CLXXI.—*Nicotine Tetrachloroiodide.*

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THE authors have shown (J., 1924, **125**, 183, 1980) that many organic bases form stable tetrachloroiodides, those of the simpler nitrogen bases and of diazonium salts having been described. As might be expected, similar derivatives of many alkaloids can be prepared, among which the tetrachloroiodide of nicotine presents features of interest, since no other equally well-crystallised derivative of nicotine is known.

Nicotine tetrachloroiodide separates quantitatively when a solution of the base in hydrochloric acid is added to a similar solution of iodine trichloride. Since nicotine is a di-tertiary base, one molecule combines with two equivalents of tetrachloroiodic acid and the compound has the constitution $C_{10}H_{14}N_2,2HICl_4$.

Nicotine tetrachloroiodide is a very stable substance; it can be kept without alteration for an indefinite period in an ordinary corked specimen tube, and does not lose weight when exposed for a considerable period in a vacuum desiccator over lime. It is decomposed by aqueous alkalis, and more slowly by water alone, giving mainly a mixture of free nicotine and nicotinic acid, together with iodate and iodide.

The preparation of pure nicotine free from the small quantities of related alkaloids and other substances with which it is associated in the tobacco plant has hitherto presented considerable difficulty.

The tetrachloroiodide affords a ready means of effecting this separation, since it can be obtained from the crude material in a state of purity with very little loss by recrystallisation from glacial acetic acid. On decomposing the pure tetrachloroiodide with sodium sulphite and making the solution alkaline with potash, pure nicotine is liberated, and can be extracted with ether.

Well-crystallised *tetrachloroiodides* are also yielded by nicotinic acid (I), methyl *N*-methylnicotinate (II), and trigonelline (nicotinic acid methyl betaine) (III).

$CO_2H\cdot C_5H_4N\cdot HICl_4$ (I.) $CO_2Me\cdot C_5H_4NMe\cdot ICl_4$ (II.) $CO_2H\cdot C_5H_4NMe\cdot ICl_4$ (III.)

EXPERIMENTAL.

Nicotine Tetrachloroiodide.—Ten g. of pure nicotine, dissolved in 20 c.c. of cooled concentrated hydrochloric acid, were added to a solution of iodine trichloride prepared by saturating a suspension of 8 g. of iodine in 100 c.c. of concentrated hydrochloric acid with chlorine. A thick yellow precipitate at once separated. A slow stream of chlorine was passed through the mixture for a short time. The precipitate was then filtered off, washed with a little concentrated hydrochloric acid, and recrystallised from hot glacial acetic acid containing a little iodine trichloride, a slow stream of chlorine being passed through the solution during cooling; *nicotine tetrachloroiodide* separated in very beautiful, orange prisms, m. p. 150° (decomp.) (Found: Cl, 40·7; I, 35·8. $C_{10}H_{16}N_2Cl_8I_2$ requires Cl, 40·5; I, 36·1%).

Nicotinic Acid Tetrachloroiodide.—To a solution of 10 g. of nicotinic acid in 150 c.c. of concentrated hydrochloric acid, 20 g. of powdered iodine were added. Chlorine was then passed until the whole was saturated. *Nicotinic acid tetrachloroiodide* separated as a bright yellow precipitate. This was filtered off and recrystallised from a mixture of equal parts of concentrated hydrochloric acid and glacial acetic acid to which a little iodine trichloride had been added, small yellow needles, m. p. 137°, very slowly separating (yield, 30 g. Theoretical yield, 31·5 g.) (Found: Cl, 36·35. $C_6H_5O_2N,HICl_4$ requires Cl, 36·1%).

Nicotinic acid tetrachloroiodide is insoluble in water and concentrated hydrochloric acid. It is decomposed by aqueous sodium sulphite, nicotinic acid being re-formed.

Methyl N-*methylnicotinate tetrachloroiodide*, prepared similarly, crystallises from hot glacial acetic acid, containing a little iodine trichloride, in bright yellow needles, m. p. 110° (Found: Cl, 33·6. $C_8H_{10}O_2NCl_4I$ requires Cl, 33·7%).

Trigonelline similarly forms a *tetrachloroiodide*, which crystallises from a mixture of glacial acetic acid and hydrochloric acid, to which a little iodine trichloride has been added, in small, bright yellow prisms, m. p. 122° (Found: Cl, 34·7. $C_7H_8O_2NCl_4I$ requires Cl, 34·9%).

Decomposition of Nicotine Tetrachloroiodide by Sodium Sulphite.—Nicotine tetrachloroiodide (50 g.), suspended in 80 c.c. of water and cooled to 0°, was added gradually, with constant stirring, to a cooled solution of 40 g. of sodium sulphite in 200 c.c. of water. Sodium hydroxide (40 g., dissolved in 100 c.c. of water) was then added, and the whole extracted four times with ether. After the extract had been dried with anhydrous potassium carbonate, and the ether evaporated, the residue was distilled in a current of hydrogen, 10 g. of pure nicotine, b. p. 249—250°, being obtained (yield, 90%).

Preparation of Pure Nicotine Tetrachloroiodide from Technical Nicotine.—Two recrystallisations from glacial acetic acid were found sufficient to free the crude nicotine tetrachloroiodide from the tetrachloroiodides of the other bases present in technical nicotine.

100 G. of commercial nicotine were dissolved in 200 c.c. of concentrated hydrochloric acid and added to a solution of iodine trichloride obtained by passing excess of chlorine through a suspension of 80 g. of iodine in 400 c.c. of concentrated hydrochloric acid. The thick yellow precipitate which separated was twice recrystallised from 750 c.c. of hot glacial acetic acid (containing a little iodine trichloride), 372 g. of pure nicotine tetrachloroiodide, m. p. 150°, being obtained.

Isolation of Pure Nicotine from Tobacco.—Two hundred g. of dried, powdered tobacco (dark rag tobacco) were ground with a solution of 80 g. of sodium hydroxide in 1000 c.c. of water and steam-distilled. The bulk of the nicotine came over in the first 1400 c.c. and when 1800 c.c. had been collected, no nicotine could be detected in the distillate. The aqueous distillate was cooled, saturated with hydrogen chloride, and a solution of iodine trichloride in hydrochloric acid (containing 12 g. of iodine) was added. The thick yellow precipitate which separated was filtered off and twice recrystallised from 50 c.c. of glacial acetic acid containing a little iodine trichloride, 22 g. of pure nicotine tetrachloroiodide being obtained. This, when decomposed with 10 g. of sodium sulphite and extracted as described above, yielded 4·5 g. of pure nicotine.

Decomposition of Nicotine Tetrachloroiodide by Caustic Alkalis.—Ten g. of nicotine tetrachloroiodide were added gradually to a cooled solution of 4 g. of sodium hydroxide in 50 c.c. of water. Much heat was developed and a small quantity of tarry matter separated, which was filtered off. The filtrate was extracted repeatedly with ether. On evaporation of the ether, 1·5 g. of nicotine were obtained. The aqueous liquid from which the nicotine had been extracted was then made acid with hydrochloric acid and evaporated to dryness, and the residue extracted with a little concentrated hydrochloric acid. The acid extract was added to excess of a solution of tetrachloroiodic acid; 1·7 g. of nicotinic acid tetrachloroiodide then separated as a bright yellow solid.

Ten g. of nicotine tetrachloride thus yielded nicotine and nicotinic acid corresponding to 6·75 g. and 3·16 g., *i.e.*, to 99% of the tetrachloroiodide used.

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