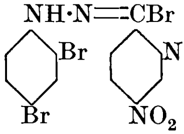
CCCLXXXVIII.—*The Action of Bromine and of Chlorine upon 2 : 4-Dinitrobenzaldehyde-phenyl- and -*p*-tolyl-hydrazones.*

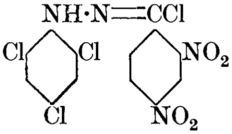
By Frederick Daniel Chattaway and Arthur B. Adamson.

The action of halogens upon the aryl hydrazones of 2 : 4-dinitrobenzaldehyde is of particular interest since, owing to the presence of a nitro-group in an ortho-position in the aldehyde nucleus, the ω-halogenated derivatives might be expected to yield explosive compounds, containing a three-membered nitrogen ring, similar to those derived from aryl hydrazones of *o*-nitrobenzaldehyde (J., 1925, **127**, 2407; 1930, 159, 845). The action of bromine and of chlorine upon 2 : 4-dinitrobenzaldehyde-phenyl- and -*p*-tolyl-hydrazones has therefore been studied.

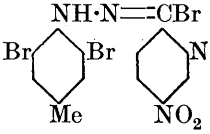
Both halogens substitute in the *o*- and *p*-positions in the phenyl residue and in the *o*-positions in the *p*-tolyl residue as well as in the ω-position. As with other hydrazones containing a phenyl residue, chlorination proceeds further than bromination, the final products being respectively



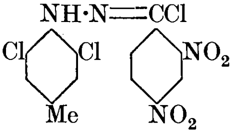
and



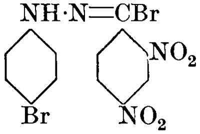
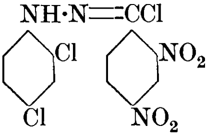
whilst in the case of the *p*-tolylhydrazone the final products are



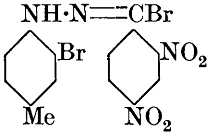
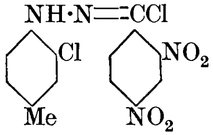
and



The first products of regulated halogenation which have been isolated are in the case of the phenylhydrazone

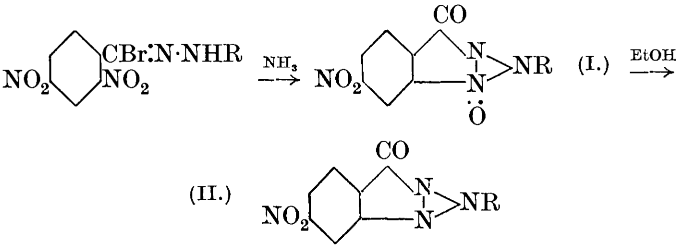

and


and in the case of the *p*-tolylhydrazone


and


All these ω-halogenated derivatives may be obtained by the action of bromine and chlorine respectively upon suitably substituted phenyl- and *p*-tolyl-hydrazones of 2 : 4-dinitrobenzaldehyde, the ω-hydrogen atom being in each case easily replaced by halogen.

The ω-halogen compounds resemble those derived from the corresponding *o*-nitrobenzaldehyde hydrazones, but they are much more stable. ω-*Bromo*-2 : 4-*dinitrobenzaldehyde*-3-*bromo* - p - *tolylhydrazone* and ω-*bromo*-2 : 4-*dinitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, when treated with ammonia, lose hydrogen bromide, forming the explosive *nitro*endo*aryliminoketodihydrobenz*iso*diazole oxides* (I), which are easily reduced to the corresponding *nitro*endo*arylimino-ketodihydrobenz*iso*diazoles* (II).


(I.)

(II.)

($R = C_6H_3MeBr$ or $C_6H_2MeBr_2$)

In the other cases examined, ammonia had no action upon the ω-halogen compounds except under conditions which brought about almost complete decomposition into tarry matter.

EXPERIMENTAL.

ω-*Bromo*-2 : 4-*dinitrobenzaldehyde*-4-*bromophenylhydrazone*.—To a suspension of 3 g. of 2 : 4-dinitrobenzaldehydephenylhydrazone (1 mol.) in 50 c.c. of acetic acid was added a solution of 1 c.c. of bromine (2 mols.) in 10 c.c. of acetic acid. A clear solution was formed from which ω-*bromo*-2 : 4-*dinitrobenzaldehyde*-4-*bromophenylhydrazone* slowly separated as a yellow solid. This crystallises from acetic acid, in which it is moderately easily soluble, in orange-brown plates, m. p. 176° (decomp.) (Found : Br, 35·9. $C_{13}H_8O_4N_4Br_2$ requires Br, 36·0%).

ω-*Bromo*-2 : 4-*dinitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone*.—Excess of bromine (5 c.c.) was added to a suspension of 3 g. of 2 : 4-dinitrobenzaldehydephenylhydrazone in 50 c.c. of acetic acid and the mixture was heated at 100° for 30 minutes to complete the bromination. On cooling, ω-*bromo*-2 : 4-*dinitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone* separated as an orange solid. It crystallises from acetic acid, in which it is moderately easily soluble, in orange prisms, m. p. 202° (decomp.) (Found : Br, 45·7. $C_{13}H_7O_4N_4Br_3$ requires Br, 45·9%).

ω-*Chloro*-2 : 4-*dinitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*.—Chlorine was slowly passed into a suspension of 4 g. of 2 : 4-dinitrobenzaldehydephenylhydrazone in 50 c.c. of acetic acid. The hydrazone dissolved and ω-*chloro*-2 : 4-*dinitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* separated as an orange solid. Chlorination was stopped when there was no further separation of solid. The *product* crystallised from acetic acid, in which it was moderately easily soluble, in flattened orange prisms, m. p. 196° (decomp.) (Found : Cl, 27·1. $C_{13}H_7O_4N_4Cl_3$ requires Cl, 27·3%).

ω-*Chloro*-2 : 4-*dinitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* was obtained as a yellow solid when a suspension of 4 g. of 2 : 4-dinitrobenzaldehydephenylhydrazone in 50 c.c. of acetic acid was saturated with chlorine. It crystallises from acetic acid, in which it is easily soluble, in two polymorphic modifications. Rapid cooling of the solution yields slender, bright yellow prisms of a labile form which, on warming in contact with the mother-liquor, slowly dissolves and orange prisms of the stable form separate. Both forms melt at 129°, transformation occurring before melting (Found : Cl, 33·4. $C_{13}H_6O_4N_4Cl_4$ requires Cl, 33·5%).

These ω-halogenated compounds are not affected by prolonged boiling with alcohol. When they are dissolved in benzene and ammonia gas is passed into the solution, they do not react at the ordinary temperature, but when the temperature is raised, rapid decomposition takes place and tarry products are formed, from which no definite compound has been isolated. Similar decomposition occurs when the ω-halogenated compounds are heated with a solution of anhydrous sodium acetate in acetic acid.

ω-*Bromo*-2 : 4-*dinitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone*.—This separated as an orange solid when 1 c.c. (2 mols.) of bromine in 10 c.c. of acetic acid was added to a suspension of 3 g. (1 mol.) of

2 : 4-dinitrobenzaldehyde-*p*-tolylhydrazone in 60 c.c. of acetic acid. It crystallises from acetic acid, in which it is easily soluble, in flattened orange prisms, m. p. 141° (Found : Br, 35·0. $C_{14}H_{10}O_4N_4Br_2$ requires Br, 34·9%).

6-*Nitro*-1 : 2-endo-3′-*bromo*-p-*tolylimino* - 3 - *keto* - 2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*oxide* separates as a bright yellow solid when ammonia gas is passed into a cold solution of ω-bromo-2 : 4-dinitrobenzaldehyde-3-bromo-*p*-tolylhydrazone in benzene. Rapidly crystallised from hot alcohol, in which it is sparingly soluble, it separates in bright yellow, rhombic tablets, explosion point 133° (Found : Br, 20·9. $C_{14}H_9O_4N_4Br$ requires Br, 21·2%).

When the explosive compound (2 g.) is boiled for several hours with alcohol (25 c.c.), it is converted into 6-*nitro*-1 : 2-endo-3′-*bromo*-p-*tolylimino*-3-*keto*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole*. This crystallises from acetic acid, in which it is easily soluble, in colourless prisms, m. p. 250° (Found : Br, 21·9. $C_{14}H_9O_3N_4Br$ requires Br, 22·1%).

ω-*Bromo*-2 : 4-*dinitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, prepared by the action of an excess of bromine upon 2 : 4-dinitrobenzaldehyde-*p*-tolylhydrazone, crystallises in two polymorphic forms. It separates from acetic acid, in which it is easily soluble, as the labile form in bright yellow prisms, which when allowed to stand in contact with the mother-liquor, slowly dissolve and the stable form separates in more compact orange prisms. Both forms melt at 152°, transformation occurring before melting (Found : Br, 44·5. $C_{14}H_9O_4N_4Br_3$ requires Br, 44·7%).

The action of ammonia upon its solution in benzene yields 6-*nitro*-1 : 2-endo-3′ : 5′-*dibromo*-p-*tolylimino*-3-*keto*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*oxide*. Rapidly crystallised from alcohol, in which it is sparingly soluble, it separates in bright yellow, six-sided plates, explosion point 142° (Found : Br, 35·0. $C_{14}H_8O_4N_4Br_2$ requires Br, 35·1%).

When boiled with alcohol for several hours, this explosive compound yielded 6-*nitro*-1 : 2-endo-3′ : 5′-*dibromo*-p-*tolylimino*-3-*keto*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole*, which crystallises from acetic acid, in which it is easily soluble, in colourless prisms, m. p. 279° (Found : Br, 36·1. $C_{14}H_8O_3N_4Br_2$ requires Br, 36·3%).

ω-*Chloro*-2 : 4-*dinitrobenzaldehyde*-3-*chloro*-p-*tolylhydrazone*, obtained by regulated chlorination of 2 : 4-dinitrobenzaldehyde-*p*-tolylhydrazone in acetic acid, crystallises from acetic acid, in which it is moderately easily soluble, as a felted mass of bright orange prisms, m. p. 170° (decomp.) (Found : Cl, 19·3. $C_{14}H_{10}O_4N_4Cl_2$ requires Cl, 19·2%), and ω-*chloro*-2 : 4-*dinitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone*, prepared by the action of an excess of chlorine upon a suspension of 2 : 4-dinitrobenzaldehyde-*p*-tolylhydrazone in acetic acid, in bright yellow prisms, m. p. 151° (decomp.) (Found Cl, 26·4. $C_{14}H_9O_4N_4Cl_3$ requires Cl, 26·4%).

Although explosive benz*iso*diazole oxides derived from these two ω-chloro-compounds were probably formed when ammonia was passed into their solutions in benzene, they could not be isolated in a state of purity from the tarry products of the reaction.

The following hydrazones, prepared in the course of this investigation, were converted into the respective ω-halogen compounds by the action of bromine and chlorine upon acetic acid suspensions of the hydrazones.

2 : 4-*Dinitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, bright red needles, m. p. 204° (Found : Br, 35·8. $C_{13}H_8O_4N_4Br_2$ requires Br, 36·0%), 2 : 4-*dinitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, bright red prisms, m. p. 207° (Found : Cl, 20·1. $C_{13}H_8O_4N_4Cl_2$ requires Cl, 20·0%), 2 : 4-*dinitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone*, crimson prisms, m. p. 179° (Found : Br, 21·2. $C_{14}H_{11}O_4N_4Br$ requires Br, 21·6%), 2 : 4-*dinitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, labile form, bright red prisms, stable form, purple prisms, m. p. 182° (Found : Br, 34·7. $C_{14}H_{10}O_4N_4Br_2$ requires Br, 34·9%), 2 : 4-*dinitrobenzaldehyde*-3-*chloro*-p-*tolylhydrazone*, dark red needles, m. p. 192° (Found : Cl, 10·7. $C_{14}H_{11}O_4N_4Cl$ requires Cl, 10·6%), and 2 : 4-*dinitrobenzaldehyde*-3 : 5-*dichloro*-p-*tolylhydrazone*, labile form, bright red prisms, stable form, purple prisms, m. p. 200° (Found : Cl, 19·1. $C_{14}H_{10}O_4N_4Cl_2$ requires Cl, 19·2%).

THE QUEEN'S COLLEGE LABORATORY,
OXFORD.
[*Received, September 2nd*, 1931.]