

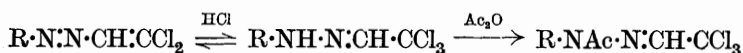
CXXXIX.—*The Interaction of Halogen-substituted  
p-Tolyldrazines with Chloral.*

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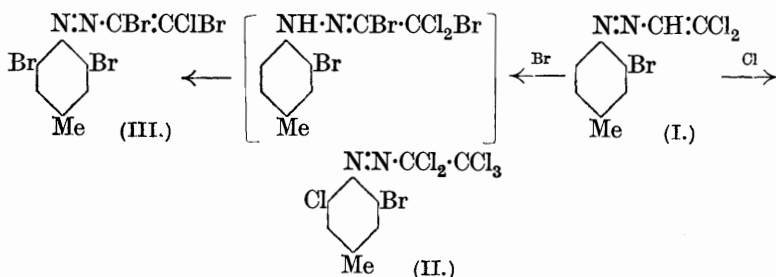
It has been shown (J., 1927, 2850; 1928, 2757) that the final products of the interactions of chloral with various halogen-substituted phenylhydrazines differ with the nature of the medium

in which they occur. The investigation has now been extended to the action of chloral upon 3-bromo- and 3:5-dibromo-*p*-tolylhydrazine.

When either of these hydrazines reacts with chloral in aqueous solution, a pale yellow hydrazone at first separates. This loses hydrogen chloride rapidly when warmed, a crimson azo-ethylene being formed. The elimination of the hydrogen chloride is reversible, and when a solution of the azo-ethylene in acetic anhydride is saturated with the gas the corresponding *trichloroacetaldehyde-N-acetylbromo-p-tolylhydrazone* is formed, though at the same time much of the azo-ethylene is converted into tarry matter. The reaction may be represented thus, where R denotes 3-bromo- or 3:5-dibromo-tolyl:



When 3-bromo- (I) and 3:5-dibromo-*o*-tolueneazo- $\beta\beta$ -dichloroethylene are fully chlorinated, 5-chloro-3-bromo- (II) and 3:5-dibromo-*p*-tolueneazopentachloroethane respectively are produced.



The action of bromine upon the two azo-ethylenes, however, is not so far-reaching: addition at the ethylene linkage, followed by elimination of hydrogen chloride, occurs, substitution in the *p*-tolyl residue also taking place if the 5-position is unoccupied.

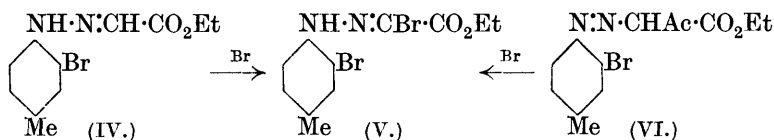
If the reaction between chloral and 3-bromo- or 3:5-dibromo-*p*-tolylhydrazine is carried out in any alcoholic solution, the corresponding alkyl glyoxylate bromotolylhydrazone is produced, the equilibrium between the first-formed hydrazone and the corresponding azo-ethylene being continually disturbed by the hydrolysis of the trichloromethyl group:



When the alcoholic solutions of chloral and the hydrazine are mixed and warmed, a bright azo-colour is produced which gradually disappears as action proceeds and the azo-ethylene disappears. At the same time a considerable amount of tarry matter is produced.

The formation of tarry by-product predominates when the pure isolated azo-ethylene is heated with an alcoholic solution of hydrogen chloride, only a poor yield of the alkyl glyoxylate being thus obtained. It appears to be due to the azo-ethylene polymerising or decomposing when heated in presence of hydrogen chloride, tarry matter being formed as soon as the temperature exceeds 70–80°. The glyoxylic acid hydrazones when formed are unaffected by hydrogen chloride, and then esterification, and hydrolysis of the resulting esters, in presence of hydrogen chloride may easily be brought about.

The regulated action of bromine upon *ethyl glyoxylate 3-bromo-p-tolylhydrazone* (IV) does not further substitute the tolyl nucleus but yields *ethyl bromoglyoxylate 3-bromo-p-tolylhydrazone* (V) identical with the product formed by the action of bromine upon ethyl 3-bromo-*p*-tolueneazoacetate (VI):



#### E X P E R I M E N T A L.

*3-Bromo-p-tolueneazo-ββ-dichloroethylene* (I).—When a solution of 10 g. (1 mol.) of 3-bromo-*p*-tolylhydrazine hydrochloride and 10 g. (1 mol. + slight excess) of chloral hydrate in 70 c.c. of water was warmed slowly, a pale yellow hydrazone separated at 40–50° which lost hydrogen chloride at 65–70°, darkened, and was converted into oily drops of *3-bromo-p-tolueneazo-ββ-dichloroethylene* which solidified on cooling. The product separated from boiling alcohol, in which it was readily soluble, in deep crimson plates, m. p. 67° (Found: Cl, 24.1; Br, 27.2. C<sub>9</sub>H<sub>7</sub>N<sub>2</sub>Cl<sub>2</sub>Br requires Cl, 24.2; Br, 27.2%).

*Trichloroacetaldehyde - N - acetyl - 3 - bromo - p - tolylhydrazone*, CCl<sub>3</sub>·CH:N·N·Ac·C<sub>6</sub>H<sub>3</sub>MeBr.—A solution of 5 g. of the azo-ethylene (I) in 10 c.c. of acetic anhydride was warmed to 70° and saturated with dry hydrogen chloride. On cooling, the above *acetyl* compound separated as a viscid mass. After repeated crystallisation from acetic acid, in which it was easily soluble, it was obtained in colourless prisms, m. p. 187° (decomp.) (Found: Cl, 28.45; Br, 21.4. C<sub>11</sub>H<sub>10</sub>ON<sub>2</sub>Cl<sub>3</sub>Br requires Cl, 28.6; Br, 21.5%). The same compound slowly separated when a solution of equivalent quantities of chloral and 3-bromo-*p*-tolylhydrazine hydrochloride in a suitable amount of glacial acetic acid was kept at the ordinary temperature.

*5-Chloro-3-bromo-p-tolueneazopentachloroethane* (II).—A suspension of 5 g. of 3-bromo-*p*-tolueneazo-ββ-dichloroethylene in 10 c.c. of

acetic acid was saturated with chlorine, the temperature not being allowed to rise above 30°. When the resulting clear solution was poured into water, a viscid yellow liquid separated which, on being heated for a few minutes with dilute acetic acid, was converted into 5-chloro-3-bromo-*p*-tolueneazopentachloroethane. This crystallised from boiling alcohol, in which it was moderately easily soluble, in yellow prisms, m. p. 113° (Found : Cl, 48.9; Br, 18.3.  $C_9H_5N_2Cl_6Br$  requires Cl, 49.1; Br, 18.4%). It could be heated with acetic anhydride without change and when strongly reduced yielded 3-bromo-*p*-toluidine.

3-Bromo-*p*-tolueneazo- $\beta$ -chloro- $\alpha\beta$ -dibromoethylene (formula as III).—5 G. (1 mol.) of 3-bromo-*p*-tolueneazo- $\beta\beta$ -dichloroethylene and 8 g. of anhydrous sodium acetate were suspended in 20 c.c. of cooled acetic acid and 4 g. (1 mol. + excess) of bromine were added. Considerable heat was developed and, on cooling, 3-bromo-*p*-tolueneazo- $\beta$ -chloro- $\alpha\beta$ -dibromoethylene separated. It dissolved easily in boiling alcohol, from which it separated in small, orange-red, irregular plates, m. p. 91° (Found : Cl, 8.4; Br, 57.0.  $C_9H_6N_2ClBr_3$  requires Cl, 8.5; Br, 57.5%).

Ethyl Glyoxylate 3-Bromo-*p*-tolylhydrazone (IV).—10 G. (1 mol.) of 3-bromo-*p*-tolylhydrazine hydrochloride were suspended in 60 c.c. of ethyl alcohol, 10 g. (1 mol. + excess) of chloral hydrate added, and the mixture warmed. The liquid became dark crimson and finally deep yellow. After 15 minutes, the bulk of the alcohol was distilled off; ethyl glyoxylate 3-bromo-*p*-tolylhydrazone, which separated on cooling, crystallised from boiling alcohol, in which it was easily soluble, in pale yellow prisms, m. p. 60° (Found : Br, 27.8.  $C_{11}H_{13}O_2N_2Br$  requires Br, 28.0%).

Ethyl Bromoglyoxylate 3-Bromo-*p*-tolylhydrazone (V).—(a) From ethyl glyoxylate 3-bromo-*p*-tolylhydrazone. 6 G. of bromine (1 mol. + excess) were added to a solution of 5 g. (1 mol.) of ethyl glyoxylate 3-bromo-*p*-tolylhydrazone in 25 c.c. of acetic acid, and the mixture heated at 50–60° for 30 minutes. On cooling, ethyl bromoglyoxylate 3-bromo-*p*-tolylhydrazone separated. It crystallised from boiling alcohol, in which it was easily soluble, in short, very pale yellow prisms, m. p. 98° (Found : Br, 43.8.  $C_{11}H_{12}O_2N_2Br_2$  requires Br, 43.9%). (b) From ethyl 3-bromo-*p*-tolueneazoacetate. 6 G. (1 mol. + excess) of bromine, dissolved in 5 c.c. of acetic acid, were added to 5 g. (1 mol.) of the azoacetate suspended in 20 c.c. of acetic acid and the mixture was heated at 50–60° for 30 minutes. On cooling, ethyl bromoglyoxylate 3-bromo-*p*-tolylhydrazone, m. p. 98°, identical with the substance obtained as above, separated.

Similar reactions were carried out with 3:5-dibromo-*p*-tolyl-

hydrazine, and the following compounds prepared : 3 : 5-Dibromo-p-tolueneazo- $\beta\beta$ -dichloroethylene, crimson needles, m. p. 50°, from alcohol (Found : Cl, 19.0 ; Br, 42.6.  $C_9H_6N_2Cl_2Br_2$  requires Cl, 19.0 ; Br, 42.9%).

3 : 5-Dibromo-p-tolueneazopentachloroethane, yellow prisms, m. p. 128°, from alcohol (Found : Cl, 36.9 ; Br, 33.2.  $C_9H_5N_2Cl_5Br_2$  requires Cl, 37.1 ; Br, 33.4%).

3 : 5-Dibromo-p-tolueneazo- $\beta$ -chloro- $\alpha\beta$ -dibromoethylene (III), deep crimson, slender prisms, m. p. 87°, from alcohol (Found : Cl, 7.1 ; Br, 63.8.  $C_9H_5N_2ClBr_4$  requires Cl, 7.15 ; Br, 64.45%).

Ethyl glyoxylate 3 : 5-dibromo-p-tolylhydrazone, yellow needles, m. p. 83°, from alcohol (Found : Br, 43.8.  $C_{11}H_{12}O_2N_2Br_2$  requires Br, 43.95%).

Glyoxylic acid 3 : 5-dibromo-p-tolylhydrazone, pale yellow prisms, m. p. 163° (decomp.), from acetic acid (Found : Br, 47.5.  $C_9H_8O_2N_2Br_2$  requires Br, 47.6%).

Ethyl bromoglyoxylate 3 : 5-dibromo-p-tolylhydrazone, white prisms, m. p. 64°, from alcohol (Found : Br, 53.3.  $C_{11}H_{11}O_2N_2Br_3$  requires Br, 54.2%).

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