CXXIV.—*Tetrachloroiodides of the Alkaloids.*

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MANY of the commoner alkaloids yield well-characterised tetrachloroiodides when a solution of the alkaloid in concentrated hydrochloric acid is added to excess of a solution of tetrachloroiodic acid made by saturating with chlorine a suspension of finely powdered iodine in concentrated hydrochloric acid.

These alkaloidal tetrachloroiodides are all decomposed by a solution of sodium sulphite, the base being liberated. When they are treated with a solution of potassium iodide acidified with acetic acid, iodine is quantitatively liberated. This reaction has been used for the analysis of these compounds.

Hexamethylenetetramine also forms a stable tetrachloroiodide.

The tetrachloroiodides of many quaternary bases are easily made by saturating a solution of the iodide in concentrated hydrochloric acid with chlorine.

EXPERIMENTAL.

The solution of tetrachloroiodic acid used was obtained by suspending finely powdered iodine (15 g.) in concentrated hydrochloric acid (80 c.c.) and saturating it with chlorine.

Quinine Tetrachloroiodide, $C_{20}H_{24}O_2N_2,2HICl_4$.—When a solution of 10 g. of quinine hydrochloride in 50 c.c. of concentrated hydrochloric acid was added to 60 c.c. of tetrachloroiodic acid solution, *quinine tetrachloroiodide* separated immediately as a bright yellow, microcrystalline powder. This was filtered off and dissolved in 150 c.c. of boiling glacial acetic acid, the solution was cooled, and 300 c.c. of concentrated hydrochloric acid were added; the tetrachloroiodide thus obtained, after being dried in a desiccator over phosphoric oxide and a few lumps of lime, melted at 114° (decomp.) (Found: Cl, 32·3. $C_{20}H_{26}O_2N_2Cl_8I_2$ requires Cl, 32·9%).

Cinchonine tetrachloroiodide, $C_{19}H_{22}ON_2,2HICl_4$, was similarly prepared and purified. It separated as a bright yellow, microcrystalline powder, m. p. 85° (decomp.) (Found: Cl, 33·4. $C_{19}H_{24}ON_2Cl_8I_2$ requires Cl, 34·0%).

Strychnine Tetrachloroiodide, $C_{21}H_{22}O_2N_2,HICl_4$.—A solution of 5 g. of strychnine in 20 c.c. of chloroform was saturated with hydrogen chloride and added to the solution formed by dissolving 3 g. of iodine in 20 c.c. of chloroform and saturating it with chlorine. *Strychnine tetrachloroiodide* separated at once as a pale yellow, microcrystalline powder, m. p. 91° (decomp.) (Found: Cl, 23·3. $C_{21}H_{23}O_2N_2Cl_4I$ requires Cl, 23·5%).

Morphine tetrachloroiodide, $C_{17}H_{19}O_3N,HICl_4$, was prepared from 5 g. of morphine hydrochloride, dissolved in 40 c.c. of concentrated hydrochloric acid, and 10·5 c.c. of tetrachloroiodic acid solution. It crystallised from glacial acetic acid, in which it was very easily soluble, in small, pale orange needles, which melt at 78° (decomp.), and rapidly decompose when kept, even in a sealed tube (Found: Cl, 25·4. $C_{17}H_{20}O_3NCl_4I$ requires Cl, 25·6%).

Codeine tetrachloroiodide, $C_{18}H_{21}O_3N,HICl_4$, was prepared similarly from 2 g. of codeine, dissolved in 20 c.c. of concentrated hydrochloric acid, and 4·5 c.c. of tetrachloroiodic acid solution. It crystallised from glacial acetic acid, containing a little iodine trichloride, in which it was easily soluble, in pale orange needles, but it was not found possible to dry the compound without slight decomposition occurring.

Cocaine Tetrachloroiodide, $C_{17}H_{21}O_4N,HICl_4$.—When a solution of 1 g. of cocaine hydrochloride in 5 c.c. of concentrated hydrochloric acid was added to 5 c.c. of tetrachloroiodic acid solution prepared as above, *cocaine tetrachloroiodide* separated as a bright yellow solid. It crystallised from glacial acetic acid, containing a little iodine trichloride, in which it was moderately easily soluble, in small, pale yellow, irregular, flat plates, m. p. 141° (decomp.) (Found: Cl, 25·3. $C_{17}H_{22}O_4NCl_4I$ requires Cl, 24·75%).

Hexamethylenetetramine tetrachloroiodide, $(CH_2)_6N_4,HICl_4$, separated in bright yellow prisms, m. p. 147° (decomp.), when a solution of 5 g. of hexamethylenetetramine in 25 c.c. of concentrated hydrochloric acid was added to 30 c.c. of tetrachloroiodic acid solution (Found: Cl, 34·2. $C_6H_{13}N_4Cl_4I$ requires Cl, 34·6%). It cannot be recrystallised, as when heated with glacial acetic acid it decomposes into formaldehyde and ammonium tetrachloroiodide.

1-*Methylpyridine Tetrachloroiodide*, $C_5H_5NMeICl_4$.—5 G. of pyridine methiodide were dissolved in 25 c.c. of concentrated hydrochloric acid and a stream of chlorine was passed through the cooled solution. Iodine at first separated, but gradually disappeared and the bright yellow 1-*methylpyridine tetrachloroiodide* separated.

It crystallised from boiling glacial acetic acid containing a little iodine trichloride, in which it was sparingly soluble, in clusters of small yellow needles, m. p. 180° (decomp.) (Found: Cl, 39·0. $C_6H_8NCl_4I$ requires Cl, 39·1%).

1 : 2-*Dimethylpyridine tetrachloroiodide* separates from boiling glacial acetic acid, in which it is rather sparingly soluble, in bright yellow, irregular, twinned plates, m. p. 185° (decomp.) (Found: Cl, 37·5. $C_7H_{10}NCl_4I$ requires Cl, 37·7%).

1 : 2 : 4 : 6-*Tetramethylpyridine tetrachloroiodide* separates from boiling glacial acetic acid, in which it is fairly easily soluble, in bright yellow, irregular, flat plates, m. p. 130° (decomp.) (Found: Cl, 35·2. $C_9H_{14}NCl_4I$ requires Cl, 35·1%).

1-*Methylquinoline tetrachloroiodide* separates from glacial acetic acid, in which it is somewhat sparingly soluble, in pale yellow prisms, m. p. 191° (Found: Cl, 34·15. $C_{10}H_{10}NCl_4I$ requires Cl, 34·4%).

6-*Chloro*-1-*methylquinoline tetrachloroiodide* separates from boiling glacial acetic acid, in which it is sparingly soluble, in long yellow needles, m. p. 167° [Found: Cl (added), 31·7. $C_{10}H_9NCl_5I$ requires Cl (added), 31·7%].

6-*Bromo*-1-*methylquinoline tetrachloroiodide* crystallises from glacial acetic acid in bright yellow needles, m. p. 176° (Found: Cl, 29·1. $C_{10}H_9NCl_4BrI$ requires Cl, 28·9%).

N-*Methylstrychnine tetrachloroiodide* separates from glacial acetic acid, in which it is moderately easily soluble, in minute, pale yellow needles which, when heated, decompose without melting (Found: Cl, 22·9. $C_{22}H_{25}O_2N_2Cl_4I$ requires Cl, 23·0%).

NN-*Dimethylnicotine bistetrachloroiodide* separates from boiling glacial acetic acid, in which it is somewhat sparingly soluble, in fine yellow needles, m. p. 145° (Found: Cl, 38·6. $C_{12}H_{20}N_2Cl_8I_2$ requires Cl, 38·9%).

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