

68. *Derivatives of 4 : 4'-Diaminodiphenylmethane.*

By G. D. PARKES and R. H. H. MORLEY.

THE action of two molecular proportions of bromine upon 4 : 4'-diacetamidodiphenylmethane yields 3 : 3'-dibromo-4 : 4'-diacetamidodiphenylmethane, from which the free base can be obtained on hydrolysis. This base and 4 : 4'-diaminodiphenylmethane can be diazotised and the bisdiazonium salts yield dihydrazines on reduction. These substances show the normal behaviour of arylhydrazines and from them a series of dihydrazones has been prepared, and their properties recorded for reference.

4 : 4'-Diaminodiphenylmethane was prepared (1) by nitration of diphenylmethane and reduction of the 4 : 4'-dinitrodiphenylmethane formed by tin and hydrochloric acid, (2) by the condensation of formaldehyde with aniline in presence of caustic alkali, followed by transformation of the resulting methylenediphenyldi-imide by heating with aniline hydrochloride. The latter is the more convenient and less wasteful process, 186 g. of aniline yielding 150 g. of base as compared with 45 g. of product from 100 g. of diphenylmethane.

3 : 3'-Dibromo-4 : 4'-diacetamidodiphenylmethane.—10 G. of 4 : 4'-diacetamidodiphenylmethane and 8 g. of anhydrous sodium acetate were dissolved in boiling glacial acetic acid, and 12 g. of bromine in 20 c.c. of glacial acetic acid added. Bromination proceeded readily,

and after the slight excess of bromine had been boiled off, the mixture was poured on ice. The 3 : 3'-dibromo-4 : 4'-diacetamidodiphenylmethane (10 g.) obtained crystallised from alcohol in colourless plates, m. p. 198°, easily soluble in glacial acetic acid and moderately soluble in alcohol (Found : Br, 35.7. $C_{17}H_{16}O_2N_2Br_2$ requires Br, 35.9%).

3 : 3'-Dibromo-4 : 4'-dibenzamidodiphenylmethane (11 g.), obtained similarly from 10 g. of 4 : 4'-dibenzamidodiphenylmethane and 11 g. of bromine, crystallised from glacial acetic acid in white prisms, m. p. 217° (Found : Br, 27.9. $C_{27}H_{20}O_2N_2Br_2$ requires Br, 28.1%).

3 : 3'-Dibromo-4 : 4'-diaminodiphenylmethane (14 g.), m. p. 119° (Found : N, 7.8. $C_{13}H_{12}N_2Br_2$ requires N, 7.9%), was prepared by refluxing 50 g. of 3 : 3'-dibromo-4 : 4'-diacetamidodiphenylmethane with 75 c.c. of concentrated hydrochloric acid and 350 c.c. of alcohol for 5 hours; its dihydrochloride (35 g.), which separated on cooling, crystallised from hot water in white rhombic plates, m. p. 285° (decomp.) (Found : N, 6.4. $C_{13}H_{12}N_2Br_2 \cdot 2HCl$ requires N, 6.5%).

The position of the bromine atoms in this compound was established by eliminating the amino-groups by the Sandmeyer method or by the action of Fehling's solution on the corresponding dihydrazine, and oxidation of the resulting dibromodiphenylmethane to dibromobenzophenone, which was identical with authentic 3 : 3'-dibromobenzophenone (Dittrich, *Ber.*, 1890, 23, 3614).

4 : 4'-Dihydrazinodiphenylmethane.—100 G. of 4 : 4'-diaminodiphenylmethane, dissolved in 300 c.c. of concentrated hydrochloric acid and 500 c.c. of water, were diazotised at 0° with 70 g. of sodium nitrite; on addition to a cold saturated aqueous solution of 400 g. of sodium sulphite, the diazosulphonate separated in yellow needles. 100 C.c. of concentrated hydrochloric acid were added and the whole was warmed slowly to 70° while sulphur dioxide was passed in. Another 400 c.c. of concentrated hydrochloric acid were then added; on cooling, 4 : 4'-dihydrazinodiphenylmethane dihydrochloride separated. A solution of this in boiling water was filtered and, after addition of concentrated hydrochloric acid, allowed to cool, the salt separating in colourless plates, very sparingly soluble in hot water. 4 : 4'-Dihydrazinodiphenylmethane (35 g.), obtained from the dihydrochloride in the usual way, crystallised from alcohol in very pale yellow needles, m. p. 141°.

3 : 3'-Dibromo-4 : 4'-dihydrazinodiphenylmethane was prepared similarly, 45 g. of 3 : 3'-dibromo-4 : 4'-diaminodiphenylmethane and 400 g. of sodium sulphite being used; it crystallised from alcohol in almost colourless prisms, m. p. 161° (Found : N, 14.5. $C_{13}H_{14}N_4Br_2$ requires N, 14.5%). The dihydrochloride (yield, 10—15 g.) separated from hot dilute hydrochloric acid in colourless plates, m. p. 279° (decomp.) (Found : N, 12.1. $C_{15}H_{14}N_4Br_2 \cdot 2HCl$ requires N, 12.2%).

The following dihydrazones were prepared by warming 1 g. of the appropriate dihydrazine dihydrochloride with a slight excess of the carbonyl compound in alcohol in presence of excess of anhydrous sodium acetate: 4 : 4'-bis-(o-nitrobenzylidenehydrazino)diphenylmethane (2.2 g.), deep purple-red plates from acetic acid, m. p. 189° (Found : N, 16.9. $C_{27}H_{22}O_4N_6$ requires N, 17.0%); 4 : 4'-bis-(m-nitrobenzylidenehydrazino)diphenylmethane (2.0 g.), fine red flattened prisms from acetone, m. p. 192° (Found : N, 16.9%); 4 : 4'-bis-(p-nitrobenzylidenehydrazino)diphenylmethane (2.2 g.), red irregular plates from acetic acid, m. p. 218° (Found : N, 16.9%); 4 : 4'-bis-salicylidenehydrazinodiphenylmethane (2.3 g.), buff-yellow, flattened prisms from dioxan or acetic acid, m. p. 252°; the crystals are phototropic, turning red in sunlight; the colour is lost on heating in a steam-oven (Found : N, 12.6. $C_{27}H_{24}O_2N_4$ requires N, 12.75%); 4 : 4'-bis-(β-phenylethylidenehydrazino)diphenylmethane (4.2 g.), almost white, lustrous plates from benzene, m. p. 174° (Found : N, 12.5. $C_{23}H_{28}N_4$ requires N, 12.65%); 4 : 4'-bis-γ-(phenyl-α-methylallylidenehydrazino)diphenylmethane (3.8 g.), pale yellow, lustrous, hexagonal plates from benzene, m. p. 222° (Found : N, 11.3. $C_{23}H_{32}N_4$ requires N, 11.55%). For the following, approx. 0.45 g. of the dihydrazine dihydrochloride were used. 3 : 3'-Dibromo-4 : 4'-bis(benzylidenehydrazino)diphenylmethane (0.2 g.), buff-yellow plates from glacial acetic acid, m. p. 165° (Found : N, 9.8. $C_{27}H_{22}N_4Br_2$ requires N, 9.9%); 3 : 3'-dibromo-4 : 4'-bis-o-nitrobenzylidenehydrazinodiphenylmethane (0.3 g.), red microscopic needles from glacial acetic acid, m. p. 234°, very sparingly soluble in acetic acid, ethyl acetate, and acetone, and insoluble in alcohol (Found : Br, 24.3. $C_{27}H_{20}O_4N_6Br_2$ requires Br, 24.5%); 3 : 3'-dibromo-4 : 4'-bis-(m-nitrobenzylidenehydrazino)diphenylmethane (0.3 g.), orange-red powder from benzene, m. p. 278°, insoluble in ethyl acetate, acetic acid, acetone, and alcohol, very sparingly soluble in benzene (Found : Br, 24.4%); 3 : 3'-dibromo-4 : 4'-bis-(p-nitrobenzylidenehydrazino)diphenylmethane (0.3 g.), red powder from ethyl acetate, m. p. 255° (decomp.), insoluble in acetic acid, alcohol, and benzene, very sparingly soluble in acetone and ethyl acetate (Found : Br, 24.5%); 3 : 3'-dibromo-4 : 4'-bis-salicylidenehydrazinodiphenylmethane (0.25 g.), buff-yellow powder from

dioxan-alcohol, m. p. 236° (decomp.), insoluble in alcohol, acetic acid, and benzene (Found : N, 9.3. $C_{27}H_{22}O_2N_4Br_2$ requires N, 9.4%); 3:3'-dibromo-4:4'-bis-(p-hydroxybenzylidene-hydrazino)diphenylmethane (0.25 g.), silvery plates (which soon darkened in air) from alcohol, m. p. 238° (decomp.) (Found : N, 9.5%).

THE DYSON PERRINS LABORATORY, UNIVERSITY OF OXFORD.

[Received, January 3rd, 1936.]
