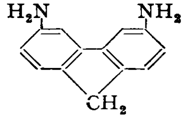
414. 3 : 6-*Disubstituted Fluorenes. Part I. The Attempted Introduction of a* 6 : 6′-*Methylene Bridge Directly into* 3 : 3′-*Diaminodiphenyl and Some of its Derivatives.*

By A. Barker and C. C. Barker.

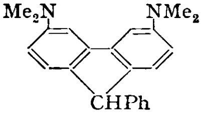
Earlier claims to have prepared 3 : 6-bisdimethylamino-9-phenylfluorene from 3 : 3′-bisdimethylaminodiphenyl and benzylidene chloride, and the lactone of *o*-3 : 6 : 9-trihydroxy-9-fluorenylbenzoic acid from 3 : 3′-dihydroxydiphenyl and phthalic anhydride, are refuted.

It is also shown that fluorene derivatives are not formed by condensing formaldehyde with 3 : 3′-diaminodiphenyl, 3 : 3′-bisdimethylaminodiphenyl, or 3 : 3′-bisdimethylamino-4 : 4′-dimethyldiphenyl. Formaldehyde appears to attack such amines only at a vacant 4-position.

Present knowledge of 3 : 6-disubstituted fluorenes is limited to 3 : 6-dibromofluorene, obtained from 3 : 6-dibromophenanthraquinone by Courtot and Kronstein (*Chim. et Ind.* [special number], 1941, **45**, 72), and 3 : 6-dimethylfluorene, obtained from 2-amino-4 : 4′-dimethylbenzophenone by Chardonnens and Wurmli (*Helv. Chim. Acta*, 1946, **29**, 922). The unknown 3 : 6-diaminofluorene (I) is thus of interest, both as a precursor, and as the parent substance of the unknown fluorene analogue of Michler's hydrol. The absorption spectrum of the colour salt of the latter, together with those of related dyes, might yield information about the configuration of the fluorene molecule.



(I)



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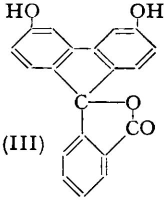
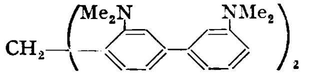


(III)



(IV)

The literature indicates that derivatives of this amine can be synthesised from the corresponding diaminodiphenyl and formaldehyde. Thus, Adam (*Compt. rend.*, 1886, **103**, 207) obtained fluorene and bis-4-diphenylylmethane, from methylene dichloride and diphenyl in the presence of aluminium chloride, although Meyer and Wesche (*Ber.*, 1917, **50**, 442) failed to repeat the preparation, and Weiler (*Ber.*, 1874, **7**, 1188) obtained only bis-4-diphenylylmethane from diphenyl and dimethoxymethane in the presence of concentrated sulphuric acid. Dutt (*J.*, 1926, 1171) claims to have prepared 3 : 6-bisdimethylamino-9-phenylfluorene (II), from benzylidene chloride and 3 : 3′-bisdimethylaminodiphenyl, and also the lactone (III) of *o*-3 : 6 : 9-trihydroxy-9-fluorenylbenzoic acid, from phthalic anhydride and 3 : 3′-dihydroxydiphenyl, both condensations being effected with aluminium chloride.

Products (II) and (III) are analogues of the leuco-base of malachite green and phenolphthalein, respectively, and their formation suggests the possibility of introducing a 6 : 6′-methylene bridge into diphenyl when powerful *para*-directing groups occupy the 3 : 3′-positions. Emde (*Chem. Zentr.*, 1915, II, 278), however, failed to obtain 3 : 6-diaminofluorene from 3 : 3′-diaminodiphenyl and formaldehyde, and attempts by the present authors confirmed that none was formed. This result was not regarded as decisive, since the action of formaldehyde on primary aromatic amines is often complex, and the condensation of formaldehyde with the tertiary base 3 : 3′-bisdimethylaminodiphenyl was therefore examined.

Dutt (*loc. cit.*) claimed to have prepared 3 : 3′-bisdimethylaminodiphenyl, m. p. 126—128°, by the methylation of 3 : 3′-diaminodiphenyl with methyl sulphate. In the present work, 3 : 3′-diaminodiphenyl dihydrobromide was methylated with methyl alcohol at 147°, and, after extensive purification, 3 : 3′-bisdimethylaminodiphenyl, m. p. 34·5°, was isolated and characterised. The same material was obtained by heating *m*-bromo-*NN*-

dimethylaniline with palladised calcium carbonate, hydrazine hydrate, and alcoholic potassium hydroxide. Considerable doubt is therefore thrown on the authenticity of Dutt's material. Moreover, condensation of authentic 3 : 3′-bisdimethylaminodiphenyl with benzylidene chloride, as described by Dutt, gave non-crystalline products which yielded no colour when oxidised in acid solution with lead peroxide—contrary to Dutt's claim to have prepared 3 : 6-bisdimethylamino-9-phenylfluorene and to have oxidised it to a coloured carbinol.

Attempts to repeat Dutt's preparation of (III) were equally unsuccessful, and it would appear that his claim, to have prepared these two compounds and to have measured the absorption maxima of their colour salts, is invalid.

The condensation of 3 : 3′-bisdimethylaminodiphenyl dihydrochloride and aqueous formaldehyde, in equimolecular amounts, gave no 3 : 6-bisdimethylaminofluorene. When the amount of formaldehyde was halved, the 3 : 3′-bisdimethylaminodiphenyl reacted completely to form a crystalline base, $C_{33}H_{40}N_2$, which is believed to be di-(3 : 3′-bisdimethylamino-4-diphenylyl)methane (IV). From this it would appear that a successful fluorene synthesis might be achieved when the reactive 4 : 4′-positions in the starting amine are occupied. Accordingly, 3 : 3′-bisdimethylamino-4 : 4′-dimethyldiphenyl was treated with formaldehyde, but the amine was recovered unchanged. This can only be attributed to steric hindrance at the 6 : 6′-positions, since *o*-dimethylaminotoluene condenses almost quantitatively with formaldehyde to give 4 : 4′-bisdimethylamino-3 : 3′-dimethyldiphenylmethane. This supports the structure (IV) for the base $C_{33}H_{40}N_4$, and indicates that a successful synthesis of 3 : 6-disubstituted fluorenes by the attempted route is unlikely.

EXPERIMENTAL

3 : 3′-*Bisdimethylaminodiphenyl.*—(*a*) 3 : 3′-diaminodiphenyl dihydrobromide (7·37 g.) and methyl alcohol (3·60 c.c.) were heated in a sealed tube for 11 hr. at 147° ± 2°. The product was made alkaline with dilute sodium hydroxide and extracted with ether. The dried extract (Na_2SO_4) was evaporated and the residue refluxed for 15 min. with acetic anhydride (15 c.c.) which was then removed at reduced pressure. The residue was dissolved in ether, and the filtered solution was washed with dilute sodium hydroxide and dried, the solvent removed, and the residue slowly distilled at 170° (bath-temp.)/10^{-3} mm. Two fractions, (i) (1·98 g.) and (ii) (0·65 g.), were collected. A solution of the partially solid (i) in benzene was adsorbed on activated alumina (1·4 × 15 cm.); elution in benzene (150 c.c.) gave 3 : 3′-*bisdimethylaminodiphenyl* (1·5 g.), m. p. 34·5° (Found : C, 78·9; H, 8·3; N, 12·0. $C_{16}H_{20}N_2$ requires C, 79·9; H, 8·3; N, 11·7%). The *dimethiodide* formed needles, m. p. 262—263° (decomp.), from aqueous alcohol (Found : C, 41·4; H, 4·8; N, 5·4; I, 47·8. $C_{16}H_{20}N_2,2CH_3I$ requires C, 41·2; H, 5·0; N, 5·3; I, 48·4%), and the *dipicrate*, micro-crystals, m. p. 202—203° (decomp.), from acetic acid (Found : N, 15·8. $C_{16}H_{20}N_2,2C_6H_3O_7N_3$ requires N, 16·0%).

(*b*) A mixture of *m*-bromo-*NN*-dimethylaniline (30·0 g.), methyl alcoholic potassium hydroxide (300 c.c.; 5% w/v), hydrazine hydrate (50% aqueous solution; 7·5 c.c.), and palladised calcium carbonate (15 g.; 0·5% of Pd) was heated in a steel autoclave at 135—140° for 90 min. (255 lb./in.^{2}). The bulk of the alcohol was removed, giving a sludge which was extracted with hot benzene. After drying of the solution (Na_2SO_4) and removal of the solvent, a viscous oil was obtained which gave a semisolid fraction (6·0 g.), b. p. 195°/2 mm. Similar fractions from three experiments were combined (16·6 g.) and slowly distilled at 165—180° (bath-temp.)/10^{-3} mm., giving three fractions : (i) 1·89 g., $n_D^{12\cdot5}$ 1·6335; (ii) 13·0 g., $n_D^{12\cdot5}$ 1·6440; and (iii) 1·35 g., $n_D^{12\cdot5}$ 1·6460. The middle fraction was purified by chromatography in benzene on activated alumina, 3 : 3′-bisdimethylaminodiphenyl, m. p. 33—34°, appearing in the fore-runnings. The m. p. was not depressed on admixture of the material with that from (*a*).

The Reaction of Formaldehyde with 3 : 3′-*Bisdimethylaminodiphenyl.*—3 : 3′-Bisdimethylaminodiphenyl dihydrochloride (1·76 g.; prepared by passing dry hydrogen chloride into a solution of the base in methyl alcohol and adding ether) was heated in a sealed tube with water (4·0 c.c.) and formalin (39·1% w/v; 0·215 c.c.) at 55° for 12 hr. and then at 95° for 30 hr. Basification of the solution yielded a white solid (1·4 g.), m. p. 60—70°, which gave a negligible amount of sublimate at 180°/10^{-3} mm. and therefore contained no 3 : 6-bisdimethylaminofluorene. This material was purified on alumina by using benzene as eluant. The fore-runnings yielded a syrup which solidified on addition of ethyl alcohol, giving *di*-(3 : 3′-*bisdimethylamino*-4-

diphenylyl)methane, m. p. 137—137·5° (from ethyl alcohol) [Found: C, 80·1; H, 8·0; N, 11·4%; *M* (micro-Rast), 495. $C_{33}H_{40}N_4$ requires C, 80·4; H, 8·2; N, 11·4%; *M*, 492].

3 : 3′-*Diamino*-4 : 4′-*dimethyldiphenyl*.—4 : 4′-Dimethyl-3 : 3′-dinitrodiphenyl, m. p. 178·5—179·5° (Adams and Patterson, *J. Amer. Chem. Soc.*, 1935, **57**, 762) was purified by sublimation at 155°/10^{-4} mm., followed by crystallisation from acetic acid. Dennett and Turner (*J.*, 1926, 480) give m. p. 175—176°. This nitro-compound (29 g.), iron pin dust (50 g.), concentrated hydrochloric acid (5·0 c.c.), and ethyl alcohol (85%; 500 c.c.) were vigorously stirred and refluxed for 40 hr. Sodium carbonate (5·0 g.) was added, refluxing continued for 30 minutes, and the iron sludge then removed. The liquors were concentrated to 200 c.c., concentrated hydrochloric acid (50 c.c.) was added, and the precipitated amine hydrochloride removed, washed with benzene, and basified with dilute sodium hydroxide. Sublimation of the resulting amine at 180°/10^{-3} mm., followed by crystallisation from aqueous alcohol, gave 3 : 3′-*diamino*-4 : 4′-*dimethyldiphenyl* (18·0 g.), m. p. 121° (Found: C, 79·2; H, 7·5; N, 13·2. $C_{14}H_{16}N_2$ requires C, 79·3; H, 7·5; N, 13·2%).

3 : 3′-*Bisdimethylamino*-4 : 4′-*dimethyldiphenyl*.—Trimethyl phosphate (2·5 c.c.) was added dropwise to 3 : 3′-diamino-4 : 4′-dimethyldiphenyl (2·0 g.) at 170°, and the temperature was raised to 195—200° for 1 hr. The product was refluxed for 1 hr. with aqueous sodium hydroxide (16% w/v; 30 c.c.), diluted with water, and extracted with ether. Evaporation of the dried extract gave a product, which, after being refluxed with acetic anhydride (6·0 c.c.) for 1 hr. and then freed from the acetic anhydride, was dissolved in dilute hydrochloric acid, the impurities extracted with benzene, and the aqueous layer basified. The precipitated solid (2·15 g.; m. p. 63—66°) was purified by chromatography on activated alumina, light petroleum (b. p. 60—80°) being used as eluant. The fore-runnings gave 3 : 3′-*bisdimethylamino*-4 : 4′-*dimethyldiphenyl* (1·8 g.), m. p. 67·5—68·5° (from light petroleum followed by methyl alcohol) (Found: C, 80·1; H, 9·0; N, 10·5. $C_{18}H_{24}N_2$ requires C, 80·6; H, 9·0; N, 10·4%).

Grateful acknowledgment is made to Distillers Co. Ltd. and to Imperial Chemical Industries Limited for grants. One of us (A. B.) thanks the University College of Hull for a Research Studentship, and the Lancashire County Council for personal grants.

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[*Received, April 1st*, 1953.]