XVIII.—*Studies in the Naphthalene Series. Part II. Diaryl- and Triaryl-methane Derivatives of Dimethyl-α-naphthylamine.*

By Basker Gokhle and Frederick Alfred Mason.

Whilst the chemistry of the diphenyl- and triphenyl-methane series of intermediates and dyes has been exhaustively investigated, as instanced by Michler's hydrol, Michler's ketone, malachite-green, crystal-violet, etc., very little has been done regarding the chemistry of diaryl- and triaryl-methane derivatives containing two or three naphthalene nuclei.

As regards dinaphthylmethane derivatives, Friedländer and Wellmann (*Ber.*, 1898, **21**, 3123) condensed benzaldehyde and *p*-dimethylaminobenzaldehyde with dimethyl-α-naphthylamine to give the leuco-bases $C_6H_5{\cdot}CH(C_{10}H_6{\cdot}NMe_2)_2$ and

$NMe_2{\cdot}C_6H_4{\cdot}CH(C_{10}H_6{\cdot}NMe_2)_2$

respectively, but were unable to obtain the corresponding dyes owing to the surprising resistance of the leuco-bases to oxidation.

The only comprehensive investigation upon di- and tri-arylmethane derivatives containing one or more naphthalene nuclei is that of Noelting (*Ber.*, 1904, **37**, 1901), who prepared phenyldinaphthylmethane derivatives from *p*-dimethylaminobenzaldehyde and various substituted naphthalene derivatives; the same chemist also prepared eight diaminonaphthyl ketones by heating *p*-dimethyl (or diethyl)-aminobenzo-alkyl- or -aryl-anilides with phosphoryl chloride and then with dimethylaniline; such as

$NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_{10}H_6{\cdot}NHMe$, $NEt_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_{10}H_6{\cdot}NHPh$,

etc. From these mixed ketones Noelting obtained various leucotriarylmethane compounds such as $(NMe_2{\cdot}C_6H_4)_2CH{\cdot}C_{10}H_6{\cdot}NHMe$ and $(NHEt{\cdot}C_{10}H_6)_2CH{\cdot}C_6H_4{\cdot}NMe_2$, which were oxidised to blue or green dyes. Only one trinaphthylmethane derivative was prepared, tri-1 : 1′ : 1″-ethylaminonaphthylmethane, which was oxidised to a blue dye (compare also Badische Anilin & Soda Fabrik, D.R.-PP. 27032, 27789; Bayer & Co., D.R.-P. 66712; Nathanson and Müller, *Ber.*, 1889, **22**, 1875).

It was therefore of considerable interest to attempt the preparation of analogous derivatives from dimethyl-α-naphthylamine, for which purpose it was necessary to examine methods for the preparation of dimethyl-α-naphthylamine (compare J., 1930, 1757), of tetramethyldiaminonaphth-hydrol and of the corresponding ketone.

For the preparation of 4 : 4′-*tetramethyldiamino*-1 : 1′-*dinaphthylcarbinol* $(NMe_2{\cdot}C_{10}H_6)_2CH{\cdot}OH$, the corresponding 4 : 4′-tetramethyldiaminodinaphthylmethane was used as the starting material: it was prepared by a slight modification of Morgan's method (J., 1900, **77**, 283) by condensing dimethyl-α-naphthylamine with formaldehyde in glacial acetic acid solution in presence of hydrochloric acid, and also by using methylal in place of formaldehyde.

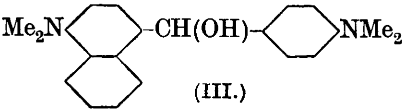
The base was oxidized with difficulty to the desired hydrol by the use of chloroanil in nearly boiling glacial acetic acid; the yield, however, was small (about 2%). The pure hydrol forms minute clusters of microscopic navicular crystals from benzene–ligroin, readily distinguished under the microscope from the rosettes of, apparently, triclinic crystals of the methane base; it dissolves in cold glacial acetic acid to a nearly colourless solution which gradually becomes blue; the colour is greatly intensified on heating, but diminishes again on standing, so that presumably there is in solution an equilibrium between the normal colourless salt (I) and the blue quinonoid salt (II). Michler's hydrol exists in acetic acid solution chiefly or exclusively in the coloured form; this conclusion is borne

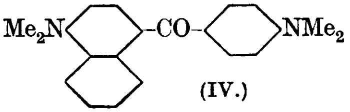
$$\text{(I.)}\ \mathrm{NMe_2\cdot C_{10}H_6\cdot CH(OH)\cdot C_{10}H_6\cdot NHMe_2Ac} \rightleftharpoons$$
$$\text{(II.)}\ \mathrm{NMe_2\cdot C_{10}H_6\cdot CH{:}C_{10}H_6{:}NMe_2Ac + H_2O}$$

out by the spectrophotometric examination of the solutions as indicated in the accompanying curves.

Attempts to prepare the corresponding tetramethyldiaminodinaphthyl ketone by a variety of different methods known to work smoothly and successfully in the case of Michler's ketone were all unsuccessful, the initial material being either recovered unchanged or, as with chloroanil, almost entirely converted into complex oxidation or condensation products. It does not therefore appear to be possible to obtain the ketone by any known method.

The corresponding " mixed " phenylnaphthyl derivatives, namely, 4 : *4'-tetramethyldiaminophenyl-*1*-naphthylcarbinol* (III) and the corresponding 4 : *4'-tetramethyldiaminophenyl-*1*-naphthyl ketone* (IV),


(III.)


(IV.)

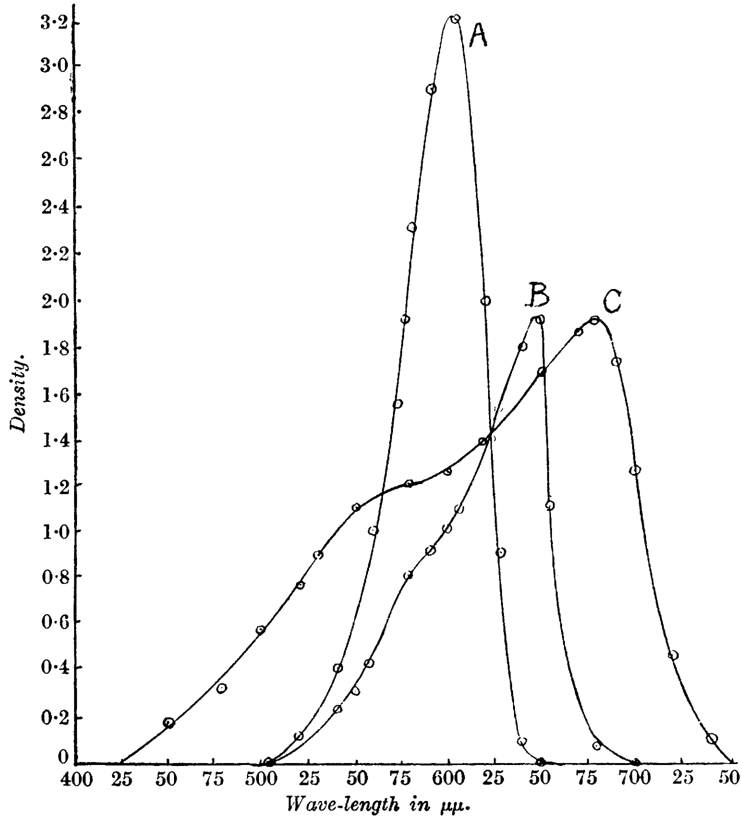
were also prepared, the latter by condensing the *chloride* of 4-*dimethylamino-*1*-naphthoic acid* with dimethylaniline by means of aluminium chloride; on reduction with sodium amalgam in alcohol, it gave the corresponding hydrol, which dissolved in glacial acetic acid to a brilliant blue solution.

As it was impossible to obtain the trinaphthyl analogue of crystal-violet *viâ* the tetramethyldiaminodinaphthyl ketone, the attempt was made to prepare the corresponding leuco-compound, 4 : 4' : 4''-*hexamethyltriaminotrinaphthylmethane*, $\mathrm{CH(C_{10}H_6\cdot NMe_2)_3}$, by condensing dimethyl-α-naphthylamine with orthoformic ester in presence of anhydrous zinc chloride as used by Welter (*J. pr. Chem.*, 1893, **48**, 231) for the synthesis of leucaniline; this method failed, but on replacing the zinc chloride by aluminium chloride the condensation was effected and the desired product obtained.

Here also, however, it was found impossible to oxidise the leuco-base to a colouring matter, lead peroxide, chloroanil, and other oxidising agents being completely without effect.

Note upon the Colours of 4 : *4'-Tetramethyldiaminodiphenylcarbinol* (*A*), 4 : *4'-Tetramethyldiaminophenylnaphthylcarbinol* (*B*), *and* 4 : *4'-Tetramethyldiaminodinaphthylcarbinol* (*C*) *in Glacial Acetic Acid Solution.*—As has been pointed out above, a characteristic property of Michler's hydrol and its analogues is the deep blue colour shown by their solutions in glacial acetic acid and it appeared of interest, therefore, to measure their absorption curves in such solutions and to ascertain how far the positions of the absorption maxima agree with the theory developed in particular by Moir (see, for instance, Formànek, " Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege," 1908, p. 104; Moir,

Fig. 1.



Absorption curves of hydrols in glacial acetic acid:
A. 4 : 4′-*Tetramethyldiaminodiphenylcarbinol,* 1 *in* 800,000.
B. 4 : 4′-*Tetramethyldiaminophenylnaphthylcarbinol,* 1 *in* 100,000.
C. 4 : 4′-*Tetramethyldiamino*-1 : 1′-*dinaphthylcarbinol,* 1 *in* 12,500.

J., 1921, **119**, 1654; 1922, **121**, 1555, 1808; 1923, **123**, 2792; 1924, **125**, 1134; 1925, **127**, 967, 2338; 1927, 1809).

Solutions of various concentrations of the three hydrols were examined in a Hilger–Nutting spectrophotometer, and the absorption curves plotted. The peaks of the absorption curves were found to be unaffected by variations in concentration and the maxima were found to be at 603, 651, and 679 μμ respectively.

According to Moir's theory the wave-length of an ionisable dye may be calculated thus :

$$\lambda_x = K_1K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad K_n\lambda_0$$

where λ_0 is the wave-length of the absorption band of the parent substance, K_1 is the " colour factor " for a phenyl group (if a phenyl derivative), K_2 the " colour factor " for any other substituent group present, and so on. In the case of Michler's hydrol itself (curve A) we have, using Moir's figures,

$$\lambda_x = \lambda_0 \times K_{\mathrm{CH\cdot OH}} \times K^2_{(\mathrm{NMe_2})} = 1380 \times 0{\cdot}39 \times (1{\cdot}059)^2 = 603$$

For B the calculation is the same, the result being multiplied by a naphthalene/benzene substitution factor 1·07 :

$$\lambda_x = 603 \times 1{\cdot}07 = 645$$

For C the calculation becomes

$$\lambda_x = 603 \times (1{\cdot}07)^2 = 690$$

The three values observed are, 603, 651, and 679 respectively.

EXPERIMENTAL.

Preparation of 4 : 4′-*Tetramethyldiamino*-1 : 1′-*dinaphthylmethane*.—(i) *By means of formaldehyde.* To a mixture of dimethyl-α-naphthylamine (100 g.) and glacial acetic acid (400 c.c.), 40% formalin (25 c.c.) and concentrated hydrochloric acid (25 c.c.) were added successively. The mixture was kept over-night, boiled for a few minutes, cooled, and poured into ice-water (2—4 l.) ; most of the desired base was then precipitated as a light creamy solid, and more was obtained by rendering the aqueous layer just alkaline with ammonia. The combined product was filtered off, washed well, pressed on a porous tile, and dried cautiously at 90°. After recrystallisation from benzene–ligroin (1 : 4) it formed colourless microscopic crystals (89 g.), m. p. 181—182·5° (Morgan gives m. p. 176°). It is advisable to use a large bulk of water for the precipitation to avoid the formation of the desired base as a gummy product, as described by Morgan.

(ii) *By means of methylal.* A mixture of dimethyl-α-naphthylamine (10 g.), glacial acetic acid (20 c.c.), methylal (7 c.c.), and concentrated hydrochloric acid (2 c.c.), having been kept overnight, was boiled for 2 hours, cooled, and poured into ice-water (500 c.c.), and a slight excess of ammonia added. The base separated as a pasty orange mass which, when dried and recrystallised from benzene–ligroin, yielded 6·0 g. of the desired base in a pure form (yield, 57% of the theoretical).

(iii) *By means of sulphuric acid.* Dimethyl-α-naphthylamine

(10 g.) and concentrated sulphuric acid (25 c.c.) were cautiously mixed, with ice-cooling, and methylal (5 c.c.) was added. After standing for 3 hours at room temperature, the mixture was heated on the water-bath for 20 minutes and poured on ice. After neutralisation with ammonia the " methane base " was precipitated as a pale yellow substance, the yield of pure recrystallised product being 5·0 g., *i.e.*, 47% of the theoretical.

Oxidation of 4 : 4′-*Tetramethyldiamino*-1 : 1′-*dinaphthylmethane*.—The " methane base " was surprisingly resistant to the action of oxidising agents such as lead peroxide and warm dilute hydrochloric acid or sulphuric acid. Of 5 g. of the base in concentrated sulphuric acid, after being stirred with lead peroxide for 4 hours at room temperature, 3 g. were recovered; the remainder was converted into a tarry product containing no trace of the expected hydrol.

Chloric acid activated by osmic acid in glacial acetic acid solution (K. A. Hofmann, E.P. 20593, 1913), and potassium permanganate in dilute sulphuric acid or in acetone solution, also failed to give any definite product, most of the base being recovered unchanged in each case.

Oxidation with chloroanil. A cold solution of the methane base in glacial acetic acid, on addition of chloroanil and gentle warming, gradually became greenish-blue; finally, when heated to incipient ebullition, the liquid became deep violet-blue owing, as was shown later, to the formation of the desired 4 : 4′-*tetramethyldiamino*-1 : 1′-*dinaphthylcarbinol*. The isolation and identification of the hydrol, however, proved to be a difficult task and was complicated by the fact that the impure hydrol and the crude " methane base " both melt between 160° and 180°.

After many experiments, the best yield of the hydrol was obtained as follows : glacial acetic acid (50 c.c.) was warmed on the water-bath to 80° and an intimate powdered mixture of the methane base (5 g.) and chloroanil (7 g.) was added gradually during 20 minutes with occasional shaking. The blue liquid was then heated cautiously at 110° for 10 minutes, and the flask cooled in ice for an hour; the pasty product was well shaken with cold 10% hydrochloric acid (150 c.c.), excess of dilute aqueous ammonia and ice were added to the filtered liquid, and the resultant grey precipitate was filtered off, pressed on a porous plate, dried in the air at room temperature, and extracted with ether. The dried extract on evaporation deposited much brown resinous matter, together with a small amount of microcrystalline hydrol; this was cautiously washed with a few drops of benzene and recrystallised from benzene–ligroin (yield, about 0·1 g.) (Found : C, 83·0; H, 7·3; N, 8·7.

$C_{25}H_{26}ON_2$ requires C, 81·1; H, 7·3; N, 7·6%). Probably, therefore, the product was still slightly contaminated with unoxidised base. The very poor yield of product obtained effectually prevented any further investigation into the properties of the compound, in particular its ability to form leuco-triarylmethane derivatives.

The hydrol, after recrystallisation from ether–benzene, melted at 184—186° in a pre-heated melting-point apparatus, the " methane base " in the same apparatus melting at 181—182·5°, whilst a mixed melting point gave 177—179°. It is, however, difficult to give the melting point accurately, as slight incipient decomposition occurs according to the rate of heating.

The purified hydrol gave a colourless or faintly green solution in cold glacial acetic acid, the colour becoming an intense deep blue-violet on warming, and fading again slowly on cooling in ice. In concentrated hydrochloric or sulphuric acid the hydrol dissolved to a deep yellow solution.

4-*Dimethylamino*-1-*naphthoyl Chloride*.—The corresponding acid was prepared by the method of Friedländer and Wellmann (*loc. cit.*) by heating together dimethyl-α-naphthylamine (34 g.) and a benzene solution (42 c.c.) of carbonyl chloride (14 g.) in a sealed tube at 60—70° for 4 hours. From the reaction product, after removal of unchanged base, about 10 g. of the desired acid, m. p. 163—165°, were obtained on acidification with acetic acid.

The *chloride* was prepared by refluxing the acid (10 g.), suspended in dry ether (20 c.c.), with thionyl chloride (7·5 c.c.) for ¾ hour. The volatile constituents were removed under reduced pressure, leaving the chloride as a white solid (10·5 g.) (Found: Cl, 15·4. $C_{13}H_{12}ONCl$ requires Cl, 15·2%).

The *anilide*, prepared by refluxing the chloride with excess of aniline in benzene solution for 10 minutes, crystallised from toluene in fine colourless needles (Found: C, 78·4; H, 6·0; N, 9·5. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2; N, 9·7%).

Attempts to synthesise 4 : 4′-*Tetramethyldiamino*-1 : 1′-*dinaphthyl Ketone*.—4-Dimethylamino-1-naphthoyl chloride (5 g.) in tetrachloroethane (20 c.c.) and dimethyl-α-naphthylamine (5 c.c.) were treated with powdered aluminium chloride (5 g.) and finally heated on the water-bath: only a tarry product was obtained from which nothing could be isolated.

In the experiments carried out for the preparation of dimethylaminonaphthoic acid by heating together carbonyl chloride and the base, no trace of the desired ketone was found. A number of experiments carried out on the lines of D.R.-PP. 287994 and 289108 (oxidation to the thio-ketone by means of sulphur, etc.), a method which works well in the case of tetramethyldiaminodiphenylmethane, all gave negative results, as also did attempts to effect the oxidation by means of *p*-nitrosodimethylaniline (compare Sachs, *Ber.*, 1900, **33**, 959).

4 : 4′ : 4″ - *Hexamethyltriaminotrinaphthylmethane.* — After dimethyl-α-naphthylamine (30 g.), orthoformic ester (7·5 g.), and zinc chloride (10 g.) had been heated in an oil-bath at 130—150° for 4 hours, most of the base was recovered unchanged. Satisfactory results were obtained, however, by the use of aluminium chloride, which does not appear to have been used before in this type of condensation. Dimethyl-α-naphthylamine (30 g.) and orthoformic ester (7·5 g.) were placed in a flask provided with a stirrer and water-cooling. Finely powdered aluminium chloride (10 g.) was added slowly during ¾ hour, and the temperature raised slowly to 70°, the mixture gradually thickening to a solid paste. After extraction with dilute hydrochloric acid the solution was rendered alkaline with sodium carbonate and distilled in steam. The residual brown solid after several crystallisations from benzene–ligroin (1 : 4) formed microscopic white crystals, m. p. 266—267·5° (Found: C, 84·8; H, 7·0; N, 7·8. $C_{37}H_{37}N_3$ requires C, 84·8; H, 7·1; N, 8·0%).

4 : 4′-*Tetramethyldiaminophenyl*-1-*naphthyl Ketone* (IV).—It is well known that the acid chloride of dimethylaminobenzoic acid is formed as an intermediate stage in the production of Michler's ketone, but this method fails, as already noted, in the case of the naphthalene analogue; the acid chloride also failed to condense with dimethylaniline under similar conditions, but it was found, rather surprisingly, that by the cautious use of aluminium chloride the condensation could be effected without the formation of an undue amount of colouring matters and other by-products. To the acid chloride (10 g.) in tetrachloroethane (20 c.c.) were added dimethylaniline (20 c.c.) with ice-cooling, and then powdered aluminium chloride (10 g.) by degrees. After standing over-night the whole was heated on the water-bath for 2 hours, cooled, and poured on ice and dilute hydrochloric acid. The product was basified with sodium carbonate and the volatile constituents were removed in steam. The granular residue after two crystallisations from ether gave large well-formed rhombs, sometimes striated with blue-green streaks; m. p. 128·5—129° (Found: C, 79·3; H, 7·0; N, 8·9. $C_{21}H_{22}ON_2$ requires C, 79·3; H, 6·9; N, 8·8%).

The *ketone* is easily soluble in alcohol, ether, and dilute mineral acids to light greenish-yellow solutions. In presence of phosphoryl chloride the "mixed ketone" condensed with dimethylaniline to yield a deep blue colouring matter, presumably identical with the "Naphthoblau" of Noelting and Philipp (*Ber.*, 1908, **41**, 580; see also D.R.-P. 27789 of the Badische Anilin & Soda Fabrik, and Noelting and Saas, *Ber.*, 1913, **46**, 961).

4 : 4′-*Tetramethyldiaminophenyl*-1-*naphthylcarbinol* (III).—The "mixed ketone" (2 g.) was dissolved in alcohol (100 c.c.), 4% sodium amalgam (10 g.) added, and the whole refluxed gently for 3 hours. After cooling, the alcoholic solution was poured into water, and the clean lemon-yellow crystalline precipitate filtered off. It was purified by re-solution in alcohol and reprecipitation in water. After drying in a vacuum, it formed a pale yellow, crystalline powder, m. p. about 62—63° (Found: C, 78·7; H, 7·1; N, 8·8. $C_{21}H_{24}ON_2$ requires C, 78·8; H, 7·5; N, 8·8%).

4-Nitrosodimethyl-α-naphthylamine was prepared by the method of Friedländer and Wellmann (*loc. cit.*): Dimethyl-α-naphthylamine (8·5 g.) was dissolved in concentrated hydrochloric acid (15 c.c.) with the addition of ice, and a nearly saturated solution of 3·5 g. of sodium nitrite in water was run in during 10 minutes. After ½ hour, the yellow nitroso-compound was filtered off and pressed (yield, 9 g.). On reduction with zinc dust in acid solution the amino-compound was formed without difficulty, and the *acetyl* derivative was prepared as a colourless crystalline product, m. p. 185° (Found: C, 73·5; H, 7·1; N, 12·1. $C_{14}H_{16}ON_2$ requires C, 73·7; H, 7·0; N, 12·3%). The corresponding benzoyl derivative melted at 195°. An attempt to prepare the analogue of methylene-blue B by oxidising together a mixture of the base with dimethyl-α-naphthylamine in presence of sodium thiosulphate by means of potassium dichromate was unsuccessful, only a brown tarry product being obtained containing no identifiable colouring matter.

The authors wish to express their thanks to Messrs. L. B. Holliday & Sons, Ltd., for a gift of chloroanil.

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[*Received, June 30th,* 1930.]