

15. The Reduction of 1 : 1'-Azonaphthalene and of Some 4 : 4'-Derivatives.

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A preparation of 1 : 1'-diamino-2 : 2'-dinaphthyl is described and the ease of ring closure to 1 : 2 : 7 : 8-dibenzocarbazole is further exemplified in the reduction of some 4 : 4'-disubstituted-1 : 1'-azonaphthalenes.

THE work of Nietzki and Goll (*Ber.*, 1885, 18, 3253) and of Cumming and Steele (*J.*, 1923, 2464) on the reduction of 1 : 1'-azonaphthalene has been confirmed. The very satisfactory method of Cohen and Oesper (*Ind. Eng. Chem. Anal.*, 1936, 8, 306) for preparing naphthidine, has now been found by suitable modification to afford about 10% of 1 : 1'-diamino-2 : 2'-dinaphthyl and about 40% of 1 : 2 : 7 : 8-dibenzocarbazole. The high yield of the dibenzocarbazole indicates that the initial transformation of 1 : 1'-hydrazonaphthalene in the acid medium would appear to afford approximately equal amounts of 1 : 1'-diamino-2 : 2'-dinaphthyl and 4 : 4'-diamino-1 : 1'-dinaphthyl; ease of ring closure, however, converts about 80% of the former into the dibenzocarbazole.

The facile ring closure of 1 : 1'-diamino-2 : 2'-dinaphthyl has now been further exemplified by the reduction with acid stannous chloride in ethyl alcohol of 4 : 4'-dinitro-, 4 : 4'-dichloro-, and 4-nitro-4'-methoxy-1 : 1'-azonaphthalene, each of which affords a moderate yield of the corresponding *dibenzocarbazole* but no detectable 4 : 4'-disubstituted-1 : 1'-diamino-2 : 2'-dinaphthyl; the remainder of the reduction products are simple α -naphthylamine derivatives. When alcohol is absent from the reduction mixture, complete fission takes place at the azo-group with production of 4-substituted- α -naphthylamines. From 4 : 4'-nitro- and 4-nitro-4'-methoxy-1 : 1'-azonaphthalene the *hydrochlorides* of 3 : 6-diamino- and 3-amino-6-methoxy-1 : 2 : 7 : 8-dibenzocarbazole were obtained, but the free bases were too susceptible to oxidation for their preservation.

EXPERIMENTAL.

Reduction of 1 : 1'-Azonaphthalene.—The azo-compound (20 g.) was reduced by stannous chloride in ethyl alcohol and hydrochloric acid according to the directions of Cohen and Oesper (*loc. cit.*), and their process for separating the 4 : 4'-diamino-1 : 1'-dinaphthyl hydrochloride followed. After this had been filtered off, the filtrate was diluted with water (200 c.c.) and the white precipitate of crude 1 : 2 : 7 : 8-dibenzocarbazole (8 g.) removed and dried; it crystallised from benzene in colourless needles, m. p. 216° (Bucherer and Schmidt, *J. pr. Chem.*, 1909, 79, 375, give m. p. 216°) (Found : N, 5.2. Calc. for $C_{20}H_{12}N_2$: N, 5.2%), which gave a reddish-brown solution with concentrated sulphuric acid. When solutions of the carbazole and picric acid in xylene were mixed together, 1 : 2 : 7 : 8-dibenzocarbazole picrate separated; this crystallised from benzene in red needles, m. p. 239° (Vesely, *Ber.*, 1905, 38, 139, gives m. p. 238.5°) (Found : N, 11.5. Calc. for $C_{28}H_{18}O_7N_4$: N, 11.3%). The filtrate after removal of the carbazole was rendered alkaline by adding powdered sodium hydroxide until the precipitated tin salts were redissolved, after which the white insoluble residue of 1 : 1'-diamino-2 : 2'-dinaphthyl (2 g.) was removed and washed with water; it crystallised from benzene in colourless plates, m. p. 278–279° (Nietzki and Goll, *loc. cit.*, give m. p. 273°) (Found : N, 10.1. Calc. for $C_{20}H_{16}N_2$: N, 9.9%), which were readily soluble in dilute hydrochloric acid.

Reduction of 4 : 4'-Dinitro-1 : 1'-Azonaphthalene.—The azo-compound (5 g.) was dissolved in glacial acetic acid (250 c.c.) and reduced with stannous chloride and hydrochloric acid by the method of Nietzki and Goll (*loc. cit.*), and the mixture poured into water. The yellow precipitate (3.5 g.) was dried, dissolved in sufficient hot nitrobenzene to maintain dissolution at room temperature, and the solution saturated with hydrogen chloride and kept overnight. The yellow precipitate of 3 : 6-dinitro-1 : 2 : 7 : 8-dibenzocarbazole (1.2 g.) was insoluble in the usual solvents but separated from hot nitrobenzene in yellowish micro-crystals which sintered at ca. 385° (Found : N, 12.0. $C_{20}H_{11}O_4N_3$ requires N, 11.8%). Attempted reduction of 4 : 4'-dinitro-1 : 1'-azonaphthalene in alkaline or neutral media produced only insoluble tars. When, however, a suspension of the compound (5 g.) in gently boiling ethyl alcohol (75 c.c.) was treated gradually with a solution of stannous chloride (25 g.) in hydrochloric acid (25 c.c., *d* 1.16), dissolution occurred after about 75% of the reducing mixture had been added. The mixture was refluxed gently for 1 hour, then cooled and kept overnight; 3 : 6-diamino-1 : 2 : 7 : 8-dibenzocarbazole dihydrochloride separated as a white powder (1.6 g.) which was filtered off and washed with ether; it decomposed at ca. 360–370° (Found : Cl, 19.4. $C_{10}H_{15}N_3 \cdot 2HCl$ requires Cl, 19.2%). When to a boiling solution of 3 : 6-dinitro-1 : 2 : 7 : 8-dibenzocarbazole (1 g.) (see above) in glacial acetic acid solution was added a solution of stannous chloride (5 c.c.) in hydrochloric acid (5 c.c., *d* 1.16), a fairly vigorous reaction ensued and, on cooling, the above dihydrochloride (0.3 g.) separated (Found : Cl, 19.2%); a similar result was obtained when the 4 : 4'-dinitro-1 : 1'-azonaphthalene was reduced in glacial acetic acid solution with excess of stannous chloride and hydrochloric acid, but neither method is preferable to that described above. When a solution of the dihydrochloride (1 g.) in hydrochloric acid (5 c.c., *d* 1.16) and water (10 c.c.) was tetrazotised at 5° by addition of sodium nitrite (0.55 g.) dissolved in the minimum of water, and then boiled for 90 minutes on the water-bath with ethyl alcohol (150 c.c.), 1 : 2 : 7 : 8-dibenzocarbazole was obtained on removal of the alcohol, and, after two recrystallisations from benzene, was obtained in colourless needles, m. p. 216° (Found : N, 10.1%).

Reduction of 4 : 4'-dinitro-1 : 1'-azonaphthalene (2 g.) by crystallised stannous chloride (10 g.) dissolved in hydrochloric acid (20 c.c., *d* 1.16) gave 1 : 4-naphthylenediamine, which was isolated by dilution of the reaction mixture with water (25 c.c.) and addition of solid sodium hydroxide until the tin compounds had dissolved; the mixture was then filtered rapidly, and the solid residue boiled with a mixture of glacial acetic acid (20 c.c.) and acetic anhydride (5 c.c.) for a few minutes, filtered, and diluted with water. The precipitated diacet-1 : 4-dinaphthylenediamide crystallised from dilute acetic acid in white needles, m. p. 304—305° (Kleeman, *Ber.*, 1886, **19**, 334, gives m. p. 304°) (Found : N, 11.8. Calc. for $C_{14}H_{14}O_2N_2$: N, 11.6%).

Reduction of 4 : 4'-Dichloro-1 : 1'-azonaphthalene.—The azo-compound (1 g.) was reduced according to the directions of Nietzki and Goll (*loc. cit.*) in hot glacial acetic acid solution with stannous chloride and hydrochloric acid. No hydrochloride separated from the solution on cooling, but on pouring it into water a white precipitate of 3 : 6-dichloro-1 : 2 : 7 : 8-dibenzocarbazole formed. After several crystallisations from acetic acid it was obtained in colourless plates, m. p. 228—230° (Found : Cl, 20.8. $C_{20}H_{11}NCl_2$ requires Cl, 21.1%). When the dihydrochloride of 3 : 6-diamino-1 : 2 : 7 : 8-dibenzocarbazole (2 g.) was diazotised at 5° as above, and the filtered solution added to one of cuprous chloride (5 g.) in hydrochloric acid (50 c.c.), a vigorous reaction ensued which was completed by heating for 30 minutes on the water-bath. The precipitate was filtered off, washed with dilute ammonia to remove copper salts, and crystallised 4 times from acetic acid; 3 : 6-dichloro-1 : 2 : 7 : 8-dibenzocarbazole was thus obtained as slightly coloured plates, m. p. 226—228°, mixed m. p. with previous preparation, 227—229° (Found : Cl, 20.9%). When the azo-compound (2 g.) was reduced with stannous chloride and hydrochloric acid as above, and the reduction mixture made alkaline and steam distilled, 4-chloro-1-naphthylamine (0.5 g.) was obtained; this crystallised from light petroleum in colourless needles, m. p. 98° (Reverdin and Crépieux, *Ber.*, 1900, **33**, 682, give m. p. 98°) (Found : Cl, 19.8. Calc. for $C_{10}H_8NCl$: Cl, 20%); the acetyl derivative crystallised from ethyl alcohol in colourless needles, m. p. 186—187° (Reverdin and Crépieux, *loc. cit.*, give m. p. 186.5°).

4-Nitro-4'-methoxy-1 : 1'-azonaphthalene.—(a) *Preparation.* 4-Nitro-1-naphthylamine (5 g.) was diazotised in glacial acetic-sulphuric acid by the method of Hodgson and Walker (*J.*, 1933, 1620), and the excess of nitrous acid removed by urea from the solution, which was then stirred into a solution of 1-methoxynaphthalene (4.2 g.) in glacial acetic acid (24 c.c.), and the mixture kept for 7 days, by which time most of the coupled product had separated (7.5 g.). This 4-nitro-4'-methoxy-1 : 1'-azonaphthalene was crystallised twice from glacial acetic acid, and then several times from ethyl alcohol-benzene, whence it was obtained in thick red needles with a metallic lustre, m. p. 224.5° (Found : N, 12.0. $C_{21}H_{15}O_3N_3$ requires N, 11.8%). When diluted with a little water, the residual acetic acid solution gave a precipitate which crystallised from benzene in reddish-brown plates, m. p. 256—259° (Found : N, 12.1%), which must be the isomeric 4-nitro-1'-methoxy-1 : 2'-azonaphthalene.

(b) *Reduction.* The azo-compound (1 g.) was reduced in glacial acetic acid solution with stannous chloride and hydrochloric acid as described above; no hydrochloride separated on keeping, and the white precipitate (0.45 g.) of 3-nitro-6-methoxy-1 : 2 : 7 : 8-dibenzocarbazole, obtained when the solution was poured into water, crystallised from acetic acid in small slightly yellowish plates, m. p. 258—259° (Found : N, 8.4. $C_{21}H_{14}O_3N_2$ requires N, 8.2%), which would neither diazotise nor form a hydrochloride. Alternatively, the azo-compound (1 g.) was dissolved in ethyl alcohol (170 c.c.), sodium hydroxide added (1.5 g.) (the red solution then became blue), and the mixture stirred at 65° with zinc dust (7 g.). The colour rapidly disappeared and the cooled mixture was filtered after the addition of water (50 c.c.), the residue being then extracted with hot benzene. From the cooled extract silvery flakes of the above dibenzocarbazole were obtained which crystallised from benzene (charcoal) in colourless plates having a silvery lustre, m. p. and mixed m. p. with previous preparation, 258—259° (Found : N, 8.5%). When the azo-compound was reduced with stannous chloride and hydrochloric acid as for 4 : 4'-dinitro-1 : 1'-azonaphthalene (above), 3-amino-6-methoxy-1 : 2 : 7 : 8-dibenzocarbazole hydrochloride (1.8 g.) was obtained (Found : Cl, 9.9. $C_{21}H_{16}ON_2 \cdot HCl$ requires Cl, 10.2%), but attempts to isolate the free base were unsuccessful owing to the rapidity with which oxidation followed basification.

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