooling, the contents of the tubes were rinsed out with water, and distilled in a current of steam. The first part of the distillate consisted chiefly of alcohol with some dissolved diethoxypyridine, and this was followed by an

aqueous part which separated into two layers, the lower of which was mainly diethoxypyridine, which was separated in the usual way, dissolved in dilute hydrochloric acid, and used for the experiments detailed below.

A small part was precipitated with chloroplatinic acid, and a platinichloride, consisting of orange-yellow needles, was obtained agreeing with the description given by Weidel and Blau (*loc. cit.*). The substance is unchanged on heating to 100° , and is anhydrous. Two portions which had been heated to 100° were afterwards ignited, and gave the following results :

0.418 gave 0.110 Pt. Pt = 26.31.

0.3278 „ 0.0855 Pt. Pt = 26.08.

$[C_5H_8(OEt)_2N]_2, H_2PtCl_6$ requires Pt = 26.18 per cent.

Conversion of Diethoxypyridine into Dibromodiethoxypyridine.

A further portion of diethoxypyridine hydrochloride was mixed with bromine water, when a voluminous, white precipitate was produced consisting of colourless needles. These were practically insoluble in cold water, and only slightly soluble on boiling, but readily so in hot alcohol, from which they crystallised in somewhat flattened needles, having a pearly lustre and melting at $141-142^{\circ}$ (uncorr.) :

(1) 0.2077 gave 0.2562 CO_2 and 0.0705 H_2O . C = 33.60; H = 3.77.

(2) 0.2126 „ 0.2618 CO_2 „ 0.0665 H_2O . C = 33.58; H = 3.48.

(3) 0.127 „ 0.142 AgBr. Br = 48.75.

(4) 0.1228 „ 0.142 AgBr. Br = 49.23.

$C_9H_{11}O_2NBr_2$ requires C = 33.23; H = 3.39; Br = 49.23 per cent.

Conversion of Diethoxypyridine into Dichlorodiethoxypyridine.

Another part of the diethoxypyridine hydrochloride was precipitated by chlorine water, the bulky, crystalline precipitate collected, and recrystallised from dilute alcohol. The substance forms beautiful colourless needles when the solution is allowed to cool rapidly, but when cooled slowly, large, prismatic crystals are formed, resembling those of potassium nitrate, and melting at 124° (uncorr.). The substance dissolves only sparingly in water, but is freely soluble in alcohol, ether, or acetone :

0.1795 gave 0.2176 AgCl. Cl = 29.97.

$C_9H_{11}O_2NCl_2$ requires Cl = 30.08 per cent.

Formation of Dibromodiethoxypyridine from 3 : 5-Dibromopyridine.

Fifty grams of pure dibromopyridine, m. p. 111° , prepared by Hofmann's directions (*loc. cit.*), were treated in an exactly similar

manner to the dichloropyridine, and part of the diethoxypyridine was converted by bromine water into its bromine derivative. The crystals formed were indistinguishable in appearance, solubility, and melting point ($141\text{--}142^\circ$) from the specimen obtained by similar treatment of the dichloropyridine in question :

0.0915 gave 0.10574 AgBr. Br = 49.17 .

0.0963 „ 0.11144 AgBr. Br = 49.24 .

$\text{C}_9\text{H}_{11}\text{O}_2\text{NBr}_2$ requires Br = 49.23 per cent.

The remaining diethoxypyridine, prepared from 3 : 5-dibromopyridine, was converted by means of chlorine water into the dichlorodiethoxypyridine. The specimen thus produced was indistinguishable from that prepared from the dichloropyridine in question.

Conversion of Dichlorodiethoxypyridine into Dichlorodihydroxypyridine.

Four grams of dichlorodiethoxypyridine were heated to $150\text{--}155^\circ$ with concentrated hydrochloric acid in sealed tubes, each tube being charged with 1 gram of the substance and 20 c.c. of acid. The heating was continued for six hours, and if, on cooling, the tube is free from crystalline matter, the decomposition is complete. On opening the tubes, ethyl chloride escaped, and on evaporating the contents of the tubes to dryness on the water-bath, a slightly brown residue was obtained. This was dissolved in the least possible amount of boiling water, a small quantity of animal charcoal added, and, after digestion for a time, the solution was filtered and allowed to crystallise. The substance separates from water in fine, colourless needles containing 3 molecules of water of crystallisation, which it loses in a vacuum over sulphuric acid, or in the air-bath at $60\text{--}70^\circ$.

The undried compound when heated to $83\text{--}84^\circ$ partly melts, leaving a lower hydrate, or more probably the unmelted anhydrous substance. On continuing the heating, the whole solidified, and afterwards melted with darkening at 196° (uncorr.). The substance when dried at $60\text{--}70^\circ$ melts sharply at $194\text{--}195^\circ$ (uncorr.) to a colourless liquid :

0.2105 lost, in a vacuum over sulphuric acid, 0.0485. $\text{H}_2\text{O} = 23.04$.

0.0835, dry substance, gave 0.13312 AgCl. Cl = 39.41 .

$\text{C}_5\text{H}_3\text{O}_2\text{NCl}_2 \cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 23.07$ per cent.

$\text{C}_5\text{H}_3\text{O}_2\text{NCl}_2$ „ Cl = 39.44 „

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