CCLXI.—*The Action of Chlorine upon Chloro-substituted Hydrazones.*

By Frederick Daniel Chattaway, Thomas Deighton, and Allan Adair.

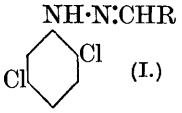
2 : 4 : 5-Trichloroaniline is easily obtained by the chlorination of 2 : 5-dichloroacetanilide, followed by hydrolysis. 2 : 3 : 4 : 6-*Tetrachloroaniline* is prepared by the regulated chlorination of 2 : 5-dichloroaniline, the presence of moisture being carefully avoided.

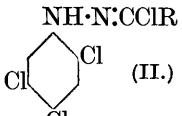
When diazotised and reduced with stannous chloride, these anilines give the corresponding *hydrazines*, which yield characteristic hydrazones with *o*-, *m*-, and *p*-nitrobenzaldehydes.

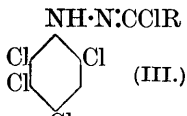
The first action of chlorine upon *m*- or *p*-nitrobenzaldehyde-2 : 5-dichlorophenylhydrazone (I) effects introduction of one chlorine atom into the 4-position of the hydrazine nucleus and one into the ω-position of the side-chain to give ω-*chloro*-m (*or* p)-*nitrobenzaldehyde*-2 : 4 : 5-*trichlorophenylhydrazone* (II), continued action giving ω-*chloro*-m(*or* p)-*nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazone* (III).

In the chlorination of *o*-nitrobenzaldehyde-2 : 5-dichlorophenyl-

hydrazone, the intermediate hydrazone (II) is so soluble that its isolation is difficult, and the final product at the ordinary temper-


(I.)


(II.)


(III.)

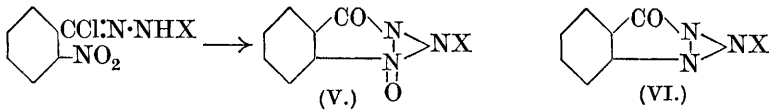
(R = *o*-, *m*-, or *p*-Nitrophenyl.)

ature is the fully chlorinated ω-*chloro*-o-*nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazone* (III). On vigorous reduction, these ω-chloro-hydrazones yield the corresponding 2 : 4 : 5-tri- or 2 : 3 : 4 : 6-tetra-chloroaniline. Their constitution is further established by their production in the regulated chlorination of nitrobenzaldehyde-2 : 4 : 5-trichloro- or -2 : 3 : 4 : 6-tetrachloro-phenylhydrazone. The presence of an ω-chlorine atom in the ω-chloro-*m*- (or *p*)-nitrobenzaldehydephenylhydrazones is shown by their reactivity with ammonia to give basic *hydrazidines* (IV):

$$X\cdot NH\cdot N{:}CHR \xrightarrow{Cl_2} X\cdot NH\cdot N{:}CClR \xrightarrow{NH_3} \underset{\text{(IV.)}}{X\cdot NH\cdot N{:}CR\cdot NH_2}$$

(X = 2 : 4 : 5-Trichloro- or 2 : 3 : 4 : 6-tetrachloro-phenyl.)

When, however, the nitro-group is in the ortho-position, the explosive *iso*diazole oxides (V) are given, which on reduction yield the *iso*diazoles (VI):


(V.) (VI.)

EXPERIMENTAL.

Although some difficulty appears to have been experienced in preparing 2 : 4 : 5-trichloro- and 2 : 3 : 4 : 6-tetrachloro-aniline (J., 1926, 3044), they are, as might be expected, readily obtained by the chlorination of 2 : 5-dichloroacetanilide and 2 : 5-dichloroaniline respectively.

Preparation of 2 : 4 : 5-*Trichloroaniline.*—7 G. of 2 : 5-dichloroacetanilide were dissolved in 30 c.c. of hot acetic acid and thoroughly saturated with chlorine; on cooling, 2 : 4 : 5-trichloroacetanilide separated as colourless needles, m. p. 184°; yield 7 g. 2 : 4 : 5-Trichloroaniline is obtained in theoretical amount by boiling the foregoing compound with alcohol containing one-eighth of its volume of concentrated hydrochloric acid. It separates from aqueous alcohol in colourless needles, m. p. 96°.

Preparation of 2 : 3 : 4 : 6-*Tetrachloroaniline.*—20 G. of 2 : 5-dichloroaniline, dissolved in 250 c.c. of dry chloroform, were saturated with chlorine, moisture being carefully excluded. The temperature rises, but cooling is undesirable. 2 : 3 : 4 : 6-Tetrachloroaniline hydrochloride, which separates, is collected and washed with dry chloroform, and the base is liberated by suspending the hydrochloride in water. 2 : 3 : 4 : 6-Tetrachloroaniline crystallises from light petroleum in white needles, m. p. 88°. Yield 25 g.

Preparation of 2 : 3 : 4 : 6-*Tetrachlorophenylhydrazine.*—12 G. of 2 : 3 : 4 : 6-tetrachloroaniline, dissolved in 20 c.c. of hot acetic acid, were poured into 70 c.c. of concentrated hydrochloric acid and diazotised at 0—5° by 4 g. of sodium nitrite in 15 c.c. of water, added during ½ hour. The solution was filtered and added during ¾ hour to a well-cooled mixture of 23 g. of stannous chloride and 30 c.c. of concentrated hydrochloric acid, whereupon 2 : 3 : 4 : 6-tetrachlorophenylhydrazine hydrochloride separated. This was collected at the pump, washed with a little concentrated hydrochloric acid, and recrystallised from a boiling mixture of 500 c.c. of water and 35 c.c. of concentrated hydrochloric acid; 8 g. of the pure hydrochloride were thus obtained, and the base was liberated by the action of aqueous sodium acetate.

The analogous trichloro-compound was similarly prepared. 2 : 4 : 5-*Trichlorophenylhydrazine* forms small colourless prisms from alcohol, m. p. 132° (Found : Cl, 50·1. $C_6H_5N_2Cl_3$ requires Cl, 50·4%). 2 : 3 : 4 : 6-*Tetrachlorophenylhydrazine*, short colourless prisms from alcohol, has m. p. 162° (Found : Cl, 58·24. $C_6H_4N_2Cl_4$ requires Cl, 57·7%).

The following hydrazones were obtained when hot alcoholic solutions of equimolecular amounts of the base and the nitrobenzaldehyde were mixed. o-*Nitrobenzaldehyde*-2 : 5-*dichlorophenylhydrazone* crystallises in two polymorphic forms from acetic acid, separating first as the labile form (orange hair-like needles), which is transformed slowly into the stable form (short six-sided orange prisms with domed ends); both forms melt at 156° (Found : Cl, 22·8. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9%). *o*-Nitrobenzaldehyde-2 : 4 : 5-trichlorophenylhydrazone, orange needles, m. p. 230°, from acetic acid. o-*Nitrobenzaldehyde*-2 : 4 : 5 : 6-*tetrachlorophenylhydrazone*, short yellow prisms from acetic acid, m. p. 184° (Found : Cl, 37·35. $C_{13}H_7O_2N_3Cl_4$ requires Cl, 37·5%). m-*Nitrobenzaldehyde*-2 : 5-*dichlorophenylhydrazone*, small yellow plates from toluene, m. p. 172° (Found : Cl, 22·75%). m-*Nitrobenzaldehyde*-2 : 4 : 5-*trichlorophenylhydrazone*, short orange prisms from nitrobenzene, m. p. 234° (Found : Cl, 30·8. $C_{13}H_8O_2N_3Cl_3$ requires Cl, 30·9%). m-*Nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazone*, yellow irregular

plates from nitrobenzene, m. p. 211° (Found : Cl, 37·4%). p-*Nitrobenzaldehyde*-2 : 5-*dichlorophenylhydrazone*, small orange prisms from acetic acid, m. p. 221° (Found : Cl, 22·8%). p-*Nitrobenzaldehyde*-2 : 4 : 5-*trichlorophenylhydrazone*, small orange prisms from nitrobenzene, m. p. 268° (Found : Cl, 30·7%). p-*Nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazone*, short yellow needles from acetic acid, m. p. 219° (Found : Cl, 37·45%).

When *o*-, *m*-, and *p*-nitrobenzaldehyde-2 : 5-dichlorophenylhydrazones were suspended in acetic acid and saturated with chlorine below 20°, *o*-, *m*-, and *p*-nitrobenzaldehyde-ω-chloro-2 : 4 : 5-trichlorophenylhydrazones were obtained. Chlorination in hot acetic acid gave nitrobenzaldehyde-ω-chloro-2 : 3 : 4 : 6-tetrachlorophenylhydrazone. These hydrazones were crystallised from acetic acid.

ω-*Chloro*-o-*nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazone*, yellow prisms, m. p. 129° (Found : Cl, 42·7. $C_{13}H_6O_2N_3Cl_5$ requires Cl, 42·9%). ω-*Chloro*-m-*nitrobenzaldehyde*-2 : 4 : 5-*trichlorophenylhydrazone*, pale yellow needles, m. p. 195° (Found : Cl, 37·7. $C_{13}H_7O_2N_3Cl_4$ requires Cl, 37·5%). ω-*Chloro*-m-*nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazone*, nodules of minute colourless crystals, m. p. 174° (Found : Cl, 42·8%). ω-*Chloro*-p-*nitrobenzaldehyde*-2 : 4 : 5-*trichlorophenylhydrazone*, small yellow prisms, m. p. 252° (Found : Cl, 37·6%). ω-*Chloro*-p-*nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazone*, pale yellow needles, m. p. 165° (Found : Cl, 42·85%).

The following basic hydrazidines were prepared by boiling the corresponding ω-chloro-nitrobenzaldehydephenylhydrazones with alcoholic ammonia. m-*Nitrobenzaldehyde*-2 : 4 : 5-*trichlorophenylhydrazidine*, brick-red needles from xylene, m. p. 210° (decomp.) (Found : Cl, 29·6. $C_{13}H_9O_2N_4Cl_3$ requires Cl, 29·6%). m-*Nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazidine*, pale yellow prisms from alcohol, m. p. 175° (decomp.) (Found : Cl, 36·1. $C_{13}H_8O_2N_4Cl_4$ requires Cl, 36·0%). p-*Nitrobenzaldehyde*-2 : 4 : 5-*trichlorophenylhydrazidine*, red prisms from nitrobenzene, m. p. 250° (decomp.) (Found : Cl, 29·7%). p-*Nitrobenzaldehyde*-2 : 3 : 4 : 6-*tetrachlorophenylhydrazidine*, dark brown needles from xylene, m. p. 230° (decomp.) (Found : Cl, 36·0%).

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