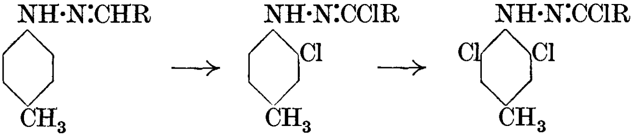
CXI.—*Intramolecular Rearrangement in the Isomeric Tetrachloro-derivatives of* p-*Tolylhydrazones.*

By Frederick Daniel Chattaway and Arthur B. Adamson.

The chlorination of the *p*-tolylhydrazones of *m*- and *p*-nitrobenzaldehyde at the ordinary temperature yields a series of compounds closely resembling the corresponding bromo-compounds.

The least halogenated products that can be isolated contain two atoms of chlorine, one in the *p*-tolyl nucleus in an *o*-position with respect to the nitrogen atom and a second in the ω-position. The same compounds are obtained by careful chlorination of the corresponding hydrazones of 3-chloro-*p*-tolylhydrazine.

Further chlorination at the ordinary temperature introduces a third atom of chlorine into the remaining *o*-position in the *p*-tolyl nucleus :



These compounds have the usual properties of ω-halogenated compounds. On boiling with sodium acetate and acetic acid they are converted into the corresponding β-*acetyl-hydrazides* of *m*- or *p*-nitrobenzoic acid, and they are converted into the corresponding *hydrazidines* by the action of concentrated aqueous ammonia.

On brominating *m*- or *p*-nitrobenzaldehyde-*p*-tolylhydrazone, only three atoms of bromine can be introduced into the molecule even when a large excess of halogen is used and the temperature allowed to rise (this vol., p. 157). When, however, an acetic acid suspension of either of these hydrazones is saturated with chlorine and the temperature allowed to rise, the resulting compound contains four atoms of chlorine in the molecule :

$$C_6H_4Me{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2 = C_{14}H_{13}O_2N_3 \longrightarrow C_{14}H_9O_2N_3Cl_4.$$

These tetrachloro- compounds are not affected by acetic anhydride and indeed can be recovered unchanged after boiling for several hours with acetic anhydride and a drop of concentrated sulphuric acid. They do not react with hot alcoholic ammonia. They liberate iodine from a solution of potassium iodide in dilute acetic acid. When treated with phenylhydrazine, they do not yield formazyl derivatives but undergo reduction to *ω-chloro*-m- or -p-*nitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone* : mild reduction with tin and cold hydrochloric acid also yields the same compound.

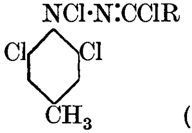
The fourth atom of chlorine cannot therefore have entered either the *p*-tolyl or the nitrobenzaldehyde nucleus.

On heating with acetic acid slightly diluted with water, they undergo a curious, exothermic, intramolecular change, considerable heat being evolved, since the mixture maintains itself at the boiling point for several minutes without external heating.

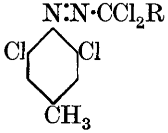
The new compounds thus formed have the same composition and molecular weight as those from which they are produced, but are much less soluble in all solvents and have much higher melting points. They have also a lighter colour, being pale yellow whilst the parent substances are deep orange, and are very unreactive. They do not react with hot alcoholic ammonia or boiling acetic anhydride, nor do they yield ω-chloro-*m*- or -*p*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone when treated with phenylhydrazine or on mild reduction. Vigorous reduction with tin and hydrochloric acid completely breaks down the molecule and yields in each case 3 : 5-dichloro-*p*-toluidine. Boiling with acetic acid and sodium acetate gives white viscid solids which cannot be crystallised but on hydrolysis yield *m*- or *p*-nitrobenzoic acid. As in the case of the parent substances, therefore, the fourth atom of chlorine in the transformation products cannot be substituted in either the *p*-tolyl or the nitrobenzaldehyde nucleus.

It seems therefore probable that the structure of these isomerides may be best represented as *ω-chloro*-m- or -p-*nitrobenzaldehyde*-3 : 5 : N-*trichloro*-p-*tolylhydrazone* (I) and 3 : 5-*dichloro*-p-*tolueneazo*-m- or -p-*nitrophenyldichloromethane* (II) :

(I.)



$(R = C_6H_4{\cdot}NO_2)$.



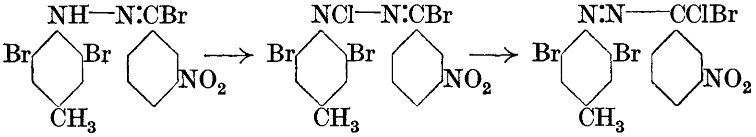
(II.)

Certain facts, however, are difficult to reconcile with this supposition. For example, one would expect the compound containing the azo-linkage to have the deeper colour, whereas it is pale yellow. Also one would expect the CCl_2 group to be reactive and easily hydrolysed, but it is remarkably stable and is not affected by boiling with concentrated hydrochloric acid or alcoholic ammonia.

The action of chlorine upon ω-bromo-*m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone yields a similar compound,

$$C_{14}H_9O_2N_3ClBr_3.$$

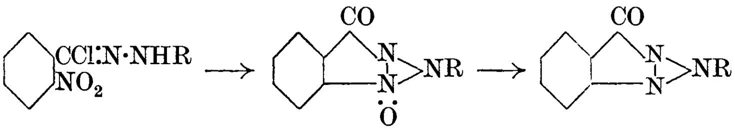
This also is converted into an isomeride of higher melting point by boiling with acetic acid slightly diluted with water :



Corresponding compounds are not produced under similar conditions by the action of chlorine upon *m*- and *p*-nitrobenzaldehyde-phenylhydrazone, the highest chlorination product being ω-chloro-*m*- or -*p*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone.

The chlorination of *o*-nitrobenzaldehyde-*p*-tolylhydrazone follows a normal course. The first product which can be isolated is ω-*chloro*-o-*nitrobenzaldehyde*-3-*chloro*-p-*tolylhydrazone*. Saturation with chlorine at the ordinary temperature yields ω-*chloro*-o-*nitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone*.

These two ω-chloro-compounds are rather more stable than the corresponding bromo-compounds and can be recrystallised unchanged from alcohol. They readily yield the corresponding *keto*endo*aryliminodihydrobenz*iso*diazole oxides*, which are violently explosive, when a little concentrated aqueous ammonia is added to their solution in benzene. On mild reduction, these explosive compounds lose one atom of oxygen and are converted into the corresponding *keto*endo*aryliminodihydrobenz*iso*diazoles* :



If the temperature is allowed to rise during the chlorination of *o*-nitrobenzaldehyde-*p*-tolylhydrazone, the hydrazone is rapidly decomposed and consequently a higher chlorination product such as is formed in the case of *m*- and *p*-nitrobenzaldehyde-*p*-tolylhydrazone cannot be obtained.

EXPERIMENTAL.

The Chlorination of m-*Nitrobenzaldehyde*-p-*tolylhydrazone.*

ω-*Chloro*-m-*nitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone*.—Chlorine was slowly passed into a suspension of 5 g. of *m*-nitrobenzaldehyde-*p*-tolylhydrazone in 50 c.c. of acetic acid. The hydrazone dissolved and almost immediately *ω-chloro-*m*-nitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone* began to separate as a bright yellow solid. When the mixture had become almost solid, chlorination was stopped and the solid collected. It crystallised from acetic acid, in which it was moderately easily soluble, in bright yellow, elongated plates, m. p. 137° (Found : Cl, 29·6. $C_{14}H_{10}O_2N_3Cl_3$ requires Cl, 29·7%).

m-*Nitrobenz*-β-*acetyl*-3 : 5-*dichloro*-p-*tolylhydrazide*, $C_6H_2Cl_2Me{\cdot}NAc{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$. —2 G. of ω-chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone, 2 g. of anhydrous sodium acetate, and 40 c.c. of acetic acid were boiled under reflux for 2 hours. The resulting solution was poured into 100 c.c. of cold water. The *hydrazide*, which separated as a white solid, crystallised from alcohol, in which it was moderately easily soluble, in small prisms, m. p 173° (Found: Cl, 18·5. $C_{16}H_{13}O_4N_3Cl_2$ requires Cl, 18·6%).

A lower chlorination product of *m*-nitrobenzaldehyde-*p*-tolylhydrazone could not be isolated in a pure state.

ω-Chloro-m-*nitrobenzaldehyde*-3 : 5 : N-*trichloro*-p-*tolylhydrazone* (I). —A suspension of 5 g. of *m*-nitrobenzaldehyde-*p*-tolylhydrazone in 50 c.c. of acetic acid was saturated with chlorine, the temperature being allowed to rise to about 60°. The bright yellow ω-chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone first separated, but this slowly redissolved, forming an orange solution. From this, on standing for 12 hours at the ordinary temperature, *ω-chloro*-m-*nitrobenzaldehyde*-3 : 5 : N-*trichloro*-p-*tolylhydrazone* slowly separated. After being washed with a very little acetic acid, this crystallised from alcohol, in which it was easily soluble, in orange four-sided prisms, m. p. 95° (Found : C, 43·1; H, 2·3; N, 10·7; Cl, 36·3; *M*, cryoscopic in benzene, 375. $C_{14}H_9O_2N_3Cl_4$ requires C, 42·8; H, 2·3; N, 10·7; Cl, 36·1%; *M*, 393).

Action of Phenylhydrazine on ω-Chloro-m-*nitrobenzaldehyde*-3 : 5 : N-*trichloro*-p-*tolylhydrazone*.—2 G. of phenylhydrazine were added to a solution of 2 g. of the hydrazone in 20 c.c. of acetic acid and warmed until a brisk reaction started. The solution became dark brown and on cooling, ω-chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone separated, m. p. 137° after several crystallisations from acetic acid.

Reduction of ω-Chloro-m-*nitrobenzaldehyde*-3 : 5 : N-*trichloro*-p-*tolylhydrazone*.—4 G. of the hydrazone were dissolved in 30 c.c. of acetic acid, 15 c.c. of hydrochloric acid and 3 g. of granulated tin were added, and the mixture was warmed gently for a few minutes. ω-Chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone separated as an oil which quickly solidified; m. p. 137° after crystallisation from acetic acid.

*Intramolecular Rearrangement of ω-Chloro-*m*-nitrobenzaldehyde-3 : 5 : N-trichloro-*p*-tolylhydrazone* (I) *into* 3 : 5-*Dichloro-*p*-tolueneazo-*m*-nitrophenyldichloromethane* (II).—5 G. of the hydrazone were dissolved in 100 c.c. of hot acetic acid, 5 c.c. of water added, and the solution raised to the boiling point. A brisk reaction took place, the mixture continued boiling for several minutes without external heating, and 3 : 5-*dichloro-*p*-tolueneazo-*m*-nitrophenyldichloromethane* separated as a pale yellow solid. The mixture was heated until there was no further separation of solid. After cooling, the product was collected and washed with alcohol, in which it was practically insoluble; it crystallised from acetic acid, in which it was moderately easily soluble, in pale yellow needles, m. p. 165° (Found : C, 43·0; H, 2·4; N, 10·6; Cl, 35·9; *M*, ebullioscopic in benzene, 388. $C_{14}H_9O_2N_3Cl_4$ requires C, 42·8; H, 2·3; N, 10·7; Cl, 36·1%; *M*, 393).

Reduction of 3 : 5-*Dichloro-*p*-tolueneazo-*m*-nitrophenyldichloromethane.*—To 5 g. of the dichloromethane, suspended in a mixture of 50 c.c. of acetic acid and 50 c.c. of hydrochloric acid, 5 g. of granulated tin were added and the mixture was heated until a clear, almost colourless solution was formed. This was cooled, made alkaline with caustic soda, and steam-distilled. 3 : 5-Dichloro-*p*-toluidine separated in the distillate as a white solid and was identified by means of its acetyl derivative, which crystallised from alcohol in colourless prisms, m. p. 207°, identical with a specimen prepared by the chlorination of aceto-*p*-toluidide.

Reaction of 3 : 5-*Dichloro-*p*-tolueneazo-*m*-nitrophenyldichloromethane with Sodium Acetate and Acetic Acid.*—A mixture of 3 g. of the dichloromethane, 3 g. of anhydrous sodium acetate, and 60 c.c. of acetic acid was boiled under reflux for 2 hours. The clear solution obtained was cooled and poured into 200 c.c. of cold water; a colourless semi-solid mass then separated which could not be made to crystallise. It was therefore boiled under reflux with a mixture of 25 c.c. of alcohol and 25 c.c. of hydrochloric acid for 2 hours; the solution obtained was cooled and made alkaline, and the alcohol distilled off. After filtration from tarry matter, the colourless liquid was acidified with hydrochloric acid; ether then extracted *m*-nitrobenzoic acid, m. p. 140° after crystallisation from water.

The Chlorination of p-*Nitrobenzaldehyde-*p*-tolylhydrazone.*

*ω-Chloro-*p*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone.*—A very slow stream of chlorine was passed into a solution of 2 g. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone in 150 c.c. of acetic acid, cooled in running water. In a few minutes *ω-chloro*-p-*nitrobenzaldehyde-3-chloro*-p-*tolylhydrazone* separated as an orange flocculent solid. Chlorination was then stopped. The product, after being washed with water, crystallised from acetic acid, in which it was moderately easily soluble, as a felted mass of slender, bright orange prisms, m. p. 163° (Found: Cl, 21·9. $C_{14}H_{11}O_2N_3Cl_2$ requires Cl, 21·9%).

3-*Chloro*-p-*tolyl*-p-*nitrobenzenylhydrazidine*,

$$C_6H_3MeCl\cdot NH\cdot N{:}C(NH_2)\cdot C_6H_4\cdot NO_2,$$

which separated when a suspension of 2 g. of ω-chloro-*p*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone in 20 c.c. of alcohol was heated with 2 c.c. of concentrated aqueous ammonia, until a clear dark purple solution was formed, and then cooled, crystallised from alcohol, in which it was moderately easily soluble, in deep purple prisms, m. p. 162° (Found: Cl, 11·8. $C_{14}H_{13}O_2N_4Cl$ requires Cl, 11·7%).

p-*Nitrobenz*-β-*acetyl*-3-*chloro*-p-*tolylhydrazide*,

$$C_6H_3MeCl\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

separated as a white solid when the solution obtained by boiling 2 g. of ω-chloro-*p*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone, 2 g. of anhydrous sodium acetate, and 40 c.c. of acetic acid under reflux for 2 hours was poured into 100 c.c. of cold water. It crystallised from alcohol, in which it was moderately easily soluble, in small colourless prisms, m. p. 164° (Found: Cl, 10·2. $C_{16}H_{14}O_4N_3Cl$ requires Cl, 10·2%).

ω-Chloro-p-*nitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone*.—This was obtained, in the same way as the *m*-nitro-compound, from 4 g. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone in 100 c.c. of acetic acid; the intermediately formed 3-chloro-*p*-tolylhydrazone separated but quickly redissolved. The 3 : 5-*dichloro*-p-*tolylhydrazone* crystallised from acetic acid, in which it was moderately easily soluble, in slender, bright yellow prisms, m. p. 139° (Found: Cl, 29·6. $C_{14}H_{10}O_2N_3Cl_3$ requires Cl, 29·7%).

3 : 5-*Dichloro*-p-*tolyl*-p-*nitrobenzenylhydrazidine* crystallises from alcohol in orange-yellow plates, m. p. 159° (Found: Cl, 21·2. $C_{14}H_{12}O_2N_4Cl_2$ requires Cl, 21·2%).

p-*Nitrobenz*-β-*acetyl*-3 : 5-*dichloro*-p-*tolylhydrazide* crystallises from alcohol in small colourless prisms, m. p. 183° (Found: Cl, 18·8. $C_{16}H_{13}O_4N_3Cl_2$ requires Cl, 18·6%).

ω-Chloro-p-*nitrobenzaldehyde*-3 : 5 : N-*trichloro*-p-*tolylhydrazone*, obtained, in the same way as the *m*-nitro-compound, from 10 g. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone in 70 c.c. of acetic acid, crystallised from acetic acid, in which it was easily soluble, in irregular orange plates, m. p. 97° (Found: C, 42·3; H, 2·6; N, 10·9; Cl, 35·9; *M*, cryoscopic in benzene, 383. $C_{14}H_9O_2N_3Cl_4$ requires C, 42·8; H, 2·3; N, 10·7; Cl, 36·1%; *M*, 393).

This compound was treated in the manner described under ω-chloro-*m*-nitrobenzaldehyde-3 : 5 : N-trichloro-*p*-tolylhydrazone and its behaviour was exactly similar. It gave ω-chloro-*p*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone, m. p. 139°, on treatment with phenylhydrazine or on reduction with tin and hydrochloric acid and was converted by boiling dilute acetic acid into 3 : 5-*dichloro*-p-*tolueneazo*-p-*nitrophenyldichloromethane*, which crystallised from acetic acid, in which it was moderately easily soluble, in bright yellow, elongated plates, m. p. 188° (Found : C, 43·1; H, 2·4; N, 10·9; Cl, 35·8; *M*, ebullioscopic in benzene, 410. $C_{14}H_9O_2N_3Cl_4$ requires C, 42·8; H, 2·3; N, 10·7; Cl, 36·1%; *M*, 393).

The azo-compound gave 3 : 5-dichloro-*p*-toluidine (acetyl derivative, m. p. 207°) on reduction with tin and hydrochloric acid and was converted by boiling acetic acid and anhydrous sodium acetate into a white viscid solid, which gave *p*-nitrobenzoic acid, m. p. 238°, on hydrolysis.

The Chlorination of ω-*Bromo*-m-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone.*

ω-*Bromo*-m-*nitrobenzaldehyde*-N-*chloro*-3 : 5-*dibromo*-p-*tolylhydrazone.*—A rapid stream of chlorine was passed into a suspension of 5 g. of ω-bromo-*m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone in 50 c.c. of hot acetic acid. From the orange solution produced, on cooling, ω-*bromo*-m-*nitrobenzaldehyde*-N-*chloro*-3 : 5-*dibromo*-p-*tolylhydrazone* slowly separated. This crystallised from alcohol, in which it was easily soluble, in deep orange prisms, m. p. 77° (Found : C, 32·0; H, 1·7; N, 8·1; Cl + Br, 52·8. $C_{14}H_9O_2N_3ClBr_3$ requires C, 31·9; H, 1·7; N, 8·0; Cl + Br, 52·3%).

By the method used in the two previous rearrangements, the chlorodibromotolylhydrazone was converted into 3 : 5-*dibromo*-p-*tolueneazo*-m-*nitrophenylchlorobromomethane*, which crystallised from acetic acid, in which it was moderately easily soluble, in pale yellow needles, m. p. 157° (Found : C, 32·1; H, 1·8; N, 7·9; Cl + Br, 52·3. $C_{14}H_9O_2N_3ClBr_3$ requires C, 31·9; H, 1·7; N, 8·0; Cl + Br, 52·3%).

The Chlorination of o-*Nitrobenzaldehyde*-p-*tolylhydrazone.*

ω-*Chloro*-o-*nitrobenzaldehyde*-3-*chloro*-p-*tolylhydrazone.*—A slow stream of chlorine was passed into a suspension of 5 g. of *o*-nitrobenzaldehyde-*p*-tolylhydrazone in 25 c.c. of acetic acid until the hydrazone just dissolved, forming a dark brown solution. From this, ω-*chloro*-o-*nitrobenzaldehyde*-3-*chloro*-p-*tolylhydrazone* slowly separated. It crystallised from alcohol, in which it was easily soluble, in orange rhombic plates, m. p. 103° (Found: Cl, 21·7. $C_{14}H_{11}O_2N_3Cl_2$ requires Cl, 21·9%).

3-*Keto*-1 : 2-endo-3′-*chloro*-p-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*Oxide*.—This separated as a bright yellow solid when a solution of ω-chloro-*o*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone (3 g.) in benzene was warmed with 3 c.c. of concentrated aqueous ammonia. It crystallised from alcohol, in which it was moderately easily soluble, in bright yellow, rhombic plates, explosion point 134° (Found : Cl, 12·1. $C_{14}H_{10}O_2N_3Cl$ requires Cl, 12·3%).

3-*Keto*-1 : 2-endo-3′-*chloro*-p-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole*.—A solution of stannous chloride (2 g.) in hydrochloric acid was added to a solution of the explosive compound (2 g.) in 5 c.c. of acetic acid and 5 c.c. of hydrochloric acid. On dilution with water, the *product* separated as a pale yellow solid. It crystallised from alcohol, in which it was easily soluble, in colourless needles, m. p. 173° (Found : Cl, 13·2. $C_{14}H_{10}ON_3Cl$ requires Cl, 13·1%).

ω-*Chloro*-o-*nitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone*.—A suspension of 5 g. of *o*-nitrobenzaldehyde-*p*-tolylhydrazone in 25 c.c. of acetic acid, cooled to the ordinary temperature in running water, was saturated with chlorine. The hydrazone dissolved and a deep yellow solution was finally obtained, from which ω-*chloro*-o-*nitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone* slowly separated. It crystallised from alcohol, in which it was easily soluble, in pale yellow, six-sided plates, m. p. 87° (Found : Cl, 29·8. $C_{14}H_{10}O_2N_3Cl_3$ requires Cl, 29·7%).

3-*Keto*-1 : 2-endo-3′ : 5′-*dichloro*-p-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*oxide*, obtained in a similar way to the preceding oxide, crystallised from alcohol, in which it was moderately easily soluble, in bright yellow, six-sided plates, explosion point 155° (Found : Cl, 21·9. $C_{14}H_9O_2N_3Cl_2$ requires Cl, 22·0%). On reduction with stannous chloride it gave 3-*keto*-1 : 2-endo-3′ : 5′-*dichloro*-p-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole*, which crystallised from alcohol, in which it was easily soluble, in colourless six-sided prisms, m. p. 202° (Found : Cl, 22·9. $C_{14}H_9ON_3Cl_2$ requires Cl, 23·2%).

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