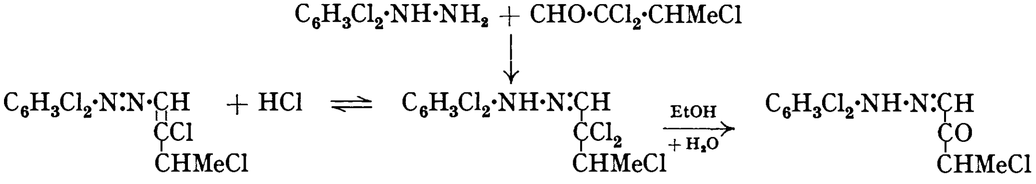
353. *The Interactions of Chloro-substituted Aldehydes with Chloro-substituted Arylhydrazines.*

By F. D. Chattaway and Allan Adair.

The interactions of chloral and of butyl chloral with 2 : 5-dichloro- and 2 : 4 : 5-trichlorophenylhydrazine hydrochlorides, although in the main following the course taken with 2 : 4-dichloro- and 2 : 4 : 6-trichloro-phenylhydrazines (Chattaway and Irving, J., 1930, 89; 1931, 751; *J. Amer. Chem. Soc.*, 1932, **54**, 263), show some points of considerable interest.

When 2 : 5-dichlorophenylhydrazine hydrochloride and butyl chloral hydrate interact in alcoholic solution at the ordinary temperature (or in hot aqueous solution), simple condensation first occurs, but the pale yellow hydrazone formed loses hydrogen chloride rapidly and a crimson azo-butylene is produced, which can be isolated if suitable precautions are observed. The separation of hydrogen chloride is reversible, loss of the crimson colour, and re-formation of the initial pale yellow hydrazone, occurring immediately if dry hydrogen chloride is led into a dry solution of the azo-butylene in benzene.

If the reaction is carried out in boiling alcohol, the final product is β-chloro-α-ketobutaldehyde-2 : 5-dichlorophenylhydrazone. The crimson colour disappears as the equilibrium is disturbed and the re-formed hydrazone is hydrolysed.



$$\begin{array}{c} C_6H_3Cl_2{\cdot}NH{\cdot}NH_2 + CHO{\cdot}CCl_2{\cdot}CHMeCl \\ \downarrow \end{array}$$

$$\begin{array}{l} C_6H_3Cl_2{\cdot}N{:}N{\cdot}CH \\ \qquad\qquad\quad\;\; \| \\ \qquad\qquad\quad\;\; CCl \\ \qquad\qquad\quad\;\; | \\ \qquad\qquad\quad\;\; CHMeCl \end{array} + HCl \rightleftharpoons \begin{array}{l} C_6H_3Cl_2{\cdot}NH{\cdot}N{:}CH \\ \qquad\qquad\qquad\; | \\ \qquad\qquad\qquad\; CCl_2 \\ \qquad\qquad\qquad\; | \\ \qquad\qquad\qquad\; CHMeCl \end{array} \xrightarrow[+H_2O]{EtOH} \begin{array}{l} C_6H_3Cl_2{\cdot}NH{\cdot}N{:}CH \\ \qquad\qquad\qquad\; | \\ \qquad\qquad\qquad\; CO \\ \qquad\qquad\qquad\; | \\ \qquad\qquad\qquad\; CHMeCl \end{array}$$

(crimson) (yellow, unstable)

If a solution of the crimson 2 : *5-dichlorobenzeneazo-βγ-dichloro-*Δ^{α}*-butylene* in benzene, or alcohol, free from hydrogen chloride, is heated for some time, the colour fades and a pale yellow isomeride, *αβ-dichlorocrotonaldehyde-*2 : *5-dichlorophenylhydrazone,*

$$C_6H_3Cl_2{\cdot}NH{\cdot}N{:}CH{\cdot}CCl{:}CMeCl,$$

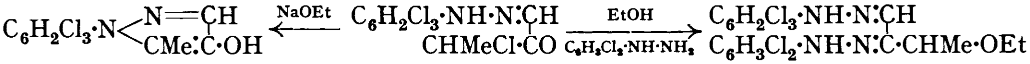
m. p. 90°, is produced. A second form of this isomeride, m. p. 116°, slowly separates when 2 : 5-dichlorophenylhydrazine hydrochloride and butyl chloral hydrate interact in acetic acid solution at the ordinary temperature.

These isomerides yield *monoacetyl* derivatives, which melt respectively at 150° and 139° and are undoubtedly *cis-trans* forms, since each combines directly with chlorine to form *ααββ-tetrachlorobutaldehyde-*2 : *5-dichloro-*N*-acetylphenylhydrazone,*

$$C_6H_3Cl_2{\cdot}NAc{\cdot}N{:}CH{\cdot}CCl_2{\cdot}CMeCl_2.$$

2 : 4 : 5-Trichlorophenylhydrazine hydrochloride reacts similarly with butyl chloral in aqueous solution, but the azo-butylene, being unstable, has not been isolated in the pure state, and the final product is *αβ-dichlorocrotonaldehyde-*2 : 4 : *5-trichlorophenylhydrazone* : no second form of this hydrazone has yet been obtained. When the reaction takes place in boiling alcohol, the crimson colour at first observed quickly disappears and *β-chloro-α-ketobutaldehyde-*2 : 4 : *5-trichlorophenylhydrazone* is formed. This compound

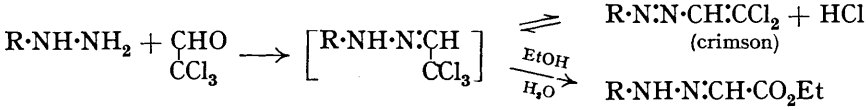
reacts (a) with an alcoholic solution of 2 : 5-dichlorophenylhydrazine, yielding an *osazone* in which the β-chlorine atom has been replaced by ethoxyl; (b) with an equivalent amount of



$$C_6H_2Cl_3\cdot N\Big<\begin{matrix}N{=}CH\\ CMe{:}C\cdot OH\end{matrix} \xleftarrow{NaOEt} \begin{matrix}C_6H_2Cl_3\cdot NH\cdot N{:}CH\\ CHMeCl\cdot CO\end{matrix} \xrightarrow[C_6H_3Cl_2\cdot NH\cdot NH_2]{EtOH} \begin{matrix}C_6H_2Cl_3\cdot NH\cdot N{:}CH\\ C_6H_3Cl_2\cdot NH\cdot N{:}C\cdot CHMe\cdot OEt\end{matrix}$$

hot alcoholic sodium ethoxide, ring closure taking place with loss of hydrogen chloride and the formation of 4-hydroxy-1-(2′ : 4′ : 5′-trichlorophenyl)-5-methylpyrazole.

The action of chloral upon 2 : 5-dichloro- or 2 : 4 : 5-trichloro-phenylhydrazine hydrochloride is similar to its action upon other halogen-substituted arylhydrazines (J., 1927, 2850). The first product is, in each case, a pale yellow, unstable hydrazone which, by a reversible loss of hydrogen chloride, passes into a crimson *azo-ethylene* which, when the reaction takes place in water (or in alcohol) at the ordinary temperature, can be isolated. In boiling alcohol, however, owing to the reversible nature of the reaction, the CCl_3 group of the initially formed hydrazone is hydrolysed and esterified, and a corresponding hydrazone of an alkyl glyoxylate is formed.



$$R\cdot NH\cdot NH_2 + \begin{matrix}CHO\\ CCl_3\end{matrix} \longrightarrow \left[\begin{matrix}R\cdot NH\cdot N{:}CH\\ CCl_3\end{matrix}\right] \begin{matrix}\rightleftharpoons R\cdot N{:}N\cdot CH{:}CCl_2 + HCl \\ \text{(crimson)} \\ \xrightarrow[H_2O]{EtOH} R\cdot NH\cdot N{:}CH\cdot CO_2Et\end{matrix}$$

When these 2 : 5-*dichloro*- and 2 : 4 : 5-*trichloro-phenylhydrazones* of ethyl glyoxylate are acted upon by chlorine, the ω-hydrogen atom is substituted. In the case of ethyl glyoxylate-2 : 5-dichlorophenylhydrazone the 4-position also is substituted, giving *ethyl ω-chloroglyoxylate*-2 : 4 : 5-*trichlorophenylhydrazone.*

EXPERIMENTAL.

2 : 5-*Dichlorobenzeneazo*-βγ-*dichloro*-Δ^α^-*butylene.*—This *compound* separated as a crimson-red solid when a well-powdered mixture of 2 : 5-dichlorophenylhydrazine hydrochloride (2 g.) and butyl chloral hydrate (2 g.) was covered with alcohol and shaken occasionally during ½ hour. After being washed with a little cold alcohol and dried, it crystallised from light petroleum (b. p. 60—80°) in large red prisms, m. p. 101° (Found : Cl, 47·7. $C_{10}H_8N_2Cl_4$ requires Cl, 47·7%). After several weeks it changed into the pale yellow αβ-dichlorocrotonaldehyde-2 : 5-dichlorophenylhydrazone, m. p. 116° (*vide infra*).

When dry hydrogen chloride was led into a benzene solution of the azo-butylene, the crimson colour faded immediately, owing to the formation of the unstable, pale yellow butyl chloral-2 : 5-dichlorophenylhydrazone. If the solution was rapidly washed free from hydrogen chloride with dilute sodium carbonate solution and then with water and dried over sodium sulphate, a neutral solution was obtained which lost hydrogen chloride when warmed, the red colour of the azo-butylene being restored.

When a benzene solution of the azo-butylene was boiled, the colour slowly faded to yellow and, on cooling, αβ-*dichlorocrotonaldehyde*-2 : 5-*dichlorophenylhydrazone*, m. p. 90°, separated in almost colourless prisms with pale blue reflex (Found : Cl, 48·2%). On treatment with acetic anhydride and a drop of sulphuric acid a *monoacetyl* derivative was obtained, which formed compact colourless prisms, m. p. 150°, from alcohol (Found : Cl, 41·5. $C_{12}H_{10}ON_2Cl_4$ requires Cl, 41·8%).

αβ-*Dichlorocrotonaldehyde*-2 : 5-*dichlorophenylhydrazone*, m. p. 116°.—6 G. of powdered 2 : 5-dichlorophenylhydrazine hydrochloride and 6 g. of butyl chloral hydrate, when covered with acetic acid (20 c.c.), dissolved in ½ hour; hydrogen chloride was evolved and the colour of the deep crimson solution faded whilst αβ-*dichlorocrotonaldehyde*-2 : 5-*dichlorophenylhydrazone* separated. This was easily soluble in boiling alcohol, and crystallised in pale yellow, flattened prisms, m. p. 116° (Found : Cl, 47·75%). The *monoacetyl* derivative, m. p. 139°, formed compact colourless prisms from alcohol (Found : Cl, 41·9%).

Either of these αβ-dichlorocrotonaldehyde-2 : 5-dichloro-*N*-acetylphenylhydrazones (m. p. 139° and 150°) was saturated with chlorine in hot chloroform solution; ααββ-*tetrachlorobutaldehyde*-2 : 5-*dichloro*-N-*acetylphenylhydrazone*, m. p. 154°, was obtained on evaporating the solvent (Found : Cl, 52·8. $C_{12}H_{10}ON_2Cl_6$ requires Cl, 51·8%). Reduction in boiling acetic acid solution with tin and hydrochloric acid gave 2 : 5-dichloroaniline, identified as 2 : 5-dichloroacetanilide, m. p. and mixed m. p. 134°.

αβ-Dichlorocrotonaldehyde-2 : 4 : 5-trichlorophenylhydrazone was obtained as a pale yellow solid when butyl chloral hydrate (1 mol.) and 2 : 4 : 5-trichlorophenylhydrazine hydrochloride (1 mol.) reacted in water at 40—50°. It formed slender, pale yellow prisms, m. p. 86°, from alcohol (Found : Cl, 53·2. $C_{10}H_7N_2Cl_5$ requires Cl, 53·4%). The *monoacetyl* derivative crystallised from alcohol in colourless compact prisms with domed ends, m. p. 123° (Found : Cl, 47·5. $C_{12}H_9ON_2Cl_5$ requires Cl, 47·4%).

β-Chloro-α-ketobutaldehyde-2 : 4 : 5-trichlorophenylhydrazone.—Butyl chloral hydrate (5 g.) and 2 : 4 : 5-trichlorophenylhydrazine hydrochloride (5 g.) were boiled with alcohol (30 c.c.) until the red colour faded to pale yellow (10 minutes). The *hydrazone*, which separated on cooling, formed pale yellow, slender prisms, m. p. 162°, from alcohol (Found : Cl, 45·3. $C_{10}H_8ON_2Cl_4$ requires Cl, 45·2%).

When an ethyl-alcoholic solution of this hydrazone was boiled with 2 : 5-dichlorophenylhydrazine, the 2 : 4 : 5 : 2′ : *5′-pentachlorodiphenylosazone* of *α-keto-β-methoxybutaldehyde* was obtained; this crystallised from pyridine–alcohol in slender yellow prisms with domed ends, m. p. 212° (Found : Cl, 37·1. $C_{18}H_{17}ON_4Cl_5$ requires Cl, 36·8%).

Action of Chloral upon 2 : 5-Dichlorophenylhydrazine.—2 : 5-Dichlorophenylhydrazine hydrochloride (8 g.), chloral hydrate (8 g.), and water (100 c.c.) were ground to a cream and gently warmed until the initially formed yellow hydrazone was converted completely into 2 : *5-dichlorobenzeneazo-ββ-dichloroethylene* (10 minutes), which separated as a red solid. This was well washed with warm water, dried, and crystallised from alcohol, in which it was readily soluble, forming orange-red needles, m. p. 93° (Found : Cl, 52·5. $C_8H_4N_2Cl_4$ requires Cl, 52·6%), unaffected by boiling alcohol in the absence of hydrogen chloride.

Ethyl Glyoxylate-2 : 5-dichlorophenylhydrazone.—This was obtained on cooling when chloral hydrate and 2 : 5-dichlorophenylhydrazine hydrochloride reacted in alcohol, the solution being first boiled until the red colour had faded to yellow. It formed yellow irregular plates, m. p. 90°, from alcohol (Found : Cl, 27·4. $C_{10}H_{10}O_2N_2Cl_2$ requires Cl, 27·2%).

Ethyl glyoxylate-2 : 4 : 5-trichlorophenylhydrazone, similarly prepared, crystallised from alcohol in almost colourless plates, m. p. 102° (Found : Cl, 36·0. $C_{10}H_9O_2N_2Cl_3$ requires Cl, 36·1%).

Ethyl ω-Chloroglyoxylate-2 : 4 : 5-trichlorophenylhydrazone.—Ethyl glyoxylate-2 : 5-di(or -2 : 4 : 5-tri)chlorophenylhydrazone (1 g.), dissolved in chloroform (10 c.c.), was saturated with chlorine, the temperature being allowed to rise. After aspiration of excess chlorine in a current of air passed through the solution, *ethyl ω-chloroglyoxylate-2 : 4 : 5-trichlorophenylhydrazone* was obtained as a yellow solid by evaporation of the chloroform on a water-bath. It was moderately easily soluble in alcohol and formed pale yellow needles (0·9 g.), m. p. 115° (Found : Cl, 43·3. $C_{10}H_8O_2N_2Cl_4$ requires Cl, 43·0%). On vigorous reduction in boiling acetic acid with tin and hydrochloric acid, 2 : 4 : 5-trichloroaniline was obtained (2 : 4 : 5-trichloroacetanilide, m. p. and mixed m. p. 182°). That this compound contains an ω-chlorine atom was shown by adding concentrated aqueous ammonia to an alcoholic solution, when, on the addition of water, *ethyl ω-aminoglyoxylate-2 : 4 : 5-trichlorophenylhydrazone* was obtained. It formed colourless hair-like prisms from aqueous alcohol; on standing in contact with its mother-liquor, it was rapidly transformed into colourless hexagonal tablets, m. p. 140° (Found : Cl, 34·2. $C_{10}H_{10}O_2N_3Cl_3$ requires Cl, 33·9%).

THE QUEEN'S COLLEGE LABORATORY, OXFORD.

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