

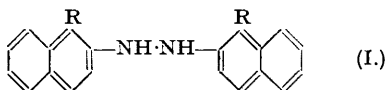
259. *The Naphthidine Transformation involving β -Positions only.*

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1 : 1'-*Dichloro-* and 1 : 1'-*dibromo-2 : 2'-diamino-3 : 3'-dinaphthyl* are most probably formed in the reduction of 1 : 1'-*dichloro-* and 1 : 1'-*dibromo-2 : 2'-azonaphthalene* by stannous chloride in ethyl alcohol-hydrochloric acid solution. 1-Bromo-2-naphthalenediazoacetate decomposes at ordinary temperatures to give 1-bromo-2-naphthaleneazo- β -naphthol.

THE naphthidine transformations already reported have involved α - and $\alpha\beta$ -positions only (Nietzki and Goll, *Ber.*, 1885, **18**, 3254; Veselý, *Ber.*, 1905, **38**, 136; Meisenheimer and Witte, *Ber.*, 1903, **36**, 4153; Hodgson and Habeshaw, this vol., p. 77). It is of interest also that,

in the transformation of 1 : 1'-hydrazonaphthalene, the 2- and 4-positions exhibit approximately equal activity (cf. Hodgson and Habeshaw, *loc. cit.*) while no mixed 1 : 1'-diamino-2 : 4'-dinaphthyl has ever been detected among the transformation products. No change involving the 2 : 3- (*i.e.*, solely β -positions) transformation has hitherto been reported, and, in view of the fact that among the possible resonance structures of a 1 : 1'-substituted-2 : 2'-hydrazonaphthalene there is one (I) which indicates that such a change might be possible, it appeared of interest



to investigate whether this 2 : 3-naphthidine change would occur in the cases of 1 : 1'-dichloro- and 1 : 1'-dibromo-2 : 2'-hydrazonaphthalenes (I; R = Cl or Br) since such compounds might be formed intermediately by the action of stannous chloride in ethyl alcohol-hydrochloric acid suspensions of 1 : 1'-dichloro- and 1 : 1'-dibromo-2 : 2'-azonaphthalenes (cf. Cohen and Oesper, *Ind. Eng. Chem. Anal.*, 1936, 8, 306).

As anticipated, dinaphthyl formation occurred and in all probability 1 : 1'-dichloro- and 1 : 1'-dibromo-2 : 2'-diamino-3 : 3'-dinaphthyls were formed, so that the naphthidine transformation had taken place between β -positions only. When the reduction of the above halogeno-azo-compounds was carried out with stannous chloride and hydrochloric acid in the absence of ethyl alcohol, cleavage occurred between the nitrogen atoms of the azo-group, and 1-chloro- and 1-bromo-2-naphthylamine were formed respectively. The constitutions of the above dinaphthyls were tentatively established by the fact of dihydrochloride formation in the cases of the chloro- and bromo-compounds, and of the tetrazotisation of the 1 : 1'-dibromo-2 : 2'-diamino-3 : 3'-dinaphthyl and subsequent coupling with alkaline β -naphthol to give a bisazo-compound. Since halogens were not displaced, it is most unlikely that dinaphthyl formation would involve the 4 : 4'-positions.

When a solution of 1-bromo-2-naphthalenediazoacetate was allowed to decompose at ordinary temperatures, 1-bromo-2-naphthaleneazo- β -naphthol was produced, an indication that 1-bromo-2-naphthol must first have been formed, by hydrolysis of the diazoacetate, and that unchanged diazo-compound subsequently coupled with it in the 1-position by displacement of the 1-bromine atom.

EXPERIMENTAL.

1 : 1'-Dichloro-2 : 2'-diamino-3 : 3'-dinaphthyl.—1 : 1'-Dichloro-2 : 2'-azonaphthalene (5 g.) (compare Hodgson, Leigh, and Turner, *J.*, 1942, 744) was boiled gently with ethyl alcohol (50 c.c.) and a solution of crystallised stannous chloride (10 g.) in hydrochloric acid (25 c.c., *d* 1.18) added gradually with shaking. During this addition, all the solid passed into solution, and, after the mixture had been kept on the boiling water-bath for 10 minutes, it was cooled and then treated with hydrochloric acid (25 c.c., *d* 1.18); 1 : 1'-dichloro-2 : 2'-diamino-3 : 3'-dinaphthyl dihydrochloride then separated (1.6 g.) in colourless crystals which were filtered off and washed with ether; it was soluble in water, evolved hydrogen chloride on treatment with concentrated sulphuric acid with formation of a yellow solution, and decomposed on heating at *ca.* 400° (Found : Cl, 33.2. $C_{20}H_{16}N_2Cl_4$ requires Cl, 33.3%).

1 : 1'-Dichloro-2 : 2'-diamino-3 : 3'-dinaphthyl was obtained as a white flocculent precipitate, which coagulated somewhat on standing and became biscuit coloured, when warm aqueous sodium carbonate was stirred into a warm aqueous solution of the above dihydrochloride; it was filtered off, washed, dried, and crystallised from benzene-light petroleum (1 : 1) in small colourless needles, m. p. 121–122° (Found : N, 8.1; Cl, 19.8. $C_{20}H_{14}N_2Cl_2$ requires N, 7.9; Cl, 20.1%), which soon became discoloured in air and were moderately soluble in ethyl alcohol; the alcoholic solution, however, rapidly oxidised and became reddish-violet, a red film forming on the wall of the glass container.

Preparation of 1-Bromo-2-naphthylamine.—A solution of β -naphthylamine (28 g.) in glacial acetic acid (200 c.c.) containing acetic anhydride (25 c.c.) was heated on the boiling water-bath for 20 minutes to complete the acetylation, and then treated dropwise with the theoretical amount of bromine (32 g.) during continuous stirring. The resulting 1-bromoaceto-2-naphthalide was precipitated by dilution with water in quantitative yield, the precipitate dissolved in alcohol (250 c.c.), hydrochloric acid (30 c.c., *d* 1.18) added, and the mixture boiled for 6 hours to complete the hydrolysis; 1-bromo-2-naphthylamine was then precipitated by addition of 20% aqueous sodium hydroxide, purified by crystallisation from light petroleum, and obtained in colourless needles, m. p. 63° (Cosiner, *Ber.*, 1881, 14, 59, gives m. p. 63°) (Found : Br, 35.8. Calc. for $C_{10}H_8NBr$: Br, 36.0%).

1-Bromo-2-naphthaleneazo- β -naphthol, obtained by diazotisation of the above amine and coupling with alkaline β -naphthol in the usual way, crystallised from toluene in dark red parallelepipeds, m. p. 169–170° (Found : N, 7.5; Br, 21.0. $C_{20}H_{13}ON_2Br$ requires N, 7.4; Br, 21.2%), which gave with concentrated sulphuric acid a bright red-violet colour turning to crimson on dilution with water.

1-Bromo-2-naphthaleneazo- β -naphthylamine, obtained by diazotisation of the above amine in aqueous hydrochloric acid and coupling with an alcoholic solution of β -naphthylamine in the presence of acetic acid and sodium acetate (cf. Hodgson and Foster, *J.*, 1941, 755), crystallised from toluene in scarlet plates, m. p. 174–175° (Found : N, 11.3; Br, 20.8. $C_{20}H_{14}N_2Br$ requires N, 11.2; Br, 21.0%), which

gave with concentrated sulphuric acid a blue colour turning to red and then to orange-yellow on addition of water.

1 : 1'-*Dibromo-2 : 2'-azonaphthalene*.—A mixture of finely divided 1-bromo-2-naphthylamine (5 g.) in hydrochloric acid (25 c.c., *d* 1.18) and water (50 c.c.) was diazotised by addition of a solution of sodium nitrite (2 g.) in water (10 c.c.) with stirring at 0°, the resulting yellow solution filtered, treated rapidly under vigorous stirring with crystallised sodium acetate (40 g.) dissolved in the minimum amount of water to remove mineral acid, and then immediately followed by a solution of crystallised sodium sulphite (10 g.) in water (50 c.c.). A light brown precipitate immediately separated (5.7 g.), and after the mixture had been stirred for 30 minutes at room temperature, when no further reaction of the precipitate with alkaline β -naphthol was detected (absence of diazo-sulphite, cf. Hodgson and Marsden, *J.*, 1943, 470), it was heated to 60° and filtered. The precipitate of 1 : 1'-*dibromo-2 : 2'-azonaphthalene* crystallised from benzene in yellow plates, m. p. 193–195° (Found : N, 6.6; Br, 36.2. $C_{20}H_{12}N_2Br_2$ requires N, 6.4; Br, 36.4%), which gave with concentrated sulphuric acid a Bordeaux-red solution turning to scarlet on addition of water.

When the solution of 1-bromonaphthalenediazonium chloride above was treated with sodium acetate only, 1-bromo-2-naphthaleneazo- β -naphthol separated on keeping; it crystallised from toluene in red parallelepipeds, m. p. and mixed m. p. with authentic specimen 168–170° (Found : N, 7.5; Br, 21.0%). If an inadequate amount of sodium acetate is added before the sodium sulphite, the resulting 1 : 1'-*dibromo-2 : 2'-azonaphthalene* is mixed with the azo- β -naphthol dye above.

1 : 1'-*Dibromo-2 : 2'-diamino-3 : 3'-dinaphthyl*.—A suspension of 1 : 1'-*dibromo-2 : 2'-azonaphthalene* (5 g.) in ethyl alcohol (50 c.c.) was heated on the boiling water-bath during the gradual addition with vigorous shaking of a solution of crystallised stannous chloride (10 g.) in hydrochloric acid (25 c.c., *d* 1.18), and the boiling continued (30 minutes) until most of the suspended matter had passed into a nearly colourless solution. The mixture was filtered hot, cooled, hydrochloric acid (20 c.c., *d* 1.18) added, the precipitate (*a*) filtered off, and the solution kept; crystals (*b*) of 1 : 1'-*dibromo-2 : 2'-diamino-3 : 3'-dinaphthyl dihydrochloride* then separated. Crystals (*b*) were filtered off and washed with ether (Found : Ionic Cl, 13.6. $C_{20}H_{14}N_2Br_2 \cdot 2HCl$ requires Cl, 13.8%). Precipitate (*a*) and crystals (*b*) were repeatedly stirred with hydrochloric acid (5 c.c., *d* 1.18) and water (10 c.c.), aqueous sodium nitrite was added until a positive reaction for free nitrous acid was obtained, the mixtures were filtered, and the resulting solutions of 1 : 1'-*dibromo-3 : 3'-dinaphthyl-2 : 2'-tetrazonium chlorides* were stirred into alkaline β -naphthol; in each case 1 : 1'-*dibromo-3 : 3'-dinaphthyl-2 : 2'-bisazo- β -naphthol* separated; this compound crystallised from toluene in red micro-plates, m. p. 315° (Found : N, 7.6; Br, 21.1. $C_{40}H_{24}O_2N_4Br_2$ requires N, 7.4; Br, 21.3%), which give a brilliant blue-violet colour with concentrated sulphuric acid.

The dihydrochloride [crystals (*b*) above] was cautiously decomposed with sodium carbonate or ammonia at about 60°; the resulting *base* crystallised from toluene–light petroleum in minute colourless needles, m. p. 117° (Found : N, 6.5; Br, 36.0. $C_{24}H_{14}N_2Br_2$ requires N, 6.3; Br, 36.2%).

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