CCXXXVIII.—*Syntheses in the Diphenyl Series.*

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THE view (this vol., p. 1200) that 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one, when heated alone or with alcoholic potassium hydroxide, decomposes into 5-bromo-3-hydroxydiphenyl and 4 : 5-dibromo-3-hydroxydiphenyl has now been shown to be correct. The constitutions of the two compounds have been proved by their syntheses from 5-bromo-3-nitro-4-aminodiphenyl through 5-bromo-3-nitrodiphenyl and 5-*bromo*-3-*aminodiphenyl* in the first case, and through 4 : 5-*dibromo*-3-*nitrodiphenyl* and 4 : 5-*dibromo*-3-*aminodiphenyl* in the second.

No trace of 4 : 5-dibromo-3-nitrodiphenyl was obtained from 5-bromo-3-nitro-4-aminodiphenyl by diazotisation in hydrobromic acid solution as described by Crossley (J., 1904, **85**, 278): the amino-group appeared to be unaffected, but the bromine formed by the interaction of the nitrous and hydrobromic acids reacted readily with the base, giving rise to 5 : 4′-dibromo-3-nitro-4-aminodiphenyl. This formed golden-orange needles, m. p. 154°. Scarborough and Waters (J., 1927, 1138), who obtained this compound by the bromination of 5-bromo-3-nitro-4-aminodiphenyl, describe it as red needles, m. p. 158°. We have repeated their experiment, carrying out the heating process for only 2 hours, and obtained the dibromo-derivative as golden-orange needles, m. p. 154°; longer heating, as carried out by them, not only diminished the yield but also produced small quantities of darker-coloured substances. Acetylation of the dibromo-compound gave a product, m. p. 153°, which was identical with a specimen kindly provided by Bell and Robinson, who prepared it by the bromination of 3-nitro-4-acetamidodiphenyl (J., 1927, 1130). Reduction of the base gave 5 : 4′-*dibromo*-3 : 4-*diaminodiphenyl*.

EXPERIMENTAL.

5-*Bromo*-3-*nitro*-4-*aminodiphenyl*.—3-Nitro-4-aminodiphenyl was brominated as described by Scarborough and Waters (*loc. cit.*). By slow crystallisation from methyl alcohol the product was obtained pure as deep orange needles, m. p. 100° (Found : Br, 27·2. Calc. : Br, 27·3%).

Acetylation of the base gave 5-bromo-3-nitro-4-acetamidodiphenyl, which crystallised from alcohol in orange-yellow needles m. p. 95°, and was identical with the compound described by Bell and Robinson (*loc. cit.*) as (5 ?)-bromo-3-nitro-4-acetamidodiphenyl, m. p. 94—95°.

5-*Bromo*-3-*aminodiphenyl*.—5-Bromo-3-nitrodiphenyl (Scarborough and Waters, *loc. cit.*) was reduced in alcoholic solution with sodium hydrosulphite. After removal of the alcohol under reduced pressure, the *base* was extracted with ether. It crystallised from light petroleum (b. p. 40—60°) in light brown prisms, m. p. 88° (Found : Br, 32·1. $C_{12}H_{10}NBr$ requires Br, 32·3%).

The *acetyl* derivative, prepared in the usual manner, crystallised from alcohol–light petroleum in white prisms, m. p. 140° (Found : Br, 26·9. $C_{14}H_{12}ONBr$ requires Br, 27·6%).

5-*Bromo*-3-*benzoyloxydiphenyl*.—5-Bromo-3-aminodiphenyl was diazotised in the usual manner in an 80% solution of sulphuric acid at 0°. After remaining for 1 hour at this temperature, the solution was gradually heated to boiling, then diluted, and extracted with ether. The dark oil remaining after removal of the ether was treated with sodium hydroxide solution. Acidification of the alkaline solution precipitated 5-bromo-3-hydroxydiphenyl as an oil which owing to the small amount available was not further purified but converted directly into its benzoyl derivative; this crystallised from alcohol in clusters of small needles, m. p. 108°, unchanged by admixture with the benzoyl derivative of 5-bromo-3-hydroxydiphenyl (this vol., p. 1203).

4 : 5-*Dibromo*-3-*nitrodiphenyl*.—4 G. of 5-bromo-3-nitro-4-aminodiphenyl were diazotised as described above. The solution was

diluted with ice-water, poured into a cold solution of cuprous bromide in hydrobromic acid, and gradually heated to boiling. Extraction of the solution with ether gave a solid which crystallised from methyl alcohol in pale yellow needles, m. p. 125° (Found : Br, 44·6. $C_{12}H_7O_2NBr_2$ requires Br, 44·8%). Oxidation with chromic acid in glacial acetic acid solution gave 4 : 5-dibromo-3-nitrobenzoic acid (m. p. 182°).

4 : 5-*Dibromo*-3-*acetamidodiphenyl*.—4 : 5-Dibromo-3-nitrodiphenyl was reduced with sodium hydrosulphite, and the brown semi-solid base obtained was converted by the usual method into the *acetyl* derivative, which crystallised from aqueous alcohol in white needles, m. p. 177° (Found : Br, 43·5. $C_{14}H_{11}ONBr_2$ requires Br, 43·4%).

On hydrolysis of the acetyl derivative with concentrated hydrochloric acid and subsequent treatment with ammonia, the base was obtained as a dark semi-solid mass, which was converted into 4 : 5-dibromo-3-hydroxydiphenyl by the diazo-reaction. This crystallised from light petroleum (b. p. 40—60°) in fine needles, m. p. 81°, and its benzoyl derivative, prepared in the usual manner, crystallised from alcohol in small, white needles, m. p. 104°. These m. p.'s were unchanged by admixture with the corresponding compounds described in this vol., p. 1203.

5 : 4′-*Dibromo*-3 : 4-*diaminodiphenyl*, obtained by reducing 5 : 4′-dibromo-3-nitro-4-aminodiphenyl with sodium hydrosulphite, crystallised from alcohol in white needles, m. p. 120° (Found : Br, 46·9. $C_{12}H_{10}N_2Br_2$ requires Br, 46·8%). The *dibenzoyl* derivative, prepared in the usual manner, was sparingly soluble in boiling alcohol, from which it separated in microscopic crystals, m. p. 278° (Found : Br, 29·2. $C_{26}H_{18}O_2N_2Br_2$ requires Br, 29·1%).

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