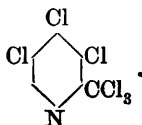


CXCVII.—*The Chlorination of Methyl Derivatives of Pyridine. Part II. 2-Methylpyridine.*

By WILLIAM JAMES SELL.

IN a former communication (Part I, Trans., 1905, 87, 799) it was shown that, when α -picoline was first saturated with hydrogen chloride and then subjected to chlorination at 105—110° as long as any action appears to take place, a mixture of chlorinated derivatives was obtained, from which a solid compound, shown to be a hexachloro-picoline, was separated. This, on examination, proved to have the constitution represented by the formula :



It was further shown (*loc. cit.*) that when this compound is carefully heated with 80 per cent. sulphuric acid it is converted into 3:4:5-trichloropicolinic acid, which is deposited when the cooled liquid is diluted with water, any 3:4:5-trichloropyridine formed by local over-heating being retained in solution.

Examination of the Liquid Product of the Chlorination of α -Picoline.

The liquid, which was drained from the crystals of hexachloropicoline by the aid of the pump and pressure, was submitted to fractional distillation under reduced pressure. The liquid commenced to distil at 148°/12 mm., the thermometer quickly rising to 153°; the receiver was changed every 5° until the thermometer registered 183°, when the distillation was practically complete. By far the largest part of the distillate passed over between 153° and 168° and remained liquid, whereas the fractions boiling at 168—183° showed signs of crystallisation on cooling, and, after some months, became almost solid. The solid from each of the last three fractions was collected, and, on crystallisation from alcohol, was found to separate in the characteristic prisms of the hexachloropicoline, m. p. 102—103°, already described, and this conclusion was confirmed by heating it with 80 per cent. sulphuric acid, when trichloropicoline, m. p. 164—165°, was isolated. That hexachloropicoline is freely soluble in the liquid products was well known, and it is not therefore surprising to find it distilling over in the last part of the distillation. Its boiling point under 12 mm. pressure is 175—180°.

In the hope of effecting some further purification by freezing out, draining, and crystallisation, the various liquid fractions were immersed in ice and then in a mixture of ice and salt, with no other result than to render them thick and syrupy. When portions were next gradually exposed in the upper part of a vessel containing liquid air, they remained clear for a time, and of the consistency of Canada balsam, ultimately becoming opaque and solid. On removal from the bath, the phenomena were repeated in the inverse order, and, after many fruitless attempts, this method of purification was abandoned.

Examination of the Various Fractions by heating with 80 per cent. Sulphuric Acid.

Portions of each fraction, b. p. 153—168°, weighing 20 grams, were mixed with 50 c.c. of 80 per cent. sulphuric acid, and heated to 130—132° in a long-necked flask provided with an air condenser ground into its neck, the heating being continued until fumes of hydrogen chloride ceased to escape. The mixture, on cooling, was next diluted with about 200 c.c. of water, and distilled in a current of

steam, when generally a few drops of apparently unaltered compound passed over, and the liquid in the flask deposited a crop of crystals on cooling.

The crystals were collected and purified by recrystallisation from water, when they were deposited in colourless needles. Those crystals which separated from the treatment of the fractions boiling at 153—158° and 158—163° melted with decomposition at 153—154°, whereas the acid obtained from the still liquid portions of the higher fractions melted at 148—149° under similar treatment as to purification. Subsequent further purification by recrystallisation, however, raised the temperature of the acid from the later fractions to 153—154°, and, as was expected and confirmed by qualitative tests, the depression was due to the crystals being more or less contaminated with trichloropicolinic acid derived from hexachloropicoline contained in the fractions of higher boiling point.

3:5-Dichloropicolinic acid is fairly soluble in boiling, and sparingly so in cold, water, freely so in boiling alcohol and in most organic solvents. The crystals are anhydrous, and gave the following numbers on analysis :

0.1855 gave 0.255 CO₂ and 0.028 H₂O. C = 37.48 ; H = 1.67.

0.3225 „ 0.4770 AgCl. Cl = 36.60.

0.0985 „ 0.1460 AgCl. Cl = 36.88.

C₆H₃O₂NCl₂ requires C = 37.50 ; H = 1.56 ; Cl = 36.97 per cent.

An aqueous solution of the acid gives the following reactions :

(1) With calcium or barium chlorides and a drop of ammonia, no precipitate.

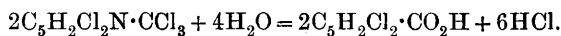
(2) With silver nitrate, a sparingly soluble, flocculent precipitate consisting of woolly needles.

(3) With mercuric chloride, a precipitate which is slowly deposited in stout, colourless needles.

(4) With ferrous sulphate, a faint brown coloration and, after long standing, a slight dark red, crystalline deposit.

(5) With copper acetate, a light blue, sparingly soluble copper salt.

The foregoing results show that a large part of the chlorination product of α-picoline, which is liquid at the ordinary temperature, consists of pentachloropicoline, C₅H₂Cl₂N·CCl₃, and that this on heating with 80 per cent. sulphuric acid, is resolved into dichloropicolinic acid and hydrogen chloride, thus :



It may be mentioned that some of the compounds described in this series of papers are isomeric with the corresponding substances obtained by Ost by the action of phosphorus pentachloride on comenamic acid (*J. pr. Chem.*, 1883, [ii], 27, 257).

Methyl-3 : 5-dichloropicolinate.

About 40 grams of the acid were converted into its methyl ester in the usual way, the substance being recrystallised from methyl alcohol. It forms stout needles, melting at 78—79° (uncorr.), and may be crystallised from water or distilled in a current of steam without change, as shown by the melting point of the material after these operations.

3 : 5-Dichloropicolinamide.

The greater part of the methyl ester was treated with an excess of strong aqueous ammonia (0·880) and left overnight in a closed flask. The *amide* was dissolved in boiling water, from which, on cooling, it crystallised in colourless needles melting sharply at 175—176° (uncorr.) :

0·1795 gave 0·2455 CO₂ and 0·0345 H₂O. C = 37·29 ; H = 2·13.

0·2593 „ 32·15 c.c. N₂ at 17·9° and 767·5 mm. N = 14·57.

C₆H₄ON₂Cl₂ requires C = 37·69 ; H = 2·09 ; N = 14·66 per cent.

Conversion of 3 : 5-Dichloropicolinic Acid into 3 : 5-Dichloropyridine.

Since the effervescence occasioned by heating the acid to its melting point seemed to indicate that it loses carbon dioxide at this temperature, an experiment was arranged which consisted in distilling about 5 grams of the acid with 20 c.c. of glycerol. The distillate, which on cooling solidified to a crystalline mass, was rinsed with cold alcohol and after pressure between folds of blotting paper crystallised from hot alcohol, from which it separated in flat, flexible needles and plates with the characteristic odour, volatility, reactions, and melting point (66—67°) of the dichloropyridine described by Königs and Geigy (*Ber.*, 1884, 17, 589, 1833), Sell and Dootson (*Trans.*, 1899, 79, 979), and shown by the author to contain the chlorine atoms in the 3 : 5-position (this vol., 1997). This was confirmed by converting a specimen of the dichloropyridine into diethoxypyridine and transforming the latter by bromine water into the characteristic dibromodiethoxypyridine, m. p. 193—140° :

Found, Br = 49·29

C₉H₁₁O₂NBr₂ requires Br = 49·23 per cent.

UNIVERSITY LABORATORY,
CAMBRIDGE.