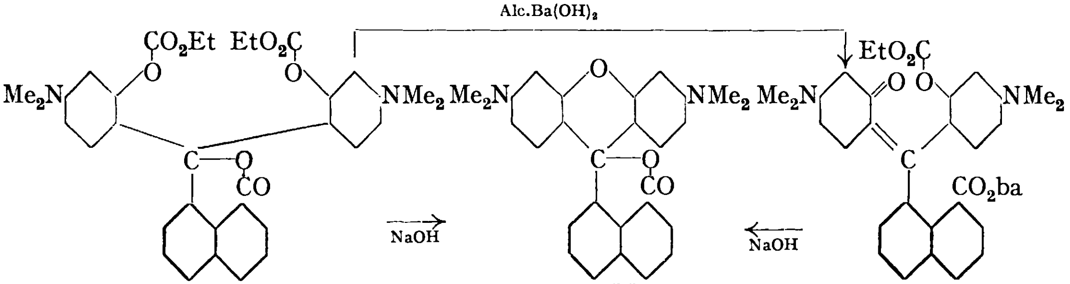
136. *The Condensation of* 1 : 8-*Naphthalyl Chloride with* m-*Ethylcarbonatodimethylaniline.*

By William R. Brown and Frederick A. Mason.

Previous attempts (J., 1933, 1264) to prepare basic phthalide derivatives analogous in structure to that suggested for the " blue sodium salt " of Rhodamine B were unsuccessful. Satisfactory results have now been obtained by condensing 1 : 8-naphthalyl chloride with m-*ethylcarbonatodimethylaniline*, 4′ : 4″-*bisdimethylamino*-2′ : 2″-*bisethylcarbonatodiphenyl*-

1 : 8-*naphthalide* (I) being obtained, though in very small yield, as a well-crystallised substance with characteristic and interesting properties :



(I.) (II.) (III.)
[Green barium salt.]

When warmed cautiously with 10% aqueous sodium hydroxide, this substance afforded a deep green solution, changing rapidly to blue, blue-violet, and then to a strongly fluorescent red, with formation of the corresponding 1 : 8-naphtharhodamine (II). If, however, a cold 10% methyl-alcoholic solution of barium hydroxide was used, a colourless solution was first obtained which, when warmed gently, became deep green and on prolonged heating turned green-blue and finally blue-red. From the deep green solution so formed there was obtained a colourless sulphate, m. p. 176—180°; this gave in methyl alcohol a pale green solution which turned *immediately* an intense deep green on the addition of barium hydroxide, but in dilute alcoholic sodium hydroxide it dissolved to a purple-blue solution which gradually became red. From its properties and general behaviour it is probably the sulphate of 4′ : 4″-bisdimethylamino-2′-hydroxy-2″-ethylcarbonatodiphenyl-1 : 8-naphthalide, the green coloration being due to the formation of (III), whilst the transient deep blue colour in aqueous alkali would be due to the formation of the alkali salt (III, with Na in place of CO_2Et), the analogue of the " blue sodium salt " of Rhodamine B. Attempts to obtain such a blue salt by treating 1 : 8-naphtharhodamine with concentrated aqueous sodium hydroxide solution gave completely negative results.

EXPERIMENTAL.

m-*Ethylcarbonatodimethylaniline.*—*m*-Hydroxydimethylaniline (137 g.) was dissolved in 10% sodium hydroxide solution (400 c.c.), and ethyl chlorocarbonate (110 g.) run in during 30 minutes with continuous agitation and ice-cooling. The still alkaline liquid was extracted with ether (2000 c.c.) in four portions. After removal of the ether, the *ethylcarbonato*-derivative was distilled under diminished pressure; b. p. 160—164°/13 mm. (Found : C, 62·8; H, 7·3; N, 6·6. $C_{11}H_{15}O_3N$ requires C, 63·1; H, 7·2; N, 6·7%). Yield, 157 g. (75% of the theoretical).

Condensation with naphthalyl chloride. 1 : 8-Naphthalyl chloride (25·3 g.; 0·1 g.-mol.) (Mason, J., 1924, **125**, 2116), dissolved in tetrachloroethane (50 c.c.), was added slowly to a solution of *m*-ethylcarbonatodimethylaniline (41·8 g.; 0·2 g.-mol.) in tetrachloroethane 100 c.c.), the liquid becoming red-brown. After cooling in ice, powdered aluminium chloride (15 g.) was added cautiously, the mixture slowly becoming purple-red. After 24 hours, carbon disulphide (300 c.c.) was added and the supernatant liquid was decanted from the tarry condensation product. This was well drained, ethyl alcohol (200 c.c.) added with stirring and cooling, and after a day the finely crystalline 4′ : 4″-*bisdimethylamino*-2′ : 2″-*diethylcarbonatodiphenyl*-1 : 8-*naphthalide* was filtered off and recrystallised from toluene, forming pale cream-coloured microscopic needles (5 g.), m. p. 253—254° (decomp.) (Found : C, 68·5; H, 6·0; N, 4·5. $C_{34}H_{34}O_8N_2$ requires C, 68·2; H, 5·6; N, 4·7%).

The chief properties of this substance have been described above. In addition, on heating for a short time with concentrated sulphuric acid the corresponding naphtharhodamine was formed; the latter was prepared more conveniently by boiling 5 g. of the condensation product with 40 c.c. of 10% potassium hydroxide solution; on acidification with acetic acid the acetate of the dye was precipitated as a fine red precipitate, almost insoluble in cold water, sparingly soluble in hot, and readily soluble in alcohol and acetone, which dyed silk from a hot acetic acid bath in bluish-red shades. The absorption spectrum in aqueous solution showed a maximum at $\lambda = 562{\cdot}5$ μμ.

4′ : 4″-*Bisdimethylamino-2′-hydroxy-2″-ethylcarbonatodiphenyl-*1 : 8-*naphthalide* (?).—The diethylcarbonato-condensation product obtained as described above (0·5 g.) was dissolved in 10% methyl-alcoholic barium hydroxide solution (10 c.c.) and methyl alcohol (10 c.c.) and heated to incipient ebullition for about 1 minute. The solution was cooled rapidly and treated with dilute sulphuric acid with ice-cooling until it was just acid to Congo-red paper. The mixture was then cautiously warmed and filtered with the aid of a pump. After 24 hours the pink solution deposited colourless crystals of the sulphate, which became bluish on drying; m. p. 176—180° (decomp.). It dissolved readily in water to a nearly colourless solution and in dilute aqueous sodium hydroxide to a purple-blue solution. The small amount of material available did not suffice for analysis, except for identification of the sulphate ion.

The authors thank Imperial Chemical Industries Ltd. and the Clayton Aniline Co. Ltd. for generous gifts of chemicals.

COLLEGE OF TECHNOLOGY, MANCHESTER.

[*Received, March* 19*th*, 1934.]