XVI.—*The Formation of Glyoxalosazones by the Interaction of Dichloroacetaldehyde and Aryl Hydrazines.*

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When chloral reacts with aryl hydrazines (Chattaway and Bennett, J., 1927, 2850; Chattaway and Daldy, J., 1928, 2756), pale yellow hydrazones are first formed. These are extremely unstable and lose hydrogen chloride very easily, brilliant crimson azo-derivatives of αα-dichloroethylene being obtained. This loss of hydrogen chloride, however, is a reversible reaction and if the acid is not removed and if the reaction is carried out in alcoholic solution, the trichloromethyl group of the original hydrazone is hydrolysed and a hydrazone of a glyoxylic ester is produced. The equilibrium being thus destroyed, the red colour at first produced disappears as the azo-αα-dichloroethylene reverts to the original hydrazone :

$$\mathrm{R{\cdot}NH{\cdot}N{:}CH{\cdot}CCl_3}\ \begin{array}{l} \rightleftarrows \mathrm{R{\cdot}N{:}N{\cdot}CH{:}CCl_2 + HCl} \\ \xrightarrow{\mathrm{R'OH}} \mathrm{R{\cdot}NH{\cdot}N{:}CH{\cdot}CO_2R'} \end{array}$$

A similar series of reactions occurs when dichloroacetaldehyde reacts with aryl hydrazines. Hydrazones are at first normally produced which quickly lose hydrogen chloride with the production of a brilliant crimson colour.

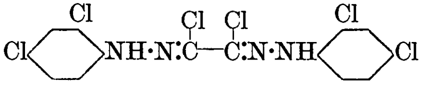
This crimson colour is undoubtedly due to the formation of azo-derivatives of α-monochloroethylene. These, however, are too unstable to allow of their isolation in a pure state and, the reactions by which they are produced being reversible, the crimson colour rapidly disappears on heating and osazones of glyoxal separate, since the dichloromethyl group of the parent hydrazones is very reactive and condenses with another molecule of the aryl hydrazine, either directly or after hydrolysis : thus, where R is C_6H_5, 4-$C_6H_4Cl(Br)$, 2 : 4-$C_6H_3Cl_2(Br_2)$, or 2 : 4 : 6-$C_6H_2Cl_3(Br_3)$,

$$\mathrm{R{\cdot}NH{\cdot}N{:}CH{\cdot}CHCl_2}\ \begin{array}{l} \rightleftarrows \mathrm{R{\cdot}N{:}N{\cdot}CH{:}CHCl + HCl} \\ \xrightarrow{\mathrm{R{\cdot}NH{\cdot}NH_2}} \mathrm{R{\cdot}NH{\cdot}N{:}CH{\cdot}CH{:}N{\cdot}NHR} \end{array}$$

In this connexion it may be recalled that αα-dichloro-5-carboxy-2-hydroxyacetophenone similarly yields an osazone with phenylhydrazine (Chattaway and Calvet, J., 1927, 687).

The glyoxalosazones are pale yellow, well-crystallised compounds, for the most part sparingly soluble in ordinary organic solvents. They melt at a high temperature, usually with decomposition, and are easily chlorinated and brominated. They also form well-crystallised diacetyl derivatives, R·NAc·N:CH·CH:N·NAcR.

The action of chlorine on the unsubstituted glyoxaldiphenylosazone, on *glyoxaldi*-p-*chlorophenylosazone*, and on *glyoxaldi*-2 : 4-*dichlorophenylosazone* yields the same product, *ωω′-dichloroglyoxaldi*-2 : 4-*dichlorophenylosazone*,



Direct halogenation does not introduce a third chlorine atom into the benzene nucleus. *ωω′-Dichloroglyoxaldi*-2 : 4 : 6-*trichlorophenylosazone*, however, is readily formed by the action of chlorine on glyoxaldi-2 : 4 : 6-trichlorophenylosazone.

Bromine acts in an exactly analogous manner, being substituted for hydrogen in the benzene nuclei and replacing the two $\omega\omega'$-hydrogen atoms.

The $\omega\omega'$-substituted halogen atoms in these compounds are remarkably unreactive. The $\omega\omega'$-halogenated osazones can be recovered unchanged even after refluxing with alcoholic ammonia for some hours. They are also not readily reduced by tin or zinc in hydrochloric or acetic acid.

The glyoxalosazones, when the $\omega\omega'$-positions are occupied by halogen atoms, are not acetylated when heated with acetic anhydride, tarry products being obtained; nor can chlorine or bromine be substituted for hydrogen in the $\omega\omega'$-positions in the diacetylosazones, even on heating in glacial acetic acid for several hours, the initial material being recovered.

EXPERIMENTAL.

Action of Phenylhydrazine upon Dichloroacetaldehyde.—As the same results were obtained whether dichloroacetaldehyde alcoholate or dichloroacetaldehyde itself was used, the former was always employed, since it is very troublesome to isolate the aldehyde.

To 150 c.c. of acetic acid were added 15·9 g. of dichloroacetaldehyde alcoholate (1 mol.) and 21 g. of phenylhydrazine (2 mols.). On being gently warmed, the solution developed a crimson colour which, as the temperature was raised to about 70°, disappeared and glyoxaldiphenylosazone separated. This compound crystallised from boiling alcohol, in which it was moderately easily soluble, in clusters of pale yellow, rhombic plates, m. p. 169—171° (compare Oddo and Cusmano, *Gazzetta*, 1911, **41**, ii, 251).

Action of p-*Chlorophenylhydrazine Hydrochloride upon Dichloroacetaldehyde Alcoholate.*—To 150 c.c. of acetic acid were added 16 g. of dichloroacetaldehyde alcoholate (1 mol.), 36 g. of *p*-chlorophenylhydrazine hydrochloride (2 mols.), and 20 g. of anhydrous sodium acetate. On warming, a brilliant crimson colour developed which on further heating disappeared and *glyoxaldi*-p-*chlorophenylosazone* separated. It crystallised from boiling alcohol or acetic acid, in both of which it was sparingly soluble, in pale yellow, quadrilateral plates, m. p. 227° (decomp.) (Found: Cl, 22·9. $C_{14}H_{12}N_4Cl_2$ requires Cl, 23·1%).

The other glyoxalosazones described in this paper were prepared in a similar manner, a deep crimson colour in each case appearing, and disappearing as the heating proceeded and the yellow osazone separated.

Glyoxaldi-2 : 4-dichlorophenylosazone crystallises from boiling acetic acid, in which it is very sparingly soluble, in clusters of pale yellow needles, m. p. 253—254° (decomp.) (Found : Cl, 37·5; C, 44·8; H, 2·6; N, 14·9. $C_{14}H_{10}N_4Cl_4$ requires Cl, 37·7; C, 44·7; H, 2·7; N, 14·9%).

Glyoxaldi-2 : 4 : 6-*trichlorophenylosazone* crystallises from acetic acid or alcohol, in both of which it is moderately easily soluble, in clusters of very pale yellow needles, m. p. 189° (Found : Cl, 47·8. $C_{14}H_8N_4Cl_6$ requires Cl, 47·8%).

Glyoxaldi-p-*bromophenylosazone* separates from either acetic acid or alcohol, in both of which it is sparingly soluble, in pale yellow, quadrilateral plates, m. p. 215° (decomp.) (Found : Br, 40·2. $C_{14}H_{12}N_4Br_2$ requires Br, 40·4%).

Glyoxaldi-2 : 4-*dibromophenylosazone* crystallises from boiling acetic acid, in which it is very sparingly soluble, in pale yellow, fine needles which darken at about 237° and melt with decomposition at 243° (Found : Br, 57·4. $C_{14}H_{10}N_4Br_4$ requires Br, 57·7%).

Glyoxaldi-2 : 4 : 6-*tribromophenylosazone* separates from acetic acid, in which it is sparingly soluble, in faintly yellow, quadrilateral plates, m. p. 226—228° (decomp.) (Found : Br, 67·25. $C_{14}H_8N_4Br_6$ requires Br, 67·4%).

All the glyoxalosazones were easily acetylated when heated with acetic anhydride containing a drop of sulphuric acid. The diacetyl derivatives are all colourless, and were crystallised from acetic acid.

Diacetylglyoxaldiphenylosazone forms quadrilateral plates, m. p. about 360° (decomp.); *diacetylglyoxaldi*-p-*chlorophenylosazone*, six-sided prisms, m. p. about 330° (decomp.) (Found : Cl, 18·0. $C_{18}H_{16}O_2N_4Cl_2$ requires Cl, 18·1%); *diacetylglyoxaldi*-2 : 4-*dichlorophenylosazone*, compact six-sided prisms, m. p. 291—292° (decomp.) (Found : Cl, 30·6. $C_{18}H_{14}O_2N_4Cl_4$ requires Cl, 30·8%); *diacetylglyoxaldi*-2 : 4 : 6-*trichlorophenylosazone*, flattened prisms, m. p. about 370° (decomp.) (Found : Cl, 40·0. $C_{18}H_{12}O_2N_4Cl_6$ requires Cl, 40·2%); *diacetylglyoxaldi*-p-*bromophenylosazone*, six-sided prisms, m. p. about 340° (decomp.) (Found : Br, 33·4. $C_{18}H_{16}O_2N_4Br_2$ requires Br, 33·3%); *diacetylglyoxaldi*-2 : 4-*dichlorophenylosazone*, slender six-sided prisms, m. p. 300° (decomp.) (Found : Br, 50·1. $C_{18}H_{14}O_2N_4Br_4$ requires Br, 50·1%); and *diacetylglyoxaldi*-2 : 4 : 6-*tribromophenylosazone*, clusters of needles, m. p. about 365° (decomp.) (Found : Br, 60·3. $C_{18}H_{12}O_2N_4Br_6$ requires Br, 60·3%).

Action of Chlorine upon Glyoxaldiphenyl-, Glyoxaldi-p-*chlorophenyl-, and Glyoxaldi*-2 : 4-*dichlorophenyl-osazones.*—When any one of these osazones was suspended in glacial acetic acid, and a rapid stream of chlorine passed in to saturation, hydrogen chloride was liberated, the suspended osazone dissolved, and ωω′-*dichloroglyoxal*-2 : 4-*dichlorophenylosazone* separated as a greenish-yellow solid. It crystallised from benzene in pale yellow, fine needles, m. p. 248—

251° (decomp.; after darkening at about 240°) (Found : Cl, 47·6. $C_{14}H_8N_4Cl_6$ requires Cl, 47·8%).

ωω′-*Dichloroglyoxaldi*-2 : 4 : 6-*trichlorophenylosazone* was similarly formed by the action of chlorine upon glyoxaldi-2 : 4 : 6-trichlorophenylosazone. It is sparingly soluble in boiling acetic acid but much more readily soluble in boiling benzene, from which it crystallises in clusters of very pale yellow, fine needles, m. p. 229—231° (decomp.) (Found : Cl, 55·1. $C_{14}H_6N_4Cl_8$ requires Cl, 55·2%).

ωω′-*Dibromoglyoxaldi*-2 : 4-*dibromophenylosazone* crystallises from benzene, in which it is moderately easily soluble, in clusters of long, fine, pale yellow needles, m. p. 205° (decomp.) (Found : Br, 67·15. $C_{14}H_8N_4Br_6$ requires Br, 67·4%); ωω′-*dibromoglyoxaldi*-2 : 4 : 6-*tribromophenylosazone* in long, fine, pale yellow needles, m. p. 230° (decomp.) (Found : Br, 73·3. $C_{14}H_6N_4Br_8$ requires Br, 73·5%); ωω′-*dibromoglyoxaldi*-2 : 4-*dichlorophenylosazone* in pale yellow needles, m. p. 270—273° (decomp.) (Found : Br, 29·8. $C_{14}H_8N_4Cl_4Br_2$ requires Br, 29·9%); and ωω′-*dichloroglyoxaldi*-2 : 4 : 6-*tribromophenylosazone* in very pale yellow, slender needles, m. p. 257° (decomp.) (Found : Cl, 8·9. $C_{14}H_6N_4Br_6Cl_2$ requires Cl, 9·1%). ωω′-*Dibromoglyoxaldi*-2 : 4 : 6-*trichlorophenylosazone* crystallises from glacial acetic acid in clusters of fine, almost colourless needles, m. p. 246° (decomp.) (Found : Br, 26·8. $C_{14}H_6N_4Cl_6Br_2$ requires Br, 26·5%).

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