65. *Some Dinaphthyl Bases. Part I. Syntheses and Properties.*

By WILLIAM MURDOCH CUMMING and GEORGE HOWIE.

SOME confusion exists in the nomenclature and constitution of the diaminodinaphthyls isolated to date. Naphthidine has been prepared by Nietzki and Goll (*Ber.*, 1885, **18**, 3252), Cumming and Steel (J., 1923, **123**, 2468), and Corbellini and Debenedetti (*Gazzetta*, 1929, **59**, 395), who record m. p. 198° for the base. By further purification we have raised it to 202°. Clemo, Cockburn, and Spence (J., 1931, 1271) describe the preparation of naphthidine by reduction of 4 : 4′-dinitro-1 : 1′-dinaphthyl and assign to the base m. p. 191°, " alone or mixed with authentic naphthidine." They claim to have proved naphthidine to be the corresponding diamino-derivative, but give no details as to how they prepared the " authentic " specimen. It may be mentioned that 2 : 2′-diamino-1 : 1′-dinaphthyl melts at 191° (Meisenheimer and Witte, *Ber.*, 1903, **36**, 4159; Cumming and Ferrier, J., 1924, **125**, 1111). Chudožilov (*Chem. Listy*, 1925, **19**, 187) records m. p. 187°. In our hands, the conditions of Clemo and co-workers did not give a product, m. p. 191°, but m. p. 196—197°, the yield (from 1 g.) being insufficient for further recrystallisation. The conditions for reduction of 4 : 4′-dinitro-1 : 1′-dinaphthyl to naphthidine, m. p. 202°, are described. The naphthidine obtained was identical with that obtained above, and is therefore 4 : 4′-diamino-1 : 1′-dinaphthyl.

The constitution of the base, 2 : 2′-diamino-1 : 1′-dinaphthyl, obtained by Meisenheimer and Witte and by Cumming and Ferrier (*locc. cit.*) was definitely established by Chudožilov (*loc. cit.*), and hence also that of the imine, 2 : 2′-imino-1 : 1′-dinaphthyl (Meisenheimer and Witte, *loc. cit.*; Walder, *Ber.*, 1882, **15**, 2173; Japp and Maitland, J., 1903, **83**, 273; Bucherer and Schmidt, *J. pr. Chem.*, 1909, **79**, 369; Kalle & Co., D.R.-P. 343,149).

Dinaphthyleneimine or dinaphthylcarbazole (Nietzki and Goll; Cumming and Steel; Bucherer and Schmidt; D.R.-P. 343,149) was synthesised by Veselý (*Ber.*, 1905, **38**, 136), who showed it to be 1 : 1′-imino-2 : 2′-dinaphthyl. The corresponding base, dinaphthyline (Nietzki and Goll; Cumming and Steel), is therefore 1 : 1′-diamino-2 : 2′-dinaphthyl. Chudožilov (*loc. cit.*) attempted the synthesis of dinaphthyline itself, but the product was impure, m. p. 253—259°. The statement of Nietzki and Goll, that dinaphthyline gives, viâ the diazonium compound, 1 : 1′-dinaphthyl (m. p. 157°), we have been unable to confirm, but on the contrary obtained 2 : 2′-dinaphthyl (m. p. 187°).

The preparation of the new base 3 : 3′-*diamino*-1 : 1′-*dinaphthyl* is described.

The reduction of 3 : 3′-dinitro-2 : 2′-dinaphthyl did not yield the corresponding base, but a non-basic yellow compound, $C_{40}H_{26}O_3N_2$, which is being further investigated.

4 : 4′-Diamino-2 : 2′-dinaphthyl could not be obtained owing to failure to prepare the corresponding dinitro-derivative (Cumming and Howie, J., 1931, 3176).

Attempts were made to prepare 2′-nitro-2-acetamido-1 : 1′-dinaphthyl and 1′-nitro-1-acetamido-2 : 2′-dinaphthyl for subsequent reduction to the monoacetyl diamines, by acetylation of the nitroamines, but under no circumstances could acetylation be effected. Further, the nitroamines were also incapable of diazotisation. These are interesting cases of steric hindrance.

EXPERIMENTAL.

4′-*Nitro*-4-*amino*-1 : 1′-*dinaphthyl*.—2 G. of 4 : 4′-dinitro-1 : 1′-dinaphthyl (Schoepfle, *J. Amer. Chem. Soc.*, 1923, **45**, 1566), suspended in 100 c.c. of alcohol, 12 c.c. of aqueous ammonia (*d* 0·88), and 4 c.c. of water, were saturated with hydrogen sulphide and refluxed (15 minutes). After cooling, a further 12 c.c. of aqueous ammonia were added and the solution was again saturated with hydrogen sulphide under reflux (15 minutes). 3 G. of sodium sulphide in 10 c.c. of water were then added and refluxing was continued until the dinitro-compound had disappeared. The clear dark brownish-red solution was kept boiling, and sufficient water added to precipitate the *nitroamine*. On removal and recrystallisation from 80% alcohol, 0·9 g. was obtained as yellowish-brown spangles, m. p. 195—196° (Found : N, 8·6. $C_{20}H_{14}O_2N_2$ requires N, 8·9%).

Ammonium hydrogen sulphide alone will not reduce the dinitrodinaphthyl to the nitroamine, and sodium sulphide or sodium hydrogen sulphide alone reacts too vigorously. The above mixture gives a smooth reduction, but when more than 2 g. of the dinitro-compound are used at a time, the proportion of diamine is considerably increased.

The base is insoluble in dilute or concentrated hydrochloric acid. The hydrochloride was obtained as colourless crystals by adding concentrated hydrochloric acid to an alcoholic solution of the base. It formed a pale yellow diazonium compound which, coupled with 2-naphthol, gave a bright red insoluble dye. It readily gave an *acetyl* derivative, pale yellow plates, m. p. 243—244° (Found : N, 7·8. $C_{22}H_{16}O_3N_2$ requires N, 7·9%).

2′-*Nitro*-2-*amino*-1 : 1′-*dinaphthyl*.—1·5 G. of 2 : 2′-dinitro-1 : 1′-dinaphthyl (Chudožilov, *loc. cit.*), reduced as above with 5 g. of sodium sulphide, gave 0·5 g. of the *nitroamine*, lemon-yellow prisms, m. p. 251° (Found : N, 9·3%).

1′-*Nitro*-1-*amino*-2 : 2′-*dinaphthyl*.—2 G. of 1 : 1′-dinitro-2 : 2′-dinaphthyl (Chudožilov, *loc. cit.*), suspended in 150 c.c. of alcohol, were reduced (¾ hour) as above with 9 g. of sodium sulphide. The *nitroamine* formed lemon-yellow woolly needles, m. p. 264° (Found : N, 8·6%). Neither the 2 : 2′-dinitro-1 : 1′- nor the 1 : 1′-dinitro-2 : 2′-dinaphthyl was affected by ammonium hydrogen sulphide.

Naphthidine (4 : 4′-*Diamino*-1 : 1′-*dinaphthyl*).—Attempts to prepare naphthidine and its diacetyl derivatives by condensation of 1-bromo-4-naphthylamine and its acetyl derivative respectively, by means of copper powder, sodium, sodium amalgam, or aluminium chloride, with and without solvents, and at temperatures up to 230°, failed. Naphthidine was finally isolated from 4 : 4′-dinitro-1 : 1′-dinaphthyl (Schoepfle, *loc. cit.*) as follows : 5 g. in 100 c.c. of glacial acetic acid, and 10 c.c. of concentrated hydrochloric acid, were gently boiled under reflux. Zinc dust was added, a little at a time, until a clear solution was obtained (1 hour). On filtration and cooling, the insoluble hydrochloride separated, which, recrystallised several times from boiling water, gave the free base on treatment with ammonia. When recrystallised several times from alcohol, 3·5 g. of naphthidine were finally obtained in silvery plates, m. p. 202°. The base is fairly readily soluble in most common organic solvents, but insoluble in water. It was found that reduction of the dinitro-compound could also be effected with zinc dust in a melt of salicylic acid, a small yield, m. p. 198—199°, being obtained. Boiling dilute hydrochloric acid and zinc dust or iron is incapable of reducing the dinitro-compound.

The base readily gave a *diacetyl* derivative, colourless microscopic needles (from nitrobenzene), m. p. 363—364°, practically insoluble in low-boiling solvents (Found : N, 7·5. $C_{24}H_{20}O_2N_2$ requires N, 7·6%) ; a *dibenzoyl* derivative by the Schotten–Baumann method, colourless plates (from nitrobenzene), m. p. 319—320°, practically insoluble in low-boiling solvents (Found : N, 5·7. $C_{34}H_{24}O_2N_2$ requires N, 5·7%) ; and a *picrate*, yellow plates, m. p. 146—147° (darkening about 140°) from benzene (Found : N, 11·9. $2C_{20}H_{16}N_2,C_6H_3O_7N_3$ requires N, 12·3%).

3 : 3′-*Diamino*-1 : 1′-*dinaphthyl*.—0·4 G. of 3 : 3′-dinitro-1 : 1′-dinaphthyl (Chudožilov, *loc. cit.*) in 30 c.c. of boiling glacial acetic acid were reduced with zinc dust. After filtration the filtrate was rendered alkaline and extracted with ether, and the ether removed. The residue, repeatedly crystallised from benzene, gave the base in colourless plates, m. p. 270°. The base is very soluble in alcohol; the hydrochloride and sulphate are extremely soluble in water. The

small quantity of the base available prevented the preparation of any derivatives.

2 : 2′-*Diamino*-1 : 1′-*dinaphthyl*.—Attempts (see naphthidine) to condense 1-bromoacet-2-naphthalide failed. The amidation of 2 : 2′-dinaphthol in an autoclave with ammonia and ammonium hydrogen sulphite, and with ammonium carbonate and calcium chloride (compare Walder, *loc. cit.*), was no more successful. Chudožilov (*loc. cit.*) reduced 2 : 2′-dinitro-1 : 1′-dinaphthyl with sodium amalgam. We obtained it by acid reduction as follows: 1 g. in 40 c.c. of boiling glacial acetic acid was reduced (2—3 minutes) with 5 g. of zinc dust. The reduction mixture was filtered into water, the precipitate washed, extracted with a little dilute hydrochloric acid, the extract made alkaline, and the base removed and recrystallised several times from alcohol; 0·1 g. was then obtained in silvery plates, m. p. 191° (Chudožilov records m. p. 187°; Meisenheimer and Witte, 191°). The base is fairly readily soluble in hot, sparingly in cold alcohol; insoluble in hot or cold light petroleum; fairly readily soluble in cold benzene. The hydrochloride and sulphate are very soluble in water. The base readily gave a *diacetyl* derivative, colourless cubes, m. p. 235—236°, from alcohol (Found : N, 7·5. $C_{24}H_{20}O_2N_2$ requires N, 7·6%); a *dibenzoyl* derivative by the Schotten–Baumann method, colourless prisms, m. p. 235°, from nitrobenzene, practically insoluble in low-boiling solvents (Found : N, 5·7. $C_{34}H_{24}O_2N_2$ requires N, 5·7%); and a *picrate*, light brownish-yellow plates, m. p. 185° (decomp.), from benzene (Found : N, 12·3. $2C_{20}H_{16}N_2,C_6H_3O_7N_3$ requires N, 12·3%).

2 : 2′-*Imino*-1 : 1′-*dinaphthyl*.—The above reduction was repeated but the reduction mixture was kept boiling for ½ hour. The solution was filtered into water, and the precipitate washed and recrystallised from alcohol. The imine formed colourless needles, m. p. 158° (Meisenheimer and Witte record 157°). It is soluble in most organic solvents other than light petroleum. Acetylation and benzoylation could not be effected; it gave a *picrate*, black needles, m. p. 218—219° (Found : N, 10·8. $C_{20}H_{13}N,C_6H_3O_7N_3$ requires N, 11·3%); treatment in glacial acetic acid solution with excess of solid sodium nitrite gave the nitroso-derivative, reddish-yellow needles, m. p. 145—146° (decomp.), from carbon tetrachloride.

Dinaphthyline (1 : 1′-*Diamino*-2 : 2′-*dinaphthyl*).—This forms colourless plates, m. p. 281°, from benzene, sparingly soluble in alcohol, slightly soluble in cold and fairly readily soluble in hot benzene. The hydrochloride and sulphate are exceedingly soluble in water, and neither has been isolated. The base reacts with excess of acetic anhydride in 24 hours in the cold to give a *diacetyl* derivative, colourless plates, m. p. 229—230°, from alcohol (Found :

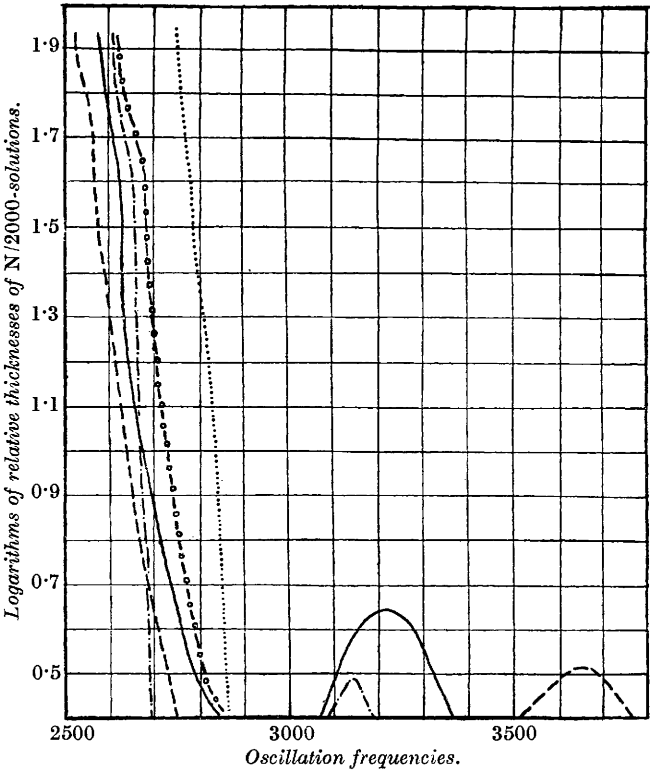
N, 7·4. $C_{24}H_{20}O_2N_2$ requires N, 7·6%). It readily gives a *dibenzoyl* derivative by the Schotten–Baumann method, colourless plates, m. p. 277—278°, from nitrobenzene (Found: N, 5·9. $C_{34}H_{24}O_2N_2$ requires N, 5·7%); mixed m. p. with dinaphthyline, 240—245°. No picrate was obtained, as the base is decomposed by hot acids. By elimination of the amino-group by the method described by Cumming and Howie (*loc. cit.*, p. 3178), 2 : 2′-dinaphthyl, m. p. 187°, was obtained.

1 : 1′-*Imino*-2 : 2′-*dinaphthyl* (*Dinaphthylcarbazole, Dinaphthyleneimine*).—This forms colourless leaflets, m. p. 221°, from glacial acetic acid, sparingly soluble in cold glacial acetic acid, fairly readily soluble in alcohol and in benzene, slightly soluble in light petroleum, soluble in cold concentrated sulphuric acid to give a bright red solution, turning dark green on addition of a drop of nitric acid. It gives a blue colour with concentrated nitric acid. The base gives an acetyl derivative, colourless plates, m. p. over 300°; a *picrate*, red needles, m. p. 242—243° (Found: N, 11·1. $C_{20}H_{13}N,C_6H_3O_7N_3$ requires N, 11·3%); a nitroso-derivative, yellow plates, m. p. over 300° (Nietzki and Goll); a benzoyl derivative, colourless plates, m. p. 119° (Cumming and Steel).

1-*Amino*-2 : 2′-*dinaphthyl*.—1 G. of 1-nitro-2 : 2′-dinaphthyl (Cumming and Howie, *loc. cit.*) in a boiling mixture of 20 c.c. of glacial acetic acid and 2 c.c. of concentrated hydrochloric acid, was reduced with zinc dust. On cooling, the hydrochloride of the base separated as lustrous plates. This was recrystallised from alcohol, and the free base liberated by addition of ammonia. From alcohol, 0·8 g. of 1-amino-2 : 2′-dinaphthyl was obtained in silvery plates, m. p. 220°, fairly readily soluble in most organic solvents, but insoluble in water. The hydrochloride and sulphate form lustrous plates. The base readily formed an *acetyl* derivative, colourless plates, m. p. 225—226° (Found: N, 4·4. $C_{22}H_{17}ON$ requires N, 4·5%).

Isolation of Compound $C_{40}H_{26}O_3N_2$.—Reduction of 3 : 3′-dinitro-2 : 2′-dinaphthyl (Cumming and Howie, *loc. cit.*) was attempted with zinc and glacial acetic acid. As reduction proceeded, a yellowish product separated, a further crop being obtained on cooling the solution after completion of the reduction. Recrystallised from benzene (carbon), it formed greenish-yellow plates, m. p. about 350°, but first beginning to decompose at 320° (Found: C, 82·5, 83·1; H, 4·5, 4·6; N, 4·8, 4·9. $C_{40}H_{26}O_3N_2$ requires C, 82·5; H, 4·5; N, 4·8%). It is almost insoluble in alcohol, glacial acetic acid, or cold benzene, and sparingly soluble in acetone. It gives a red solution in concentrated sulphuric acid, turning apple-green on addition of a drop of nitric acid. It gives no reaction with nitrous acid.

The amino-bases described above were coupled with various azo-components, the best colours being obtained from H-acid, in alkaline solution. All the colours obtained were unaffected by acids, in this respect differing markedly from the corresponding diphenyl derivatives, *e.g.*, Congo-red.



2 : 2′-*Diamino*-1 : 1′-*dinaphthyl* ———
4 : 4′-*Diamino*-1 : 1′-*dinaphthyl* (*naphthidine*) — — —
1 : 1′-*Diamino*-2 : 2′-*dinaphthyl* (*dinaphthyline*) —o—o—
2 : 2′-*Imino*-1 : 1′-*dinaphthyl* —·—·—
1 : 1′-*Imino*-2 : 2′-*dinaphthyl* (*dinaphthyl carbazole, dinaphthyleneimine*) ·····

Absorption Spectra.—The absorption spectra of *N*/2000-solutions of the bases and imines were photographed (Fig.). In the light of the iron arc, naphthidine solutions in alcohol exhibit a pale blue fluorescence; dinaphthyline, a brilliant bluish-green fluorescence; 2 : 2′-diamino-1 : 1′-dinaphthyl, a purple fluorescence; 2 : 2′-imino-1 : 1′-dinaphthyl, a violet fluorescence; and 1 : 1′-imino-2 : 2′-dinaphthyl, a purple fluorescence.

In the case of the three isomeric diamines, as the distance from the amino-groups to the bond of union of the naphthalene residues increases, the absorption passes further towards the region of lower frequency. The absorption of 1 : 1′-imino-2 : 2′-dinaphthyl is displaced towards the region of higher frequency from that of its parent base, whilst in the case of 2 : 2′-imino-1 : 1′-dinaphthyl the absorption is displaced in the other direction from its parent base.

The authors desire to record their thanks to the Department of Scientific and Industrial Research and to the Ferguson Trust for grants which have enabled one of them (G. H.) to take part in this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

[*Received, September 10th,* 1931.]