279. *The Condensation of Halogen-substituted Aldehydes with Nitromethane.*

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THE condensation of aldehydes with nitromethane was first observed by Henry (*Compt. rend.*, 1895, **120**, 1262), who found that under slightly alkaline conditions α-nitro-β-hydroxy-paraffins were formed: $R{\cdot}CHO + CH_3{\cdot}NO_2 \longrightarrow R{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$. In particular, he found (*Bull. Acad. Roy. Belg.*, 1896, **32**, 17) that chloral afforded a crystalline compound, trichloronitro*iso*propyl alcohol, but he merely described its behaviour with caustic alkalis and phosphorus pentachloride.

The condensation of the halogen-substituted aliphatic aldehydes is so characteristic that it has been further studied. Each of the three common trihalogen-substituted aldehydes, chloral, bromal, and butylchloral, combines equally readily with nitromethane in the presence of salts of weak acids yielding respectively *γγγ-trichloro-α-nitro-β-hydroxypropane*, $CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$, the *tribromo*-analogue, and *γγδ-trichloro-α-nitro-β-hydroxypentane*, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$.

They are all colourless, well-crystallised solids of low melting point, and, under a low pressure, can be distilled without decomposition. The first two products, each of which contains an asymmetric carbon atom, are inactive mixtures of the two possible active stereoisomerides, and the third, which contains two asymmetric carbon atoms, is an inactive mixture of the four possible active forms. Separation of these inactive mixtures, however, has not been effected, for both they and their esters are low-melting, and cannot without great loss be crystallised from solvents.

They are readily acetylated by acetic anhydride, the esters formed being also inactive mixtures of the active forms.

EXPERIMENTAL.

γγγ-Trichloro-α-nitro-β-hydroxypropane.—165·5 G. of chloral hydrate (1 mol.), 61 g. of nitromethane (1 mol.), and 25 g. of sodium sulphite were dissolved in 250 c.c. of water. A clear, colourless solution was thus obtained which, on heating, remained clear till the temperature approached 60°, whereupon it suddenly became cloudy and the condensation product separated as a heavy, colourless liquid. The heating was continued to 70° to complete the reaction. The whole was then cooled, and the heavy layer separated, washed with water, and distilled under reduced pressure.

γγγ-Trichloro-α-nitro-β-hydroxypropane distils at 119°/3 mm. as a colourless liquid which, on cooling (if necessary in an ice chest), slowly solidifies to a hard, colourless, crystalline mass. Several times remelted and allowed partly to solidify, with rejection of the liquid portion, the final product softened at about 44—45° and melted at 45—46°. It is difficult to crystallise from any solvent on account of its low m. p. and ready solubility in all ordinary solvents; it crystallises from the molten liquid in colourless, rhombic plates (yield 208 g.; quantitative) (Found: C, 17·32; H, 1·9; N, 6·5; Cl, 50·9. $C_3H_4O_3NCl_3$ requires C, 17·25; H, 1·92; N, 6·7; Cl, 51·04%). It does not appear to condense further with chloral for it remains unchanged when its aqueous-alcoholic solution is warmed with excess of chloral hydrate in the presence of sodium sulphite.

Other salts, *e.g.*, potassium carbonate, sodium acetate, and borax, similarly catalyse the condensation but, although they lead to a good yield, the initial product is not so pure as when sodium sulphite is used.

Acetyl derivative. 104 G. of the substance were treated with 102 g. (2 mols.) of acetic anhydride. The mixture, which became warm, was heated on a water-bath for 1 hr. and then distilled under reduced pressure. After acetic acid and excess anhydride had passed over, the *acetyl* derivative distilled at 148°/16 mm. or 160°/25 mm. as a colourless liquid which quickly solidified to a mass of colourless crystals (yield theoretical). It is very readily soluble in boiling alcohol, from which it crystallises in colourless, six-sided prisms with domed ends, m. p. 61—62° (Found: Cl, 42·58. $C_5H_6O_4NCl_3$ requires Cl, 42·51%).

γγγ-Tribromo-α-nitro-β-hydroxypropane.—50 G. of bromal hydrate (1 mol.) and 15 g. of nitromethane (1½ mols.) were shaken with 80 c.c. of water till a clear solution was obtained; 2 g. of potassium carbonate were added, and the whole warmed to 50—55°. The colourless solution became slightly yellow, and *γγγ-tribromo-α-nitro-β-hydroxypropane* separated as a heavy liquid (yield, 51 g.; theo., 54 g.).

This was separated and shaken several times with very dilute hydrochloric acid, until it became colourless; 10 c.c. of chloroform were added, the chloroform solution dried (calcium chloride), mixed with a few c.c. of low-boiling petroleum, and cooled in ice. The required compound separated in colourless, granular aggregates, readily soluble in chloroform, from which it crystallises in colourless, transparent plates, m. p. 78° (Found: Br, 70·16. $C_3H_4O_3NBr_3$ requires Br, 70·2%).

Acetyl derivative. Prepared by warming 34·2 g. of the substance with 25 g. of acetic anhydride (2½ mols.), this separated on cooling as a colourless solid. It was recrystallised from acetic acid, in which it is easily soluble and from which it separates in brilliant, colourless, stout, six-sided prisms; m. p. 70° (Found: Br, 62·54. $C_5H_6O_4NBr_3$ requires Br, 62·5%).

γγδ-Trichloro-α-nitro-β-hydroxypentane.—193·5 G. of butylchloral hydrate (1 mol.), 50 c.c. of alcohol, and 90 g. of nitromethane (1½ mols.) were added to 250 c.c. of water, and the suspension warmed to about 35°; 50 g. of sodium sulphite were added to the clear solution thus obtained, whereupon it almost at once became cloudy, a heavy liquid separating. The whole was then heated with constant shaking to 60°, and on standing it separated into two layers of about equal bulk. The colourless lower layer was separated, well washed with water, and distilled under reduced pressure; b. p. 156°/4 mm. The colourless, viscid distillate, on standing in an ice chest over-night, solidified to a beautifully crystalline, colourless mass; m. p. *ca.* 20° (yield theoretical) (Found: Cl, 44·8. $C_5H_8O_3NCl_3$ requires Cl, 45·0%). Potassium carbonate may be used as a condensing agent but the product is not so pure.

Acetyl derivative. 47·3 G. of the pentanol were heated with 40·8 g. of acetic anhydride (2 mols.) to about 140° and then distilled under reduced pressure. The *acetyl* derivative passed over at 168°/4 mm. as a thick, viscid, colourless liquid (Found: N, 5·1; Cl, 38·3. $C_7H_{10}O_4NCl_3$ requires N, 5·0; Cl, 38·2%), which did not solidify when kept in an ice-chest for several days.

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