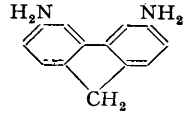
3 : 6-*Disubstituted Fluorenes. Part II.* The Preparation of* 3 : 6-*Diaminofluorene from Fluorene, and the Attempted Internuclear Cyclisation of Derivatives of* 4 : 4′-*Diaminodiphenylmethane.*

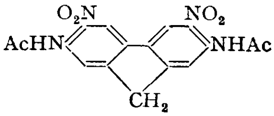
By A. Barker and C. C. Barker.

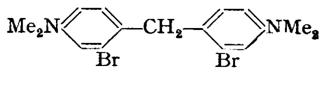
[Reprint Order No. 4792.]

3 : 6-Diaminofluorene is prepared from fluorene in eight stages, and its constitution is established, Attempts to prepare this amine, or its derivatives, from derivatives of 4 : 4′-diaminodiphenylmethane succeeded only with 4 : 4′-bisdimethylaminobenzophenone-2-diazonium sulphate which gave 3 : 6-bisdimethylaminofluorenone.

As a result of the failure of attempts to prepare 3 : 6-diaminofluorene (I) from 3 : 3′-diaminodiphenyl (Part I*) its preparation from fluorene was examined. Nitration of 2 : 7-diacetamidofluorene gave the 3 : 6-dinitro-derivative (II) which failed, however, to give 3 : 6-dinitrofluorene by successive deacetylation, tetrazotisation, and treatment with ethanol; a sparingly soluble, red product which resisted purification was obtained. Campbell and Stafford (*J.*, 1952, 299) obtained a similar product when attempting to deaminate 2-amino-3-nitrofluorene, and it seems that this is determined by the methylene group since the deamination of 4 : 4′-diamino-2 : 2′-dinitrodiphenylmethane encounters similar difficulties, whereas 2 : 7-diamino-3 : 6-dinitrofluorenone is deaminated normally.


(I)


(II)


(III)

Nitration of 2 : 7-diacetamidofluorenone gave the 3 : 6-dinitro-derivative which was identical with oxidised 2 : 7-diacetamido-3 : 6-dinitrofluorene. Deacetylation and deamination of this fluorene proceeded normally but gave a crude product from which 3 : 6-dinitrofluorenone could be isolated only by sublimation at 250—260°/10^{-4} mm. Reduction of this nitro-compound with stannous chloride gave yellow 3 : 6-diaminofluorenone which was reduced by the Huang-Minlon–Wolff–Kishner reaction to 3 : 6-diaminofluorene, the yield from fluorene amounting to 10%.

The structure of 3 : 6-diaminofluorenone, and hence of its precursors, was established by converting the base into 3 : 6-dichloro- and 3 : 6-dibromo-fluorenone by the Sandmeyer reaction. Huntress and Cliff (*J. Amer. Chem. Soc.*, 1933, **55**, 2566) prepared the former from 5 : 5′-dichlorodiphenic anhydride, and Courtot and Kronstein (*Chim. et Ind.*, Special No., 1941, **45**, 72) prepared the latter from 3 : 6-dibromophenanthraquinone. Attempts to convert 3 : 6-diaminofluorene into 3 : 6-dibromofluorene by the Sandmeyer reaction gave 3 : 6-dibromofluorenone and unidentified substances, but 3 : 6-diaminofluorenone is a useful precursor and gave 3 : 6-dihydroxyfluorenone without difficulty.

A more attractive route to 3 : 6-diaminofluorene or its derivatives was offered by the internuclear cyclisation of derivatives of 4 : 4′-diaminodiphenylmethane, but considerable difficulties were encountered. Thus, 2 : 2′-dibromo-4 : 4′-bisdimethylaminodiphenylmethane (III) gave only 4 : 4′-bisdimethylaminodiphenylmethane (33%) and starting material (54%) when heated with palladised calcium carbonate, hydrazine, and potassium hydroxide, although Busch and Weber (*J. pr. Chem.*, 1936, **146**, 47) obtained low yields of 2 : 7-diaminofluorene from 5 : 5′-diamino-2 : 2′-dibromodiphenylmethane by this method. 4 : 4′-Bisdimethylamino-2 : 2′-di-iododiphenylmethane also gave no 3 : 6-bisdimethylaminofluorene when heated with copper powder. 4 : 4′-Diacetamido- and 4 : 4′-bisdimethylamino-diphenylmethane-2-diazonium sulphates failed to cyclise when decomposed by heat or copper powder, but 4 : 4′-bisdimethylaminobenzophenone-2-diazonium sulphate gave

---

* Part I, *J.*, 1953, 2034.

3 : 6-bisdimethylaminofluorenone (12%) when heated in 88% sulphuric acid; the use of 10% acid gave only 4 : 4′-bisdimethylamino-2-hydroxybenzophenone. A similar effect was observed by Guyot and Haller (*Bull. Soc. chim.*, 1901, **25**, 750) when cyclising 4 : 4′ : 4″-trisdimethylaminotriphenylmethane-2-diazonium sulphate, and Nunn, Schofield, and Theobald (*J.*, 1952, 2800) found that 5-nitrobenzophenone-2-diazonium sulphate cyclised only in the presence of high concentrations of sulphuric acid.

EXPERIMENTAL

2 : 7-*Diamino*-3 : 6-*dinitrofluorene*.—2 : 7-Diacetamidofluorene (10 g.; cf. Morgan and Thomason, *J.*, 1926, 2691) was added during 10 min. to a stirred mixture of nitric acid (95%; 100 c.c.) and acetic anhydride (24 c.c.) at −12° (±2°). After 2 more minutes the solution was poured into ice-water, and the solid was removed, washed until acid-free, dried, extracted with hot acetic acid to remove material which inhibited crystallisation, and crystallised from nitrobenzene (100 c.c.), giving 2 : 7-*diacetamido*-3 : 6-*dinitrofluorene* (11·0 g.) as yellow needles which decomposed slowly above 290° (Found: C, 54·5; H, 3·9; N, 14·2. $C_{17}H_{14}O_6N_4$ requires C, 55·1; H, 3·8; N, 15·1%). A mixture of the nitro-compound (6·0 g.), sulphuric acid (24 c.c.), and water (6·0 c.c.) was kept at 100° for 40 min., the solution was poured on ice, and the solid washed until acid-free, dried, and crystallised from aniline, giving red-brown crystals of 2 : 7-*diamino*-3 : 6-*dinitrofluorene* which did not melt at 360° (Found: C, 54·4; H, 3·6; N, 20·6. $C_{13}H_{10}O_4N_4$ requires C, 54·5; H, 3·5; N, 19·6%).

2 : 7-*Diacetamidofluorenone*.—Fluorene, technical grade twice crystallised from acetic acid, was oxidised to fluorenone (59%) by Huntress, Hershberg, and Cliff's method (*J. Amer. Chem. Soc.*, 1931, **53**, 2720), and the ketone was nitrated to 2 : 7-dinitrofluorenone (73%) as directed by Schmidt, Retzlaff, and Haid (*Annalen*, 1912, **390**, 224). The dinitro-compound (162 g.) was added cautiously to a solution of hydrated stannous chloride (1100 g.) in a mixture of concentrated hydrochloric acid (900 c.c.) and acetic acid (1600 c.c.), and the suspension was stirred and refluxed for 1 hr. The mixture was cooled, and the solid removed and washed with concentrated hydrochloric acid, then with water until the filtrate just became violet. The residue was dissolved in boiling water, the filtered solution basified with sodium hydroxide, and the precipitate washed with water, dried, and crystallised from nitrobenzene (1250 c.c.), giving 2 : 7-diaminofluorenone (108 g.), m. p. 284—286°. Schmidt, Retzlaff, and Haid (*loc. cit.*) employed tin and hydrochloric acid and gave m. p. 290°; Courtot (*Ann. Chim.*, 1930, **14**, 87) used ethanolic ammonium sulphide, but attempts to repeat his work gave crystalline, brown substances, m. p. 245—250°.

Acetylation of the amine with acetic anhydride in acetic acid gave pinkish-red 2 : 7-*diacetamidofluorenone* (94%), m. p. 348—349° (from nitrobenzene) (Found: C, 68·9; H, 5·0; N, 9·5. $C_{17}H_{14}O_3N_2$ requires C, 69·4; H, 4·8; N, 9·5%).

2 : 7-*Diamino*-3 : 6-*dinitrofluorenone*.—(*a*) 2 : 7-Diacetamidofluorenone (128 g.) was added during 10 min. to a stirred mixture of nitric acid (95%; 1550 c.c.) and acetic anhydride (350 c.c.) at 0—5°. After 12 more minutes the solution was poured into ice-water, and the solid washed until acid-free, and dried, giving 2 : 7-*diacetamido*-3 : 6-*dinitrofluorenone* (150 g.), which crystallised from nitrobenzene in orange needles, m. p. 335—336° (Found: C, 53·2; H, 3·1; N, 15·0. $C_{17}H_{12}O_7N_4$ requires C, 53·1; H, 3·1; N, 14·6%). Hydrolysis of this compound as described for its fluorene analogue gave the corresponding *amine* as a bronze-coloured powder which did not melt at 400°, sparingly soluble in hot pyridine, hot aniline, or hot nitrobenzene (Found: C, 52·3; H, 2·5; N, 19·5. $C_{13}H_8O_5N_4$ requires C, 52·0; H, 2·7; N, 18·7%).

(*b*) A solution of 2 : 7-diacetamido-3 : 6-dinitrofluorene (1·4 g.) and chromium trioxide (2·0 g.) in acetic acid (50 c.c.) was refluxed for 3 hr., and cooled, and the separated solid (0·65 g.) dried and crystallised from nitrobenzene, giving 2 : 7-diacetamido-3 : 6-dinitrofluorenone, m. p. and mixed m. p. with a sample from (*a*) 335—336°.

3 : 6-*Dinitrofluorenone*.—Nitrosylsulphuric acid, prepared from sodium nitrite (36 g.) and sulphuric acid (200 c.c.), was added at 0—5° during 15 min. to a solution of 2 : 7-diamino-3 : 6-dinitrofluorenone, obtained by hydrolysing the diacetyl compound (65 g.) with water (123 c.c.) and sulphuric acid (227 c.c.). After 40 min. the solution was run into hypophosphorous acid (50%; 835 c.c.) at 0—5° and kept at that temperature overnight. Water (1500 c.c.) was added and the separated solid (44 g.) washed until acid-free, dried, sublimed at 250—260°/10^{-4} mm., then crystallised from nitrobenzene (120 c.c.), giving yellow leaflet of 3 : 6-*dinitrofluorenone* (22 g.), m. p. 342—345°, raised to m. p. 344—346° when chromatographed in pyridine on activated alumina (Found: C, 57·8; H, 2·3; N, 10·2. $C_{13}H_6O_5N_2$ requires C, 57·8; H, 2·3; N, 10·4%).

The sublimation was slow, 10 g. of sublimate collecting in 12 hr. on a condensing surface of 10 in.^{2}.

3 : 6-*Diaminofluorenone.*—Reduction of 3 : 6-dinitrofluorenone (m. p. 342—345°; 40 g.) by the procedure used with 2 : 7-dinitrofluorenone gave a crude product which was purified by passing its filtered solution in pyridine down an alumina column (16 × 2·5 cm.). The eluate (1500 c.c.) was evaporated to 170 c.c., and water (340 c.c.) slowly added, giving 3 : 6-*diaminofluorenone* (27 g.), m. p. 249—251°, sparingly soluble in benzene, alcohol, or acetone, and crystallising from pyridine–alcohol in small orange needles, m. p. 252—253° (Found : C, 74·2; H, 4·7; N, 13·1. $C_{13}H_{10}ON_2$ requires C, 74·3; H, 4·8; N, 13·3%).

3 : 6-*Diaminofluorene.*—A stirred mixture of 3 : 6-diaminofluorenone (2·0 g.), trimethylene glycol (14 c.c.), hydrazine hydrate (100%; 1 c.c.), and sodium hydroxide (1·0 g.) was heated to 165° during 10 min.; a deep red precipitate was formed. The temperature was then raised to 200° during 30 min., to 205° during 1 hr., and to 215° during 3 hr. The clear amber-coloured solution was cooled and diluted with water (30 c.c.), and the crystalline product sublimed at 190—200°/10^{-3} mm. and crystallised from aniline (4·5 c.c.), giving long, pale yellow needles of 3 : 6-*diaminofluorene* (1·47 g.), m. p. 260—262°, sparingly soluble in hot ethanol, acetone, or benzene, more soluble in hot pyridine, readily soluble in hot aniline and hot nitrobenzene (Found : C, 78·7; H, 6·0; N, 14·2. $C_{13}H_{12}N_2$ requires C, 79·6; H, 6·1; N, 14·3%).

3 : 6-*Dihydroxyfluorenone.*—Nitrosylsulphuric acid, from sodium nitrite (1·05 g.) and sulphuric acid (10 c.c.), was added dropwise to a solution of 3 : 6-diaminofluorenone (1·6 g.) in sulphuric acid (10 c.c.), and the solution was kept for 20 min., then poured on ice (100 g.). After 2 hr. the excess of nitrous acid was destroyed with sulphamic acid, the solution was boiled for 10 min. and cooled, the precipitate dissolved in aqueous alkali, the deep red solution filtered and acidified, and the product sublimed at 210/10^{-4} mm., then crystallised from ethanol (15 c.c.), giving deep yellow, feathery needles of 3 : 6-*dihydroxyfluorenone*, m. p. 345—348° (decomp.) (Found : C, 72·9; H, 3·6. $C_{13}H_8O_3$ requires C, 73·6; H, 3·8%).

3 : 6-*Dichloro- and* 3 : 6-*Dibromo-fluorenone.*—3 : 6-Diaminofluorenone was tetrazotised in hydrochloric acid and treated with cuprous chloride; the product was sublimed at 210°/10^{-4} mm. and crystallised from benzene, giving 3 : 6-dichlorofluorenone (50%) as yellow needles, m. p. 299—301° (Found : C, 62·7; H, 2·4; Cl, 28·3. Calc. for $C_{13}H_6OCl_2$: C, 62·7; H, 2·4; Cl, 28·5%). Huntress and Cliff (*loc. cit.*) give m. p. 301°. The oxime had m. p. 250—252° (Found : C, 59·0; H, 3·0; N, 5·2. Calc. for $C_{13}H_7ONCl_2$: C, 59·1; H, 2·7; N, 5·3%). Huntress and Cliff (*loc. cit.*) give m. p. 243·5°. 3 : 6-Dibromofluorenone, prepared in an analogous manner, formed small, yellow leaflets (from benzene–xylene), m. p. 323—324°. Courtot and Kronstein (*loc. cit.*) give m. p. 321° (Found : Br. 47·0. Calc. for $C_{13}H_6OBr_2$: Br, 47·3%). The oxime had m. p. 262—263° (Found : N, 3·9. Calc. for $C_{13}H_7ONBr_2$: N, 4·0%). Courtot and Kronstein (*loc. cit.*) give m. p. 262—263°.

2-*Acetamido*-4 : 4′-*bisdimethylaminobenzophenone.*—Nitration of 4 : 4′-bisdimethylaminodiphenylmethane gave the 2-nitro-derivative (76%), m. p. 96—98°, removal of the 2 : 2′-dinitroderivative by fractional basification replacing the ethanol extraction used by Ullmann and Marie (*Ber.*, 1901, **34**, 4314), who give m. p. 95°. Reduction of the nitro-compound in 90% ethanol with iron pin-dust and hydrochloric acid, followed by acetylation, gave 2-acetamido-4 : 4′-bisdimethylaminodiphenylmethane (70%), m. p. 140—141°. Kliegl (*Ber.*, 1906, **39**, 1273) gives m. p. 138°. Oxidation of this amine with chloranil gave 2-acetamido-4 : 4′-bisdimethylaminobenzophenone (78%), m. p. 165—167°. Kliegl (*loc. cit.*) gives m. p. 162°.

3 : 6-*Bisdimethylaminofluorenone.*—The aforementioned ketone (5·0 g.) was hydrolysed with sulphuric acid (25·5 c.c.) and water (9·0 c.c.) at 100° for 1 hr. and the amine suspension was diazotised at 0° with nitrosylsulphuric acid prepared from sodium nitrite (1·08 g.) and sulphuric acid (12·5 c.c.). After being kept overnight at room temperature the diazonium solution was kept at 70° until a sample gave no red colour with water. The product was precipitated with ammonia, dried, and eluted from a short alumina column with dry pyridine until a sample of the eluate, diluted with ethanol, gave no orange-red fluorescence in ultra-violet light. The pyridine was removed, and the residue crystallised from ethanol (15 c.c.) containing potassium hydroxide (1·0 g.), giving deep orange crystals of 3 : 6-*bisdimethylaminofluorenone* (0·5 g.), m. p. 249—250° (Found : C, 76·0; H, 6·8; N, 9·8. $C_{17}H_{18}ON_2$ requires C, 76·7; H, 6·8; N, 10·5%). Attempted cyclisation in 10% sulphuric acid gave pale yellow 4 : 4′-*bisdimethylamino*-2-*hydroxybenzophenone*, m. p. 172°, insoluble in aqueous but soluble in ethanolic potassium hydroxide (Found : C, 71·7; H, 7·1; N, 9·6. $C_{17}H_{20}O_2N_2$ requires C, 71·8; H, 7·1; N, 9·8%).

4 : 4′-*Diacetamido*-2-*aminodiphenylmethane.*—4 : 4′-Diaminodiphenylmethane was nitrated as described by Epstein (D.R.-P. 139,989; *Chem. Zentr.*, 1903, I, 798) but separation of the

2-nitro- from the 2 : 2′-dinitro-derivative by fractional basification of the sulphates, nitrates, or chlorides failed because partial neutralisation precipitated the salts. By dissolving the bases in acetic acid and adding 4 vol. of water the dinitro-compound was precipitated, leaving in solution 4 : 4′-diamino-2-nitrodiphenylmethane (60%), m. p. 88·5—90° (from ethanol) (Found : N, 17·7. Calc. for $C_{13}H_{13}O_2N_3$: N, 17·3%). Epstein gives m. p. 100—101°. The *diacetyl* derivative (94%), m. p. 220—223°, formed cream-coloured crystals from aqueous acetic acid (Found : C, 62·3; H, 5·0; N, 12·9. $C_{17}H_{17}O_4N_3$ requires C, 62·4; H, 5·2; N, 12·8%). A suspension of this nitro-compound (7·8 g.) in ethanol (95 c.c.) was stirred with hydrochloric acid (25 c.c.) and hydrated stannous chloride (21 g.) for 20 hr. at 20°, then kept overnight at 0°. White amine stannichloride separated and was collected, washed with a little ethanol, suspended in water, and decomposed with hydrogen sulphide. The mixture was filtered at 40° and the residue extracted with boiling wate r(4 × 100 c.c.), giving a solution which deposited the aminehydrochloride on cooling. Basification with ammonia gave 4 : 4′-*diacetamido*-2-*aminodiphenylmethane* (2·2 g.), m. p. 226—227° (needles from methanol) (Found : C, 68·1; H, 6·4; N, 13·9. $C_{17}H_{19}O_2N_3$ requires C, 68·6; H, 6·5; N, 14·1%).

4 : 4′-*Bisdimethylamino*-2 : 2′-*di-iodo- and* 2 : 2′-*Dibromo*-4 : 4′-*bisdimethylamino-diphenylmethane.*—*m*-Iodo-*NN*-dimethylaniline (9·0 g.), aqueous formaldehyde (40%; 1·3 c.c.), and hydrochloric acid (0·2 c.c.) were stirred at 20° for 12 hr., 40° for 24 hr., then 100° for 6 hr., and the product was crystallised from ethanol (180 c.c.), giving 4 : 4′-bisdimethylamino-2 : 2′-di-iododiphenylmethane (5·0 g.), m. p. 122—123°. Mascarelli, Toschi, and Zambonini (*Atti R. Accad. Lincei*, 1910, **19**, ii, 341) give m. p. 123° for material prepared in low yield from 2 : 2′-diamino-4 : 4′-bisdimethylaminodiphenylmethane. The 2 : 2′-dibromo-compound was prepared in a similar manner from *m*-bromo-*NN*-dimethylaniline.

UNIVERSITY COLLEGE, HULL.

[*Received, November* 13*th*, 1953.]