## ACTION OF CHLORINE UPON CHLORO-SUBSTITUTED HYDRAZONES. 1925

# CCLXI.—The Action of Chlorine upon Chlorosubstituted Hydrazones.

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2:4:5-TRICHLOROANILINE is easily obtained by the chlorination of 2:5-dichloroacetanilide, followed by hydrolysis. 2:3:4:6-*Tetra-chloroaniline* 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  $\omega$ -position of the side-chain to give  $\omega$ -chloro-m (or p)-nitrobenzaldehyde-2:4:5-trichlorophenylhydrazone (II), continued action giving  $\omega$ -chloro-m(or p)-nitrobenzaldehyde-2:3:4:6-tetrachlorophenylhydrazone (III).

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

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



ature is the fully chlorinated  $\omega$ -chloro-o-nitrobenzaldehyde-2:3:4:6tetrachlorophenylhydrazone (III). On vigorous reduction, these  $\omega$ -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  $\omega$ -chlorine atom in the  $\omega$ -chlorom- (or p)-nitrobenzaldehydephenylhydrazones is shown by their reactivity with ammonia to give basic hydrazidines (IV):

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

(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):



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°.

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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  $\frac{1}{2}$  hour. The solution was filtered and added during  $\frac{3}{4}$  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<sub>13</sub>H<sub>7</sub>O<sub>2</sub>N<sub>3</sub>Cl<sub>4</sub> requires Cl, 37.5%). m-Nitrobenzaldehyde-2:5-dichlorophenylhydrazone, small yellow plates from toluene, m. p. 172° 22.75%). m-Nitrobenzaldehyde-2:4:5-trichloro-(Found : Cl, phenylhydrazone, 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

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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- $\omega$ -chloro-2: 4: 5-trichlorophenylhydrazones were obtained. Chlorination in hot acetic acid gave nitrobenzaldehyde- $\omega$ -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<sub>13</sub>H<sub>6</sub>O<sub>2</sub>N<sub>3</sub>Cl<sub>5</sub> requires Cl, 42·9%). ω-Chloro-m-nitrobenzaldehyde-2:4:5-trichlorophenylhydrazone, pale yellow needles, m. p. 195° (Found : Cl, 37·7. C<sub>13</sub>H<sub>7</sub>O<sub>2</sub>N<sub>3</sub>Cl<sub>4</sub> 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-2:3:4:6tetrachlorophenylhydrazone, pale yellow needles, m. p. 165° (Found : Cl, 42·85%).

The following basic hydrazidines were prepared by boiling the corresponding  $\omega$ -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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