CCCCVIII.—*Investigations in the Diphenyl Series. Part IV. Halogenation of* 4-*Aminodiphenyl.*

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THE divergence in the action of chlorine and of bromine on 4-acetylaminodiphenyl in acetic acid solution was briefly recorded in Part I (this vol., p. 1242). Bromine, unlike chlorine, gives rise to two isomerides, *viz.*, 3- and 4′-bromo-4-acetylaminodiphenyl, which comprise about 50% and 30% of the product, respectively; small quantities of the corresponding bromo-bases are sometimes produced by hydrolysis. The orientation of the two principal products has been determined as follows: 4′-bromo-4-aminodiphenyl obtained by hydrolysis of its acetyl derivative is identical with 4′-bromo-4-aminodiphenyl prepared from benzidine by the usual method; the 3-bromo-4-aminodiphenyl similarly obtained was converted into 3 : 5-dibromo-4-aminodiphenyl, which has been described by Scarborough and Waters (this vol., p. 557).

The results of the bromination of 4-acetylaminodiphenyl herein described differ considerably from those recorded by those authors, who did not observe the formation of 3-bromo-4-acetylaminodiphenyl.

3-Bromo-4-aminodiphenyl was the only product isolated from the interaction of *N*-bromoacetanilide and 4-aminodiphenyl.

3 : 5-Dibromo-4-aminodiphenyl is converted with great readiness into a monoacetyl and a diacetyl derivative, which melt respectively at 212° and 184°; it seems likely, therefore, that the acetyl derivative of 3 : 5-dibromo-4-aminodiphenyl, m. p. 162°, described by Scarborough and Waters is a mixture. It is somewhat remarkable that this base should undergo di-acetylation with great readiness, a property which is shared by (3 : 5 ?)-dibromo-4′-nitro-4-aminodiphenyl.

A striking difference in stability is shown by the *N*-halogeno-derivatives of 4-acetylaminodiphenyl, for whilst *N*-chloro-4-acetylaminodiphenyl and 4′ : *N*-dichloro-4-acetylaminodiphenyl can be obtained pure and exhibit the normal degree of stability, 3 : *N*-dichloro-4-acetylaminodiphenyl and *N*-bromo-4-acetylaminodiphenyl lose halogen with great readiness and cannot be obtained pure.

The failure to obtain the latter compound is unfortunate, as it was hoped that its behaviour on treatment with acetic acid might explain the divergence in the action of bromine and of chlorine on 4-acetylaminodiphenyl referred to above. 4′ : *N*-Dichloro-4-acetylaminodiphenyl in acetic acid solution undergoes transformation to 3 : 4′-dichloro-4-acetylaminodiphenyl, which was also isolated in small quantity (5%) from the products of the action of hot acetic acid on the unstable 3 : *N*-dichloro-4-acetylaminodiphenyl.

This result may be compared with the behaviour of *oN*-dichloroacetanilide, which does not undergo complete conversion into 2 : 4-dichloroacetanilide even when heated in acetic acid solution at 100° for many hours (Chattaway and Orton, J., 1900, **77**, 797).

3 : 4′-Dichloro-4-acetylaminodiphenyl was identified by conversion into 3 : 5 : 4′-trichloro-4-acetylaminodiphenyl, a compound which has been described by Scarborough and Waters (*loc. cit.*).

Only one product could be isolated from the bromination of 4-dimethylaminodiphenyl, and from its great solubility and low m. p. it is presumed to be 3-bromo-4-dimethylaminodiphenyl.

In the case of diphenyl derivatives with an ortho-para-directing group in position 4, it would therefore seem possible to draw the following conclusions: (1) Whilst migration substitution can occur only in the 3-position, direct substitution can take place in positions 3 and 4′. (2) When a second ortho-para-directing substituent of almost equal power is present in position 3, substitution occurs in the 4′-position and migration substitution is inhibited.

EXPERIMENTAL.

3-*Bromo*-4-*acetylaminodiphenyl*.—Bromine (27·8 g.) dissolved in glacial acetic acid (30 c.c.) was added to a solution of 4-acetylaminodiphenyl (35 g.) in glacial acetic acid (400 c.c.), and the mixture maintained at 30—40° for an hour. The crystalline precipitate that separated (27 g.) was collected after some time, ground with dilute sodium carbonate solution, washed, dried, and well shaken with cold benzene (100 c.c.), in which 4′-bromo-4-acetylaminodiphenyl is only sparingly soluble. The filtered extract was evaporated to dryness and the residue recrystallised from alcohol; after removal of a further quantity of the less soluble 4′-bromo-isomeride, impure 3-bromo-4-acetylaminodiphenyl was obtained. The greater portion of this compound, however, remained in the acetic acid solution, from which it was obtained (29·5 g.) by precipitation with water. Extraction of this material, when dry, with cold benzene removed much of the 4′-bromo-isomeride present (more than 5%), but even fractional crystallisation from alcohol usually failed to raise the m. p. above 146°, since this procedure did not completely remove the admixed 4′-bromo-4-acetylaminodiphenyl, unchanged 4-acetylaminodiphenyl and some dibrominated material. Complete purification of the material of m. p. 146° was effected most conveniently by hydrolysis : the resulting crude 3-bromo-4-aminodiphenyl, after crystallisation and reacetylation, gave the pure *acetyl* derivative, which separated from alcohol or light petroleum in long, glistening needles, m. p. 161° (Found : Br, 27·9. $C_{14}H_{12}ONBr$ requires Br, 27·6%).

3-*Bromo*-4-*aminodiphenyl*, obtained from its acetyl derivative by hydrolysis with alcoholic hydrogen chloride or 65% sulphuric acid, crystallised from aqueous alcohol in almost colourless, small plates, m. p. 66° (Found : C, 57·8; H, 4·0. $C_{12}H_{10}NBr$ requires C, 58·0; H, 4·0%). When mixed with cold acetic anhydride, this substance dissolved at once, and almost immediately separated in the form of its acetyl derivative. To a solution of the free base in cold acetic acid, bromine (1 mol.) was added; the yellow precipitate which formed was washed with sodium carbonate solution and dissolved in alcohol, from which it separated in needles, m. p. 118°, identical with the 3 : 5-dibromo-4-aminodiphenyl obtained by the direct bromination of 4-aminodiphenyl.

4′-Bromo-4-acetylaminodiphenyl requires heating with 75% sulphuric acid at 120—130° for some hours before hydrolysis is complete.

3 : 5-*Dibromo*-4-*acetylaminodiphenyl* was obtained by heating a mixture of 3 : 5-dibromo-4-aminodiphenyl (24 g.), acetic acid (120 c.c.), and acetic anhydride (14 c.c.) under reflux for 2 hours and pouring the reaction mixture into water. The dried precipitate was extracted with carbon tetrachloride (250 c.c.), and the residue (22 g.) crystallised from alcohol, from which it separated in long needles, m. p. 212° (Found : C, 45·5; H, 3·2. $C_{14}H_{11}ONBr_2$ requires C, 45·5; H, 3·0%).

3 : 5-*Dibromo*-4-*diacetylaminodiphenyl*, obtained by the process described above when a higher concentration of acetic anhydride was used, crystallised from carbon tetrachloride in short needles, m. p. 184° (Found : C, 46·8; H, 3·1. $C_{16}H_{13}O_2NBr_2$ requires C, 46·7; H, 3·2%).

(3 ?) - *Bromo* - 4 - *dimethylaminodiphenyl*.—To 4-dimethylaminodiphenyl (8 g.) dissolved in acetic acid, bromine (6·5 g.), diluted with acetic acid, was added and after ¼ hour the reaction mixture was poured into water and neutralised with ammonia. The precipitate was dissolved in dilute hydrochloric acid, reprecipitated with ammonia, and crystallised from methyl alcohol, forming lustrous plates, m. p. 82° (Found : C, 60·9; H, 5·2. $C_{14}H_{14}NBr$ requires C, 60·8; H, 5·1%).

(3 : 5 ?)-*Dibromo-4′-nitro-4-acetylaminodiphenyl.*—4′-Nitro-4-aminodiphenyl (3·5 g.) (obtained in 70—75% yield by the method of Willstätter, *Ber.*, 1906, **39**, 3478) was warmed with bromine (5·5 g.) and acetic acid (30 c.c.) for several hours, and the mixture poured into water. After several recrystallisations from benzene the product formed pale yellow needles, m. p. 184° (Found : C, 40·3; H, 2·5. $C_{14}H_{10}O_3N_2Br_2$ requires C, 40·6; H 2·4%). On boiling with acetic anhydride for 1 hour, this compound was converted into (3 : 5 ?)-*dibromo-4′-nitro-4-diacetylaminodiphenyl*, which crystallised from acetic acid in needles, m. p. 228° (Found : C, 42·1; H, 2·7. $C_{16}H_{12}O_4N_2Br_2$ requires C, 42·1; H, 2·6%). The positions assigned to the bromine atoms could not be confirmed, as 3 : 5-dibromo-4-acetylaminodiphenyl, under conditions sufficiently powerful to cause nitration, gave a product from which only a dinitro-derivative could be obtained in a pure state.

3 : 5-*Dibromodinitro-4-acetylaminodiphenyl* crystallised from acetic acid in clusters of small needles, m. p. 269—270° (Found : C, 36·9; H, 2·4. $C_{14}H_9O_5N_3Br_2$ requires C, 36·6; H, 2·0%). By boiling for 1 hour with acetic anhydride it was converted into 3 : 5-*dibromodinitro-4-diacetylaminodiphenyl*, which crystallised from aqueous acetic acid in stout needles, m. p. 140° (Found : C, 38·8; H, 2·3. $C_{16}H_{11}O_6N_3Br_2$ requires C, 38·4; H, 2·2%).

Action of N-*Bromoacetanilide on 4-Aminodiphenyl.*—*N*-Bromoacetanilide (5·3 g.; Chattaway and Orton, J., 1899, **75**, 1046) was dissolved in chloroform and added slowly to a chloroform solution of 4-aminodiphenyl (4 g.); a deep red colour developed. The residue obtained from the solution after evaporation was hydrolysed with alcoholic hydrogen chloride, and the freed aniline removed by steam-distillation. Recrystallisation of the product yielded only 3-bromo-4-aminodiphenyl.

4′ : N-*Dichloro-4-acetylaminodiphenyl.*—Finely-divided 4′-chloro-4-acetylaminodiphenyl (6·9 g.), obtained by pouring an alcoholic solution into water, was suspended in water (300 c.c.) containing potassium bicarbonate (7 g.) and mixed with sodium hypochlorite (excess of *N*/4-solution) and the whole was maintained at 60° for an hour. The product separated from carbon tetrachloride or from chloroform–light petroleum in almost colourless, small plates, m. p. 128°. The compound solidified just above its m. p. and then melted at 181° (Found : Cl, 12·4, by estimation of the iodine liberated from potassium iodide. $C_{14}H_{11}ONCl_2$ requires Cl, 12·7%).

3 : 4′-*Dichloro-4-acetylaminodiphenyl* was easily prepared by dissolving the chloroamine in warm acetic acid; it separated on cooling and crystallised from carbon tetrachloride in large, colour

less needles, m. p. 184° (Found : C, 59·9; H, 3·9. $C_{14}H_{11}ONCl_2$ requires C, 60·0; H, 3·9%). It was also obtained in small quantity from 3-chloro-4-acetylaminodiphenyl, which, with hypochlorous acid, gave an unstable chloroamine. This substance, on solution in acetic acid, gave as the principal product of the reaction 3-chloro-4-acetylaminodiphenyl accompanied by less than 5% of 3 : 4′-dichloro-4-acetylaminodiphenyl.

When an acetic acid solution of the latter compound was mixed with an excess of sodium hypochlorite solution, 3 : 5 : 4′-trichloro-4-acetylaminodiphenyl (compare Scarborough and Waters, *loc. cit.*) was obtained, the view that the dichloro-4-acetylaminodiphenyl is the 3 : 4′-isomeride thus being confirmed.

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