

310. Some 1:1'- and 2:2'-Dinaphthyl Derivatives and a New Synthesis of 3:3'-Dinitro-1:1'-dinaphthyl.

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3:3'-Dinitro-1:1'-dinaphthyl, formerly prepared by the action of copper on 1-iodo-3-nitronaphthalene, is now synthesised from naphthidine.

4:4'-DIACETAMIDO-1:1'-DINAPHTHYL readily dinitrated to give 3:3'-dinitro-4:4'-diacetamido-1:1'-dinaphthyl which was hydrolysed by boiling ethyl-alcoholic sulphuric acid to 3:3'-dinitro-4:4'-diamino-1:1'-dinaphthyl, a compound easily bisdiazotised by a nitrosyl-glacial acetic acid procedure (cf. Hodgson and Walker, *J.*, 1933, 1620; Schoutissen, *J. Amer. Chem. Soc.*, 1933, 55, 4535). Replacement of both diazo-groups by hydrogen was effected by means of ethanol to give 3:3'-dinitro-1:1'-dinaphthyl in over 80% yield, a compound previously prepared in poor yield by the action of copper on 1-iodo-3-nitronaphthalene (cf. Cumming and Howie, *J.*, 1931, 3179; Chudožilov, *Chem. Listy*, 1925, 19, 187). Reduction to 3:3'-diamino-1:1'-dinaphthyl by the procedure of Cumming and Howie (*loc. cit.*) was confirmed, and so the 3:3'-positions taken up by the nitro-groups in the original nitration of 4:4'-diacetamido-1:1'-dinaphthyl were established. Replacement of the amino- by hydroxyl groups in 3:3'-dinitro-3:3'-diamino- or 3:3'-diacetamido-1:1'-dinaphthyl to give 3:3'-dinitro-4:4'-dihydroxy-1:1'-dinaphthyl was effected by boiling aqueous sodium hydroxide, and the *disodium* salt of this compound was sparingly soluble in cold water.

1:1'-Diacetamido-2:2'-dinaphthyl is dinitrated in the 4:4'-positions to give 4:4'-dinitro-1:1'-diacetamido-2:2'-dinaphthyl, as proved by hydrolysis with ethanol and concentrated sulphuric acid to give the known 3:6-dinitro-1:2:7:8-dibenzocarbazole (Hodgson and Habeshaw, this vol., p. 77).

EXPERIMENTAL.

Nitration of 4:4'-Diacetamido-1:1'-dinaphthyl.—The diacetyl compound (1.9 g.), prepared by the addition of acetic anhydride to a boiling solution of naphthidine in glacial acetic acid (cf. Cumming and Howie, *J.*, 1932, 528), was added gradually in a finely divided state with stirring to nitric acid (35 c.c., *d* 1.42), the temperature being maintained below 15°; the solution darkened as the solid dissolved and, after about 15 minutes, a yellow precipitate of 3:3'-dinitro-4:4'-diacetamido-1:1'-dinaphthyl began to separate. After being stirred for 30 minutes from the final addition of the acetyl compound, the mixture was poured into water, the yellow precipitate (1.95 g., m. p. 332–335°) filtered off, washed acid free with water, dried, and crystallised first from nitrobenzene in which it was moderately soluble and then from glacial acetic acid in which it was sparingly soluble, to give yellow micro-crystals, m. p. 342–343° (Found: N, 12.5. $C_{24}H_{18}O_6N_4$ requires N, 12.2%).

3:3'-Dinitro-4:4'-diamino-1:1'-dinaphthyl.—This was obtained by refluxing the diacetyl derivative above (5 g.) for 10 hours with ethanol (50 c.c.) and dilute sulphuric acid (50 c.c., *d* 1.08); the solution deepened in colour and on being poured into water (600 c.c.) afforded the free *amine* (4.5 g.) which was filtered off, washed with water until acid-free and then with ethyl acetate, and crystallised once from nitrobenzene in which it was readily soluble at the boil and twice from glacial acetic acid in which it was moderately soluble, to give bright yellow micro-plates, m. p. 338–339° (Found: N, 14.8. $C_{20}H_{14}O_4N_4$ requires N, 15.0%).

3:3'-Dinitro-1:1'-dinaphthyl.—This was prepared by addition of finely powdered 3:3'-dinitro-

4 : 4'-diamino-1 : 1'-dinaphthyl (5.7 g.) to a mixture of sodium nitrite (7 g.) in sulphuric acid (60 c.c., *d* 1.84) below 40°; a deep green solution was formed which was diluted with glacial acetic acid at such a rate that the temperature was kept between 45° and 50°, and the colour became golden-brown. After being stirred for 1 hour, the mixture was added gradually to ethanol (200 c.c.) and, when the reaction had moderated, the whole was heated on the water-bath under the reflux for 1 hour, after which the volatile portion was removed by distillation until the residual volume was *ca.* 100 c.c.; it was then poured into water (500 c.c.). The light brown precipitate of 3 : 3'-dinitro-1 : 1'-dinaphthyl (4.6 g.) was filtered off, washed acid free with water, crystallised once from nitrobenzene and twice from glacial acetic acid, and so obtained in golden yellow plates, *m. p.* 280—281° (Cumming and Howie, *loc. cit.*, give *m. p.* 281°; Chudožilov, *loc. cit.*, gives *m. p.* 262—264°) (Found : N, 8.3. Calc. for $C_{20}H_{12}O_4N_2$: N, 8.1%). This compound (2.4 g.), when boiled for 5 hours with glacial acetic acid (180 c.c.) and zinc dust (20 g.) during the gradual addition of hydrochloric acid (2 c.c., *d* 1.18), was reduced to 3 : 3'-diamino-1 : 1'-dinaphthyl which was removed from the cold reaction mixture, after it had been made alkaline with solid sodium hydroxide, by ether extraction; after removal of the ether from the dried extract, the residue of the crude 3 : 3'-diamino-1 : 1'-dinaphthyl crystallised from benzene in white plates, *m. p.* 269—270° (Cumming and Howie, *loc. cit.*, give *m. p.* 270°) (Found : N, 10.1. Calc. for $C_{20}H_{16}N_2$: N, 9.9%).

3 : 3'-Dinitro-4 : 4'-dihydroxy-1 : 1'-dinaphthyl.—This was formed when 3 : 3'-dinitro-4 : 4'-diamino-1 : 1'-dinaphthyl (2 g.) was refluxed with 20% aqueous sodium hydroxide (50 c.c.) for 2 hours; when the red *disodium* salt of the dihydroxy-compound began to be deposited, the mixture was filtered hot, and, on cooling, an almost quantitative yield was obtained in reddish-brown crystals (Found : Na, 10.8. $C_{20}H_{10}O_6N_2Na_2$ requires Na, 11.0%), which were sparingly soluble in cold but readily so in hot water. When the sodium salt was mixed with dilute acids, 3 : 3'-dinitro-4 : 4'-dihydroxy-1 : 1'-dinaphthyl was liberated and crystallised from glacial acetic acid in which it was moderately soluble in yellow micro-plates, *m. p.* 319—320° (Found : N, 7.6. $C_{20}H_{12}O_6N_2$ requires N, 7.4%).

3 : 3'-Diamino-4 : 4'-diacetamido-1 : 1'-dinaphthyl.—This was obtained when a solution of 3 : 3'-dinitro-4 : 4'-diacetamido-1 : 1'-dinaphthyl (2 g.) in boiling glacial acetic acid (150 c.c.) was treated gradually with zinc dust (20 g.) during 45 minutes, the mixture refluxed a further 30 minutes, and filtered hot into water (500 c.c.). The flocculent precipitate was extracted with boiling water (100 c.c.) containing hydrochloric acid (50 c.c., *d* 1.18) and the filtered extract cooled; the *dihydrochloride* of 3 : 3'-diamino-4 : 4'-diacetamido-1 : 1'-dinaphthyl then separated (1.2 g.) in white feathery needles which did not melt (Found : ionic chlorine, 14.9. $C_{24}H_{22}O_2N_4 \cdot 2HCl$ requires Cl, 15.1%), and were only sparingly soluble in cold water but readily so in hot water and dilute acids. After basification with dilute ammonia, the white precipitate of 3 : 3'-diamino-4 : 4'-diacetamido-1 : 1'-dinaphthyl was crystallised from glacial acetic acid, giving white micro-crystals which carbonised at 390° (Found : N, 13.9. $C_{24}H_{22}O_2N_4$ requires N, 14.1%), and were almost insoluble in benzene, xylene, or ethanol.

1 : 1'-Diacetamido-2 : 2'-dinaphthyl.—This was prepared by stirring a suspension of 1 : 1'-diamino-2 : 2'-dinaphthyl (1.7 g.) in acetic anhydride (25 c.c.) for 24 hours at room temperature (cf. Cumming and Howie, *J.*, 1932, 531); attempts to make this compound more rapidly by hot acetylation resulted in the formation of 1 : 2 : 7 : 8-dibenzocarbazole, which crystallised from benzene in white needles, *m. p.* 216° (Bucherer and Schmidt, *J. pr. Chem.*, 1909, 79, 375, give *m. p.* 216°) (Found : N, 5.4. Calc. for $C_{20}H_{13}N$: N, 5.2%).

Dinitration of 1 : 1'-Diacetamido-2 : 2'-dinaphthyl.—1 : 1'-Diacetamido-2 : 2'-dinaphthyl (0.95 g.) was stirred into nitric acid (25 c.c., *d* 1.42) below 15°. After 30 minutes' stirring, 4 : 4'-dinitro-1 : 1'-diacetamido-1 : 1'-dinaphthyl began to separate, and at this stage the mixture was poured into water (120 c.c.), and the precipitated dinitro-compound (0.5 g.) dissolved in a hot mixture of glacial acetic acid and xylene (1 : 1) from which it separated in light yellow micro-needles, *m. p.* 341—342° (Found : N, 12.5. $C_{24}H_{18}O_6N_4$ requires N, 12.3%). When this compound (1 g.) was refluxed for 10 hours with ethanol (10 c.c.) and sulphuric acid (10 c.c., *d* 1.08), and the mixture poured into water, there separated 3 : 6-dinitro-1 : 2 : 7 : 8-dibenzocarbazole which crystallised from nitrobenzene in yellow micro-crystals; these had no *m. p.* but sintered at *ca.* 385° (cf. Hodgson and Habeshaw, *loc. cit.*) (Found : N, 12.1. Calc. for $C_{20}H_{11}O_4N_3$: N, 11.8%).

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