

## Reduction of Chloral Hydrate and Chloral Acylchlorides.

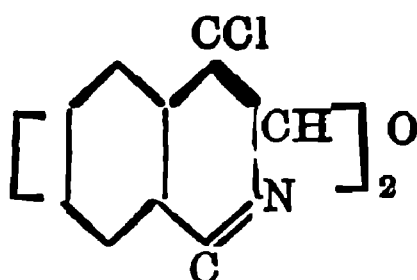
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Chloral hydrate has been reduced with aluminium amalgam giving a product (b. p. 96-98°), which consists mainly of dichloraldehyde hydrate as it gives dichloroethylidene diacetate,  $\text{CHCl}_2 \cdot \text{CH}(\text{OCOCH}_3)_2$  (Delacre, *Bull. Soc. Chim.*, 1930, **48**, 715) with acetic anhydride and sulphuric acid and dichloroacetal with alcohol and sulphuric acid and dichloraldehyde by distillation with sulphuric acid. Dichloraldehyde is further confirmed by the preparation from it of  $\alpha\beta\beta$ -trichloroethyl acetate,  $\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OCOCH}_3$  (Delacre, *loc. cit.*) by the action of acetyl chloride and of glyoxime by the action of hydroxylamine.

Chloral acetylchloride,  $\text{CCl}_3 \cdot \text{CHCl} \cdot \text{OCOCH}_3$ , was reduced by Curie and Milliet (*Compt. rend.*, 1901, **133**, 745; *Ber.*, 1876, **9**, 1611) by means of zinc and acetic acid. They described the reduction product as  $\alpha\beta$ -dichloroethyl acetate,  $\text{CH}_2\text{Cl} \cdot \text{CHCl} \cdot \text{OCOCH}_3$  (*cf.* Natterer, *Monatsch.*, 1882, **3**, 453), who prepared it by the action of acetyl chloride on chloraldehyde hydrate. This seemed to be unlikely and hence a study of the reduction product was taken up. The same product is obtained by reducing chloral diacetate,  $\text{CCl}_3 \cdot \text{CH}(\text{OCOCH}_3)_2$  with zinc and acetic acid. This shows that the presence of a Cl atom in the  $\alpha$ -position in the reduction product is unlikely. The reduction product absorbs two atoms of bromine. It behaves like dichloraldehyde towards phenylhydrazine, semicarbazide, etc., and gives dichloraldehyde hydrate on treatment with concentrated ammonia solution. All these properties show that the reduction product is  $\beta$ -dichlorovinylacetate,  $\text{CCl}_2 : \text{CH} \cdot \text{OCOCH}_3$ . This can hydrolyse to form dichlorovinyl alcohol which would give rise to dichloraldehyde.

$\beta$ -Dichlorovinyl acetate gives with dry ammonia  $\beta$ -dichlorovinylamine. The latter gives with benzoyl chloride and caustic soda a

substance m.p. 199° (decomp.) to which the following constitution is provisionally given



Other  $\beta$ -dichlorovinyl esters were prepared by reduction of the condensation products of chloral with acyl chlorides with zinc and acetic acid.

#### EXPERIMENTAL.

*Preparation of chloral acylchlorides.*—The acid (1 mol.) was heated with thionyl chloride (2 mols.) on a water-bath with a reflux condenser till the evolution of  $\text{SO}_2$  and  $\text{HCl}$  slackened. The mixture was then cooled and chloral (a little more than 1 mol.) was added. The mixture was then shaken with a few drops of concentrated sulphuric acid when the condensation took place with the evolution of heat. The condensation is less vigorous the higher the molecular weight of the acid and in some cases it is necessary to start the reaction by heating the mixture. The condensation products are liquids and some of them decompose on distilling under reduced pressure. In such cases the substance was washed, dried and reduced with zinc and acetic acid.

*Reduction of chloral hydrate.*—Chloral hydrate (84 g.) was dissolved in water (100 c.c.) and reduced with aluminium amalgam prepared from aluminium foil (13.5 g.) and added in three lots. The mixture was extracted several times with ether and a liquid (66 g. b. p. 96–98°) was obtained on removing the ether. This gave dichloraldehyde with partial decomposition on distillation with sulphuric acid.

*$\gamma$ -Dichlorocrotonic acid.*—Dichloraldehyde (13 g.) was mixed with malonic acid (12 g.) and pyridine (15 g.). The reaction which immediately started with evolution of  $\text{CO}_2$  was completed by heating on the water-bath. The mixture was heated with dilute sulphuric acid and extracted with ether. A sticky liquid which was obtained on the removal of ether gave a crystalline solid (2.5 g.) on the addition of a little water. The solid forms white feathery plates from water, m.p. 100–01°, (Found: Cl, 45.72; Eq. wt. 153.8.  $\text{C}_4\text{H}_4\text{O}_3\text{Cl}_2$

requires Cl, 45.75 per cent; Eq. wt., 154.9). The mother liquor from above gave a sticky residue which solidified on keeping in a desiccator. This was purified from chloroform and gave short prisms, m.p. 117-18°. It was found to be an acid containing chlorine and of Eq. wt., 203.9.

*β-Dichlorovinyl acetate*.—Chloral acetylchloride (100 g.) (Meyer and Dulk, *Annalen*, 1874, 171, 67), prepared by treating water-free chloral with an equivalent quantity of acetyl chloride in the presence of sulphuric acid, was reduced by shaking in a bottle with acetic acid (150 c.c.) and zinc dust (60 g.) which was added in small quantities at a time. After the reduction was complete, the mixture was filtered to remove zinc acetate and unchanged zinc and the filtrate diluted with water. The heavy oily liquid (60 g.) separating was dried over sulphuric acid and distilled at 148-49°. (Found: Cl, 45.8, M. W. 154.5.  $C_4H_4O_2Cl_2$  requires Cl, 45.8 per cent; M. W., 154.9). Curie and Milliet (*loc. cit.*) recorded the b.p. as 146°. The same product is obtained by the reduction of chloral diacetate (Meyer and Dulk, *loc. cit.*) with zinc and acetic acid in a similar way.

*β-Dichloro-αβ-dibromoethyl acetate* was obtained as a liquid by treating *β*-dichlorovinyl acetate with bromine, b.p. 127°/40 mm. (Found: Br, 50.72.  $C_4H_4O_2Cl_2Br_2$  requires Br, 50.72 per cent). The product decomposes on keeping.

*β-Dichlorovinylamine*.—*β*-Dichlorovinyl acetate (80 g.) was mixed with chloroform (50 c.c.) and a few g. of powdered anhydrous sodium sulphate and a brisk current of dry ammonia was passed through the mixture which was cooled with water. After 2 hours when the smell of the ester disappeared, the mixture was washed with water and dried over caustic soda and the chloroform was evaporated off. The sticky residue on dissolving in alcohol and keeping gave a white solid (2.5 g.), which crystallised in needles from alcohol, m.p. 109°. (Found: N, 12.0; Cl, 63.4.  $C_2H_5NCl_2$  requires N, 12.5; Cl, 63.4 per cent).

It gave with benzoyl chloride in presence of caustic soda a solid which crystallised in needles, m.p. 199° (decomp.) from alcohol. (Found: N, 8.8; Cl, 20.8.  $C_{18}H_{10}ON_2Cl_2$  requires N, 8.6; Cl, 20.8 per cent).

*Action of aqueous ammonia*.—*β*-Dichlorovinyl acetate (72 g.) was dissolved in concentrated aqueous ammonia while cooling in ice. The solution was quickly acidified with dilute sulphuric acid and extracted with ether. The liquid (40 g.) that remained after removal

of ether was identified with the reduction product of chloral hydrate.

$\beta$ -Dichlorovinyl acetate gave with malonic acid in presence of pyridine  $\gamma$ -dichlorocrotonic acid, with phenylhydrazine glyoxal-*osazone*, m. p.  $179^\circ$  (Found: N, 23.5.  $C_{14}H_{14}N_4$  requires N, 23.5 per cent) and with semicarbazide hydrochloride disemicarbazone of glyoxal. (Found: N, 49.3.  $C_4H_8O_2N_6$  requires N, 48.9 per cent).

*Chloralpropionyl chloride*, b. p.  $120^\circ/40$  mm. (Found: Cl, 59.4.  $C_5H_6O_2Cl_4$  requires Cl, 59.1 per cent).

$\beta$ -Dichlorovinyl propionate, b. p.  $90-92^\circ$ . (Found: Cl, 42.0.  $C_5H_6O_2Cl_2$  requires Cl, 42.0 per cent).

$\beta$ -Dichloro- $\alpha\beta$ -dibromoethyl propionate, b. p.  $145-46^\circ/39$  mm. (Found: Br, 48.3.  $C_5H_6O_2Cl_2Br_2$  requires Br, 48.6 per cent).

*Chloral-n-butyryl chloride*, b. p.  $128^\circ/36$  mm. (Found: Cl, 55.6.  $C_6H_8O_2Cl_4$  requires Cl, 55.9 per cent).

$\beta$ -Dichlorovinyl *n*-butyrate, b. p.  $100-101^\circ/36$  mm. (Found: Cl, 39.1.  $C_6H_8O_2Cl_2$  requires Cl, 38.7 per cent).

$\beta$ -Dichloro- $\alpha\beta$ -dibromoethyl *n*-butyrate, b. p.  $162-64^\circ/40$  mm. (Found: Br, 46.5.  $C_6H_8O_2Cl_2Br_2$  requires Br, 46.3 per cent).

$\beta$ -Dichlorovinyl benzoate was obtained as needles, m. p.  $34-35^\circ$ . (Found: Cl, 32.6.  $C_9H_6O_2Cl_2$  requires Cl, 32.7 per cent).

$\beta$ -Dichlorovinyl cinnamate was obtained as needles, m. p.  $70^\circ$ . (Found: Cl, 29.2.  $C_{11}H_8O_2Cl_2$  requires Cl, 29.3 per cent).

$\beta$ -Dichloro- $\alpha\beta$ -dibromoethyl dibromocinnamate was obtained as needles, m. p.  $87-88^\circ$  (Found: Br, 57.0.  $C_{11}H_8O_2Cl_2Br_4$  requires Br, 56.8 per cent).

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