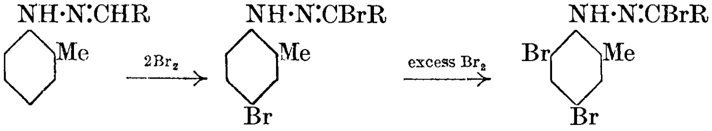
CCCLXXXVII.—*The Action of Bromine upon* o-*Tolylhydrazones and* o-*Nitrophenylhydrazones.*

By Frederick Daniel Chattaway and Arthur B. Adamson.

The action of bromine upon the *o*-tolylhydrazones of *o*-, *m*-, and *p*-nitrobenzaldehydes is very similar to its action upon the corresponding *p*-tolylhydrazones (J., 1930, 157, 843).

When an excess of bromine is used, substitution takes place in the ω-position and in the 3- and 5-positions in the *o*-tolylhydrazine nucleus. When only the calculated quantity (2 mols.) of bromine is used, the hydrogen atom in the ω-position and one in the 3-position in the *o*-tolylhydrazine nucleus are replaced. If less than this amount of bromine is used, the product, even under carefully regulated conditions, is chiefly a mixture of this dibromo-derivative and the unsubstituted hydrazone.

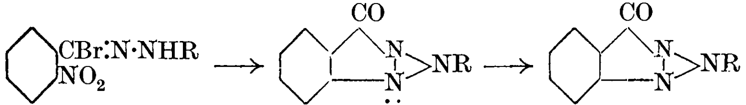


(R = *o*-, *m*-, or *p*-$C_6H_4{\cdot}NO_2$)

All these ω-bromo-compounds are very reactive. Those derived from *m*- and *p*-nitrobenzaldehyde-*o*-tolylhydrazones react with ammonia, yielding the corresponding hydrazidines, and when boiled with an acetic acid solution of sodium acetate, give the corresponding β-acetylhydrazides of *m*- or *p*-nitrobenzoic acid.

$$R{\cdot}NAc{\cdot}NH{\cdot}COR' \xleftarrow{CH_3{\cdot}CO_2Na} R{\cdot}NH{\cdot}N{:}CBrR' \xrightarrow{NH_3} R{\cdot}NH{\cdot}N{:}C(NH_2)R'$$

The ω-bromo-derivatives (I) of *o*-nitrobenzaldehyde-*o*-tolylhydrazone behave differently. They do not yield hydrazidines or β-acetylhydrazides but, when heated with alcohol or when treated with ammonia, readily lose hydrogen bromide and form the explosive *keto*endo*aryliminodihydrobenz*iso*diazole oxides* (II) (compare J., 1930, 159, 845), which may be reduced to the corresponding *benz*iso*diazoles* (III).



(I.) (II.) (III.)

($R = C_6H_3MeBr$ or $C_6H_2MeBr_2$)

Since all the ω-halogen derivatives of arylhydrazones containing a nitro-group in an ortho-position in the aldehyde nucleus lose hydrogen bromide or hydrogen chloride in this way, it was of interest to examine the behaviour of similar ω-halogen derivatives of hydrazones containing a nitro-group in an ortho-position in the hydrazine nucleus.

The action of bromine upon benzaldehyde-*o*-nitrophenylhydrazone and upon *o*-, *m*-, and *p*-nitrobenzaldehyde-*o*-nitrophenylhydrazones causes in each case substitution in the ω-position and in the *p*-position in the hydrazine nucleus.

The ω-bromo-derivatives thus obtained closely resemble the other ω-halogen compounds previously described. Those derived from benzaldehyde- and *m*- and *p*-nitrobenzaldehyde-*o*-nitrophenylhydrazones, when acted upon by ammonia, yield characteristic hydrazidines, and when boiled with an acetic acid solution of sodium acetate, are converted into corresponding β-acetylhydrazides.

The one derived from *o*-nitrobenzaldehyde-*o*-nitrophenylhydrazone again behaves similarly to other ω-halogen-*o*-nitrobenzaldehydehydrazones and yields an explosive benz*iso*diazole oxide.

The nitro-group therefore behaves like other groups substituted in the hydrazine nucleus and, like them, modifies only to a limited extent the properties of the derived compounds.

EXPERIMENTAL.

ω-*Bromo*-m-*nitrobenzaldehyde*-3-*bromo*-o-*tolylhydrazone*. — A solution of 2·1 c.c. (2 mols.) of bromine in 10 c.c. of acetic acid was slowly added to a suspension of 5 g. (1 mol.) of *m*-nitrobenzaldehyde-*o*-tolylhydrazone in 100 c.c. of acetic acid. A dark-coloured solution was formed from which ω-*bromo*-m-*nitrobenzaldehyde*-3-*bromo*-o-*tolylhydrazone* separated as a yellow solid. This crystallised from acetic acid, in which it was moderately easily soluble, in slender, bright yellow prisms, m. p. 164° (Found : Br, 38·6. $C_{14}H_{11}O_2N_3Br_2$ requires Br, 38·7%).

ω-*Bromo*-m-*nitrobenzaldehyde*-3 : 5-*dibromo*-o-*tolylhydrazone.*—To a suspension of 5 g. of *m*-nitrobenzaldehyde-*o*-tolylhydrazone in 100 c.c. of acetic acid, 4 c.c. (excess) of bromine were added and the mixture was heated for some time at 100° to complete the reaction. On cooling, ω-*bromo*-m-*nitrobenzaldehyde*-3 : 5-*dibromo*-o-*tolylhydrazone* separated as a bright yellow solid. It crystallises from acetic acid, in which it is moderately easily soluble, in bright yellow plates, m. p. 152° (Found : Br, 49·0. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%).

ω-*Bromo*-p-*nitrobenzaldehyde*-3-*bromo*-o-*tolylhydrazone.*—This was prepared in a similar manner by the action of bromine (2 mols.) upon *p*-nitrobenzaldehyde-*o*-tolylhydrazone (1 mol.). It crystallises in two polymorphic forms, separating from hot acetic acid, in which it is moderately easily soluble, in bright yellow needles of a labile form which, on standing in the mother-liquor, quickly dissolve and compact orange prisms of the stable form separate, m. p. 186° (Found: Br, 38·8. $C_{14}H_{11}O_2N_3Br_2$ requires Br, 38·7%).

ω-*Bromo*-p-*nitrobenzaldehyde*-3 : 5-*dibromo*-o - *tolylhydrazone.*—This was obtained by the action of a large excess of bromine upon *p*-nitrobenzaldehyde-*o*-tolylhydrazone. It crystallises from acetic acid, in which it is moderately easily soluble, in slender, bright yellow prisms, m. p. 175° (Found : Br, 48·7. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%).

The following hydrazidines were prepared by the action of 2 c.c. of concentrated aqueous ammonia upon a suspension of 2 g. of the ω-bromo-compound in 40 c.c. of alcohol. They are moderately easily soluble in alcohol and readily dissolve in concentrated hydrochloric acid, forming colourless solutions from which colourless unstable hydrochlorides may be obtained.

3-*Bromo*-o-*tolyl*-m-*nitrobenzenylhydrazidine* crystallises from alcohol in red plates, m. p. 149° (Found : Br, 22·8. $C_{14}H_{13}O_2N_4Br$ requires Br, 22·9%), 3 : 5-*dibromo*-o-*tolyl*-m-*nitrobenzenylhydrazidine* in yellow needles, m. p. 150° (Found : Br, 37·5. $C_{14}H_{12}O_2N_4Br_2$ requires Br, 37·4%), 3-*bromo*-o-*tolyl*-p-*nitrobenzenylhydrazidine* in very dark red prisms with a pronounced green reflex, m. p. 152° (Found: Br, 23·0. $C_{14}H_{13}O_2N_4Br$ requires Br, 22·9%), and 3 : 5-*dibromo*-o-*tolyl*-p-*nitrobenzenylhydrazidine* in orange-red needles, m. p. 171° (Found : Br, 37·4. $C_{14}H_{12}O_2N_4Br_2$ requires Br, 37·4%).

m-*Nitrobenz*-β-*acetyl*-3 : 5-*dibromo*-o-*tolylhydrazide.*—A mixture of ω-bromo-*m*-nitrobenzaldehyde-3 : 5-dibromo-*o*-tolylhydrazone (2 g.), anhydrous sodium acetate (2 g.), and 40 c.c. of acetic acid was boiled under reflux for 2 hours. The colourless solution so formed was poured into 400 c.c. of cold water; m-*nitrobenz*-β-*acetyl*-3 : 5-*dibromo*-o-*tolylhydrazide* then separated as a white solid. It crystallises from alcohol, in which it is moderately easily soluble, in colourless prisms, m. p. 176° (Found : Br, 33·6. $C_{16}H_{13}O_4N_3Br_2$ requires Br, 33·9%).

p-*Nitrobenz*-β-*acetyl*-3-*bromo*-o-*tolylhydrazide*, prepared similarly from ω-bromo-*p*-nitrobenzaldehyde-3-bromo-*o*-tolylhydrazone, crystallises from alcohol in colourless prisms, m. p. 195° (Found : Br, 20·5. $C_{16}H_{14}O_4N_3Br$ requires Br, 20·4%).

ω-*Bromo*-o-*nitrobenzaldehyde*-3-*bromo*-o-*tolylhydrazone*.—This separated in yellow crystals from the solution obtained by adding 2·1 c.c. of bromine (2 mols.) in 10 c.c. of acetic acid to a suspension of 5 g. of *o*-nitrobenzaldehyde-*o*-tolylhydrazone (1 mol.) in 50 c.c. of acetic acid. It decomposes when warmed with acetic acid but may be recrystallised from a mixture of benzene and high-boiling petroleum, from which it separates in yellow plates which darken in colour when exposed to light; m. p. 106° (Found: Br, 38·7. $C_{14}H_{11}O_2N_3Br_2$ requires Br, 38·7%).

When boiled for a few minutes with alcohol or when ammonia gas is passed into the solution in benzene, it loses hydrogen bromide and is converted into the explosive 3-*keto*-1 : 2-endo-3′-*bromo*-o-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*oxide*, which separates as a bright yellow solid. This crystallises from alcohol, in which it is moderately easily soluble, in bright yellow prisms, explosion point 151° (Found : Br, 24·4. $C_{14}H_{10}O_2N_3Br$ requires Br, 24·4%).

3-*Keto*-1 : 2-endo-3′-*bromo*-o-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole*.—Excess of a solution of stannous chloride in hydrochloric acid was added to a cooled solution of the explosive compound in a mixture of equal parts of acetic and concentrated hydrochloric acids. On dilution with water, 3-*keto*-1 : 2-endo-3′-*bromo*-o-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* separated as a pale yellow solid. It crystallises from dilute acetic acid in very pale yellow, hair-like needles, m. p. 181° (Found : Br, 25·3. $C_{14}H_{10}ON_3Br$ requires Br, 25·3%).

ω-*Bromo*-o-*nitrobenzaldehyde*-3 : 5-*dibromo*-o-*tolylhydrazone*.—This could not be prepared by the direct bromination of *o*-nitrobenzaldehyde-*o*-tolylhydrazone (compare J., 1930, 159), but was obtained as a yellow solid by the addition of 2·1 c.c. of bromine (1 mol.) to a suspension of 10 g. of *o*-nitrobenzaldehyde-3 : 5-dibromo-*o*-tolylhydrazone (1 mol.) in 100 c.c. of acetic acid. It crystallises from a mixture of benzene and high-boiling petroleum in yellow flattened prisms which rapidly darken on exposure to light; m. p. 137° (Found: Br, 49·0. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%).

When ammonia gas was passed into a solution of this compound in benzene, 3-*keto*-1 : 2-endo-3′ : 5′-*dibromo*-o-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*oxide* separated as a bright yellow solid. This crystallises from alcohol in bright yellow tablets, explosion point 145° (Found: Br, 39·1. $C_{14}H_9O_2N_3Br_2$ requires Br, 38·9%).

ω-*Bromobenzaldehyde*-4-*bromo*-2-*nitrophenylhydrazone*.—5 G. of benzaldehyde-*o*-nitrophenylhydrazone were suspended in 100 c.c. of warm acetic acid, and 3 c.c. of bromine (slight excess) added. On cooling, ω-*bromobenzaldehyde*-4-*bromo*-2-*nitrophenylhydrazone* separated as an orange solid. It crystallises from acetic acid, in which it is moderately easily soluble, in orange-yellow prisms, m. p. 166° (Found: Br, 40·3. $C_{13}H_9O_2N_3Br_2$ requires Br, 40·1%).

ω-*Bromo*-m-*nitrobenzaldehyde*-4-*bromo*-2-*nitrophenylhydrazone*, prepared similarly from *m*-nitrobenzaldehyde-*o*-nitrophenylhydrazone, crystallises from acetic acid as a felted mass of bright orange prisms, m. p. 201° (Found: Br, 35·8. $C_{13}H_8O_4N_4Br_2$ requires Br, 36·0%), and ω-*bromo*-p-*nitrobenzaldehyde*-4-*bromo*-2-*nitrophenylhydrazone*, obtained similarly from *p*-nitrobenzaldehyde-*o*-nitrophenylhydrazone, in bright orange prisms, m. p. 242° (Found: Br, 35·8%).

4-*Bromo*-2-*nitrophenylbenzenylhydrazidine*, prepared in the usual way, crystallises from alcohol, in which it is rather sparingly soluble, in almost black prisms with a green reflex; m. p. 188° (Found: Br, 24·0. $C_{13}H_{11}O_2N_4Br$ requires Br, 23·9%).

4-*Bromo*-2-*nitrophenyl*-m-*nitrobenzenylhydrazidine* is so sparingly soluble in the usual organic solvents that it cannot be crystallised from them; it crystallises from hot aniline, in which it is easily soluble, in dark brown needles, m. p. 245° (decomp.) (Found: Br, 20·7. $C_{13}H_{10}O_4N_5Br$ requires Br, 21·0%). The *hydrochloride* crystallises from a mixture of equal parts of alcohol and hydrochloric acid in pale yellow plates, m. p. 235° (decomp.) (Found: Cl, 8·2. $C_{13}H_{10}O_4N_5Br,HCl$ requires Cl, 8·5%).

4-*Bromo*-2-*nitrophenyl*-p-*nitrobenzenylhydrazidine* crystallises from a mixture of equal parts of aniline and alcohol as a felted mass of brown needles, m. p. 249° (Found: Br, 20·8. $C_{13}H_{10}O_4N_5Br$ requires Br, 21·0%).

m-*Nitrobenz*-β-*acetyl*-4-*bromo*-2-*nitrophenylhydrazide*, prepared from ω-bromo-*m*-nitrobenzaldehyde-4-bromo-2-nitrophenylhydrazone in the manner described for the *o*-tolylhydrazide, crystallises from alcohol in colourless shining plates, m. p. 173° (Found: Br, 18·7. $C_{15}H_{11}O_6N_4Br$ requires Br, 18·9%).

ω-*Bromo*-o-*nitrobenzaldehyde*-4-*bromo*-2-*nitrophenylhydrazone*.—Excess of bromine (4 c.c.) was added to a suspension of 5 g. of *o*-nitrobenzaldehyde-*o*-nitrophenylhydrazone in 100 c.c. of hot acetic acid and the mixture was heated until a clear orange solution was formed. On cooling, *ω-bromo-*o*-nitrobenzaldehyde-4-bromo-2-nitrophenylhydrazone* separated as an orange solid. It crystallises from acetic acid in deep orange prisms, m. p. 137° (Found : Br, 35·9. $C_{13}H_8O_4N_4Br_2$ requires Br, 36·0%).

When ammonia gas was passed into a solution of this compound in benzene, 3-*keto*-1 : 2-endo-4′-*bromo*-2′-*nitrophenylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*oxide* separated as a bright yellow solid. It crystallises from alcohol in bright yellow prisms, explosion point 142° (Found : Br, 21·8. $C_{13}H_7O_4N_4Br$ requires Br, 22·0%).

THE QUEEN'S COLLEGE LABORATORY,
OXFORD.

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