37. *Octahydrodinaphthyline and Octahydronaphthidine.*

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An improved procedure for the preparation of dinaphthyline and of naphthidine is described. These compounds have been reduced to the corresponding *octahydro*-derivatives and converted into *tetramethyl* derivatives. This work was intended as the first stage of an investigation of the effect of condensed rings on the resolvability and ease of racemisation of certain diphenyl derivatives of the type investigated by Shaw and Turner (J., **1933**, 135). Unfortunately, neither tetramethyldinaphthyline nor tetramethyloctahydrodinaphthyline forms quaternary derivatives, so it is now proposed to use a different series of substances for the investigation. The preparation and properties of those reduced dinaphthyl derivatives which have been obtained are recorded.

THE methods described by Nietzki and Goll (*Ber.*, 1885, **18**, 3259) and Cumming and Steel (J., **1923**, **123**, 2468) for the preparation of dinaphthyline from azonaphthalene by a benzidine change are not entirely satisfactory, the former on account of the ease with which hydrazonaphthalene is oxidised in the air before it can be transformed into dinaphthyline, the latter owing to decomposition and polymerisation during the evaporation of alcohol in the final stages. A modified procedure embodying some features of both methods has been found to give improved yields. Naphthidine is formed at the same time and can be isolated.

By reduction with sodium and amyl alcohol ar-*octahydrodinaphthyline* and ar-*octahydronaphthidine* have been obtained. Although naphthidine forms a quaternary ammonium compound fairly easily, corresponding salts of dinaphthyline and of its octahydro-derivative could not be obtained.

EXPERIMENTAL.

Dinaphthyline.—1-Naphthylamine was converted into 4-amino-1 : 1′-azonaphthalene and then into azonaphthalene as described by Michaelis and Erdmann (*Ber.*, 1895, **28**, 2198) and Nietzki and Goll (*loc. cit.*). Azonaphthalene (4 g.), suspended in a boiling solution of 8·5 g. of potassium hydroxide in 800 c.c. of methylated spirit, was reduced with zinc dust. The use of potassium hydroxide in preference to sodium hydroxide, and of methylated spirit instead of absolute alcohol, was found to accelerate the reaction without diminishing the yield, reduction being complete after 2 hours' boiling. When colourless, the boiling solution was rapidly decanted into a mixture of 95 c.c. of concentrated hydrochloric acid and 100 c.c. of water, kept for 24 hours in a tightly corked flask, and then poured into 4 l. of water; unchanged azonaphthalene was precipitated and was removed by filtration. From the clear, almost colourless filtrate, on neutralisation with concentrated potassium hydroxide solution, 3·2 g. of a mixture of dinaphthyline and naphthidine were obtained. The mixture was dissolved in 50 c.c. of 3% hydrochloric acid at 70—80° in an atmosphere of nitrogen, 50 c.c. of concentrated hydrochloric acid added, and the precipitated naphthidine hydrochloride removed. The filtrate, on neutralisation, yielded 1·8 g. of dinaphthyline, and 1·2 g. of naphthidine were obtained from the precipitated hydrochloride.

ar-*Octahydrodinaphthyline.*—1 G. of finely powdered dinaphthyline was suspended in 60 g. of boiling amyl alcohol, 4 g. of sodium added during 1 hour (the final b. p. was 180°), the hot solution poured into 200 c.c. of water, and, after shaking, the amyl alcohol layer separated. The amyl alcohol was removed in steam and the solid remaining was dissolved in hot 3% hydrochloric acid and reprecipitated, after filtration, by alkali. The precipitate was washed free from chloride, dried in a desiccator, recrystallised from 20 c.c. of boiling alcohol, and finally dried in a vacuum at 100°. ar-*Octahydrodinaphthyline* was thus obtained in colourless plates (0·53 g.), m. p. 213° (Found: C, 82·1; H, 8·0; N, 9·6. $C_{20}H_{24}N_2$ requires C, 82·2; H, 8·2; N, 9·6%).

ar-Octahydrodinaphthyline is stable when dry, but is oxidised slowly in contact with the air if damp or in solution in alcohol. It dissolves readily in dilute acids, but it was not possible to isolate a crystalline hydrochloride. No formation of the corresponding amine takes place on boiling solutions in hydrochloric acid (either dilute or concentrated) or acetic acid, and the original compound can be recovered unchanged. With sulphuric acid, of such concentration that the b. p. is above 150°, blackening takes place but no amine is formed. A cooled acid solution of *ar*-octahydrodinaphthyline can be tetrazotised, forming a clear yellow solution which gives a bright red azo-compound with alkaline β-naphthol and an amorphous iodo-derivative (which could not be obtained crystalline) when treated with potassium iodide solution (cf. Mascarelli and Benati, *Atti R. Accad. Lincei*, 1907, **16**, II, 565). This behaviour indicates that reduction has taken place in the unsubstituted rings.

Attempts to acetylate or benzoylate *ar*-octahydrodinaphthyline were fruitless (compare 2 : 2′-diaminodiphenyl, which can only be acetylated with difficulty; Tauber, *Ber.*, 1891, **24**, 199). *ar*-Octahydronaphthyline was dissolved in dry benzene (0·4 g. in 3 c.c.), excess of phenyl *iso*cyanate added, and the mixture kept for 3 days. The *bis*-NN′-*phenylcarbamyl*-ar-*octahydrodinaphthyline* formed was contaminated with carbanilide, from which it was separated with difficulty by precipitation from benzene solution by addition of light petroleum (b. p. 40—60°). It formed fine colourless needles, m. p. 168° (Found : C, 76·4; H, 6·1. $C_{34}H_{34}O_2N_4$ requires C, 77·0; H, 6·4%).

ar-*Octahydronaphthidine*.—This was prepared by reducing naphthidine in the same way as dinaphthyline. After steam-distillation the sticky tarry material was removed and dissolved in a small quantity of alcohol and a few drops of concentrated hydrochloric acid were added, followed by 25 c.c. of hot water. This dissolved the ar-*octahydronaphthidine* as its hydrochloride and the impurities were filtered off. The hot filtrate was heated with 25 c.c. of concentrated hydrochloric acid; on cooling, *ar*-octahydronaphthidine hydrochloride separated. This was dissolved in hot water, and the base liberated as a white flocculent precipitate by addition of alkali. The base was very soluble in alcohol and the usual solvents, but did not crystallise when hot saturated solutions cooled; m. p. 50° (Found : C, 82·0; H, 7·95; N, 9·2. $C_{20}H_{24}N_2$ requires C, 82·2; H, 8·2; N, 9·6%). The *diacetyl* derivative was obtained by adding 4 c.c. of acetic anhydride to a fine suspension of 0·5 g. of the base obtained by dissolving it in the least possible quantity of alcohol, adding 5 c.c. of water, and warming on a water-bath. Colourless crystalline plates slowly separated during an hour and were recrystallised from nitrobenzene; m. p. 317° (Found : N, 7·6. $C_{24}H_{28}O_2N_2$ requires N, 7·45%).

Tetramethyl-ar-*octahydrodinaphthyline*.—1·5 G. of *ar*-octahydrodinaphthyline were dissolved in the smallest possible quantity of alcohol, 100 c.c. of water added (so producing a fine suspension), the mixture heated on a water-bath, and methyl sulphate and anhydrous potassium carbonate added (15 g. of each) in small quantities with vigorous shaking during 1 hour (the mixture being kept just alkaline). After a further ½ hour's heating, the solution had become acidic and the suspended amine dissolved. A small quantity of tar was removed, and the filtrate made alkaline. The precipitated *tetramethyl*-ar-*octahydrodinaphthyline* was washed with water, dried, and recrystallised from alcohol, from which it separated in colourless plates, m. p. 154° (Found : N, 8·1. $C_{24}H_{32}N_2$ requires N, 8·05%).

Tetramethyldinaphthyline was prepared similarly, but extra care was necessary to keep the reaction mixture alkaline during methylation in order to prevent formation of the imine of dinaphthyline (which proceeds very readily in presence of acid). It was sparingly soluble in alcohol, but easily soluble in benzene, from which it separated in colourless plates, m. p. 212° (Found : N, 8·4. $C_{24}H_{24}N_2$ requires N, 8·2%). Reduction of tetramethyldinaphthyline with sodium and amyl alcohol gave an octahydro-derivative identical with the product of methylation of *ar*-octahydrodinaphthyline.

Tetramethylnaphthidine was prepared from naphthidine in the same way. It was very easily soluble in alcohol and other organic solvents and would not separate from them in a crystalline condition.

Hexamethylnaphthidineammonium Di-iodide.—0·4 G. of tetramethylnaphthidine was dissolved in 2 c.c. of methyl iodide. After 24 hours the quaternary *salt* was separated and recrystallised from methyl alcohol, from which it separated in clusters of needles, m. p. 220° (decomp.) (Found : I, 40·2. $C_{26}H_{30}N_2I_2$ requires I, 40·7%).

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