CCCLXXXI.—*The Interaction of Chloral and Arylhydrazines.*

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OWING to the violence with which the hydrazone initially formed decomposes, the behaviour of chloral with phenylhydrazine has been little studied. When, however, a 2 : 4-dihalogen-substituted phenylhydrazine is used, the decomposition occurs more quietly and the final products can be isolated. These differ according to the nature of the solvent in which interaction occurs. When any alcohol is used as the solvent, the 2 : 4-dihalogen-substituted phenylhydrazone of the corresponding alkyl glyoxylate (III) is produced identical with the ester yielded by the corresponding dihalogen-substituted phenylhydrazone of glyoxylic acid :

$$\begin{tikzcd}
 & \text{(I.) } C_6H_3X_2\cdot NH\cdot N{:}CH\cdot CCl_3 \arrow[dr, "ROH"] & \\
C_6H_3X_2\cdot NH\cdot NH_2 \arrow[ur, "CHO\cdot CCl_3"] \arrow[dr, "CHO\cdot CO_2H"'] & & C_6H_3X_2\cdot NH\cdot N{:}CH\cdot CO_2R \text{ (III.)} \\
 & \text{(II.) } C_6H_3X_2\cdot NH\cdot N{:}CH\cdot CO_2H \arrow[ur, "ROH"'] &
\end{tikzcd}$$

Bromal behaves in an exactly similar manner, although the reaction is not so vigorous as when chloral is used.

When, on the other hand, interaction takes place in water or acetic acid, one molecule of water and one molecule of hydrogen chloride are eliminated and beautifully crystalline, brilliant red compounds formed. When strongly reduced, these yield 2 : 4-dihalogen-substituted aniline; the chlorine atom lost in the decomposition must therefore be one of those contained in the chloral. They are unaffected by heating with acetic anhydride, whilst their intense red colour recalls that of compounds containing an azo-group. Bromine replaces one hydrogen atom not in the nucleus, the substitution product still retaining its red colour.

These red compounds therefore appear to be αα-dichloro-β-2 : 4-dihalogenobenzeneazoethylenes (IV), and the bromine substitution products αα-dichloro-β-bromo-β-2 : 4-dihalogenobenzeneazoethylenes (V), formed thus :

(I.) ⟶ (IV.) $C_6H_3X_2\cdot N\colon N\cdot CH\colon CCl_2$ ⟶ (V.) $C_6H_3X_2\cdot N\colon N\cdot CBr\colon CCl_2$.

When the azoethylenes are heated with alcohols they are converted into the corresponding alkyl glyoxylate arylhydrazones (III), but the reaction is not so rapid as that by which the latter compounds are formed from the chloral hydrazones.

EXPERIMENTAL.

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Ethyl Alcohol.*—When 21·5 g. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.) and 16·5 g. of chloral hydrate (1 mol.) were added to 100 c.c. of ethyl alcohol, the liquid became yellow, but little action appeared to take place at the ordinary temperature. On heating, the colour deepened to dark orange and at about 60° hydrogen chloride was evolved, much heat liberated, and the liquid boiled spontaneously for several minutes. The bulk of the alcohol was then slowly distilled off ; the residual clear deep yellow liquid, on cooling, deposited bright yellow crystals of *ethyl glyoxylate* 2 : 4-*dichlorophenylhydrazone*, the yield being practically theoretical. This substance is easily soluble in warm alcohol and separates in pale yellow, very slender prisms, m. p. 121·5° (Found : C, 45·8 ; H, 3·8 ; N, 11·1 ; Cl, 27·2. $C_{10}H_{10}O_2N_2Cl_2$ requires C, 46·0 ; H, 3·8 ; N, 10·8 ; Cl, 27·2%). It yielded ethyl alcohol and glyoxylic acid 2 : 4-dichlorophenylhydrazone on hydrolysis, and 2 : 4-dichloroaniline on reduction.

Methyl glyoxylate 2 : 4-*dichlorophenylhydrazone* crystallises in pale yellow, slender prisms, m. p. 136·5° (Found : C, 43·9 ; H, 3·4 ; Cl, 28·8. $C_9H_8O_2N_2Cl_2$ requires C, 43·7 ; H, 3·2 ; Cl, 29·0%), n-*propyl glyoxylate* 2 : 4-*dichlorophenylhydrazone* in short, pale yellow, flattened prisms, m. p. 65° (Found : Cl, 25·6. $C_{11}H_{12}O_2N_2Cl_2$ requires Cl, 25·8%), and n-*butyl glyoxylate* 2 : 4-*dichlorophenylhydrazone* in slender, yellow, flattened prisms, m. p. 59° (Found : Cl, 24·3. $C_{12}H_{14}O_2N_2Cl_2$ requires Cl, 24·5%).

Action of 2 : 4-*Dibromophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Methyl Alcohol.*—2 : 4-Dibromophenylhydrazine hydrochloride (15 g. ; 1 mol.), chloral hydrate (8 g. ; 1 mol.), and methyl alcohol (60 c.c.), when heated together under reflux on a water-bath for an hour, reacted vigorously with liberation of hydrogen chloride. A deep yellow liquid was obtained, from which *methyl glyoxylate* 2 : 4-*dibromophenylhydrazone* separated on cooling.

It crystallises from boiling methyl alcohol, in which it is moderately easily soluble, in slender, pale yellow, flattened prisms, m. p. 136° (Found: C, 32·2; H, 2·5; Br, 47·6. $C_9H_8O_2N_2Br_2$ requires C, 32·1; H, 2·4; Br, 47·6%).

Similar esters were obtained when chloral was allowed to interact with 2 : 4-dibromophenylhydrazine, 2-chloro-4-bromophenylhydrazine, and 4-chloro-2-bromophenylhydrazine in presence of alcohols and were all found to be identical with the corresponding esters prepared from glyoxylic acid.

Ethyl glyoxylate 2 : 4-*dibromophenylhydrazone* crystallises in slender, pale yellow, flattened prisms, m. p. 119° (Found: Br, 45·6. $C_{10}H_{10}O_2N_2Br_2$ requires Br, 45·7%), n-*propyl glyoxylate* 2 : 4-*dibromophenylhydrazone* in short, pale yellow, flattened prisms, m. p. 75° (Found: Br, 44·0. $C_{11}H_{12}O_2N_2Br_2$ requires Br, 43·9%), and *ethyl glyoxylate* 2-*chloro*-4-*bromophenylhydrazone* (Found: Cl, 11·6; Br, 26·3. $C_{10}H_{10}O_2N_2ClBr$ requires Cl, 11·6; Br, 26·2%) and *ethyl glyoxylate* 4-*chloro*-2-*bromophenylhydrazone* in slender, pale yellow prisms, m. p. 120° and 115°, respectively.

Glyoxylic Acid 2 : 4-*Dichlorophenylhydrazone.*—Glyoxylic acid (made by the electrolytic reduction of oxalic acid) and 2 : 4-dichlorophenylhydrazine hydrochloride reacted at once in aqueous solution at 60° and the *hydrazone* separated as a yellow solid. It is sparingly soluble in water, very easily soluble in alcohol, and crystallises from hot aqueous alcohol in pale yellow needles, decomp. about 150° (Found: Cl, 30·3. $C_8H_6O_2N_2Cl_2$ requires Cl, 30·4%).

The 2 : 4-*dibromophenylhydrazone* of glyoxylic acid resembles the dichloro-hydrazone very closely. It crystallises in pale yellow needles, decomp. about 150° (Found: Br, 49·5. $C_8H_6O_2N_2Br_2$ requires Br, 49·7%).

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Bromal dissolved in Ethyl Alcohol.*—A mixture of 11 g. of 2 : 4-dichlorophenylhydrazine hydrochloride, 14 g. of bromal, and 100 c.c. of ethyl alcohol was boiled under reflux for an hour, hydrogen bromide being liberated in quantity and ethyl bromide (recognisable by its odour) formed. The bright yellow liquid obtained, on cooling, deposited ethyl glyoxylate 2 : 4-dichlorophenylhydrazone, m. p. 121·5°, identical in every respect with that prepared both from chloral and from glyoxylic acid.

Methyl glyoxylate 2 : 4-dibromophenylhydrazone, m. p. 136°, was similarly obtained when 2 : 4-dibromophenylhydrazine hydrochloride was heated with bromal dissolved in methyl alcohol.

Action of 2 : 4-*Dichlorophenylhydrazine Hydrochloride on Chloral Hydrate dissolved in Acetic Acid or Water.*—To a solution of 16·5 g. (1 mol.) of chloral hydrate in 100 c.c. of acetic acid, 21·5 g. (1 mol.)

of 2 : 4-dichlorophenylhydrazine hydrochloride and 33 g. of anhydrous sodium acetate (4 mols.) were added. The liquid became pale yellow, but little apparent change occurred until the temperature was raised to about 60°; obvious action then took place and the liquid became bright red. It was heated on a water-bath for ½ hour to complete the reaction and poured into water; *αα-dichloro-*β*-2 : 4-dichlorobenzeneazoethylene* (IV) then separated as a scarlet-red solid.

If aqueous solutions of equivalent quantities of chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride are mixed and slowly heated, the same compound separates at about 80° as a crimson, viscid liquid which solidifies on cooling and from which the supernatant liquid, now strongly acid from the hydrogen chloride set free in the reaction, can be decanted.

The red solid is readily soluble in boiling chloroform, acetic acid, and alcohol, and separates from warm alcohol in slender, flattened, golden-red prisms, m. p. 84·5° (Found : C, 35·6; H, 1·6; N, 10·2; Cl, 52·5; *M*, cryoscopic in benzene, 262. $C_8H_4N_2Cl_4$ requires C, 35·6; H, 1·5; N, 10·4; Cl, 52·6%; *M*, 270). It does not react with acetic anhydride. When it was boiled with ethyl alcohol for 8 hours, a deep orange-coloured liquid was obtained from which, on cooling, ethyl glyoxylate 2 : 4-dichlorophenylhydrazone separated.

*Action of Bromine upon αα-Dichloro-*β*-2 : 4-dichlorobenzeneazoethylene.*—To a solution of 5 g. (1 mol.) of αα-dichloro-β-2 : 4-dichlorobenzeneazoethylene in 20 c.c. of warm acetic acid, 3·5 g. (1 mol.) of bromine in 5 c.c. of acetic acid were added. The bromine slowly disappeared and the solution became paler in colour. The solution was then poured into water; *αα-dichloro-*β*-bromo-*β*-2 : 4-dichlorobenzeneazoethylene* (V) separated as a brownish-red solid. It is easily soluble in warm acetic acid or alcohol and separates in small, red needles, m. p. 90° (Found : Cl, 40·5; Br, 22·7. $C_8H_3N_2Cl_4Br$ requires Cl, 40·7; Br, 22·9%).

*αα-Dichloro-*β*-2 : 4-dibromobenzeneazoethylene* crystallises in slender, orange-red, flattened prisms, m. p. 96·5° (Found : Cl, 19·9; Br, 44·9. $C_8H_4N_2Cl_2Br_2$ requires Cl, 19·8; Br, 44·6%), *αα-dichloro-*β*-2-chloro-4-bromobenzeneazoethylene* in small, slender, orange-red prisms, m. p. 84° (Found : Cl, 33·6; Br, 25·3. $C_8H_4N_2Cl_3Br$ requires Cl, 33·8; Br, 25·4%), and *αα-dichloro-*β*-4-chloro-2-bromobenzeneazoethylene* in slender, orange-red prisms, m. p. 81°.

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