167. *The Mercuration of Pyridine.*

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SACHS and EBERHARTINGER (*Ber.*, 1923, **56**, 2223) have described the mercuration of pyridine by heating it with mercuric acetate at 175—180°. They state that when the reaction product is poured into water, and brine added, the precipitate produced (A) is 3 : 5-dichloromercuripyridine, and that the precipitate (B) formed when the filtrate from A is treated with potassium iodide is 3-iodomercuripyridine. A is described as a light brown powder insoluble in all solvents, including pyridine, decomposing at 220°, and giving 3 : 5-dibromopyridine when warmed with bromine, while B is a yellow amorphous powder, melting crude at 68—69°, insoluble in the ordinary organic solvents except pyridine, from which, however, it cannot be crystallised, and giving with bromine 3-bromopyridine.

We repeated this preparation, and obtained the same precipitates, but the reactions of B showed that it could not have the formula

assigned to it by Sachs and Eberhartinger, and investigation showed that A and B were not single substances. The main constituent of B was found to be a yellow crystalline compound, m. p. 154°, which gave pyridine and mercuric oxide when boiled with sodium hydroxide, and from which we could not obtain 3-bromopyridine. It was shown to be *pyridine tri-iodomercuriate*, $C_5H_5N,HHgI_3$. A consisted of about 70% of 3-chloromercuripyridine mixed with other substances, insoluble in pyridine, which were not further examined. That the mercury had entered the ring in the 3-position was shown by the action of bromine, which gave 3-bromopyridine, and further by the action of arsenic trichloride, which led to the production of a pyridylarsonic acid identical with that obtained from 3-aminopyridine (as will be described in a subsequent paper).

EXPERIMENTAL.

3-Chloromercuripyridine.—Mercuric acetate (1000 g.) was heated with pyridine (2000 c.c.) in ten lots in an autoclave at 180° for 2 hours. The product was filtered from the insoluble residue (265 g.) and diluted with four times its volume of water. An equal volume of brine was added, and the precipitate filtered off and dried (1350 c.c. of pyridine were recovered from the filtrate by steam distillation). The precipitate (405 g.) was extracted three times with 1000 c.c. of pyridine, and the soluble portion recovered by the gradual addition of water (3000 c.c.). The crude *3-chloromercuripyridine* (273 g.) melted at 225—240°; 10 g., crystallised three times from 50% aqueous pyridine, and then from alcohol, gave 2·5 g. of white needles, m. p. (decomp.) 278—280° (Found: C, 18·9; H, 1·75; Cl, 10·9, 11·1; Hg, 64·5, 64·0. C_5H_4NClHg requires C, 19·2; H, 1·3; Cl, 11·3; Hg, 63·9%).

10 G. of the crude product were warmed on a water-bath with bromine (5 g.) and sodium bromide (10 g.) in water (20 c.c.), made alkaline, and steam distilled. The distillate was extracted with ether, and the extract distilled (0·9 g., 170—171°). It was compared with a specimen of 3-bromopyridine, prepared by the method of Räth (*Annalen*, 1931, **486**, 100) from nitropyridine made by direct nitration of pyridine. Mercurichloride, m. p. and mixed m. p. 203°; picrate, m. p. and mixed m. p. 154°.

Pyridine Tri-iodomercuriate.—Mercuric acetate (100 g.) and pyridine (200 g.) were heated as above, and after precipitation with brine the filtrate was treated with potassium iodide solution. An oil separated, which solidified on addition of a little acetic acid. The yellow solid formed (24·1 g.; m. p., crude, 65—85°) was very soluble in pyridine and acetone, soluble in methyl, ethyl, and amyl alcohols, and slightly soluble in ethyl acetate, benzene, and water.

Crystallised from glacial acetic acid, it gave yellow needles, m. p. 152—154° (Found : N, 1·9; I, 57·1, 58·1; Hg, 30·5. $C_5H_6NI_3Hg$ requires N, 2·1; I, 57·6; Hg, 30·3%). 10 G. of the crude product gave on distillation 8·1 g., b. p. 230—236°/1 mm., which crystallised from alcohol in yellow plates, m. p. 154°; mixed m. p. with the needles from acetic acid, 152—154°.

The same substance was formed directly from its constituents when molecular proportions of pyridine, hydriodic acid, and mercuric iodide were heated together on a water-bath. The whole solidified to a yellow mass, which, crystallised from acetic acid or alcohol, had m. p. 154°, and mixed m. p. with the above compound 154°.

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