

and the filtrate was evaporated to yield (III) which was crystallised from dry benzene, m.p. 128° . (III) was also obtained from PCl_5 (1 mol) and (I), the reaction product being treated with petroleum ether to remove POCl_3 . (Found : Cl, 62.6. $\text{C}_4\text{H}_5\text{ONCl}_4$ requires Cl, 63.0 per cent).

β -Trichloro- α -anilinoethylacetamide (IV), which was obtained by spontaneous interaction of (III) (3 g.) and aniline (1.5 g.) in benzene, was washed with dilute hydrochloric acid and crystallised from chloroform, m.p. 146° . (Found : Cl, 37.4. $\text{C}_{10}\text{H}_{11}\text{ON}_2\text{Cl}_3$ requires Cl, 37.8 per cent).

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Condensation of Chloral and Bromal with Polyhydric Alcohols.

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This paper describes the preparations and reactions of the condensation products of chloral and bromal with ethylene glycol and glycerol, and of chloral with erythritol. Bromal is found to be more reactive than chloral.

The results are shown diagrammatically in Figs. 1 and 2.

EXPERIMENTAL.

s-Di-(β -trichloro- α -hydroxy-ethoxy)ethane (I) was prepared by the method of Forcrand (*Bull. Soc. chim.*, 1889, *iii*, 2, 256).

Anhydrodichloral-glycol (II) was obtained by keeping a solution of (I) in acetic anhydride and a few drops of concentrated sulphuric acid for 4 hours and diluting with water or by refluxing a mixture of (I) and acetyl chloride in equal proportions for 30 minutes and pouring into water. (II) separates from alcohol in cubes, m.p. 144° . (Found: Cl, 62.8. $\text{C}_6\text{H}_6\text{O}_3\text{Cl}_6$ requires Cl, 62.8 per cent).

It is stable towards hot concentrated nitric acid, boiling alkali solutions and strong ammonia in a sealed tube at 110° . Hot concentrated sulphuric acid changes it back into the original substances.

The diacetyl derivative of (I) (III) was obtained by keeping a

solution of (I) (12 g.) and acetic anhydride (15 c.c.) for 4 hours and fractionating the product, b. p. 132-134°/15 mm. (Found: Cl, 48.5. $C_{10}H_{12}O_6Cl_6$ requires Cl, 48.2 per cent).

β -Trichloroethylideneglycol (IV) was formed by the distillation of (I) at atmospheric pressure, m. p. 42°; b. p. 200°. (Found: Cl, 55.6. $C_4H_5O_2Cl_3$ requires Cl, 55.5 per cent).

$\beta\beta$ -Dichloroethylideneglycol (V) was obtained by the reduction of (IV) (15 g.) with zinc dust (6 g.) and glacial acetic acid (25 c.c.). The mixture was mechanically shaken for 5 hours and the filtrate nearly neutralised with Na_2CO_3 paste and extracted with ether, b. p. 118°/25 mm. (Found: Cl, 45.5. $C_4H_6O_2Cl_2$ requires Cl, 45.2 per cent).

$\alpha\beta$ -Di-(β' -trichloro- α' -hydroxyethoxy)- γ -hydroxypropane (VI) was obtained by keeping a mixture of glycerol (25 g.), chloral (80 g.) and sulphuric acid (20 c.c.) overnight. The resulting mixture was washed with dilute methyl alcohol and extracted with chloroform, b. p. 145-50°/15 mm. (Found: Cl, 55.1. $C_7H_{10}O_5Cl_6$ requires Cl, 55.0 per cent).

Action of Nitric Acid on (VI).—A mixture of (VI) (30 g.) and concentrated nitric acid (70 c.c.) was kept at 0° for 12 hours. The mixture was diluted with water (15 c.c.) and the product (VII) separating on keeping for further 24 hours was recrystallised from methyl alcohol, m. p. 192-93°. (Found: Cl, 55.3; Equiv. 380. $C_7H_6O_5Cl_6$ requires Cl, 55.5 per cent. Equiv. 383).

Sodium Salt.—(Found: Na, 5.1; H_2O , 10.1. $C_7H_5O_5Cl_6Na$, $2\frac{1}{2} H_2O$ requires Na, 4.9; H_2O , 10 per cent). *Barium salt.*—(Found: Ba, 14.5; H_2O , 3.9. $C_{14}H_{10}O_{10}Cl_{12}Ba$, $2H_2O$ requires Ba, 14.7; H_2O , 3.8 per cent).

This action of nitric acid confirms the structure assigned to (VI).

Distillation of (VI) at 70 mm. pressure yields (VIII), b. p. 162-64°/25 mm. Yoder (*J. Amer. Chem. Soc.*, 1923, **45**, 476) obtained the compound by heating glycerol, chloral hydrate and zinc chloride under pressure. The acetyl derivative boils at 205°/120 mm. (Found: Cl, 40.2; $C_7H_9O_4Cl_3$ requires Cl, 40.4 per cent).

The nitrate of (VIII) (IX) separated after heating (VIII) with a mixture of nitric and sulphuric acids (2:1; 3 c.c.) for 2 minutes and keeping overnight. It crystallises from methyl alcohol in white needles, m. p. 64°. (Found: Cl, 40.1. $C_5H_6O_5NCl_3$ requires Cl, 39.9 per cent).

α - β -(β' -Trichloroethylidenedioxy)- γ -chloropropane (X) was prepared by the action of PCl_5 (equal weight) on (VIII). The reaction mixture was poured on to crushed ice and extracted with ether, b. p. $130^\circ/15$ mm. (Found: Cl, 58.9. $\text{C}_3\text{H}_6\text{O}_2\text{Cl}_4$ requires Cl, 59.1 per cent).

The methyl derivative of (VIII) was obtained by the action of dimethyl sulphate (equal weight) in the presence of $2N$ -alkali. The alkaline mixture was shaken for nearly 8 hours and the product extracted with ether, b. p. $140.42^\circ/15$ mm. (Found: Cl, 45.4. $\text{C}_8\text{H}_9\text{O}_3\text{Cl}_3$ requires Cl, 45.2 per cent).

(XII) was obtained from (VIII) on reduction with zinc dust and acetic acid. [See preparation of (V)], b. p. $160^\circ/20$ mm. (Found: Cl, 38.1. $\text{C}_5\text{H}_9\text{O}_3\text{Cl}_2$ requires Cl, 37.9 per cent). The acetyl derivatives (XIII) boils at $188^\circ/30$ mm. (Found: Cl, 31.2. $\text{C}_7\text{H}_{10}\text{O}_4\text{Cl}_2$ requires Cl, 31.0 per cent).

Di- α - β -(β' -trichloro- α' -hydroxyethyl)-ether of erythritol.—Erythritol (10 g.) and freshly distilled chloral (25 g.) were heated at 100° for 1 hour and the mixture diluted with water. The product is insoluble in the usual solvents in the cold and decomposes on heating in alcohol, ethyl acetate or glacial acetic acid. It was washed with warm dilute methyl alcohol and dried, m.p. 167.71° . (Found: Cl, 50.7. $\text{C}_8\text{H}_{12}\text{O}_6\text{Cl}_6$ requires Cl, 51.0 per cent). The tetraacetyl derivative was obtained by the action of acetic anhydride and a few drops of sulphuric acid. It separates from hot alcohol in cubic crystals, m.p. 164° . (Found: Cl, 36.2. $\text{C}_{16}\text{H}_{20}\text{O}_{10}\text{Cl}_6$ requires Cl, 36.4 per cent).

s-Di(β -tribromo- α -hydroxyethoxy)-ethane.—Ethylene glycol (5 g.) and bromal hydrate (25 g.) were heated for 1 hour at 130.40° . The liquid on dilution with water was extracted with ether, b.p. $145.47^\circ/25$ mm. (Found: Br, 77.0. $\text{C}_6\text{H}_8\text{O}_4\text{Br}_6$ requires Br, 76.9 per cent). The diacetyl derivative boils at $196^\circ/135$ mm. (Found: Br, 67.6. $\text{C}_{10}\text{H}_{12}\text{O}_6\text{Br}_6$ requires Br, 67.8 per cent).

β -Tribromoethylideneglycol.—A mixture of ethylene glycol (10 g.), bromal hydrate (25 g.) and concentrated sulphuric acid (10 c.c.) was kept for 3 days and the solid separating (18 g.) was crystallised from alcohol, m.p. 103.104° . The substance was also obtained by distilling dibromalglycol at ordinary pressure. It is stable towards hot alkalis. (Found: Br, 73.7. $\text{C}_4\text{H}_5\text{O}_2\text{Br}_3$ requires Br, 73.8 per cent).

α - β -Di(β' -tribromo- α' -hydroxyethoxy)- γ -hydroxypropane (XIV) (Formula similar to VI) was obtained as with the dibromal ethylene

glycol, b.p. $205^{\circ}/25$ mm. (Found: Br, 73.5. $C_7H_{10}O_5Br_6$ requires Br, 73.4 per cent). The *triacetyl* derivative boils at $190^{\circ}/155$ mm. (Found: Br, 61.6. $C_{13}H_{16}O_8Br_6$ requires Br, 61.5 per cent).

$\alpha\beta$ -(β' -tribromoethylidene)-glycerol (XV) (Formula similar to VIII) was obtained by the distillation of (XIV) under reduced pressure, b.p. $210^{\circ}/60$ mm. (Found: Br, 67.5. $C_5H_7O_3Br_3$ requires Br, 67.6 per cent).

Tri-(β' -tribromo- α' -hydroxyethyl) ether of glycerol (XVI).—A mixture of glycerol (10 g.), bromal hydrate (35 g.) and concentrated sulphuric acid (10 c.c.) was kept for 2 days, diluted with water and extracted with ether. The product could not be distilled unchanged without decomposition under a pressure of 20 mm. (Found: Br, 76.6. $C_9H_{11}O_6Br_9$ requires Br, 77.0 per cent).

γ -(β' -Tribromo- α' -hydroxyethyl) ether of $\alpha\beta$ -(β' -tribromoethylidene)-glycerol (XVII) was obtained by distilling (XVI) under reduced pressure, b.p. $145^{\circ}/20$ mm. (Found: Br, 75.2. $C_7H_8O_4Br_6$ requires Br, 75.4 per cent).

FIG. 1.



