

L.—*The Nitration of s-Trihalogen Anilines.*

By K. J. P. ORTON.

IN the hope of possibly throwing further light on the process of substitution in anilines, I have studied the carefully regulated action of nitric acid on those anilines in which chlorine or bromine occupies the positions 2, 4, and 6 in the benzene nucleus relatively to the amino-group; namely, those positions into which a substituting group most readily finds its way. That the nitro-group is capable of displacing bromine, at least, from these positions in phenols has been shown by Armstrong and Harrow (*Trans.*, 1876, **30**, 448), who obtained 2:6-dibromo-4-nitrophenol and 2-bromo-4:6-dinitrophenol from *s*-tribromophenol. Thiele and Eichwede (*Annalen*, 1900, **311**, 363), by the action of amyl nitrite on this phenol, replaced, not the para-, but an ortho-bromine atom, 2:4-dibromo-6-nitrophenol being thus formed. Further, from *s*-tribromoaniline by the action of nitric acid, Losanitsch (*Ber.*, 1882, **15**, 474) obtained 2:6-dibromo-4-nitroaniline.

In their behaviour \* with nitric acid (diluted with acetic acid), the anilines investigated divide themselves sharply into two classes; (1) anilines with a bromine atom in the para-position relatively to the amino-group, *s*-tribromoaniline, 2-chloro-4:6-dibromoaniline, and 2:6-dichloro-4-bromoaniline, (2) anilines with a chlorine atom in the para-position relatively to the amino-group, 4-chloro-2:6-dibromoaniline, 2:4-dichloro-6-bromoaniline, and *s*-trichloroaniline. The crystalline aniline nitrate initially formed dissolves on heating, producing solutions of characteristically different colours in the two classes; when a bromine atom is in the para-position, the solution is finally *orange-yellow*; when a chlorine atom is in the para-position, the solution is finally *crimson* (see experimental part). From anilines of the first class, bromine is evolved, and there is obtained a product which possesses a nitro-group in the para-position instead of an atom of bromine. The amount of the dihalogen-nitroaniline represents about 75 per cent. of the original *s*-trihalogen aniline. From anilines of the second class, neither chlorine nor bromine is evolved, nor is an aniline obtained in which a nitro-group has replaced the *p*-chlorine atom. Further, in no case was the replacement of an *o*-bromine atom observed. In this respect, the behaviour of these anilines with nitric acid is analogous to their behaviour with acetylchloroamino-

\* In these experiments, an investigation of the *final* products of the action of nitric acid on these anilines was not intended. This has been done in the case of *s*-tribromoaniline by Losanitsch (*loc. cit.*), dibromodinitromethane, tetrabromobenzene, bromanil, oxalic and picric acids being isolated. Doubtless, these similarly constituted substances undergo degradation in much the same manner.

benzenes, when only the *p*-bromine atom is replaced by chlorine (Trans, 1901, 79, 822). From 2 : 3 : 4 : 6-tetrabromoaniline in which one meta-position is also occupied by bromine, only 2 : 3 : 6-tribromo-4-nitroaniline is formed, although replacement of an *o*-bromine atom might be expected from analogy with the action of chlorine, bromine, and nitric acid on meta-substituted anilines, and anilides, which always yield a considerable proportion of the ortho-derivative.

Lastly, in no case was hydrogen in the meta-position replaced by the nitro-group under the conditions employed.

During the period of heating of the acetic acid solution of the aniline and nitric acid (aniline nitrate), there is present a small amount of the nitroamine of the aniline, thus from *s*-trichloroaniline is obtained 1-nitroamino-2 : 4 : 6-trichlorobenzene,  $C_6H_2Cl_3 \cdot NH \cdot NO_2$ . These nitroamines would appear to be formed in this reaction by the elimination of water from the aniline nitrate, just as aniline acetates on heating lose water and become acetyl-amino-derivatives.\* At no period of the experiment did the nitroamine amount to more than 5—10 per cent. of the aniline used. As under the conditions, namely, heating in acetic acid solution in the presence of a mineral acid, the nitroamines themselves undergo change, no great quantity can at *any one time* be present. When a nitroamine in which a bromine atom is in the para-position relatively to the amino-group is dissolved in acetic acid to which one or two drops of sulphuric acid have been added, the nitro-group is transferred to the nucleus and displaces the *p*-bromine atom; † whereas a nitroamine with a chlorine atom in the para-position, under identical treatment, yields no nitroaniline but gives a deep crimson solution, similar in appearance to that obtained directly from the aniline and nitric acid. From the crimson solutions from both sources, red *substances* can be isolated in very small amount; these have not yet been obtained in sufficient quantity for a thorough analysis or investigation. Experiments are now in progress having as their object the preparation of these compounds.

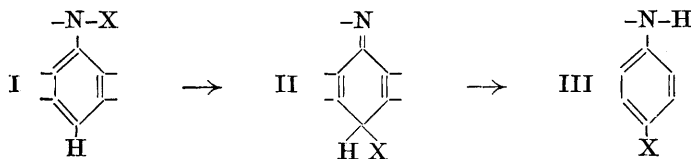
Up to the point of the formation of the nitroamine from the aniline nitrate, there is a complete parallelism in the action of nitric acid on these two classes of *s*-trihalogen anilines (namely, the one class with a *p*-bromine atom and the other with a *p*-chlorine atom); as the nitroamines in each class are under an identical influence, the tendency

\* So far as I am aware *s*-trisubstituted nitroaminobenzenes have not hitherto been prepared; nor have nitroaminobenzenes been obtained by the direct action of nitric acid on anilines. These substances were prepared by Bamberger, Pinnow, and others, by oxidation of alkaline solutions of benzenediazotates, by the action of nitrogen pentoxide on anilines in chloroform solution, and by adding the dry aniline nitrate to acetic anhydride.

† By a similar means, Bamberger brought about the transformation of nitroaminobenzenes into *o*- and *p*-nitroanilines.

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in each case must be for the nitro-group to replace the *p*-halogen atom. It was suggested (*loc. cit.*) that in the transformation of the acetylchloro- and acetylchloro-aminobenzenes (I), into *o*- and *p*-chloro- and bromo-acetanilides (III), an iminoquinone (II) formed a transient intermediate stage.



From this point of view (which was originally foreshadowed by Lapworth, *Trans.*, 1898, **73**, 450), it would be expected that both with a *p*-bromo-, and a *p*-chloro-aniline the nitroamine would pass into an iminoquinone in which both the nitro-group and the bromine atom are attached to the same carbon atom; in the one case, the bromine is eliminated, and a *p*-nitroaniline produced; in the other case, the chlorine is not eliminated, but some derivative of the iminoquinone type is formed. It is possible that the red substance above mentioned is such a derivative.

It is open to doubt whether, in the ordinary nitration of anilides, the stages observed in the action of nitric acid on these *s*-trihaloanilines actually occur; the nitroamino-derivatives of the anilides have never been obtained; it is possible that the nitrating agent reacts directly with an acyliminoquinone (compare Lapworth, *Trans.*, 1901, **79**, 1267; Thiele, *Annalen*, 1899, **303**, 87).

## EXPERIMENTAL.

*Reaction of Nitric Acid with s-Tribromoaniline and the s-Dihaloanilines.*

*s*-Tribromoaniline.—Losanitsch (*loc. cit.*) heated *s*-tribromoaniline with nitric acid diluted with acetic acid and obtained 2:6-dibromo-4-nitroaniline, but he does not state the proportion of nitric acid used, or give the details of the experiment.

Five grams of the aniline were covered with 50 c.c. of glacial acetic acid (m. p. 15.2°) a quantity insufficient to completely dissolve this base at the ordinary temperature. To the solution containing some solid in suspension were added 7—8 c.c. of nitric acid (sp. gr. 1.5), which was colourless and free from nitrous acid\*; a crystalline precipitate of the aniline nitrate immediately separated. The mixture was

\* In the presence of nitrous acid, diazotisation took place to a large extent, confusing the direct interaction of the aniline and nitric acid.

now heated on the water-bath, when the nitrate dissolved, forming a solution which rapidly became deep orange, and then lighter in tint and more yellow than orange in colour. After about 20—30 minutes, the evolution of bromine had become very obvious, and on cooling 2:6-dibromo-4-nitroaniline (3·5 grams) separated in a nearly pure state. It melted at 205°; its acetyl derivative melted at 235°, and the acetylchloroamino-derivative at 109—110°; the last named contained Cl as :NCl = 9·33 per cent. (instead of 9·51 per cent.). A careful search was made in the mother liquors for 2:4-tribromo-6-nitroaniline, and for 2:4:6-tribromo-3-nitroaniline. The mother liquors were precipitated by water, and the solid thus obtained extracted with aqueous sodium carbonate (to remove any nitroamino-derivative), and then distilled in steam. The fact that the distillate was colourless indicated the absence of any *o*-nitroaniline (this vol., p. 496). Small amounts of *s*-tribromoaniline were alone found.

*1-Nitroamino-2:4:6-tribromobenzene*,  $C_6H_2Br_3 \cdot NH \cdot NO_2$ .—In order to isolate the nitroamine, the acetic acid solution at any time during the period of 5 to 15 minutes from the beginning of heating was poured on to ice; the yellow solid which separated was collected and washed free from acid. It was then extracted with cold dilute aqueous sodium carbonate. The remaining yellow solid, consisting mainly of unchanged *s*-tribromoaniline and 2:6-dibromo-4-nitroaniline, was filtered from the alkaline liquor, from which, on addition of a mineral acid, the nitroamine separated as a white precipitate. From 10 grams of aniline, 0·4 gram of nitroamine was obtained. It is readily soluble in all organic solvents except petroleum; from dilute acetic acid or dilute alcohol, it crystallises in flesh-coloured needles. In cold water, the nitroamine is insoluble; 1500 c.c. of hot water are required to dissolve 1 gram; from this solution, it crystallises in slender, long, often curved, flesh-coloured needles, melting and decomposing at 143—144° with evolution of oxides of nitrogen:

0·1634 gave 0·246 AgBr. Br = 64·04.

$C_6H_2O_2N_2Br_3$  requires Br = 63·98 per cent.

This substance is acid to litmus; on addition of aqueous sodium hydroxide to an aqueous solution of its sodium salt, the latter separates in pearly white plates:

0·3444 gave 0·053  $Na_2SO_4$ . Na = 5·62.

$C_6H_2O_2N_2Br_3Na$  requires Na = 5·79 per cent.

When the nitroamine is dissolved in acetic acid to which a drop of sulphuric acid has been added, the colour of the solution becomes orange, and after some time 2:6-dibromo-4-nitroaniline separates.

*2-Chloro-4:6-dibromoaniline* was treated in a perfectly similar

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manner with nitric acid. 2-Chloro-6-bromo-4-nitroaniline was the main product; it melted at  $177^{\circ}$ , yielded an acetyl derivative melting at  $221^{\circ}$  and was in every respect identical with the synthetical product (this vol., p. 496). The nitroamine obtained in this case melted and decomposed at  $137^{\circ}$ ; as only a small quantity of the aniline was used, there was not sufficient of the nitroamine for analysis. From 2:6-dichloro-4-bromoaniline, 2:6-dichloro-4-nitroaniline (m. p.  $188^{\circ}$ ) was obtained; its acetyl derivative melted at  $210-211^{\circ}$ . The nitroamine was only obtained in very small quantity, and melted and decomposed at  $136-137^{\circ}$ .

*Reaction of Nitric Acid with s-Trichloroaniline and with s-Dihalogen-p-chloroanilines.*

*s-Trichloroaniline.*—Five grams of the aniline were dissolved in 50 c.c. of acetic acid and 8 c.c. of pure nitric acid added, whereupon the nitrate of the base immediately crystallised out. On heating the mixture on the water-bath, the solution became purple as the nitrate dissolved, and then rapidly changed to magenta, which more slowly became crimson. No chlorine was evolved. After 30 minutes' heating, a very small quantity (0.05 gram) of hexachloroazobenzene separated; on recrystallisation from chloroform and alcohol, it was obtained in long, lustrous, red needles, melting at  $188^{\circ}$ , identical in melting point, solubility, &c., with the specimen previously prepared by the action of acetylchloroamino-2:4-dichlorobenzene on *s*-trichloroaniline (Trans., 1901, 79, 467).

1-Nitroamino-2:4:6-trichlorobenzene,  $C_6H_2Cl_3 \cdot NH \cdot NO_2$ , was isolated in a manner completely similar to that used for the tribromoderivative, and resembles the latter very closely in appearance and properties. It crystallises from much hot water in long, flesh-coloured needles, melting and decomposing at  $135^{\circ}$ :

0.1402 gave 14.2 c.c. of moist nitrogen at  $17^{\circ}$  and 775 mm.  $N = 11.93$ .  
0.1486 „ 0.266 AgCl.  $Cl = 44.26$ .

$C_6H_3O_2N_2Cl_3$  requires  $Cl = 44.06$ ;  $N = 11.63$  per cent.

Its sodium salt crystallises in glistening plates, and is very soluble in water or alcohol.

A solution in glacial acetic acid to which one drop of sulphuric acid has been added soon becomes crimson in colour. At the ordinary temperature, the nitroamine changes only slowly, but on heating on the water-bath it rapidly decomposes, the colour of the solution quickly deepening.

To isolate any substance or substances which may have been formed, the crimson solution obtained either from the nitroamine, or directly by

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the action of nitric acid on an acetic acid solution of the aniline, was poured on to ice; the red solid was collected, washed free from acid, and extracted with aqueous sodium carbonate to remove any nitroamine. The solid was now fractionally crystallised from petroleum (b. p.  $50-80^{\circ}$ ); finally, a small amount of a *substance* was obtained, which crystallised in elongated, brilliant red plates melting and decomposing at  $143^{\circ}$ , and very soluble in the usual solvents. It dissolved in concentrated sulphuric acid with a reddish-brown coloration; on addition of water and on warming, the solution became colourless. A solution in acetone was immediately reduced by zinc dust and acetic acid with the production of a colourless substance, crystallising in needles from petroleum melting at  $188^{\circ}$ . Sufficient of these substances (0.2 gram from 20 grams of aniline) could not be obtained by the above method for a complete investigation.

2 : 4-*Dichloro-6-bromoaniline* and 4-*chloro-2 : 6-dibromoaniline* behave in a completely analogous manner; from each, nitroamines were obtained, decomposing at nearly the same temperature,  $137-138^{\circ}$ . Azobenzenes were formed in small amount. From the red solutions, obtained as in the case of *s*-trichloroaniline, no attempt was made to isolate the corresponding red substances.

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