CV.—*Chloroamines as Halogenating Agents. Iodination by a Chloroamine and an Iodide.*

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CHLORINE, bromine chloride, and iodine chloride are respectively formed by the reaction between hydrogen chloride, hydrogen bromide and hydrogen iodide and a chloroamine, according to the equation $>NCl + HX = >NH + XCl$; and a method of chlorination based on the first of these reactions has already been developed (Orton and King, J., 1911, **99**, 1185: Orton and Bradfield, J., 1927, 986). It is now shown that by utilisation of the third reaction (Chattaway, J., 1905, **87**, 145; Orton and W. J. Jones, P., 1909, **25**, 306) the preparation of an acetic acid solution of iodine chloride, which has long been in use as an iodinating agent, is very greatly facilitated, and a method of iodination involving the reaction between dichloramine-T and hydrogen iodide, or, better, sodium iodide, has been applied in the first instance to the preparation of typical iodoanilines, some of them not hitherto described.

EXPERIMENTAL.

Preparation and Use of the Iodinating Reagent.—The reagent may be prepared by slowly adding to an acetic acid solution of dichloramine-T the calculated amount of hydrogen iodide, also dissolved in acetic acid. The first action of hydrogen iodide liberates iodine : $>NCl + 2HI \longrightarrow >NH + HCl + I_2$. The hydrogen chloride formed reacts with another molecule of the chloroamine, liberating chlorine, which combines with the iodine to give a solution with the characteristic orange-yellow colour of iodine chloride. An alternative procedure is to add the calculated quantity of hydrogen chloride to an acetic acid solution of dichloramine-T, containing in solution and suspension the required amount of iodine. It was hoped that by employing a small quantity of hydrogen chloride, a constant low concentration of iodine chloride could be maintained (compare Orton and King, Orton and Bradfield, *locc. cit.*), the acid being re-formed in the substitution by iodine chloride. However, chlorine is produced in the system and even in the presence of a considerable excess of iodine, some chlorination occurred.

Finally, it was found most satisfactory to employ the iodide, not as hydrogen iodide, but as the finely powdered sodium salt, which is added in small amounts, with shaking, to a solution of dichloramine-T in glacial acetic acid, little or no liberation of iodine occurring. It should be noted that the reduction in acidity consequent upon the presence of sodium or potassium ions affects favourably the rate of iodination of anilines.

The general method of employment of the solution of iodine chloride, prepared as above, is to add it slowly to a solution of the aniline in acetic acid. With the simpler anilines, the calculated quantity of the reagent is used, and the reaction proceeds at the ordinary temperature. With substituted anilines, an excess of the reagent and a water-bath temperature are frequently advantageous. The iodo-compound is precipitated by dilution.

The Action of the Reagent on Aniline, 2 : 4-*Dichloroaniline and* 2-*Chloro*-4-*bromoaniline.*—Aniline, with one equivalent of the reagent yields *p*-iodoaniline, with three equivalents, tri-iodoaniline. 2 : 4 - Dichloro-6-iodoaniline (Körner and Contardi, *Atti R. Accad. Lincei*, 1913, **22**, 823; Dains, Vaughan, and Janney, *J. Amer. Chem. Soc.*, 1918, **40**, 930), obtained from 2 : 4-dichloroaniline and two equivalents of the reagent, forms an *acetyl* derivative,* thick needles, m. p. 198—199° (Found : X,† 59·7. $C_8H_6ONCl_2I$ requires X, 60·0%). In a similar way, 2-chloro-4-bromoaniline yields 2-*chloro*-4-*bromo*-6-*iodoaniline* as colourless needles, m. p. 95—96° (Found : X, 74·0. $C_6H_4NClBrI$ requires X, 72·9%). The *acetyl* derivative forms colourless needles, m. p. 213° (Found : X, 64·8. $C_8H_6ONClBrI$ requires X, 64·8%). No iodination of 2 : 4-dichloroaniline could be detected after 60 hours' heating at 100° with iodine, in the presence or absence of sodium acetate.

Action of the Reagent on Acetanilide.—On heating acetanilide for 15 minutes with two equivalents of the reagent, *p*-iodoacetanilide is produced (yield, 80%). Prolonged heating gives a poor yield of di-iodo-derivative. The bromination of *p*-iodoacetanilide with double the calculated quantity of bromine, in 70% acetic acid, for 20 minutes at 70°, yields 2-*bromo*-4-*iodoacetanilide* as rhombs, m. p. 143° (Found : X, 61·6. C_8H_7ONBrI requires X, 60·9%). Hydrolysis with 10% aqueous-alcoholic hydrochloric acid, or 10% alcoholic sodium hydroxide, gives 2-*bromo*-4-*iodoaniline*, which crystallises as thick needles, m. p. 75—76° (Found : X, 69·5. C_6H_5NBrI requires X, 69·5%). Slight displacement of the iodine occurs during hydrolysis.

2-*Chloro*-6-*bromo*-4-*iodoaniline* is prepared by chlorination of the above aniline with dichloramine-T and hydrochloric acid. It crystallises from alcohol in fine white needles, m. p. 113—114° (Found : X, 71·6. $C_6H_4NClBrI$ requires X, 72·9%). The *acetyl*

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* Prepared by the method of Smith and Orton (J., 1908, **93**, 1249), which has proved successful with all the *s*-trisubstituted anilines described in this paper.

† In all the analyses given in this paper, X denotes mixed halogens.

derivative crystallises from alcohol in fine white needles, m. p. 221° (Found: X, 65·1. $C_8H_6ONClBrI$ requires X, 64·8%). The third *s*-chlorobromoiodoaniline, isomeric with the two described in the foregoing, was prepared by Körner and Contardi (*loc. cit.*).

Action of the Reagent on o-*Nitroaniline.*—An 80% yield of 4-iodo-2-nitroaniline, m. p. 122°, is obtained by heating *o*-nitroaniline with 1½ equivalents (50% excess) of the reagent for 20—30 minutes. Further heating with an additional quantity of the reagent yields the 4 : 6-di-iodo-derivative (compare Brenans, *Compt. rend.*, 1902, **135**, 177; *Bull. Soc. chim.*, 1902, **27**, 963). Chlorination of 4-iodo-2-nitroaniline with dichloramine-T and hydrochloric acid gives 2-*chloro*-4-*iodo*-6-*nitroaniline* as orange needles, m. p. 124° (Found: X, 54·7. $C_6H_4O_2N_2ClI$ requires X, 54·4%); the *acetyl* derivative forms straw-coloured needles, m. p. 227° (Found: X, 48·2. $C_8H_6O_3N_2ClI$ requires X, 47·7%) : and bromination in acetic acid in the cold gives 2-*bromo*-4-*iodo*-6-*nitroaniline* as orange needles, m. p. 117—118° (Found: X, 60·7. $C_6H_4O_2N_2BrI$ requires X, 60·4%), the *acetyl* derivative of which forms straw-coloured needles, m. p. 222° (Found: X, 54·0. $C_8H_6O_3N_2BrI$ requires X, 53·8%).

Action of the Reagent on 4-*Chloro*-2-*nitro- and* 4-*Bromo*-2-*nitro-anilines.*—One equivalent (4 g.) of 4-chloro-2-nitroaniline, prepared by chlorinating *o*-nitroaniline by the usual chloroamine method, was heated for 3 hours on the water-bath with 2 equivalents of the reagent. On cooling, 0·85 g. of orange needles separated, m. p. 136—137°. Gradual dilution gave 1·6 g., m. p. 127°, and 1·2 g., m. p. 80—90°, this impure product being purified through the *acetyl* derivative described below. 4-*Chloro*-2-*iodo*-6-*nitroaniline* forms orange needles, m. p. 137—138° (Found: X, 54·2. $C_6H_4O_2N_2ClI$ requires X, 54·4%), diazotisation of which with amyl nitrite in alcoholic solution yielded 3-chloro-5-iodo-1-nitrobenzene, m. p. 70° (Körner and Contardi, *loc. cit.*). 4-*Chloro*-2-*iodo*-6-*nitroacetanilide* crystallises from alcohol in very pale straw-coloured needles, m. p. 207° (Found: X, 47·1. $C_8H_6O_3N_2ClI$ requires X, 47·7%).

The iodination in a similar manner of 4-bromo-2-nitroaniline, obtained by bromination of *o*-nitroaniline in acetic acid, in the presence of sodium acetate, gave 4-*bromo*-2-*iodo*-6-*nitroaniline* as orange needles, m. p. 146—147° (Found: X, 59·8. $C_6H_4O_2N_2BrI$ requires X, 60·4%). The *acetyl* derivative forms pale yellow needles, m. p. 215° (Found: X, 54·0. $C_8H_6O_3N_2BrI$ requires X, 53·8%). Diazotisation of the aniline in ethyl alcohol with amyl nitrite gave 3-bromo-5-iodo-1-nitrobenzene, m. p. 97° (Körner and Contardi, *loc. cit.*).

The description of the above anilines completes the list of *s*-trisubstituted anilines in which one of the positions 2 : 4 : 6 is occupied by the nitro-group and the other two are filled by chlorine, bromine, or iodine atoms.

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