

XV.—*The Interaction of Butyl Chloral Hydrate and 2 : 4-Dihalogen-substituted Phenylhydrazines.*

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WHEN butyl chloral hydrate reacts with phenylhydrazine, the hydrazone initially formed decomposes almost at once with such violence that the course of the reaction cannot easily be followed. When, however, a 2 : 4-dihalogen-substituted phenylhydrazine is used, the decomposition proceeds more quietly and the final products can be isolated. As in the reactions between the halogen-substituted phenylhydrazines and ordinary chloral (Chattaway and Bennett, J., 1927, 2850; Chattaway and Daldy, J., 1928, 2756), these final

products differ according to the nature of the solvent in which the reaction takes place.

The first product of the interaction of butyl chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride in aqueous solution is a viscous crimson mass which cannot be obtained in a condition suitable for analysis, since, from the moment of its formation, whether alone or in contact with a solvent, it continually evolves hydrogen chloride, yielding finally a well-crystallised substance of the composition $C_{10}H_8N_2Cl_4$. This appears to have been formed from a molecule of butyl chloral and a molecule of 2 : 4-dichlorophenylhydrazine by the elimination of a molecule of water and a molecule of hydrogen chloride :



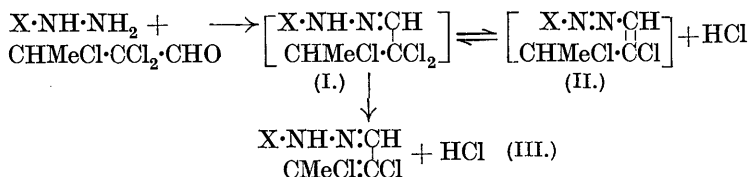
When strongly reduced, it yields 2 : 4-dichloroaniline; the halogen atom eliminated in the reaction must therefore have been one of those in the butyl chloral residue. Its pale yellow colour indicates that, unlike the compound formed in the corresponding reaction of ordinary chloral, it has no azo-linkage in its molecule. It is unsaturated and combines directly with two atoms of bromine to give a colourless *dibromo*-addition compound, $C_{10}H_8N_2Cl_4Br_2$. With acetic anhydride it yields a colourless *monoacetyl* derivative, pointing to the presence of a single imino-group in the molecule. This acetyl derivative is still unsaturated and gives on careful chlorination a colourless dichloro-addition compound of the composition $C_{10}H_7N_2Cl_4(CO \cdot CH_3)Cl_2$.

These reactions appear to show that it is $\alpha\beta$ -*dichlorocrotonaldehyde*-2 : 4-*dichlorophenylhydrazone* (III) formed by the elimination of hydrogen chloride from the unstable butyl chloral 2 : 4-dichlorophenylhydrazone (I) which is without doubt formed initially.

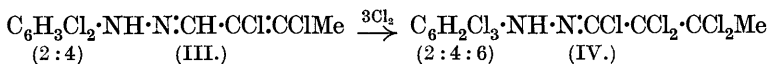
As in the analogous reactions between halogen-substituted phenylhydrazines and chloral (see above), or dichloroacetaldehyde (Chattaway and Farinholt, this vol., p. 94), it seems probable that butyl chloral 2 : 4-dichlorophenylhydrazone also loses hydrogen chloride in a reversible manner to give a crimson azobutylene derivative of the constitution $C_6H_3Cl_2 \cdot N : N \cdot CH : CCl \cdot CHClMe$, 2 : 4-dichlorobenzeneazo- $\beta\gamma$ -dichloro- Δ^{α} -butylene (II).

In virtue of its azo-structure this compound would be intensely red and, although it is not formed to an extent large enough to permit of its isolation, it nevertheless gives a deep crimson azo-colour to the viscous mass obtained in the early stage of the condensation.

The course of the reaction where $X = C_6H_3Cl_2(2 : 4)$ may be represented as follows :

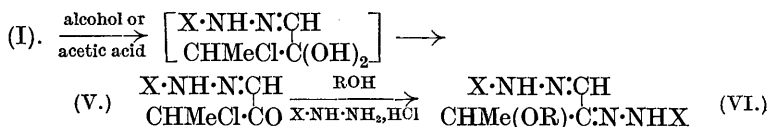


Although $\alpha\beta$ -dichlorocrotonaldehyde-2 : 4-dichlorophenylhydrazone (III) combines readily with two atoms of bromine at the ordinary temperature and without further substitution, a similar addition compound with chlorine cannot be obtained, since simultaneous substitution always takes place. The final product of the chlorination is $\alpha\alpha\beta\beta\omega$ -pentachlorobutaldehyde-2 : 4 : 6-trichlorophenylhydrazone (IV), in which two atoms of chlorine have added on to the double bond, a third has entered the nucleus, and a fourth has displaced the methine hydrogen atom :



When butyl chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride react in alcohol or acetic acid, the reaction pursues a different course and a well-crystallised yellow compound (V) of the composition $\text{C}_{10}\text{H}_9\text{ON}_2\text{Cl}_3$ is ultimately obtained. This appears to have been derived from butyl chloral 2 : 4-dichlorophenylhydrazone (I) by replacement of two atoms of chlorine by an atom of oxygen. When strongly reduced, it yields 2 : 4-dichloroaniline ; the halogen atoms lost in the decomposition must therefore have been in the butyl chloral residue. Its yellow colour indicates that there is no azo-group in the molecule, and the presence of an imino-group is established by the formation of a colourless monobenzoyl derivative, $\text{C}_{10}\text{H}_8\text{ON}_2\text{Cl}_3(\text{CO}\cdot\text{C}_6\text{H}_5)$.

It must therefore have the structure β -chloro- α -ketobutaldehyde-2 : 4-dichlorophenylhydrazone (V). When heated with a substituted phenylhydrazine in any alcoholic solution, it yields a sparingly soluble osazone (VI) in which the ketonic oxygen has been replaced by a hydrazine residue, and also the one remaining chlorine atom in the aldehyde residue has been simultaneously replaced by an alkoxy-group :



When the reaction between butyl chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride is carried out in methyl

alcohol, the latter reaction takes place so readily that the ketonic hydrazone (V) and the sparingly soluble methoxyl-osazone (VI) are formed together, but they may be separated by fractional crystallisation.

EXPERIMENTAL.

The Action of 2 : 4-Dichlorophenylhydrazine Hydrochloride on Butyl Chloral Hydrate in Water : Formation of $\alpha\beta$ -Dichlorocrotonaldehyde-2 : 4-dichlorophenylhydrazone (III).—To 20 g. (1 mol.) of 2 : 4-dichlorophenylhydrazine hydrochloride dissolved in 1000 c.c. of water at 75° acidified with 5 c.c. of concentrated hydrochloric acid, was added a solution of 18 g. (1 mol.) of butyl chloral hydrate and 13 g. of sodium acetate in 250 c.c. of water, also at 75°. The liquid immediately became turbid owing to the separation of yellow oily droplets, which turned first pink and then red, finally coalescing to form a viscous crimson mass. When cold, the supernatant liquid was decanted and the red viscous material was extracted with chloroform, in which it was readily soluble. The chloroform solution, after drying over calcium chloride, was kept at the ordinary temperature in an open dish for 4 days until the evolution of hydrogen chloride, which had been continuous from the first, had apparently ceased.

The chloroform had then evaporated, leaving a semi-crystalline mass. The crystals were separated, washed free from viscous material with light petroleum, and recrystallised repeatedly from boiling alcohol (animal charcoal).

$\alpha\beta$ -Dichlorocrotonaldehyde-2 : 4-dichlorophenylhydrazone crystallises from boiling alcohol or acetic acid, in which it is readily soluble, in pale yellow, long, slender, flattened prisms, m. p. 112° (Found : C, 40.5; H, 3.0; N, 9.4; Cl, 47.7. $C_{10}H_8N_2Cl_4$ requires C, 40.3; H, 2.7; N, 9.4; Cl, 47.65%).

Reduction of $\alpha\beta$ -Dichlorocrotonaldehyde-2 : 4-dichlorophenylhydrazone.—3 G. of the hydrazone were dissolved in 20 c.c. of glacial acetic acid and boiled with excess of granulated tin and 20 c.c. of concentrated hydrochloric acid. When the pale yellow colour had completely disappeared (1 hour), the hot solution was made alkaline with aqueous caustic soda and steam-distilled. 2 : 4-Dichloroaniline (1 g.) in the distillate was identified by conversion into its acetyl derivative, which, alone or mixed with an authentic specimen, melted at 145.5°.

The Action of Bromine upon $\alpha\beta$ -Dichlorocrotonaldehyde-2 : 4-dichlorophenylhydrazone.—When bromine (1 mol.), dissolved in a few c.c. of glacial acetic acid, was added to a cold saturated solution of the hydrazone in glacial acetic acid, $\alpha\beta$ -dichloro- $\alpha\beta$ -dibromobutaldehyde-2 : 4-dichlorophenylhydrazone separated. It dissolved

readily in hot glacial acetic acid, from which it separated in colourless compact prisms, m. p. 126—127° (decomp.) (Found : Cl, 31·3; Br, 35·3. $C_{10}H_8N_2Cl_4Br_2$ requires Cl, 31·0; Br, 34·9%).

Action of Chlorine upon $\alpha\beta$ -Dichlorocrotonaldehyde-2 : 4-dichlorophenylhydrazone.—A rapid stream of chlorine was passed into a suspension of 6·5 g. of the hydrazone in 20 c.c. of glacial acetic acid. The temperature rose somewhat, hydrogen chloride was freely evolved, and the solid dissolved, giving an almost colourless solution. When no further change appeared to be taking place ($\frac{1}{2}$ hour), the solution was set aside for 24 hours, during which $\alpha\alpha\beta\beta\omega$ -pentachlorobutaldehyde-2 : 4 : 6-trichlorophenylhydrazone (IV) (7·6 g.) slowly separated. It crystallised from boiling acetic acid or alcohol, in which it was readily soluble, in very slender, colourless prisms, m. p. 84—85° (Found : Cl, 64·7. $C_{10}H_6N_2Cl_8$ requires Cl, 64·8%).

Reduction of $\alpha\alpha\beta\beta\omega$ -Pentachlorobutaldehyde-2 : 4 : 6-trichlorophenylhydrazone.—2 G. of the octachloro-compound were reduced by boiling in acetic acid solution with tin and hydrochloric acid. 2 : 4 : 6-Trichloroaniline, separated from the solution, made alkaline, by steam distillation, was identified by conversion into its acetyl derivative, m. p. 208—209°.

Acetylation of $\alpha\alpha\beta\beta\omega$ -Pentachlorobutaldehyde-2 : 4 : 6-trichlorophenylhydrazone.—A solution of the hydrazone in acetic anhydride containing a drop of concentrated sulphuric acid was boiled for several minutes. On cooling, $\alpha\alpha\beta\beta\omega$ -pentachlorobutaldehyde-N-acetyl-2 : 4 : 6-trichlorophenylhydrazone separated. It crystallised from boiling acetic acid, in which it was readily soluble, in colourless rhombic plates, m. p. 108—109° (Found : Cl, 58·85. $C_{12}H_8ON_2Cl_8$ requires Cl, 59·1%).

The Action of Acetic Anhydride upon $\alpha\beta$ -Dichlorocrotonaldehyde-2 : 4-dichlorophenylhydrazone.—When warmed with acetic anhydride containing a drop of concentrated sulphuric acid, the hydrazone reacted with evolution of heat to give a clear brown solution, from which $\alpha\beta$ -dichlorocrotonaldehyde-N-acetyl-2 : 4-dichlorophenylhydrazone separated on cooling. It crystallised from boiling alcohol or acetic acid, in which it was easily soluble, in six-sided prisms, m. p. 122·5° (Found : C, 42·2; H, 3·5; N, 8·5; Cl, 41·6; *M*, cryoscopic in benzene, 329, 333. $C_{12}H_{10}ON_2Cl_4$ requires C, 42·4; H, 3·0; N, 8·2; Cl, 41·7%; *M*, 340).

Action of Chlorine upon $\alpha\beta$ -Dichlorocrotonaldehyde-N-acetyl-2 : 4-dichlorophenylhydrazone.—A slow stream of chlorine was passed into a suspension of 2 g. of the acetylhydrazone in 10 c.c. of glacial acetic acid, cooled to prevent any marked rise in temperature. The clear solution obtained was set aside for 4 hours. On cautious

addition of water, $\alpha\alpha\beta\beta$ -tetrachlorobutaldehyde-N-acetyl-2 : 4-dichlorophenylhydrazone separated; this was moderately easily soluble in boiling alcohol, from which it separated in colourless compact prisms, m. p. 97—98° (Found : Cl, 51·7. $C_{12}H_{10}ON_2Cl_6$ requires Cl, 51·8%).

The Action of 2 : 4-Dichlorophenylhydrazine Hydrochloride upon Butyl Chloral Hydrate in Ethyl Alcohol : Formation of β -Chloro- α -ketobutaldehyde-2 : 4-dichlorophenylhydrazone (V).—20 G. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.), 18 g. of butyl chloral hydrate (1 mol.), and 150 c.c. of ethyl alcohol were gently warmed together. As the reactants dissolved, a bright red colour was developed and, when the boiling point of the alcohol was reached, a vigorous reaction set in, hydrogen chloride was freely evolved, and the alcohol continued to boil for some time without further heating. The bright red colour gradually disappeared and the solution became pale yellow.

Half the alcohol was then distilled off and the concentrated solution left to cool; the yellow crystals thus obtained, after being washed with a little cold ligroin, separated from boiling alcohol, in which they readily dissolved, in pale yellow, very slender, hair-like prisms, m. p. 129° (Found : C, 43·2; H, 3·3; N, 10·3; Cl, 38·0. $C_{10}H_9ON_2Cl_3$ requires C, 42·9; H, 3·3; N, 10·0; Cl, 38·0%).

β -Chloro- α -ketobutaldehyde-2 : 4-dichlorophenylhydrazone was also formed when the reaction was carried out in acetic acid solution, the evolution of hydrogen chloride being naturally more marked in this case.

The Action of Benzoyl Chloride upon β -Chloro- α -ketobutaldehyde-2 : 4-dichlorophenylhydrazone.—4 G. of benzoyl chloride (1 mol. + excess) were added to 2 g. of the hydrazone dissolved in 6 g. of pyridine. After 30 hours, the deep orange-coloured reaction mixture was poured into dilute hydrochloric acid and the oily layer which separated was washed with aqueous alkali to remove excess of benzoyl chloride. When digested with a few c.c. of warm alcohol, the oil solidified to a mass of crystals. β -Chloro- α -ketobutaldehyde-N-benzoyl-2 : 4-dichlorophenylhydrazone crystallises from boiling alcohol, in which it is sparingly soluble, in small, colourless, compact prisms, m. p. 166·5° (Found : Cl, 28·0. $C_{17}H_{13}O_2N_2Cl_3$ requires Cl, 27·75%).

The Interaction of 2 : 4-Dichlorophenylhydrazine Hydrochloride with β -Chloro- α -ketobutaldehyde-2 : 4-dichlorophenylhydrazone in Methyl Alcohol : Formation of α -Keto- β -methoxybutaldehyde-2 : 4-dichlorophenylhydrazone (VI).—2 G. (1 mol.) of the hydrazone and 1·5 g. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.) in 20 c.c. of methyl alcohol were boiled for about 5 minutes and cooled. The osazone obtained was readily soluble in boiling pyridine, from which

it separated in compact, bright yellow prisms, m. p. 196° (decomp.). It is very sparingly soluble in boiling alcohol, but may be recrystallised from boiling benzene [Found : C, 46·8; H, 3·8; N, 12·9; Cl, 32·95; OMe, by Hewitt and Moore's modification (J., 1902, 81, 318) of Zeisel's method, 7·1. $C_{16}H_{13}N_4Cl_4(OMe)$ requires C, 47·0; H, 3·7; N, 12·9; Cl, 32·7; OMe, 7·15%].

The corresponding *ethoxy-osazone*, similarly prepared in ethyl-alcoholic solution, crystallised from boiling alcohol, in which it was sparingly soluble, in dull yellow, irregular plates, m. p. 162° (decomp.) [Found : Cl, 31·5; OEt, 8·9. $C_{16}H_{13}N_4Cl_4(OEt)$ requires Cl, 31·65; OEt, 9·95%].

The Interaction of 2 : 4-Dichlorophenylhydrazine Hydrochloride and Butyl Chloral Hydrate in Methyl Alcohol.—When a powdered mixture of 20 g. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.) and 18 g. of butyl chloral hydrate (1 mol.) suspended in 50 c.c. of methyl alcohol was treated in the way described for the reaction in ethyl alcohol (p. 92), the same phenomena were observed as in that case; when cold, the reaction mixture had almost solidified to a pulp of crystals. These were separated and extracted with 50 c.c. of boiling ethyl alcohol, a quantity (A) remaining undissolved. The solution, on cooling, deposited yellow needle-like crystals which, after repeated crystallisation from alcohol, melted at 129° (8 g.), alone or mixed with β -chloro- α -ketobutaldehyde-2 : 4-dichlorophenylhydrazone (Found : Cl, 37·9. Calc. : Cl, 38·0%).

The material (A), after being extracted twice more with 50 c.c. of boiling ethyl alcohol, left a yellow crystalline residue sparingly soluble in most of the common organic solvents; this separated from boiling pyridine, in which it was moderately easily soluble, in bright yellow, compact prisms (9 g.), m. p. 196° (decomp.), identical with the methoxy-osazone described above (Found : Cl, 32·7. Calc. : Cl, 32·7%).

Similar series of reactions were carried out with 2-chloro-4-bromophenylhydrazine and 2 : 4-dibromophenylhydrazine, the following compounds, all crystallised from alcohol, being prepared :—

$\alpha\beta$ -Dichlorocrotonaldehyde-2 : 4-dibromophenylhydrazone, slender, hair-like, dull yellow prisms, m. p. 119·5° (Found : C, 30·7; H, 2·3; N, 7·3; Cl, 18·3; Br, 41·3. $C_{10}H_8N_2Cl_2Br_2$ requires C, 31·0; H, 2·1; N, 7·2; Cl, 18·3; Br, 41·3%).

$\alpha\beta$ -Dichloro- $\alpha\beta$ -dibromobutaldehyde-2 : 4-dibromophenylhydrazone, colourless compact prisms, m. p. 132—133° (decomp.) (Found : Cl, 13·1; Br, 58·7. $C_{10}H_8N_2Cl_2Br_4$ requires Cl, 13·0; Br, 58·5%).

$\alpha\beta$ -Dichlorocrotonaldehyde-N-acetyl-2 : 4-dibromophenylhydrazone, colourless, compact, rhombic plates, m. p. 141° (Found : Cl, 16·5; Br, 37·3. $C_{12}H_{10}ON_2Cl_2Br_2$ requires Cl, 16·5; Br, 37·3%).

$\alpha\beta$ -Dichlorocrotonaldehyde-2-chloro-4-bromophenylhydrazone, slender, pale yellow prisms, m. p. 118° (Found : C, 35.2; H, 2.3; N, 8.2; Cl, 31.0; Br, 23.3. $C_{10}H_8N_2Cl_3Br$ requires C, 35.0; H, 2.35; N, 8.2; Cl, 31.1; Br, 23.3%).

$\alpha\beta$ -Dichlorocrotonaldehyde-N-acetyl-2-chloro-4-bromophenylhydrazone, colourless plates, m. p. 134° (Found : C, 37.8; H, 2.65; N, 7.3; Cl, 27.75; Br, 20.85. $C_{12}H_{10}ON_2Cl_3Br$ requires C, 37.5; H, 2.6; N, 7.3; Cl, 27.7; Br, 20.8%).

β -Chloro- α -ketobutaldehyde-2-chloro-4-bromophenylhydrazone, very slender, lemon-yellow prisms, m. p. 135° (Found : C, 37.1; H, 2.9; N, 8.6; Cl, 21.9; Br, 24.7. $C_{10}H_9ON_2Cl_2Br$ requires C, 37.05; H, 2.8; N, 8.65; Cl, 21.9; Br, 24.7%).

β -Chloro- α -ketobutaldehyde-2 : 4-dibromophenylhydrazone, very slender, pale yellow prisms, m. p. 143.5° (Found : Cl, 9.7; Br, 43.6. $C_{10}H_9ON_2ClBr_2$ requires Cl, 9.6; Br, 43.4%).

β -Chloro- α -ketobutaldehyde-N-benzoyl-2 : 4-dibromophenylhydrazone, colourless compact prisms, m. p. 183.5° (Found : Cl, 7.5; Br, 33.75. $C_{17}H_{13}O_2N_2ClBr_2$ requires Cl, 7.5; Br, 33.8%).

α -Keto- β -methoxybutaldehyde-2 : 4-dibromophenylosazone, bright yellow prisms, m. p. 194° (decomp.), from pyridine or alcohol (Found : C, 33.8; H, 2.8; N, 9.2; Br, 52.3. $C_{17}H_{16}ON_4Br_4$ requires C, 33.3; H, 2.6; N, 9.2; Br, 52.25%).

α -Keto- β -ethoxybutaldehyde-2 : 4-dibromophenylosazone, yellow, six-sided plates, m. p. 177° (decomp.) (Found : Br, 50.6. $C_{18}H_{18}ON_4Br_4$ requires Br, 50.8%).

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