

XLIX.—*The Action of Acetylchloro- and Acetylbromo-aminobenzenes on Amines and Phenylhydrazine.*

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THE action of chloro- and bromo-amino-derivatives on other compounds has been but little investigated, chiefly owing to the fact that these substances either have been prepared with difficulty, or do not easily lend themselves to manipulation. Some of the acetylchloro- and acetylbromo-aminobenzenes recently described by us are, however, extremely easily obtained in a pure and dry state, and can be used for studying the reactions of this group with other classes of compounds.

In this paper we propose to consider the action of these substituted aminobenzenes on amines and phenylhydrazine.

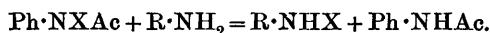
The earliest experiments of this nature were those of Hofmann (*Ber.*, 1882, 15, 407), who found that *s*-tribromoaniline was formed in the action of acetbromoamide on aniline.

Bender later (*Ber.*, 1886, 19, 2272) obtained 2 chloro-*p*-nitroaniline by the action of acetylchloroaminobenzene on *p*-nitroaniline, whilst Hentschell (*Ber.*, 1897, 30, 2643) recently tried the action of nitrogen chloride (NCl_3) dissolved in benzene on aniline and on monomethylaniline, from both of which *s*-trichloro-derivatives were obtained. A small quantity of the aniline was converted into azobenzene.

All amines react readily with the acetylchloro- and acetylbromoaminobenzenes. The course of the reaction can generally be followed best by using solutions of the dry reagents in anhydrous solvents such as chloroform or benzene. Other solvents, such, for example, as alcohol, acetic acid, or ether, may be used and do not affect the general course of the reaction, but as they cannot be obtained so readily in an anhydrous condition, the reaction does not proceed so cleanly, and the products are not easily purified.

Throughout these experiments we have employed the nitrogen chloride and bromide derived from 2:4-dichloroacetanilide, both of which are prepared in quantity without any difficulty. Further, 2:4-dichloroacetanilide, which is always regenerated in the reaction, is only slightly soluble in cold chloroform, whilst the other product or products are very soluble.

The first reaction of an amine with a nitrogen chloride or bromide is represented by the equation (where $\text{X} = \text{Cl}$ or Br):



In the case of the aliphatic amines, the chloroamines can be isolated. The bromoamines, however, decompose so readily that we have not been able to isolate them.

With all anilines, further reactions follow. Either the halogen wanders into the nucleus and takes up ortho- and para-positions relatively to the NH_2 group, or azobenzenes are formed with elimination of hydrogen chloride or hydrogen bromide. The latter reaction only plays a subordinate part, except when positions 2, 4, and 6 in the nucleus are occupied, and wandering of the halogen cannot therefore take place.

When 1 mol. of a nitrogen chloride or bromide interacts with 1 mol. of an aniline, it is found that the monohalogen derivative is almost exclusively formed. Thus aniline yields only *o*- and *p*-monochloroanilines and no 2:4-dichloroaniline, whilst *p*-chloroaniline yields only 2:4-dichloroaniline and no 2:4:6-trichloroaniline. When more than one aniline is present, the nitrogen halogen derivative always reacts preferentially with the least substituted base. In one

experiment, 1 mol. of the nitrogen chloride, dissolved in chloroform, was added to a chloroform solution containing 1 mol. of *p*-chloro-aniline, and 1 mol. of 2:4-dichloroaniline. Only a trace of *s*-trichloroaniline was recognisable in the product, while no unchanged *p*-chloroaniline was discovered.

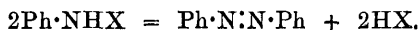
As weighed quantities of the pure substituted nitrogen chlorides can be used, this reaction affords a very simple means of introducing one atomic proportion of chlorine into an aniline. The yields are nearly quantitative and the products readily isolated in a pure state. It provides also a convenient method of chlorinating anilines already substituted in both the 2- and 4-positions. As is well known, the chlorination of anilides only leads to the entrance of chlorine into the para- and one ortho-position. Although, with anilines, chlorine itself can effect substitution in *both* ortho-positions, in many cases much oxidation of the aniline takes place, and the yield is consequently small.

With aniline and monomethylaniline, both the *o*- and *p*-monochloro-derivatives are formed. About equal proportions of each are obtained in the case of the former, a result which is noteworthy, as our previous observations have shown that in the transformation of acetylchloroaminobenzene, *p*-chloroacetanilide is the chief product, only some 5 per cent. of *o*-chloroacetanilide being produced (Trans., 1900, 77, 797).*

On the other hand, *p*-bromoaniline appears to be exclusively formed when aniline interacts with a nitrogen bromide.

Metasubstituted anilines also yield *o*- and *p*-chloro-derivatives, whilst from ortho-substituted anilines only 2:4-di-derivatives are produced.

The formation of azobenzenes from the first formed halogen-amino-compounds may be represented by the following equation:



The formation of azo-derivatives takes place best, at least in unsubstituted bases (for example, aniline and *o*- and *p*-toluidine), when excess of the base is used, as the acid then appears as a hydrochloride (or hydrobromide). Thus, in one experiment with aniline,

* In this connection may be mentioned the experiments of Loeb (*Ber.*, 1896, 29, 1895) on the electrolysis of a hydrochloric acid solution of nitrobenzene. He found that *o*-chloroaniline was formed in large proportion together with the *p*-chloro-derivative.

Again it has been observed that the nature of the acyl group replacing the aminic hydrogen of aniline affects the proportion of the *o*- and *p*-derivatives formed on nitration. Thus Lellmann (*Annalen*, 1883, 221, 6) found that benzanilide yielded more *o*-nitro-derivative than did acetanilide.

75 per cent. of the amine was converted into *o*- and *p*-chloroanilines, whilst as much as 25 per cent. appeared as azobenzene.*

With nitrogen bromides, on the other hand, these anilines yield very little azo-compound.

Anilines which are substituted in positions 2, 4, and 6, such as *s*-trichloroaniline and *s*-tribromoaniline, yield chloro- and bromo-amino-derivatives, which cannot undergo transformation, and especially readily form azo-compounds. The bromoamino-derivatives undergo this decomposition more readily than the chloroamino-derivatives.

Action of Acetylchloroamino- and Acetylbromoamino-2 : 4-dichlorobenzene on Amines.

Dibenzylamine.—Acetylchloroamino-2 : 4-dichlorobenzene (1 mol.), dissolved in a little dry chloroform, was added to dibenzylamine (1 mol.) dissolved in the same solvent. Little heat was developed. The dichloroacetanilide which separates was filtered off and the chloroform evaporated. The residue crystallised from petroleum (b. p. 50–80°) in large rhombs melting at 56°, and proved to be the dibenzylchloroamine, $(C_6H_5 \cdot CH_2)_2NCl$, described by Berg (*Bull. Soc. Chim.*, 1893, [ii], 26, 189).

0.2506 liberated $I = 21.35$ c.c. $N/10$ iodine. Cl as $:NCl = 15.11$.

$C_{14}H_{14}NCl$ requires Cl as $:NCl = 15.33$ per cent.

When acetylbromoamino-2 : 4-dichlorobenzene was employed, a similar reaction took place, but the dibenzylbromoamine formed was so unstable that it could not be isolated.

Other primary and secondary aliphatic amines gave similar results. For example, when an ethereal solution of the nitrogen chloride was added to an aqueous solution of methyl- or ethyl-amine, dichloroacetanilide immediately separated. On evaporating the ether, methyl- or ethyl-chloroamine was left as an oil, which was exceedingly irritating to the eyes, and set free iodine from potassium iodide.

Aniline.—A solution of the nitrogen chloride (12 grams or 1 mol.) in chloroform was gradually added to a cooled chloroform solution of

* It is very probable that the preparation of azobenzene and azotoluene by the action of dry bleaching powder on the respective bases in the presence of chloroform depends on the formation of the chloroamino-derivatives. Schmitt (*J. pr. Chem.*, 1878, **18**, 195; 1879, **19**, 314) found that the azobenzene produced represented one-third of the aniline. He does not account for the remaining two-thirds of the base, and does not seem to have anticipated the formation of chloroanilines. In the presence of water, no azo-compounds are formed, a fact which points to the action not being one of direct oxidation.

aniline (23 grams or 5 mols.). The reaction was accompanied by development of heat, and the solution became highly coloured. A mixture of dichloroacetanilide and aniline hydrochloride separated; the latter weighed 1.76 grams.

The chloroform mother liquor was partially evaporated, and petroleum added to precipitate the remainder of the anilide. The anilines were now extracted with hydrochloric acid. After evaporating the solvents, a residue of azobenzene remained, 1.14 grams being obtained instead of 1.23 grams which theoretically corresponds with the quantity (1.76 grams) of aniline hydrochloride.

In another experiment, in which 4 mols. of the nitrogen chloride to 5 mols. of aniline were used, the anilines were separated by fractionally distilling in steam from sulphuric acid. *o*- and *p*-Chloroanilines were obtained in nearly equal amounts.

Monomethylaniline.—The chloroamine and methylaniline dissolved in chloroform were mixed in molecular proportion. Much colour was developed in the reaction. The anilines were separated as in the previous experiment. The final fraction was acetylated and proved to be

Acetyl-4-chloromethylaniline.—It crystallised from petroleum in pearly, white plates melting at 92°.

0.1935 gave 0.151 AgCl. Cl = 19.3.

$C_9H_{10}ONCl$ requires Cl = 19.31 per cent.

On hydrolysis, *p*-chloromethylaniline boiling at 240° was obtained. The latter was also prepared for comparison by heating methyl iodide with *p*-chloroaniline at 100° in a sealed tube and isolated in the usual manner through its nitroso-derivative.

o-Chloromethylaniline was contained in the first fraction from the distillation with steam. It was purified by distillation under reduced pressure, and boils at 95–96° under 12 mm., and at 218° under 760 mm. pressure. For comparison, this compound was synthesised from *o*-chloroaniline and methyl iodide.

0.2726 gave 0.2782 AgCl. Cl = 25.23.

C_7H_8NCl requires Cl = 25.04 per cent.

The quantity of *p*-chloromethylaniline formed in the reaction of a nitrogen chloride on methylaniline largely exceeds that of the *o*-chloro-derivative.

o-, *m*-, and *p*-*Toluidines*.—With each of these bases, considerable quantities of the corresponding azotoluene were formed. Thirty to forty per cent. of *p*-toluidine appeared as azo-compound. In addition, *o*-toluidine yielded 5-chloro-*o*-toluidine (melting at 30°); *m*-toluidine, 6-chloro-*m*-toluidine (melting at 83°); and *p*-toluidine, 3-chloro-*p*-toluidine, the acetyl derivative of which melted at 118°.

Ortho-substituted Anilines.—*o*-Chloroaniline is almost entirely converted into 2:4-dichloroaniline, very little azo-compound being formed.

o-Nitroaniline yielded the 2-nitro-4-chloroaniline of Körner (*Jahresb.*, 1875, 351). It melted at 116—117°, and gave an acetyl derivative melting at 102°, which we have also obtained by the nitration of *p*-chloroacetanilide (Chattaway and Orton, *Ber.*, 1900, 33, 3062).

Meta-substituted Anilines.—*m*-Bromoaniline yields a mixture of two chlorobromoanilines, which were separated by distilling in a current of steam from sulphuric acid. The larger portion, which distilled over first, was 2-chloro-5-bromoaniline melting at 45° (Clarke, *Amer. Chem. J.*, 1892, 14, 561). Its acetyl derivative was sparingly soluble in 50 per cent. acetic acid, from which it separated in needles melting at 141°.

0.0977 gave 0.1317 AgCl + AgBr and 0.0457 Cl + Br. Cl = 14.68 ;
Br = 32.09.

C₈H₇ONClBr requires Cl = 14.26 ; Br = 32.17 per cent.

The smaller portion, which distilled over after complete neutralisation of the acid, was 3-bromo-4-chloroaniline melting at 78° (Wheeler and Valentine, *Amer. Chem. J.*, 1895, 17, 697). Its acetyl derivative melts at 130°, and crystallises in rhombs fairly soluble in 50 per cent. acetic acid.

0.2649 gave 0.3558 AgCl + AgBr and 0.1238 Cl + Br. Cl = 14.39 ;
Br = 32.35.

C₈H₇ONClBr requires Cl = 14.26 ; Br = 32.17 per cent.

m-Nitroaniline.—3-Nitro-4-chloroaniline is the chief product, although other chloronitroanilines are formed. After evaporation of the chloroform, the residue was recrystallised from petroleum and then acetylated. The anilide was repeatedly crystallised from dilute alcohol, and then melted at 145°. This anilide has been prepared by us from 3-nitro-4-chloroaniline, obtained by nitration of *p*-chloroaniline (Chattaway and Orton, *loc. cit.*).

m-Chloroaniline, when treated with acetyl bromoamino-2:4-dichlorobenzene, yielded 3-chloro-4-bromoaniline, melting at 67—68° (Wheeler and Valentine, *loc. cit.*).

Para-substituted Anilines.—*p*-Chloro-, *p*-bromo-, and *p*-nitro-anilines all readily yield monochloro-derivatives, in which chlorine is in the ortho-position relatively to the amino-group ; azo-compounds are formed only in small quantities.

2:4-Disubstituted Anilines.—These anilines react with chloro- and bromo-amino-compounds, with a smaller evolution of heat than do less substituted anilines, and the formation of azo-derivatives takes place only

to a slight extent. 2:4-Dichloroaniline yields 2:4:6-trichloroaniline; 2:4-dibromoaniline, 2:4-dibromo-6-chloroaniline; and 2-chloro-*p*-nitroaniline, 2:6-dichloro-*p*-nitroaniline.

s-Trisubstituted Anilines.—On mixing solutions of these anilines in chloroform with solutions of acetylchloro- or acetylbromo-amino-2:4-dichlorobenzene, crystals of dichloroacetanilide begin immediately to separate. No heat is developed in the reaction. The chloroamino-derivative of *s*-trichloroaniline can be obtained in an impure state, as a faintly coloured oil, on evaporation of the solvent. It soon becomes deep-red from decomposition into the azo-compound, a change which also takes place in the solution after a short time. The bromoamino-derivative decomposes still more readily.

2:4:6:2':4':6'-Hexachloroazobenzene, hitherto unknown, can thus be readily prepared from *s*-trichloroaniline. Chloroform solutions of acetylbromoamino-2:4-dichlorobenzene and trichloroaniline are mixed; after separation of the anilide, the filtered solution is evaporated, and the residue recrystallised from a mixture of alcohol and chloroform. The azo-compound separates in fine, dark red needles melting at 188°, insoluble in alcohol, but very soluble in chloroform or benzene.

0.147 gave 0.326 AgCl. Cl = 54.83.

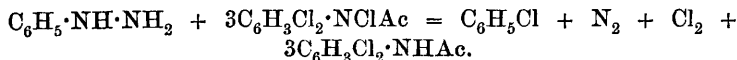
C₁₂H₄N₂Cl₆ requires Cl = 54.7 per cent.

It is reduced by tin and hydrochloric acid to trichloroaniline.

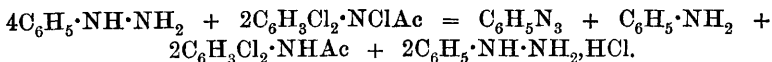
Tribromoaniline, on similar treatment, gave hexabromoazobenzene melting at 213° (Pechmann and Nold, *Ber.*, 1898, 31, 564).

The Action of Nitrogen Halogen Compounds on Phenylhydrazine.

All chloro-, bromo-, and iodo-amines interact very readily with phenylhydrazine. Two reactions take place, according as the nitrogen halogen compound or the hydrazine is in excess. Thus when phenylhydrazine is added to an excess of acetylchloroamino-2:4-dichlorobenzene, nitrogen, chlorine, chlorobenzene, and the regenerated anilide are formed. The final result is represented by the equation:



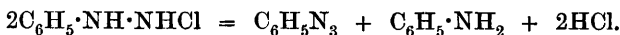
In this reaction, much heat is developed. When excess of the hydrazine is present, the final result of the reaction (which is not accompanied by much development of heat) is represented thus:



A hydrazino-halogen compound is probably the first product,

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which then decomposes into azimidobenzene, aniline, and hydrogen chloride.*



Nitrogen iodide reacts with phenylhydrazine in a similar manner ; and as in this case it is impossible to exclude water, the presence of the latter does not modify the course of the reaction.

(1) Action of acetylchloroamino-2:4-dichlorobenzene on excess of phenylhydrazine.

A solution of the nitrogen chloride dissolved in chloroform was slowly run into chloroform containing a large excess of phenylhydrazine. The hydrochloride of the base immediately separated together with the anilide. After filtration, the mother liquor was repeatedly extracted with dilute hydrochloric acid, and then evaporated. The oil which remained was purified by distillation in steam. It was insoluble in hydrochloric acid, and contained no halogen. On treating a solution in chloroform with excess of bromine, fine needles of 2:4:6-tribromoaniline hydrobromide separated. The liquid is therefore azimidobenzene.

The hydrochloric acid extracts were evaporated to a small bulk, and after filtering off the phenylhydrazine hydrochloride, the mother liquor was made alkaline and distilled in steam. The oil which distilled over proved to be aniline, and yielded acetanilide on treatment with acetic anhydride.

In one experiment, in which 16 grams of acetylchloroamino-2:4-dichlorobenzene were used, 13.11 grams of 2:4-dichloroacetanilide, 2.24 grams of hydrogen chloride, 3.12 grams of aniline, and 2 grams of azimidobenzene were obtained, whilst 13.69, 2.34, 2.75, and 4.02 grams respectively are required by the equation. The low yield of the azimidobenzene is undoubtedly due to some loss in the evaporation of the large quantity of chloroform.

(2) Action of phenylhydrazine on excess of acetylchloroamino-2:4-dichlorobenzene.

The solution of phenylhydrazine in chloroform was slowly added to the solution of the nitrogen chloride. Heat was developed, and much gas given off. After removal of the anilide by filtration, and evaporation of the chloroform, the residual oil was distilled in steam. It proved to be chlorobenzene, boiling at 132°.

* Fischer (*Annalen*, 1877, **190**, 67) found that iodine has two reactions with phenylhydrazine, according as one or the other substance is in excess. With the halogen in excess, iodobenzene, nitrogen and hydriodic acid are produced, and with hydrazine in excess azimidobenzene, aniline, and phenylhydrazine hydriodide. As we find that these reactions can take place equally well in the absence of water, it is very probable that this action is not a simple oxidation, as Fischer suggests, but depends on the formation of an iodohydrazine.

(3) Action of nitrogen iodide ($\text{NH}_3 \cdot \text{NI}_3$) on phenylhydrazine.

In this case, as it was impossible to dry the nitrogen iodide, the latter was added to an aqueous emulsion of phenylhydrazine. The reaction takes place very readily and in the presence of excess of phenylhydrazine without marked development of heat. Azimido-benzene, aniline, and hydriodic acid (as phenylhydrazine hydriodide) were formed.

(4) Action of iodine on phenylhydrazine in anhydrous solution.

With excess of phenylhydrazine, little heat was developed. After removal of the hydriodide of the base by filtration, the solution was thoroughly extracted with hydrochloric acid. On evaporation of the chloroform, azimidobenzene was left. The acid extract contained aniline, together with the excess of phenylhydrazine.

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