41. *Some Dinaphthyl Bases. Part II. Reduction of* 1 : 1′-*Azoxy- and* 1 : 1′-*Azo-naphthalenes. Isolation of* 1 : 1′-*Hydrazonaphthalene.*

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CUMMING and HOWIE (J., 1932, 528) have synthesised naphthidine (4 : 4′-diamino-1 : 1′-dinaphthyl), dinaphthyline (1 : 1′-diamino-2 : 2′-dinaphthyl), and dinaphthyleneimine (1 : 1′-imino-2 : 2′-dinaphthyl) and established their constitutions. This part describes their preparation by reduction of 1 : 1′-azoxy- and 1 : 1′-azo-naphthalene in neutral, alkaline, and acid solutions (cf. Cumming and co-workers, J., 1923, **123**, 2464; 1924, **125**, 1111; *J. Roy. Tech. Coll. Glasgow*, 1929, 43). An interesting fact emerges from this work, *viz.*, that the " benzidine conversion " as applied to the hydrazonaphthalenes takes place with the 1 : 1′- as well as with the 2 : 2′-derivative, in acid, neutral, and alkaline solutions.

Nietzki and Goll (*Ber.*, 1885, **18**, 3252) by alkaline reduction of 1 : 1′-azonaphthalene, and Cumming and Steel (J., 1923, **123**, 2464) by neutral reduction of 1-nitronaphthalene, obtained colourless plates, m. p. 275°, and needles, m. p. 274°, respectively. The latter compound on recrystallisation from alcohol containing sulphur dioxide to prevent oxidation gave a different modification, plates, m. p. 271°; mixed m. p. 269·5°. Both papers describe this compound, m. p. 275°, as 1 : 1′-hydrazonaphthalene. Cumming and Steel advanced the view that the two compounds, m. p. 274° and 271°, are represented by $R{\cdot}NH{\cdot}NHR$ and $R{\cdot}N{:}NH_2R$, corresponding to the *s*.- and *as*.-azoxynaphthalenes. The formulation of the *as*.-form is now considered unsatisfactory, and in any case we have proved that sulphur dioxide is capable of converting the hydrazo-compound into dinaphthyline, m. p. 281°.

By neutral reduction of *s*.-azoxynaphthalene, and by alkaline reduction of *s*.- and *as*.-azoxy- and azo-naphthalenes we obtained, in fair yield, colourless plates, m. p. 153° (turning red). This compound showed a tendency to turn yellow on keeping, and an alcoholic solution of the solid gradually turned red in air and deposited on concentration under reduced pressure 1 : 1′-azonaphthalene, m. p. 186—187°, identified by mixed m. p. On treatment with acids, even sulphurous and carbonic acids, it gave dinaphthyline, m. p. 281°, identical with that obtained by Cumming and Howie (*loc. cit.*). In one experiment when an attempt was made to isolate it from its alcoholic solution by addition of water, a compound, m. p. 275° showing no depression when mixed with dinaphthyline, was obtained. The compound, m. p. 153°, is therefore 1 : 1′-hydrazonaphthalene and undergoes conversion with very great readiness. At its m. p. it is converted into 1 : 1′-azonaphthalene and 1-naphthylamine.

We decided, in the light of these facts, to repeat the work of Nietzki and Goll and of Cumming and Steel. We obtained the compound, m. p. about 274°, and were able to procure, thanks to Mr. Steel, the actual specimen made by him in 1923, m. p. 274°. Both those compounds gave no depression when mixed with dinaphthyline, and showed no tendency to oxidise in alcoholic solution. We therefore conclude that the statement in both papers, that the compound oxidised to the azo-compound in alcoholic solution, referred to the alcoholic solution of the reduction product. Their azo-compound was undoubtedly formed by oxidation of the hydrazo-compound, but the compound actually isolated by them was dinaphthyline.

The constitutions of the compounds obtained in this work were established by comparison with those obtained in Part I.

EXPERIMENTAL.

1 : 1′-*Azonaphthalene.*—1 : 1′-Azoxynaphthalene, prepared in 32% yield by the method of Cumming and Steel (*loc. cit.*), could not be reduced to the azo-stage by neutral reduction using 5% excess of Zn. The method of Nietzki and Goll (*loc. cit.*) was modified as follows: 9 g. of 4-amino-1 : 1′-azonaphthalene, prepared by coupling 1-naphthylamine to diazotised 1-naphthylamine, in 900 c.c. of abs. EtOH and 26 c.c. of conc. H_2SO_4 were treated with excess of amyl nitrite and the whole was refluxed until it was deep red. Addition of H_2O pptd. a brownish mass, which, recryst. several times from AcOH (carbon), yielded orange-red needles, m. p. 188°; a further yield was obtained by addition of H_2O to the filtrate (total, 3 g.). The method of Hantzsch and Schmiedel (*Ber.*, 1897, **30**, 82) *viâ* 1-naphthalene*syn*diazonium sulphonate yielded in our hands only 2·5 g. of azonaphthalene from 20 g. of 1-naphthylamine, but is nevertheless the more convenient. Cumming and Steel record m. p. 186°, and Hantzsch and Schmiedel 188—189°, for azonaphthalene. The variation may be explained by the fact that 1 : 1′-azonaphthalene begins to sublime at about 170°.

1 : 1′-*Hydrazonaphthalene.*—(1) 3 G. of *s*.-1 : 1′-azoxynaphthalene were reduced according to Cumming and Steel (*loc. cit.*) with Zn dust (4·5 g.) until the solution became colourless. The solid matter, obtained by concn. almost to dryness of the solution under reduced press., was quickly dried and extracted with light petroleum. The white crystals formed gave, after 5 fractional recrystns. from the same solvent, 1 : 1′-*hydrazonaphthalene*, colourless plates, m. p. 153°, turning bright red (Found: C, 84·3; H, 5·7; N, 9·9; *M*, 242. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·6; N, 9·9%; *M*, 284). The filtrate from the reduction when cooled deposited white needles, $9Zn(OH)_2,4NH_4Cl,6H_2O$ (see Cumming and Howie, *J. Roy. Tech. Coll. Glasgow*, 1929, 49). 1 : 1′-Hydrazonaphthalene is insol. in H_2O, sparingly sol. in EtOH and in light petroleum, but readily in C_6H_6; a dil. HCl suspension, treated with a drop of bleaching powder solution, gave a bluish-violet colour, discharged by excess of bleaching powder solution. Naphthidine, m. p. 202°, also was obtained from the reduction product.

(2) 4 G. of *s*.-1 : 1′-azoxynaphthalene in 300 c.c. of EtOH containing 8 g. of NaOH were heated to boiling, and reduced as quickly as possible with a large excess of Zn until the solution was nearly colourless. Without filtration the most of the EtOH was removed under reduced press. During concn. the reduction was completed, the solution becoming colourless. The residue was removed, quickly dried, and extracted with C_6H_6. This solution on concn. gave

1 : 1′-hydrazonaphthalene (1·3 g.), m. p. 153° after two recrystns. from C_6H_6. Prolonged heating at the b. p. must be avoided, otherwise dinaphthyline also is formed.

(3) 1 G. of *as*.-1 : 1′-azoxynaphthalene (see Cumming and Howie, J., 1931, 3184) in 100 c.c. of EtOH containing 3 g. of NaOH was reduced as in (2). 1 : 1′-Hydrazonaphthalene, m. p. 153°, was obtained.

(4) 1 G. of 1 : 1′-azonaphthalene, suspended in 150 c.c. of EtOH containing 4·5 g. of NaOH, was reduced as in (2), and the reduction mixture quickly filtered into H_2O containing NH_4HS. The ppt. was removed, rapidly dried, and extracted with C_6H_6. Treatment of the C_6H_6 solution as above gave 1 : 1′-hydrazonaphthalene, m. p. 153°.

Naphthidine.—(5) 1 G. of *as*.-1 : 1′-azoxynaphthalene was treated as in (1), and the dried residue extracted with C_6H_6. After concn. of the C_6H_6 solution to about 20 c.c., naphthidine separated on cooling, colourless plates, m. p. 202° after several recrystns. from EtOH. By further concn. of the filtrate traces of 1 : 1′-hydrazonaphthalene and dinaphthyleneimine were obtained.

(6) The method of Cumming and Steel (*loc. cit.*), reduction with $SnCl_2$, produced from *s*.- and *as*.-azoxynaphthalene a poor yield of naphthidine, silvery plates, m. p. 202°. (The *s*.-form is more readily reduced in acid solution than the *as*.-form, whilst in alkaline solution the reverse holds.)

(7) The method of Nietzki and Goll (*loc. cit.*), reduction with $SnCl_2$, gave a nearly theoretical yield of naphthidine, m. p. 202°, from 1 : 1′-azonaphthalene.

Dinaphthyline.—(8) 1 G. of 1 : 1′-azonaphthalene, reduced as in (1) to the colourless stage, was filtered into H_2O containing NH_4HS to prevent oxidation. The yellowish ppt. was extracted with abs. EtOH and the crystals were recrystallised several times from the same solvent, a small yield of dinaphthyline, needles, m. p. 281°, being obtained.

(9) 4 G. of *s*.-1 : 1′-azoxynaphthalene were reduced as in (2) in presence of 30 g. of NaOH and the reduction mixture was refluxed for ½ hr. before concn. The dried residue, extracted and recryst. from C_6H_6, gave 0·9 g. of dinaphthyline, colourless plates, m. p. 281°; a mixed m. p. with that obtained by conversion of 1 : 1′-hydrazonaphthalene in acid solution showed no depression.

Dinaphthyleneimine.—(10) 2 G. of *s*.-1 : 1′-azoxynaphthalene in 300 c.c. of EtOH at 40° were treated with HCl aq. and Zn dust until the solution was colourless. After rapid filtration, and concn. under reduced press. to small bulk, the residue was dried and extracted with light petroleum. The product, recryst. from the same solvent, yielded dinaphthyleneimine, colourless leaflets, m. p. 221°. The same result was obtained when HCl was replaced by AcOH. In one reduction below 30°, dinaphthyleneimine was not obtained, but its parent base, dinaphthylline, along with a little naphthidine.

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