234. *The ααβ-Trihalogenated Butaldehydes.*

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With the exception of the well-known ααβ-trichlorobutaldehyde (butyl chloral, III), the trihalogen-substituted butaldehydes have been little studied, only one other having previously been prepared.

In the preparation of butyl chloral, Pinner (*Ber.*, 1875, **8**, 1321) obtained as a by-product a colourless, lachrymatory liquid, b. p. 147°, having the composition C_4H_5OCl, which combined readily with two atoms of bromine. These compounds he considered to be γ-chlorocrotonaldehyde ($CH_2Cl{\cdot}CH{:}CH{\cdot}CHO$) and γ-chloro-αβ-dibromobutaldehyde ($CH_2Cl{\cdot}CHBr{\cdot}CHBr{\cdot}CHO$) respectively.

His conclusions, however, are incorrect, since, by the elimination of hydrogen chloride from αβ-dichlorobutaldehyde (I), Moureu, Murat, and Tampier (*Bull. Soc. chim.*, 1921, **29**, 29) obtained a monochlorocrotonaldehyde, b. p. 146—148° (identical with Pinner's compound), which was undoubtedly α-chlorocrotonaldehyde (II) because on addition of two atoms of chlorine it yielded butyl chloral (III). Pinner's bromine addition compound must therefore have been α-chloro-αβ-dibromobutaldehyde (IV). The present paper describes the preparation of this aldehyde, and of the hitherto undescribed αβ-dichloro-α-bromobutaldehyde (V; X = Cl) and ααβ-tribromobutaldehyde (V; X = Br) (butyl bromal).

$$\underset{\text{(I.)}}{CH_3{\cdot}CHCl{\cdot}CHCl{\cdot}CHO} \xrightarrow{-HCl} \underset{\text{(II.)}}{CH_3{\cdot}CH{:}CCl{\cdot}CHO} \xrightarrow{Cl_2} \underset{\text{(III.)}}{CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO}$$

These compounds have been prepared from α-chloro- and α-bromo-crotonaldehyde (obtained by the elimination of hydrogen halide from the dichloro- and dibromo-addition products of crotonaldehyde) by the addition of two equivalents of the appropriate halogen.

$$CH_3{\cdot}CH{:}CCl{\cdot}CHO \xrightarrow{Br_2} CH_3{\cdot}CHBr{\cdot}CBrCl{\cdot}CHO \quad \text{(IV.)}$$

$$CH_3{\cdot}CH{:}CBr{\cdot}CHO \xrightarrow{X_2} CH_3{\cdot}CHX{\cdot}CXBr{\cdot}CHO \quad \text{(V.)}$$

These three aldehydes resemble butyl chloral closely in appearance and properties, but the progressive replacement of chlorine by bromine is accompanied by an increasing tendency to lose hydrogen halide, and to decompose profoundly on standing, or more especially on heating.

They slowly combine with water to form stable, colourless, crystalline *monohydrates*, $CH_3·CHX·CX_2·CH(OH)_2$, and the readiness with which this occurs diminishes as the bromine content of the molecule increases. Further, αβ-dichloro-α-bromobutaldehyde hydrate may be sublimed unchanged when cautiously heated, but both α-chloro-αβ-dibromobutaldehyde hydrate and butyl bromal hydrate dissociate on heating and do not readily recombine with the eliminated water. These hydrates separate in a pure state when the free aldehydes are left in contact with water, but it has not been found possible to recrystallise them.

The aldehydes combine with alcohols with the evolution of heat, but crystalline compounds have not been obtained.

When warmed with a little fuming nitric acid, butyl bromal and α-chloro-αβ-dibromobutaldehyde, or their hydrates, are oxidised to the corresponding ααβ-trihalogenated butyric acids, identical with those obtained by the addition of bromine to the corresponding α-bromo- and α-chloro-crotonic acids (cf. Michael and Norton, *Amer. Chem. J.*, 1880, **2**, 14; Sarnow, *Annalen*, 1872, **164**, 105).

αβ-Dichloro-α-bromobutyric acid is similarly obtained by the oxidation of αβ-dichloro-α-bromobutaldehyde, but is difficult to purify since it readily loses hydrogen halide.

When kept with concentrated sulphuric acid at the ordinary temperature, these aldehydes are decomposed profoundly. Hence the formation of para-polymerides of the type obtained from butyl chloral (cf. Chattaway and Kellett, J., 1928, 2709) has not been observed.

Like butyl chloral, each of these aldehydes reacts with amides, and condensation products with formamide, acetamide, benzamide, and urea have been prepared. $CH_3·CHX·CX_2·CHO + NH_2·CO·R \longrightarrow CH_3·CHX·CX_2·CH(OH)·NH·CO·R$. These *compounds* are readily obtained by cautiously fusing together equivalent quantities of the amide and aldehyde hydrate. They are all colourless crystalline solids, practically insoluble in water but readily soluble in hot alcohol, from which they crystallise well. They melt with decomposition, the tendency to decompose on heating increasing with the bromine content of the parent aldehyde.

The ααβ-trihalogenated butaldehydes gave in every case only a single amide condensation product: the suggestion (cf. Schiff, *Ber.*, 1892, **25**, 1690) that isomerides of such compounds may be formed seems, therefore, to be devoid of foundation.

EXPERIMENTAL.

α-Chlorocrotonaldehyde (II) was obtained in 70—80% yield by heating αβ-dichlorobutaldehyde (I) with aqueous sodium acetate. It boiled at 53—54°/20 mm. (cf. Moureu, Murat, and Tampier, *loc. cit.*). α-Bromocrotonaldehyde, b. p. 72°/30 mm., was obtained similarly in 75—85% yield from the dibromo-aldehyde (cf. Claisen, *Ber.*, 1911, **44**, 1164).

Preparation of α-Chloro-αβ-dibromobutaldehyde (IV).—18·3 G. of bromine (1 mol.) were added drop by drop to 12 g. of α-chlorocrotonaldehyde (1 mol.), moisture being excluded, and the temperature being kept below 0° (mechanical stirrer). Each drop of bromine was instantly decolorised until the exact equivalent had been added, whereupon the required aldehyde was obtained as a colourless viscous liquid with a smell resembling that of butyl chloral. It could not be distilled without decomposition, even in a vacuum. It slowly combined with water to give a colourless, crystalline mass of the *monohydrate*, m. p. 45—50° (Found: Cl, 12·3; Br, 56·4. $C_4H_5OClBr_2,H_2O$ requires Cl, 12·6; Br, 56·6%).

Oxidation of α-Chloro-αβ-dibromobutaldehyde to α-Chloro-αβ-dibromobutyric Acid.—5 G. of the aldehyde hydrate were digested for several hours on the water-bath with 20 c.c. (excess) of fuming nitric acid. On cooling, a viscous liquid remained, which soon solidified to a colourless crystalline mass of α-chloro-αβ-dibromobutyric acid. After recrystallisation from hot concentrated nitric acid, in which it readily dissolved, it formed colourless prisms, m. p. 91—92° (Sarnow, *loc. cit.*, gives m. p. 92°) (Found: Cl, 12·85; Br, 57·8. Calc. for $C_4H_5O_2ClBr_2$: Cl, 12·7; Br, 57·6%).

Preparation of αβ-Dichloro-α-bromobutaldehyde (V; X = Cl).—A slow stream of dry chlorine was passed into 27 g. of α-bromocrotonaldehyde (1 mol.) cooled in a freezing mixture, until a gain in weight of 12·9 g. (1 mol.) had taken place: any unabsorbed chlorine was then removed by a current of dry air. αβ-Dichloro-α-bromobutaldehyde was thus obtained as a thick, colourless, lachrymatory liquid, decomposing on attempted distillation in a vacuum. It combines slowly with water at the ordinary temperature to give the *monohydrate*, which can be sublimed on very careful heating, recombination after dissociation occurring sufficiently readily, with the formation of colourless flattened prisms, m. p. 70° (Found: Cl, 29·5; Br, 33·2. $C_4H_5OCl_2Br,H_2O$ requires Cl, 29·8; Br, 33·6%).

On oxidation with fuming nitric acid as described above, this aldehyde yielded αβ-dichloro-α-bromobutyric acid, which could not, however, be obtained perfectly pure owing to the ease with which it lost hydrogen halide.

Preparation of Butyl Bromal, ααβ-Tribromobutaldehyde (V; X = Br).—32 G. of bromine (1 mol.) were added very slowly to 30 g. of α-bromocrotonaldehyde (1 mol.), moisture being excluded, and care being taken that the temperature did not rise above 0° (mechanical stirrer). Each drop of bromine was instantly decolorised until the exact equivalent had been added; any slight excess was removed by cautious addition of a little α-bromocrotonaldehyde. ααβ-Tribromobutaldehyde was thus obtained as a rather viscous, colourless liquid with a smell resembling that of butyl chloral. It could not be distilled, even under reduced pressure, without profound decomposition. It combined slowly with water to form the *monohydrate*, which separated as compact, colourless prisms, m. p. 42—45° (Found: Br, 72·9. $C_4H_5OBr_3,H_2O$ requires Br, 73·4%). The hydrate readily lost its combined water when placed in a desiccator over calcium chloride or concentrated sulphuric acid. It was not possible to recrystallise it since a similar loss of water took place when it was dissolved in ordinary organic solvents. On oxidation with fuming nitric acid it yielded ααβ-tribromobutyric acid as colourless prisms, m. p. 112° (Michael and Norton, *loc. cit.*, give m. p. 115°) (Found: Br, 73·1. Calc. for $C_4H_5O_2Br_3$: Br, 73·8%).

Acet-ββγ-tribromo-α-hydroxybutylamide.—1 G. of acetamide (1 mol.) and 6 g. of butyl bromal hydrate (1 mol. + slight excess) were warmed together cautiously upon the water-bath until a crystalline nucleus appeared in the clear melt first formed. Heating was immediately discontinued, and the whole cooled; the substituted *amide* then solidified; it crystallised from boiling alcohol, in which it was readily soluble, as thin, colourless, nacreous plates, m. p. 140° (decomp.) (Found: Br, 65·4. $C_6H_{10}O_2NBr_3$ requires Br, 65·2%).

Benz-ββγ-tribromo-α-hydroxybutylamide.—5 G. of butyl bromal hydrate and 1·7 g. of benzamide were heated together as described above (the slightest overheating leads to violent decomposition, with the formation of tarry products). The *amide* crystallised from alcohol, in which it is moderately soluble, in long, slender, colourless, flattened prisms, m. p. 142° (decomp.) (Found: Br, 56·3. $C_{11}H_{12}O_2NBr_3$ requires Br, 55·8%).

The following aldehyde–amide condensation products, prepared similarly, were all crystallised from boiling alcohol. *Form-ββγ-tribromo-α-hydroxybutylamide*, colourless, flattened prisms, m. p. 133° (decomp.) (Found: Br, 68·25. $C_5H_8O_2NBr_3$ requires Br, 67·7%). *ββγ-Tribromo-α-hydroxybutylurea* (butyl bromal urea), slender, colourless, flattened prisms, m. p. 104° (decomp.). (Found: Br, 64·4. $C_5H_9O_2N_2Br_3$ requires Br, 65·0%). *Acet-β-chloro-βγ-dibromo-α-hydroxybutylamide*, colourless plates, m. p. 142° (decomp.) (Found: Cl, 10·95; Br, 49·3. $C_6H_{10}O_2NClBr_2$ requires Cl, 11·0; Br, 49·4%). *Benz-β-chloro-βγ-dibromo-α-hydroxybutylamide*, long, slender, colourless prisms, m. p. 144° (decomp.) (Found: Cl, 9·1; Br, 41·0. $C_{11}H_{12}O_2NClBr_2$ requires Cl, 9·2; Br, 41·5%). *Form-β-chloro-βγ-dibromo-α-hydroxybutylamide*, small, faintly yellow prisms, m. p. 136° (decomp.) (Found: Cl, 11·4; Br, 51·2. $C_5H_8O_2NClBr_2$ requires Cl, 11·5; Br, 51·7%). *β-Chloro-βγ-dibromo-α-hydroxybutylurea*, small, colourless, flattened prisms, m. p. 112° (decomp.) (Found: Cl, 10·9; Br, 48·9. $C_5H_9O_2N_2ClBr_2$ requires Cl, 10·95; Br, 49·3%). *Form-βγ-dichloro-β-bromo-α-hydroxybutylamide*, colourless prisms, m. p. 140° (decomp.) (Found: Cl, 26·85; Br, 30·3. $C_5H_8O_2NCl_2Br$ requires Cl, 26·8; Br, 30·2%). *Acet-βγ-dichloro-β-bromo-α-hydroxybutylamide*, well-formed, colourless, hexagonal plates, m. p. 165° (decomp.) (Found: Cl, 25·4; Br, 28·7. $C_6H_{10}O_2NCl_2Br$ requires Cl, 25·4; Br, 28·65%). *Benz-βγ-dichloro-β-bromo-α-hydroxybutylamide*, long, slender, colourless, flattened prisms, m. p. 157° (decomp.) (Found: Cl, 20·8; Br, 23·4. $C_{11}H_{12}O_2NCl_2Br$ requires Cl, 20·8; Br, 23·4%). *βγ-Dichloro-β-bromo-α-hydroxybutylurea*, very small colourless prisms, m. p. 153° (decomp.) (Found: Cl, 25·3; Br, 28·4. $C_5H_9O_2N_2Cl_2Br$ requires Cl, 25·3; Br, 28·55%).

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