XXIV.—*The Action of Bromine upon the* p-*Tolylhydrazones of Benzaldehyde and of the Nitrobenzaldehydes.*

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BROMINE reacts very readily with the *p*-tolylhydrazones of benzaldehyde and of the nitrobenzaldehydes.

When 2 mols. of bromine are allowed to act upon 1 mol. of any one of the hydrazones, one atom of bromine enters the *p*-tolyl nucleus in an *o*-position with respect to the nitrogen atom and a second the ω-position.

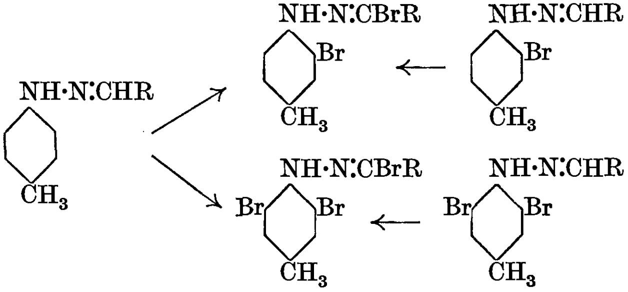
The action of 1 mol. of bromine upon 1 mol. of hydrazone yields a mixture of the oω-*dibromo*-derivative and unchanged hydrazone.

The *o*ω-dibromo-hydrazones are also obtained by the action of 1 mol. of bromine upon the hydrazones of 3-bromo-*p*-tolylhydrazine.

When a large excess of bromine is used, a third atom of bromine can be introduced into the remaining *o*-position in the *p*-tolyl nucleus. A larger excess of halogen is required to effect complete tribromination of benzaldehyde- and *p*-nitrobenzaldehyde-*p*-tolylhydrazones than of *m*-nitrobenzaldehyde-*p*-tolylhydrazone.

Compounds containing more than three atoms of bromine in the molecule cannot be obtained by the direct bromination of these hydrazones.

The course of the reactions may be represented thus :



In these ω-bromo-hydrazones the ω-bromine atom is very reactive. When heated with sodium acetate and acetic acid, they are converted into the corresponding β-*acetyl-hydrazides* of benzoic or nitrobenzoic acid :

$$R'\cdot NH\cdot N{:}CBrR \longrightarrow [R'\cdot NAc\cdot N{:}C(OH)R] \longrightarrow R'\cdot NAc\cdot NH\cdot COR$$

These hydrazides may be hydrolysed with aqueous-alcoholic hydrochloric acid, a substituted *p*-tolylhydrazine and an acid corresponding to the aldehyde forming the original hydrazone being produced. When only one *o*-bromine atom is present in the *p*-tolyl nucleus, the β-acetyl group of the hydrazide is removed by hydrolysis

$$C_6H_3MeBr\cdot NAc\cdot NH\cdot COR \longrightarrow C_6H_3MeBr\cdot NH\cdot NH_2 + R\cdot CO_2H + CH_3\cdot CO_2H,$$

but when both *o*-positions are occupied by bromine atoms, this acetyl group is protected and an α-acetylated dibromo-*p*-tolylhydrazine is obtained :

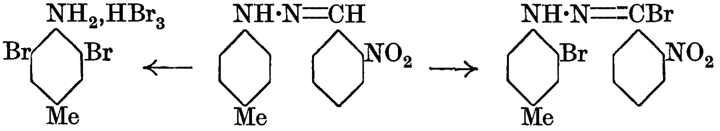
$$C_6H_2MeBr_2\cdot NAc\cdot NH\cdot COR \longrightarrow C_6H_2MeBr_2\cdot NAc\cdot NH_2 + R\cdot CO_2H.$$

The ω-bromo-hydrazones are converted into the corresponding *hydrazidines* by the action of concentrated aqueous ammonia :

$$R'\cdot NH\cdot N{:}CBrR \longrightarrow R'\cdot NH\cdot N{:}C(NH_2)R.$$

These are highly-coloured weak bases and form colourless crystalline hydrochlorides which are rather unstable and sparingly soluble in alcohol or dilute hydrochloric acid.

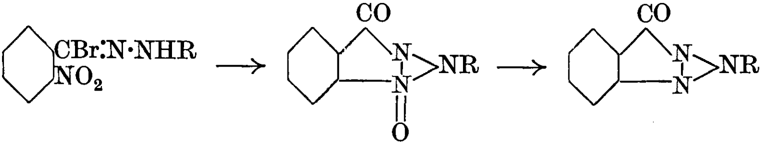
o-Nitrobenzaldehyde-*p*-tolylhydrazone does not behave in quite the same way as its isomerides, this hydrazone being rather less stable. When 2 mols. of bromine are used, an ω-*bromo*-compound is obtained in the normal manner. A larger proportion of bromine has no further action at the ordinary temperature, but when the temperature is allowed to rise, the hydrazone breaks down and the bright orange *perbromide* of 3 : 5-dibromo-*p*-toluidine is formed :



Although not produced by the direct bromination of *o*-nitrobenzaldehyde-*p*-tolylhydrazone, ω-*bromo*-o-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone* is readily obtained by brominating *o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, the ω-position being easily substituted.

The ω-bromo-compounds derived from *o*-nitrobenzaldehyde-*p*-tolylhydrazone have different properties from those derived from other *p*-tolylhydrazones and readily lose hydrogen bromide, forming the violently explosive keto*endo*aryliminodihydrobenz*iso*diazole oxides (I) (the so-called *iso*diazomethane derivatives) (J., 1925, **127**, 2407).

This loss takes place even on cautious recrystallisation from alcohol. When boiled for several hours with alcohol, the explosive compounds lose one atom of oxygen and form keto*endo*aryliminodihydrobenz*iso*diazole derivatives (II) (J., 1927, 323).



(I.) (II.)

If bromination is carried out in the presence of sodium acetate, the formation of the ω-bromo-compound and the elimination of hydrogen bromide from this take place successively and the explosive compound is obtained as the product of the one operation (J., 1925, **127**, 2408).

When *o*-nitrobenzaldehyde-*p*-tolylhydrazone is brominated in the presence of sodium acetate, no substitution occurs in the *p*-tolyl nucleus at the ordinary temperature, even when excess of bromine is used, and consequently the explosive compound formed under these conditions contains no halogen.

EXPERIMENTAL.

ω-*Bromo*-m-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone*.—To a suspension of 5 g. (1 mol.) of *m*-nitrobenzaldehyde-*p*-tolylhydrazone in 70 c.c. of acetic acid was slowly added a solution of 2·1 c.c. (2 mols.)

of bromine in 10 c.c. of acetic acid. The hydrazone dissolved, forming an orange solution from which ω-*bromo*-m-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone* separated as a bright yellow solid. After being washed with water, this crystallised from acetic acid, in which it was moderately easily soluble, in long, slender, bright yellow prisms, m. p. 145·5° (Found : Br, 39·1. $C_{14}H_{11}O_2N_3Br_2$ requires Br, 38·7%).

ω-*Bromo*-m-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone.*—A solution of 3·1 c.c. (3 mols.) of bromine in 10 c.c. of acetic acid was added to a suspension of 5 g. (1 mol.) of *m*-nitrobenzaldehyde-*p*-tolylhydrazone in 100 c.c. of the same solvent. The dibromo-compound separated as a bright yellow solid, which became paler as it was converted into the tribromo-compound. The mixture was heated on a water-bath to complete the reaction and cooled, and the solid collected. ω-*Bromo*-m-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone* crystallises from acetic acid, in which it is moderately easily soluble, in pale yellow prisms, m. p. 154·5° (Found : Br, 48·8. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%).

The same compound was easily prepared by the action of 1 mol. of bromine upon *m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone.

ω-*Bromo*-p-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone.*—This was obtained in a similar manner by the action of 2·1 c.c. (2 mols.) of bromine upon 5 g. (1 mol.) of *p*-nitrobenzaldehyde-*p*-tolylhydrazone suspended in 100 c.c. of acetic acid. It crystallised from acetic acid, in which it was moderately easily soluble, as a felted mass of bright orange needles, m. p. 176° (Found : Br, 39·1. $C_{14}H_{11}O_2N_3Br_2$ requires Br, 38·7%).

ω-*Bromo*-p-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone.*—When 3 mols. of bromine were used to 1 mol. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone, the product was almost exclusively ω-bromo-*p*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone. Not until 8 mols. of bromine were used was there any appreciable formation of the tribromo-compound and to ensure complete tribromination it was found advisable to use a still larger excess of bromine.

5 G. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone (1 mol.) were suspended in 100 c.c. of acetic acid, and 10 c.c. (excess) of bromine added with vigorous shaking. The mixture was heated on a water-bath for 30 minutes to complete the reaction. ω-*Bromo*-p-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, which separated as an orange solid, crystallised from acetic acid, in which it was easily soluble, in long orange-yellow prisms, m. p. 161° (Found : Br, 48·7. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%).

ω-*Bromobenzaldehyde*-3-*bromo*-p-*tolylhydrazone.*—This was obtained by the action of 2·5 c.c. (2 mols.) of bromine upon 5 g. (1 mol.) of benzaldehyde-*p*-tolylhydrazone suspended in 25 c.c. of acetic acid. It crystallised from hot alcohol, in which it was easily soluble, in long colourless needles, m. p. 74° (Found : Br, 43·8. $C_{14}H_{12}N_2Br_2$ requires Br, 43·5%).

ω-*Bromobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*.—This could be prepared from benzaldehyde-*p*-tolylhydrazone only by the use of a large excess of bromine. 10 C.c. of bromine were added to 5 g. of the hydrazone in 25 c.c. of acetic acid. The *product* crystallised from hot acetic acid, in which it was easily soluble, in long colourless needles, m. p. 106° (Found : Br, 53·8. $C_{14}H_{11}N_2Br_3$ requires Br, 53·7%).

m-Nitrobenz-β-acetyl-3-bromo-*p*-tolylhydrazide,

$$C_6H_3MeBr\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

was obtained as a white viscid solid which could not be made to crystallise. Its constitution was shown by hydrolysis with alcohol and hydrochloric acid; it then yielded acetic acid, *m*-nitrobenzoic acid, and 3-bromo-*p*-tolylhydrazine.

m-*Nitrobenz*-β-*acetyl*-3 : 5-*dibromo*-p-*tolylhydrazide* crystallised from alcohol in fine colourless prisms, m. p. 170° (Found : Br, 33·8. $C_{16}H_{13}O_4N_3Br_2$ requires Br, 33·9%). On hydrolysis it yielded *m*-nitrobenzoic acid and α-acetyl-3 : 5-dibromo-*p*-tolylhydrazine. The latter was identified by conversion into its *m*-nitrobenzaldehydehydrazone, which crystallised from acetic acid in colourless shining plates, m. p. 218°, and was identical with the compound prepared by the action of acetic anhydride upon *m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone.

p-*Nitrobenz*-β-*acetyl*-3-*bromo*-p-*tolylhydrazide* crystallised from alcohol in colourless prisms, m. p. 173° (Found : Br, 20·6. $C_{16}H_{14}O_4N_3Br$ requires Br, 20·4%). On hydrolysis it yielded acetic acid, *p*-nitrobenzoic acid, and 3-bromo-*p*-tolylhydrazine.

p-*Nitrobenz*-β-*acetyl*-3 : 5-*dibromo*-p-*tolylhydrazide* crystallised from alcohol in colourless prisms, m. p. 183° (Found : Br, 33·7. $C_{16}H_{13}O_4N_3Br_2$ requires Br, 33·9%). On hydrolysis it yielded *p*-nitrobenzoic acid and α-acetyl-3 : 5-dibromo-*p*-tolylhydrazine.

Benz-β-*acetyl*-3 : 5-*dibromo*-p-*tolylhydrazide* crystallised from alcohol in colourless prisms, m. p. 190° (Found : Br, 37·4. $C_{16}H_{14}O_2N_2Br_2$ requires Br, 37·5%). On hydrolysis it yielded benzoic acid and α-acetyl-3 : 5-dibromo-*p*-tolylhydrazine.

The following hydrazidines were prepared by the action of 5 c.c. of concentrated aqueous ammonia upon a suspension of 5 g. of the ω-bromo-compounds in 50 c.c. of alcohol.

3-*Bromo*-p-*tolyl*-m-*nitrobenzenylhydrazidine*,

$$C_6H_3MeBr\cdot NH\cdot N{:}C(NH_2)\cdot C_6H_4\cdot NO_2,$$

crystallises from alcohol in red prisms, m. p. 136° (Found : Br, 22·8. $C_{14}H_{13}O_2N_4Br$ requires Br, 22·9%). It forms a hydrochloride which crystallises from alcohol and hydrochloric acid in colourless plates, m. p. 230° (decomp.).

3 : 5-*Dibromo*-p-*tolyl*-m-*nitrobenzenylhydrazidine* crystallises from alcohol in yellow prisms, m. p. 151° (Found : Br, 37·6. $C_{14}H_{12}O_2N_4Br_2$ requires Br, 37·4%), 3-*bromo*-p-*tolyl*-p-*nitrobenzenylhydrazidine* in deep purple prisms, m. p. 155° (Found : Br, 22·8. $C_{14}H_{13}O_2N_4Br$ requires Br, 22·9%), and 3 : 5-*dibromo*-p-*tolyl*-p-*nitrobenzenylhydrazidine* in orange-yellow rhombic plates, m. p. 145° (Found : Br, 37·2. $C_{14}H_{12}O_2N_4Br_2$ requires Br, 37·4%).

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

ω-*Bromo*-o-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone.*—2·1 C.c. of bromine (2 mols.) were added to 5 g. (1 mol.) of *o*-nitrobenzaldehyde-*p*-tolylhydrazone suspended in 50 c.c. of acetic acid. A dark brown solution was formed from which ω-*bromo*-o-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone* slowly separated in yellow crystals. Recrystallised from acetic acid, it formed yellow rhombic plates, m. p. 105° (decomp.). The recrystallisation must be rapidly effected, since the compound quickly decomposes when heated with acetic acid (Found : Br, 38·3. $C_{14}H_{11}O_2N_3Br_2$ requires Br, 38·7%).

The compound cannot be recrystallised from alcohol, as it then loses hydrogen bromide and is converted into the highly explosive 3-*keto*-1 : 2-endo-3′-*bromo*-p-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benzisodiazole* 1-*oxide* (I ; $R = C_6H_3MeBr$). This crystallises from alcohol in bright yellow, rhombic plates, explosion point 139° (Found : Br, 24·0. $C_{14}H_{10}O_2N_3Br$ requires Br, 24·1%).

When 2 g. of the explosive compound were boiled for 2 hours under reflux with 25 c.c. of alcohol, a brown solution was obtained which, on cooling, deposited 3-*keto*-1 : 2-endo-3′-*bromo*-p-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benzisodiazole.* This crystallised from alcohol in pale yellow prisms, m. p. 166° (Found : Br, 25·2. $C_{14}H_{10}ON_3Br$ requires Br, 25·3%).

The Action of Excess of Bromine upon o-*Nitrobenzaldehyde*-p-*tolylhydrazone.*—5 G. of the hydrazone were suspended in 100 c.c. of acetic acid, and 10 c.c. of bromine added. A dark brown solution was formed from which, on shaking and cooling, 3 : 5-*dibromo*-p-*toluidine perbromide* separated. This, recrystallised from a 16% solution of bromine in acetic acid, formed bright orange prisms, m. p. 134° (decomp.) (Found : Br, 78·2. $C_7H_8NBr_5$ requires Br, 79·0%).

This perbromide is fairly stable in the solid state and can be dried at 100° with only slight decomposition. It loses bromine and hydrogen bromide on being washed with water or kept for several weeks over lime in a vacuum desiccator. It is easily soluble in acetic acid and when the solution is boiled, bromine is evolved; on cooling, 3 : 5-dibromo-*p*-toluidine separates in colourless needles, m. p. 73°.

The perbromide was also prepared by the action of an excess of bromine upon a solution of *p*-toluidine in acetic acid.

ω-*Bromo*-o-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone* was obtained by the action of 1 mol. of bromine upon *o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone. It decomposes very readily when warmed with acetic acid, but can be recrystallised from a mixture of benzene and high-boiling petroleum, from which it separates in pale yellow prisms, m. p. 123° (decomp.) (Found : Br, 48·3. $C_{14}H_{10}O_2N_3Br_3$ requires Br, 48·8%).

When boiled for a few minutes with alcohol, it loses hydrogen bromide and is converted into the highly explosive 3-*keto*-1 : 2-endo-3′ : 5′-*dibromo*-p-*tolylimino*-2 : 3-*dihydro*-1 : 2-*benz*iso*diazole* 1-*oxide*, which crystallises from alcohol in bright yellow, rhombic plates, explosion point 167° (Found : Br, 39·1. $C_{14}H_9O_2N_3Br_2$ requires Br, 38·9%).

The explosive compound (2 g.), when boiled with 25 c.c. of alcohol for 6 hours, gives the corresponding *endo*aryliminobenz*iso*diazole derivative, which crystallises from alcohol in yellow rhombic plates, m. p. 190° (decomp.).

Bromination of o-*Nitrobenzaldehyde*-p-*tolylhydrazone in the Presence of Sodium Acetate.*—5 G. of this hydrazone and 5 g. of anhydrous sodium acetate were suspended in 50 c.c. of acetic acid, and 1·1 c.c. of bromine (1 mol.) added. A dark solution was formed from which crystals of the explosive 3-keto-1 : 2-*endo*-*p*-tolylimino-2 : 3-dihydro-1 : 2-benz*iso*diazole 1-oxide slowly separated. It crystallised from alcohol in bright yellow prisms, explosion point 143°. The same compound, containing no halogen, was obtained even when 2 or 3 mols. of bromine were used at the ordinary temperature.

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