278. *The Condensation of Halogen-substituted Aldehydes with Nitro-paraffins.*

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Under slightly altered conditions both chloral and butylchloral condense with nitroethane as they do with nitromethane (Chattaway and Witherington, J., 1935, 1178), yielding respectively *δδδ-trichloro-β-nitro-γ-hydroxybutane*, $CCl_3{\cdot}CH(OH){\cdot}CH(NO_2){\cdot}CH_3$, and *δδε-trichloro-β-nitro-γ-hydroxyhexane*, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(OH){\cdot}CH(NO_2){\cdot}CH_3$. Chloral also condenses, though not quite so readily, with phenylnitromethane, yielding *γγγ-trichloro-α-nitro-β-hydroxy-α-phenylpropane*, $CCl_3{\cdot}CH(OH){\cdot}CH(NO_2){\cdot}C_6H_5$.

The compounds derived from nitroethane are slightly viscid liquids, which, under low pressures, can be distilled without decomposition. That derived from phenylnitromethane and chloral is a crystalline solid. They are all readily acetylated, the *esters* formed from the butane and the hexane compound being rather viscid liquids, which, under low pressures, can also be distilled without decomposition. The ester of the compound prepared from phenylnitromethane is a crystalline solid.

All these compounds are inactive mixtures of the possible active forms, which it has not been possible to separate.

Experimental.

δδδ-Trichloro-β-nitro-γ-hydroxybutane.—10 G. (1 mol.) of nitroethane, 24 g. (1 mol.) of chloral hydrate, and 5 g. of sodium sulphite were dissolved in 50 c.c. of water, and 0·5 g. of potassium carbonate added. The clear pale yellow solution thus obtained was warmed to 40°, whereupon it became cloudy owing to separation of the heavy liquid condensation product. Heating was continued to 70° to complete the reaction. After cooling, the heavy layer of condensation product was separated, any small amount remaining suspended in the mother-liquors being extracted with chloroform. The extract, mixed with the previously separated product, was then washed with very dilute hydrochloric acid and finally with water, dried (calcium chloride), and the chloroform distilled off. The condensation product remained as a pale yellow liquid, which was distilled under diminished pressure; yield 80%.

δδδ-Trichloro-β-nitro-γ-hydroxybutane is a colourless, slightly viscid liquid, b. p. 95°/0·05 mm., 115°/2 mm.; *n* 1·5040 (Found: C, 21·8; H, 2·8; N, 6·3. $C_4H_6O_3NCl_3$ requires C, 21·6; H, 2·7; N, 6·3%).

22 G. (1 mol.) of the foregoing compound and 20 g. (2 mols.) of acetic anhydride were mixed together, and a drop of sulphuric acid added, the temperature rising to 80°. After being heated for a short time on the water-bath, the mixture was fractionated under reduced pressure, the *acetyl* derivative distilling at 98°/0·05 mm., or 125°/2 mm., as a colourless, rather viscid liquid; *n* 1·4790 (Found: N, 5·3. $C_6H_8O_4NCl_3$ requires N, 5·3%).

δδε-Trichloro-β-nitro-γ-hydroxyhexane.—19 G. (1 mol.) of butylchloral hydrate and 7·5 g. (1 mol.) of nitroethane were dissolved in 50 c.c. each of water and alcohol, 5 g. of sodium sulphite and 1 g. of potassium carbonate added, and the solution warmed to 70°. After cooling, 200 c.c. of water were added, and the condensation product, which separated as a heavy layer, was isolated as before. *δδε-Trichloro-β-nitro-γ-hydroxyhexane* is a colourless, rather viscid liquid, b. p. 138°/0·75 mm.; *n* 1·5060 (Found: N, 5·7. $C_6H_{10}O_3NCl_3$ requires N, 5·6%). Its *acetyl* derivative is a colourless, viscid liquid, b. p. 140°/0·25 mm.; *n* 1·4890 (Found: N, 5·0. $C_8H_{12}O_4NCl_3$ requires N, 4·8%).

γγγ-Trichloro-α-nitro-β-hydroxy-α-phenylpropane.—5 G. (1 mol.) of phenylnitromethane and 15 g. (2·5 mols.) of chloral hydrate were warmed together to 70°, a clear yellow liquid being obtained. To this, 2 g. of finely powdered potassium carbonate and a saturated solution of 1 g.

of potassium carbonate were added. The temperature rose to 80° and was maintained at this for 3 minutes. The mixture was then poured into excess of water, and the condensation product, which separated as a viscid mass, was extracted with ether, the extract well washed with a moderately concentrated solution of potassium carbonate, and finally with water. After drying (calcium chloride), the ether was evaporated, and the condensation product remained as a yellow, viscid liquid which solidified on standing in an ice-chest for some hours. It was recrystallised from light petroleum (b. p. 60—80°), in which it is easily soluble and from which it separates as clusters of very pale yellow, rhombic prisms, m. p. 109° (Found: Cl, 37·3. $C_9H_8O_3NCl_3$ requires Cl, 37·4%). Its *acetyl* derivative crystallises from boiling alcohol, in which it is readily soluble, as colourless, six-sided prisms with domed ends, m. p. 98° (Found: Cl, 32·5. $C_{11}H_{10}O_4NCl_3$ requires Cl, 32·6%).

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