

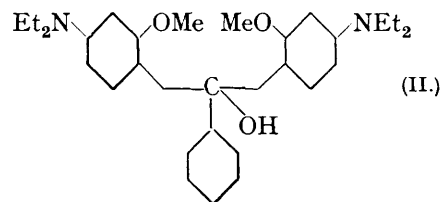
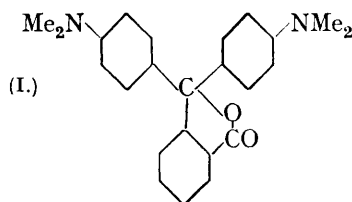
## 298. The Preparation of 4 : 4'-Bisdiethylamino-2 : 2'-dimethoxytriphenylcarbinol.

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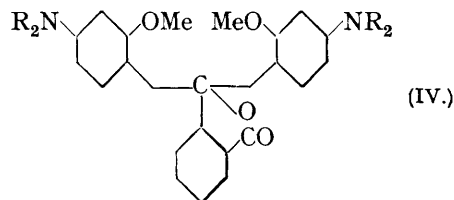
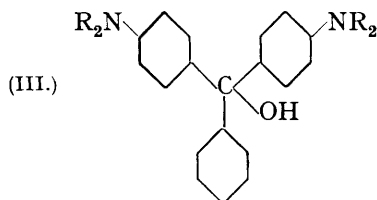
THE close connexion between the substances described in the previous communication (this vol., p. 1264) and the anilinephthaleins, such as the so-called "Phthal Grün" (I) (O. Fischer, *Annalen*, 1881, **206**, 107; Haller and Guyot, *Compt. rend.*, 1897, **125**, 221, 1153), on the one hand, and malachite-green, or brilliant-green (III), on the other (O. Fischer, *Ber.*, 1881, **14**, 2520), made it desirable to examine the colouring matter (II), *i.e.*, the 2' : 2''-dimethoxy-derivative of brilliant-green, in order to ascertain whether the presence of the two *o*-methoxy-groups would affect the stability and colour of the resulting dyestuff; and also, if possible, to prepare the corresponding phthalein (IV).

The latter objective was not attained, for in the attempted condensation of *as*-phthalyl chloride with *m*-methoxydiethylaniline by means of aluminium chloride, the main product of the reaction appeared to be rhodamine-B. In the light of other evidence, it is possible that the phthalein may have been formed in the first instance and that demethylation took place immediately with formation of the pyrone ring.

The corresponding triphenylmethane dye (II) was, however, prepared, though oxidation of the leuco-compound to the carbinol base (4 : 4'-bisdiethylamino-2 : 2'-dimethoxy-



triphenylcarbinol) took place with great difficulty, the two *o*-methoxy-groups having a powerful inhibiting action. The new dyestuff, in the form of the chloride, was found to resemble brilliant-green very closely, and dyed silk a slightly yellower shade than the



unsubstituted dye, its maximum absorption in dilute aqueous solution being at  $\lambda = 635 \mu\mu$  (as compared with  $\lambda = 627 \mu\mu$  under similar conditions, for brilliant-green).

The new dyestuff was quite stable and showed no tendency whatever to split off methyl groups and form the corresponding xanthene derivative.

### EXPERIMENTAL.

*m*-Methoxydiethylaniline.—*m*-Diethylaminophenol (42 g.; 0.25 g.-mol.) was dissolved in methyl alcohol (130 c.c.), and methyl sulphate (48 g.; 0.375 g.-mol.), diluted with an equal

volume of methyl alcohol, was run into the boiling solution simultaneously with a 10% methyl-alcoholic potassium hydroxide solution (210 c.c.; 0.375 g.-mol.) during  $\frac{3}{4}$  hour. After removal of the bulk of the alcohol by distillation, the residue was extracted with ether, any unchanged aminophenol removed by means of aqueous alkali, and the residue, after removal of the ether, distilled under diminished pressure; yield, 32 g. (72%). Alkylation in aqueous solution gave only a 51% yield. *m*-Methoxydiethylaniline forms a colourless oil, b. p. 146—148°/14 mm., darkening rapidly on keeping (Found: C, 73.4; H, 9.3; N, 7.8.  $C_{11}H_{17}ON$  requires C, 73.7; H, 9.5; N, 7.8%).

2 : 2'-Dimethoxy Brilliant-green.—The foregoing compound (10 g.) and benzaldehyde (3 g.) were boiled with concentrated hydrochloric acid (8.0 g.) for 8 hours. The sticky product was steam-distilled in presence of sodium carbonate (4 g.), the crude substance weighing 10 g. (80%). The pure 4 : 4'-bisdiethylamino-2 : 2'-dimethoxytriphenylmethane crystallised from light petroleum in small rosettes, m. p. 114° (Found: C, 77.6; H, 8.6; N, 6.4; OMe, 13.0.  $C_{29}H_{38}O_2N_2$  requires C, 78.0; H, 8.5; N, 6.3; OMe, 13.0%).

*Oxidation to the colour base.* The leuco-base was surprisingly resistant to ordinary oxidising agents such as lead peroxide and acid, and moderately satisfactory results were obtained only with chloroanil (cf. O. Fischer, *Ber.*, 1881, **14**, 2520) in ethereal suspension; the leuco-base (7.5 g.) was dissolved in ether (40 c.c.), a suspension of chloroanil (4.3 g.) in ether (50 c.c.) added, and the whole boiled for 5 hours. The deep green viscid carbinol base, left after removal of the ether, was extracted with dilute sodium hydroxide to remove tetrachloroquinol, the residue treated with concentrated hydrochloric acid, and the diluted acid extract rendered alkaline with sodium carbonate. The precipitated 4 : 4'-bisdimethylamino-2 : 2'-dimethoxytriphenylcarbinol was extracted with ether, and the solvent evaporated, leaving the base as small colourless platelets, m. p. 115°; yield 5 g. (65%).

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