CCCLIX.—*Polymerides of Aliphatic Chloroaldehydes.*

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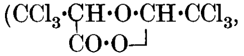
THE known polymerides of the aliphatic chloroaldehydes may be grouped in two classes, the so-called meta- and para-aldehydes. The meta-compounds are insoluble, colourless, amorphous solids, which on heating volatilise and dissociate without previously melting; they have no properties which afford a guide to their constitution, since in all reactions they revert to and react as the unpolymerised forms, and their molecular complexity is unknown. Metachloroacetaldehyde (Natterer, *Monatsh.*, 1882, **3**, 447) and metadichloroacetaldehyde (Friedrich, *Annalen*, 1881, **206**, 52) are readily formed from the free aldehydes under the influence of hydrogen chloride, whilst strong sulphuric acid causes the formation of polymerides of a different type—the para-aldehydes (Natterer, *loc. cit.*; Jacobsen, *Ber.*, 1875, **8**, 88). These are colourless, crystalline solids having sharp melting points, and being soluble in most organic solvents, though insoluble in water. They are comparatively stable, being unaffected by, *e.g.*, boiling aqueous alkalis. On distillation under ordinary pressure they dissociate, but under diminished pressure they volatilise unchanged. They are trimeric, and their constitution is usually represented by a six-atom ring.

Although chloral has long been known to give a polymeride of the meta-type, it has not hitherto been found to give one of the para-type. When, however, a solution of chloral in strong sulphuric acid is allowed to remain at the ordinary temperature, two isomeric *parachlorals* are formed in addition to the metachloral which is the main product, and they may be extracted from the latter by hot alcohol. By fractional crystallisation from the same solvent, they can be separated from each other and from chloralide



$$\left(\mathrm{CCl_3{\cdot}\underset{CO{\cdot}O}{CH}{\cdot}O{\cdot}CH{\cdot}CCl_3},\right.$$

trichloroethylidene trichlorolactic ester), which is formed to some extent at the same time and is considerably less soluble than either. The production of these polymerides appears to depend on the temperature : at or below 0°, metachloral is the sole product, whilst at 40°, a relatively large amount of chloralide is also formed.

Both isomerides show the characteristic properties of true paraldehydes : they have sharp melting points, and are readily soluble in organic solvents, though insoluble in hot or cold water. Cryoscopic molecular-weight determinations in benzene show each to be trimeric, and although they dissociate into chloral on distillation under ordinary pressure, they distil unchanged under a pressure of 15 mm. The less soluble and more soluble forms are termed α- and β-parachloral, respectively.

These two isomerides and metachloral are formed independently, for in the presence of sulphuric acid none is converted into either of the others. It seems probable that the isomerism of α- and β-parachloral is of the *cis-trans* type, corresponding to the two possibilities in the paraldehyde ring, one having all three trichloromethyl residues on the same side of the plane of the ring, and the other having two on one side and one on the other. Isomerism which has similarly been attributed to *cis-trans* forms has been observed in parabromopropaldehyde (Franke, *Annalen*, 1907, **351**, 421), in trichloralimide, $(CCl_3{\cdot}CH{:}NH)_3$ (Béhal and Choay, *Ann. Chim. Phys.*, 1892, **26**, 7, 34), and in the trithioaldehydes, $(R{\cdot}CH{:}S)_3$ (Baumann and Fromm, *Ber.*, 1891, **24**, 1426), and in the last case this type of isomerism has been confirmed, since on oxidation the *cis*-form gives only one disulphone-sulphide, whereas the *trans*-form gives two. One form is converted into the other by the action of acetyl chloride, iodine, etc. Attempts to effect interconversion of the two parachlorals by the same means have been unsuccessful, however.

It is noteworthy that this is the first time that a meta-form and two isomeric para-forms of the same aldehyde have been obtained. The assumption that the relation of the meta- and para-forms is that of *cis-trans* isomerides (compare *Ber.*, 1907, **40**, 4341) can thus no longer be accepted, at least in the case of chloral.

Paradichloroacetaldehyde does not appear to exist in isomeric forms, for sulphuric acid converts it into a single compound, which decomposes when kept for more than a few hours in contact with the acid; it is possible, however, that the failure to isolate a second isomeride is due to its still more rapid decomposition.

Butylchloral, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO$, like chloral, forms two isomeric polymerides of the para-type when kept in contact with excess of sulphuric acid; these differ in solubility and can be separated by fractional crystallisation from acetic acid. The terms α- and β- may be applied to the less soluble and more soluble forms as before. In properties they closely resemble the parachlorals, being colourless, crystalline, sharp-melting compounds, soluble in organic solvents, but insoluble in water. They are trimeric, and can be distilled unchanged under a pressure of 15 mm., but dissociate into butylchloral on distillation under ordinary pressure.

It may be noted that the α-forms of parachloral, parabutylchloral, and trichloralimide all crystallise in the orthorhombic system. Béhal and Choay (*loc. cit.*) infer from the crystal symmetry a corresponding molecular symmetry, and designate the α-form "*cis*" and the β-form "*trans*"; but this conclusion seems hardly justifiable.

Butylchloral appears not to form a polymeride of the meta-type; in fact, no meta-polymerides of chloro- or bromo-aldehydes have been observed outside the acetaldehyde group.

EXPERIMENTAL.

Preparation of α- and β-Parachloral.—The most suitable conditions for the preparation of these isomerides are (*a*) a temperature of 15—20°, and (*b*) a large excess of sulphuric acid, and it appears to be essential that the chloral should first dissolve, for metachloral is formed as a crust when a layer of chloral is left floating on the surface of the acid.

Powdered chloral hydrate (100 g.) was added slowly to concentrated sulphuric acid (1000 g.), each portion being shaken until dissolved. On standing for a few hours at the ordinary temperature, a mixture of the three polymerides with chloralide began to separate as a white powder. After 3 days, this solid was filtered off, washed with hot water until the smell of chloral could no longer be recognised, dried, powdered, and extracted with boiling alcohol (100 c.c. to 50 g. of product). The chloralide, which separated from the cold extract, was removed, and cold water added to the filtrate. The colourless precipitate was separated, dried, and boiled for a few seconds with sufficient alcohol to dissolve half of it; evaporation of the extract gave a residue rich in the β-form, and the two solids were then repeatedly recrystallised from alcohol until the two forms were obtained pure and of constant m. p.

α-*Parachloral* crystallises from boiling alcohol in compact, colourless, rhombic crystals (Found: Cl, 72·02; *M*, cryoscopic in benzene, 423. $C_6H_3O_3Cl_9$ requires Cl, 72·16%; *M*, 442). It melts at 116° *

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* It may be noted that this m. p. is very near to that of chloralide (115—116°), which, however, boils at 272° without change. The mixed m. p. of the two may be as low as 85—90°. The monoclinic crystalline form of chloralide (*Z. Kryst.*, 1877, **1**, 594) is quite different from the rhombic form of α-parachloral. Further, chloralide is decomposed by boiling aqueous alkalis.

and boils at 223°/760 mm. The b. p. was determined by the capillary-tube method; in an ordinary distillation apparatus the b. p. rises, owing to decomposition, whilst a thermometer in the vapour registers 98·0°, the b. p. of chloral. Even in a vacuum distillation apparatus under 15 mm. pressure the boiling point was found not to be constant, as some decomposition occurred, but a quantity of unchanged α-parachloral collected in the condenser.

Dr. T. V. Barker, of Brasenose College, has very kindly examined the crystals, and reports that they are orthorhombic, as shown in Fig. 1. The forms developed were *c* (001), *o* (111), and *m* (110). The axial elements, $a : b : c = 0{\cdot}8801 : 1 : 1{\cdot}4505$, were computed from the following mean measurements derived from two crystals :

$$mm\ (110 : 1\bar{1}0) = 84^\circ\ 42',\quad co\ (001 : 111) = 65^\circ\ 31'.$$

β-*Parachloral* crystallises from alcohol in long, colourless prisms (Found: Cl, 71·95%; *M*, cryoscopic in benzene, 420), too slender to admit of measurement. It melts at 152° and boils at 250° (in the capillary tube). Its behaviour on distillation is similar to that of the α-form.

Fig. 1.

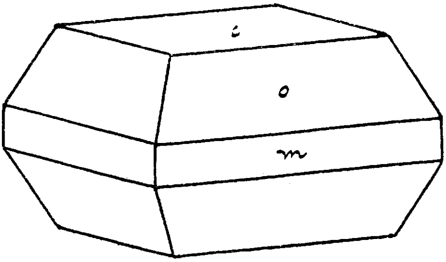
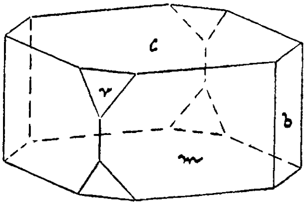


Fig. 2.



The yield of α- and β-parachloral obtained as above is not more than 1% of the chloral taken: about 2% of chloralide is also formed. These polymerides have none of the characteristic properties of chloral: they are odourless, stable to boiling aqueous alkalis, and do not react with phenylhydrazine or potassium cyanide.

Preparation of α- *and* β-*Parabutylchloral.*—In order to obtain a good yield of these polymerides, not less than 6 parts by weight of concentrated sulphuric acid to one part of butylchloral hydrate should be used. With a smaller amount polymerisation is slow, and this probably explains why Willcox and Brunel (*J. Amer. Chem. Soc.*, 1916, **38**, 2538), who used sulphuric acid for dehydrating butylchloral hydrate, failed to observe the formation of the polymerides. 150 G. of concentrated sulphuric acid were poured on 25 g. of powdered butylchloral hydrate and shaken until a homogeneous brown liquid was formed. In about 2 hours the solid polymerides began to separate, and after standing with occasional shaking for about two days, the mixture became almost solid. Ice was then added, and the caked product which separated was broken up, thoroughly washed with hot water until the smell of butylchloral could no longer be detected, dried, and fractionally crystallised from acetic acid. The total yield of the two isomerides before separation was about 80% of the butylchloral taken.

α-*Parabutylchloral* crystallises from boiling acetic acid (in which it is moderately soluble) or from boiling alcohol (in which it is sparingly soluble) in compact, colourless, rhombic crystals, m. p. 180°, b. p. 255°/760 mm. (in the capillary tube) (Found : Cl, 60·6 ; *M*, cryoscopic in benzene, 484. $C_{12}H_{15}O_3Cl_9$ requires Cl, 60·66% ; *M*, 526). Its behaviour on distillation under atmospheric pressure or in a vacuum resembles that of α-parachloral.

Mr. W. R. C. Curjel, of Keble College, has kindly examined the crystals, and reports that they are orthorhombic (Fig. 2). The axial elements are $a : b : c = 0{\cdot}8209 : 1 : 1{\cdot}4460$. The forms observed were *c* (001), *b* (010), *m* (110), *r* (101), and, less frequently, *o* (111). Mean values for the interfacial angles are :

$110 : 1\bar{1}0 = 78° 46'$
$110 : 101 = 47° 46'$
$001 : 101 = 60° 22'$
$110 : 111 = 23° 35'$
$101 : 111 = 35° 24'$

β-*Parabutylchloral* crystallises from boiling acetic acid or alcohol (in which it is considerably more soluble than the α-form) in clusters of very small, colourless crystals (Found : Cl, 60·6% ; *M*, 479), m. p. 157°, b. p. 233°/760 mm. (capillary tube). In properties and behaviour on distillation it closely resembles the polymerides already described.

Preparation of Anhydrous Butylchloral.—In order to attempt the preparation of a meta-polymeride, it was necessary to prepare anhydrous butylchloral from the hydrate. Neither the method of Willcox and Brunel (*loc. cit.*), who used sulphuric acid as dehydrating agent, nor that of Pinner (*Ber.*, 1870, **3**, 383), who distilled the hydrate in a stream of dry hydrogen chloride, was found satisfactory.

A suitable method is to distil the hydrate with about half its weight of acetic anhydride under a short fractionating column. A considerable portion of acetic acid distils at 120—130°, and the thermometer then rises rapidly to 165° (the b. p. of butylchloral), at which it remains constant practically till the end of the distillation. The fraction which distils at 165° is redistilled and dried in a vacuum desiccator. The distilling apparatus should be thoroughly dry, and the receiver protected by a calcium chloride tube, to prevent re-formation of the hydrate.

The anhydrous aldehyde is also conveniently prepared by distilling the dry polymerides under ordinary pressure; they need not be separated for this purpose, and are converted quantitatively into the unimolecular form.

Action of hydrogen chloride. Since mono- and di-chloroacetaldehyde are readily converted into meta-polymerides under the influence of hydrogen chloride (which also induces the formation of metachloral from chloral, though in this case it is much less effective than sulphuric acid), the prolonged action of hydrogen chloride in the cold on butylchloral was investigated. The chloral was saturated with the dry gas and sealed up, but no action occurred even on standing for a long period. A similar experiment was then carried out with butylchloral alcoholate (which absorbs more of the acid), the mixture being well cooled in order to avoid formation of the acetal (compare Freundler, *Bull. Soc. chim.*, 1907, **1**, 201), but no action occurred.

Action of pyridine. Chloral is rapidly converted into metachloral in the presence of $\frac{1}{12}$ mol. of pyridine (Böeseken, *Rec. trav. chim.*, 1913, **32**, 112); 9 g. of butylchloral were therefore sealed up with 0·4 g. of pyridine, the two liquids being readily miscible. After standing for 5 days, the liquid had turned dark brown, and 1·5 g. of a white solid had separated. This was filtered off and washed with a little cold alcohol and hydrochloric acid; it proved to be a mixture of the two parabutylchlorals.

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[*Received, July* 31*st*, 1928.]