

387. Trichlorohydroxy-aliphatic Amines.

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BOTH $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropane and $\gamma\gamma\delta$ -trichloro- α -nitro- β -hydroxypentane, which can be easily and quantitatively obtained by the condensation of nitromethane with chloral and butyl chloral respectively (this vol., p. 1178), are readily reduced to the corresponding amines, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$ and $\text{CH}_3\cdot\text{CHCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$. These are stable, colourless, well-crystallised compounds. Their resolution into optically active modifications has not yet been effected. They yield well-crystallised salts, among which the hydrochlorides, the sulphates, and the oxalates are the most characteristic. The hydrochlorides are easily soluble in water, the sulphates and oxalates less readily soluble, the latter separating as colourless crystalline precipitates when solutions of the hydrochlorides are added to saturated solutions of sodium sulphate and ammonium oxalate respectively. The bases yield well-crystallised N-acetyl and ON-diacetyl derivatives and well-crystallised ureas.

$\gamma\gamma\gamma$ -Trichloro- α -amino- β -hydroxypropane Hydrochloride.—To a mixture of 208.5 g. of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropane, 354 g. of tin, and 50 c.c. of water, 657 c.c. of concentrated hydrochloric acid were added, about 50 c.c. at a time, with vigorous shaking, the temperature being kept between 60° and 70° ; the rate of addition was regulated so as to keep the action brisk but not violent. When the tin had nearly all dissolved, the whole was diluted to 2 l. and heated, and the tin precipitated by hydrogen sulphide. To complete the removal of the tin it was necessary, when stannous sulphide was no longer precipitated in the original liquid, to evaporate the filtrate to dryness, redissolve the residue, and again pass hydrogen sulphide. The filtrate was evaporated to dryness, and the somewhat dark-coloured hydrochloride washed with a little anhydrous alcoholic hydrogen chloride. This removed most of the colour; the last traces were removed by redissolving the salt and adding animal charcoal. On evaporation, the hydrochloride was obtained colourless and practically pure. Recrystallised from a very little dilute hydrochloric acid, it formed long, transparent, flattened prisms with domed ends, m. p. 235° (decomp.) (Found: Cl as HCl, 16.7; total Cl, 66.3. $\text{C}_3\text{H}_6\text{ONCl}_3\cdot\text{HCl}$ requires Cl as HCl, 16.5; total Cl, 66.1%).

$\gamma\gamma\gamma$ -Trichloro- α -amino- β -hydroxypropane, obtained by mixing well-cooled solutions of the hydrochloride and potassium hydroxide, crystallised from hot alcohol, in which it was easily soluble, in long, well-shaped, colourless, transparent, six-sided prisms, m. p. 123° (Found: Cl, 59.7. $\text{C}_3\text{H}_6\text{ONCl}_3$ requires Cl, 59.7%).

The oxalate was only very slightly soluble in boiling water and separated, on cooling, in very small, transparent, colourless, short, six-sided prisms with domed ends, m. p. 220° (decomp.) (Found: N, 6.1; Cl, 47.8. $2\text{C}_3\text{H}_6\text{ONCl}_3\cdot\text{H}_2\text{C}_2\text{O}_4$ requires N, 6.3; Cl, 47.65%).

The sulphate separated from boiling water, in which it was sparingly soluble, in thin, colourless, transparent, rhombic plates, m. p. 255° (decomp.) (Found: Cl, 47.05; S, 6.9. $2\text{C}_3\text{H}_6\text{ONCl}_3\cdot\text{H}_2\text{SO}_4$ requires Cl, 46.8; S, 7.0%).

The N-acetyl derivative, formed from equivalent amounts of acetic anhydride and the base, crystallised from water, in which it was somewhat sparingly soluble, in colourless, transparent, rhombic plates, m. p. 154° (Found: Cl, 49.0. $\text{C}_5\text{H}_8\text{O}_2\text{NCl}_3$ requires Cl, 48.3%). The ON-diacetyl derivative, produced when the base was heated with excess of acetic anhydride, crystallised from acetic anhydride in short colourless prisms, m. p. 99° (Found: Cl, 40.8. $\text{C}_7\text{H}_{10}\text{O}_3\text{NCl}_3$ requires Cl, 40.6%).

$\gamma\gamma\gamma$ -Trichloro- β -hydroxy-n-propylurea, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, separated when a heated solution of 8 g. of $\gamma\gamma\gamma$ -trichloro- α -amino- β -hydroxypropane hydrochloride and 5 g.

of potassium cyanate was cooled. It was moderately easily soluble in hot water and separated in colourless, transparent, four-sided, rhombic plates, m. p. 175° (Found : Cl, 48·2. $C_4H_7O_2N_2Cl_3$ requires Cl, 48·1%).

$\gamma\delta$ -Trichloro- α -amino- β -hydroxy-n-pentane Hydrochloride.—This salt and the corresponding base were prepared and purified similarly to the propane derivatives.

The hydrochloride was recrystallised from dilute hydrochloric acid. It separated from boiling water in colourless, transparent, thin plates, m. p. about 231° (decomp.) (Found : Cl as HCl, 14·6; total Cl, 58·3. $C_5H_{10}ONCl_3 \cdot HCl$ requires Cl as HCl, 14·6; total Cl, 58·4%).

$\gamma\delta$ -Trichloro- α -amino- β -hydroxy-n-pentane crystallised from alcohol in colourless rhombic plates, m. p. 141° with darkening (Found : Cl, 51·9. $C_5H_{10}ONCl_3$ requires Cl, 51·6%).

The oxalate was formed when equivalent amounts of the base and oxalic acid were dissolved in boiling water, and crystallised in colourless, transparent, irregularly formed, rhombic plates, m. p. 232° (decomp.) (Found : Cl, 42·5. $2C_5H_{10}ONCl_3 \cdot H_2C_2O_4$ requires Cl, 42·35%).

The sulphate crystallised from water in clusters of colourless transparent prisms, m. p. 235—240° with blackening and decomposition (Found : Cl, 42·1; S, 6·1. $2C_5H_{10}ONCl_3 \cdot H_2SO_4$ requires Cl, 41·7; S, 6·3%).

The N-acetyl derivative crystallised from water in colourless, transparent, six-sided, short prisms with domed ends, m. p. 109° (Found : Cl, 42·4. $C_7H_{12}O_2NCl_3$ requires Cl, 42·8%), and the ON-diacetyl derivative from acetic anhydride in colourless, transparent, four-sided, thin plates, m. p. 136° (Found : Cl, 36·4. $C_9H_{14}O_3NCl_3$ requires Cl, 36·7%).

$\gamma\delta$ -Trichloro- β -hydroxy-n-amylurea formed beautifully shaped, colourless, transparent, six-sided plates, m. p. 205°, from alcohol (Found : Cl, 42·9. $C_6H_{11}O_2N_2Cl_3$ requires Cl, 42·7%).

Warmed with acetic anhydride, it yielded $\gamma\delta$ -trichloro- β -acetoxy-n-amylacetylurea,



which crystallised from alcohol in slender colourless prisms, m. p. 175° (Found : Cl, 32·0. $C_{10}H_{15}O_4N_2Cl_3$ requires Cl, 31·9%).

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