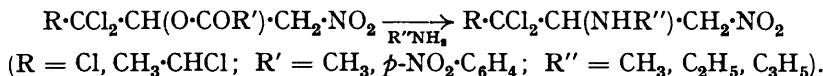


335. The Action of Amines on Esters of the Trichloronitrohydroxy-paraffins.

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METHYLAMINE, ethylamine, and allylamine react with esters of the trichloro- α -nitro- β -hydroxy-paraffins in the same manner as ammonia, aromatic amines, and hydrazines (Chattaway, this vol., p. 355). In every case the amino-residue attaches itself to the negatively substituted alkyl radical and replaces the acyloxy-group, with which the excess of amine forms a salt:



The secondary amines thus formed are relatively stable, pale yellow liquids which boil at comparatively high temperatures, under very low pressures, with little or no decomposition. They form stable well-crystallised hydrochlorides, and well-crystallised ureas with phenyl isocyanate.

$\delta\delta\delta$ -Trichloro- β -nitro- γ -acetoxybutane, $\delta\delta\delta$ -trichloro- β -nitro- γ -acetoxyhexane, and $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxy- α -phenylpropane (Chattaway, Drewitt, and Parkes, this vol., p. 1294) react similarly with amines and hydrazines, secondary amines or β -alkylarylhydrazines resulting.

In all the amines and hydrazines thus produced by the action of ammonia, amines or hydrazines on the above esters the amino- or hydrazino-residues introduced are less firmly attached to the negatively substituted carbon chain than in amines containing unsubstituted alkyl groups and may be slowly removed by protracted heating with hydrochloric acid. For this reason in their preparation, after elimination of the excess of the reacting amine or hydrazine and acidification of the product, it is better to liberate the new amine or hydrazine formed by neutralisation rather than to evaporate the solution to dryness and isolate the base as the hydrochloride.

EXPERIMENTAL.

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -methylaminopropane, CCl₃·CH(NH·CH₃)·CH₂·NO₂.—15 G. (2 mols.) of a 33% solution of methylamine in anhydrous alcohol, cooled to -10°, were added to a solution of 20 g. (1 mol.) of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxypropane in 100 c.c. of alcohol, similarly cooled. The temperature rose immediately to 30°. After 24 hours, most of the alcohol was distilled off, and much water added; $\gamma\gamma\gamma$ -trichloro- α -nitro- β -methylaminopropane then separated as a heavy liquid. The mother-liquors were extracted several times with ether, the ethereal solution mixed with the previously separated base and dried over potassium carbonate, and the ether evaporated; the base distilled at 96°/3 mm. (yield, 80%) as a pale yellow liquid, n_D 1.5050 (Found: N, 12.4. C₄H₇O₂N₂Cl₃ requires N, 12.6%).

The hydrochloride separated when a concentrated alcoholic solution of hydrogen chloride was added to an ethereal solution of the base. It crystallised from warm dilute aqueous-alcoholic hydrochloric acid in small, well-formed, colourless, four-sided, rhombic plates, which char and decompose at about 185° (Found: Cl as HCl, 13.7; total Cl, 54.9. C₄H₇O₂N₂Cl₃·HCl requires Cl as HCl, 13.8; total Cl, 55.0%).

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -phenylcarbamylmethylaminopropane was prepared by refluxing the base (1 mol.) with phenyl isocyanate (1 mol.) in dry benzene solution. It formed colourless, well-shaped, rhombic plates from alcohol, m. p. 130° (Found: Cl, 31.5. C₁₁H₁₂O₃N₃Cl₃ requires Cl, 31.3%).

By methods similar to the above, the following amines, hydrochlorides, and ureas were prepared.

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -ethylaminopropane, a pale yellow liquid, b. p. 106°/2 mm., n_D 1.4967 (Found: N, 11.8. C₅H₉O₂N₂Cl₃ requires N, 11.9%). Hydrochloride, small, colourless, irregular plates from dilute aqueous-alcoholic hydrochloric acid, m. p. 146° (Found: Cl as HCl, 13.1; total Cl, 52.3. C₅H₉O₂N₂Cl₃·HCl requires Cl as HCl, 13.1; total Cl, 52.2%). Phenylcarbamyl derivative, colourless, elongated, six-sided prisms from alcohol, m. p. 121° (Found: Cl, 29.9. C₁₂H₁₄O₃N₃Cl₃ requires Cl, 30.0%).

$\gamma\gamma\gamma$ -Trichloro- α -nitro- β -allylamino-propane, a pale yellow liquid, b. p. $106^\circ/2$ mm., n_D 1.5100 (Found : N, 11.2. $C_6H_9O_2N_2Cl_3$ requires N, 11.3%). It decomposes explosively on attempted distillation at higher temperatures and pressures. *Hydrochloride*, colourless, flattened, rhombic prisms from dilute aqueous-alcoholic hydrochloric acid, m. p. 141° (decomp.) rapidly heated (Found : Cl as HCl, 12.6; total Cl, 50.0. $C_6H_9O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 12.5; total Cl, 50.0%). A solution of this salt in dilute hydrochloric acid darkens and decomposes when heated. *Phenylcarbamyloxy* derivative, slender, colourless, flattened prisms from alcohol, m. p. 124° (Found : Cl, 29.2. $C_{13}H_{14}O_3N_3Cl_3$ requires Cl, 29.1%).

$\gamma\gamma\delta$ -Trichloro- α -nitro- β -methylamino-*n*-pentane, colourless, six-sided prisms from alcohol, m. p. 68° , b. p. $110^\circ/2$ mm. (Found : Cl, 42.6. $C_6H_{11}O_2N_2Cl_3$ requires Cl, 42.7%). *Hydrochloride*, colourless, six-sided, rhombic plates, m. p. 172° (Found : Cl as HCl, 12.5; total Cl, 49.8. $C_6H_{11}O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 12.4; total Cl, 49.7%). *Phenylcarbamyloxy* derivative, clusters of long, colourless needles from alcohol, m. p. 186° (decomp.) (Found : Cl, 28.8. $C_{13}H_{16}O_3N_3Cl_3$ requires Cl, 28.9%).

$\gamma\gamma\delta$ -Trichloro- α -nitro- β -ethylamino-*n*-pentane, a pale yellow liquid, b. p. $115^\circ/0.7$ mm. (slight decomp. and liberation of hydrogen chloride, since a slight residue of the hydrochloride of the base remains in the distilling flask) (Found : N, 10.2. $C_7H_{13}O_2N_2Cl_3$ requires N, 10.6%). *Hydrochloride*, small, colourless, irregular plates, m. p. 120° (Found : Cl as HCl, 11.7; total Cl, 47.0. $C_7H_{13}O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 11.8; total Cl, 47.1%). *Phenylcarbamyloxy* derivative, long, slender, colourless, flattened prisms from alcohol, m. p. 140° (Found : Cl, 27.7. $C_{14}H_{18}O_3N_3Cl_3$ requires Cl, 27.8%).

$\gamma\gamma\delta$ -Trichloro- α -nitro- β -allylamino-*n*-pentane, a pale yellow liquid, b. p. $116^\circ/0.5$ mm. (some decomp.). As a result of this decomposition it was found impossible to isolate the base in a pure state. *Hydrochloride*, colourless, four-sided, rhombic plates, m. p. 140° (decomp.) rapidly heated (Found : Cl as HCl, 11.5; total Cl, 45.8. $C_8H_{13}O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 11.4; total Cl, 45.5%).

*The Action of Ammonia and Amines on $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -*p*-nitrobenzoyloxypropane.*—With *p*-nitrobenzoyl chloride, $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropane yields $\gamma\gamma\gamma$ -trichloro- α -nitro- β -*p*-nitrobenzoyloxypropane, which crystallises from boiling alcohol in pale yellow, six-sided prisms, m. p. 87° (Found : Cl, 29.5. $C_{10}H_7O_6N_2Cl_3$ requires Cl, 29.8%). This reacts with ammonia, methylamine, or ethylamine like the corresponding acetoxy-compound, the *p*-nitrobenzoyloxy-group being replaced by the NHR group. The procedure being essentially the same in each case, the experimental details are given only for the reaction with methylamine.

2 G. (1 mol.) of the ester were suspended in 30 c.c. of alcohol, and 2 g. (3.5 mols.) of a 33% solution of methylamine in anhydrous alcohol added; the temperature rose about 10° . The suspended ester slowly dissolved and a new, almost colourless, crystalline solid separated. After 2 days the mixture was heated on a water-bath for 10 minutes. On cooling, methylamine *p*-nitrobenzoate (m. p. and mixed m. p. with an authentic specimen 207°) separated. This was filtered off and to the mother-liquor water was added: the clear solution obtained was extracted several times with small quantities of ether. After drying (potassium carbonate), the ether was evaporated; a pale yellow liquid (1 g.) remained, identical with the $\gamma\gamma\gamma$ -trichloro- α -nitro- β -methylaminopropane prepared from the corresponding acetic ester (Found for the hydrochloride : Cl as HCl, 13.9; total Cl, 55.2%).

*The Action of Amines upon $\delta\delta\delta$ -Trichloro- β -nitro- γ -acetoxy-*n*-butane, $\delta\delta\epsilon$ -Trichloro- β -nitro- γ -acetoxy-*n*-hexane, and $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -acetoxy- α -phenylpropane.*—The procedure employed is very similar to that previously described.

$\delta\delta\delta$ -Trichloro- β -nitro- γ -methylamino-*n*-butane, obtained from the corresponding acetoxy-derivative and methylamine, was a pale yellow liquid, b. p. $94^\circ/0.5$ mm. (Found : N, 11.6. $C_5H_9O_2N_2Cl_3$ requires N, 11.9%). *Hydrochloride*, small, colourless, four-sided plates, m. p. 194° (Found : Cl as HCl, 13.2; total Cl, 52.3. $C_5H_9O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 13.1; total Cl, 52.2%).

$\delta\delta\epsilon$ -Trichloro- β -nitro- γ -methylamino-*n*-hexane, a pale yellow liquid, b. p. $109^\circ/0.3$ mm., formed a *hydrochloride*, small, colourless, four-sided, rhombic plates, m. p. (rapidly heated) about 200° (Found : Cl as HCl, 12.0; total Cl, 47.5. $C_7H_{13}O_2N_2Cl_3 \cdot HCl$ requires Cl as HCl, 11.8; total Cl, 47.3%).

$\delta\delta\delta$ -Trichloro- β -nitro- γ -*p*-toluidino-*n*-butane crystallised from light petroleum in slender, lemon-yellow, six-sided prisms, m. p. 99 — 100° (Found : Cl, 34.3. $C_{11}H_{13}O_2N_2Cl_3$ requires Cl, 34.2%), and $\delta\delta\epsilon$ -trichloro- β -nitro- γ -*p*-toluidino-*n*-hexane in pale yellow, rhombic prisms, m. p. 82° (Found : Cl, 31.3. $C_{13}H_{17}O_2N_2Cl_3$ requires Cl, 31.4%), $\gamma\gamma\gamma$ -trichloro- α -nitro- β -*p*-toluidino- α -phenylpropane from methyl alcohol in small, pale yellow, rhombic plates, m. p. 121 — 122° (Found :

1532 *Sidgwick and Springall: Dipole Moments and the Fixation of*

Cl, 28.4. $C_{16}H_{15}O_2N_2Cl_3$ requires Cl, 28.5%), and *δδδ-trichloro-β-nitro-γ-phenylhydrazino-n-butane* from alcohol in very pale yellow, slender prisms, m. p. 108—109° (Found: Cl, 34.2. $C_{10}H_{12}O_2N_3Cl_3$ requires Cl, 34.1%). On exposure to air this hydrazine becomes bright yellow, presumably owing to the formation of an azo-compound. *γγγ-Trichloro-α-nitro-β-phenylhydrazino-α-phenylpropane* formed pale yellow, thin, four-sided, rhombic plates from alcohol, m. p. 155° (decomp.) (Found: Cl, 28.6. $C_{15}H_{14}O_2N_3Cl_3$ requires Cl, 28.4%).

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