77. *Esters of 1-Hydroxy-2-naphthoic Acid, and Naphthol-blue Dyes therefrom.*

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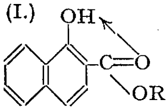
The preparation of esters of 1-hydroxy-2-naphthoic acid and naphthol-blue dyes derived from them is discussed. The stability of these dyes is compared with those derived from esters of salicylic acid.

1-Hydroxy-2-naphthoic acid was prepared by passing dry carbon dioxide for 14 hours over powdered anhydrous sodium α-naphthoxide placed in a uniformly heated tube at a constant temperature which lay between 80° and 140° according to requirements (cf. Lassar-Cohn and Loewenstein, *Ber.*, 1908, **41**, 3365). By reaction of the acid chloride with the corresponding alcohol or its sodium derivative the esters were obtained. These were but sparingly soluble in alkali probably owing to chelation as in (I).

Physical properties of the dyes $O{:}C_{10}H_5(CO_2R){:}N{\cdot}C_6H_4{\cdot}NEt_2$.

R.	Colour of dye crystals.	M. p.	Recryst. from :	Abs. max. (A.) in $COMe_2$.	Found, %.			Formula.	Required, %.		
					C.	H.	N.		C.	H.	N.
Me	Dark blue	157—158°	Dil. MeOH	6200	72·9	6·1	7·9	$C_{22}H_{22}O_3N_2$	72·9	6·1	7·7
Et	Orange	141—142	PhMe–light pet.	6260	73·6	6·4	7·3	$C_{23}H_{24}O_3N_2$	73·4	6·4	7·4
Pr	Dark brown	149—150	,,	6310	73·9	6·6	7·3	$C_{24}H_{26}O_3N_2$	73·8	6·7	7·2
Bu	Dark blue	79—80	MeOH	6340	74·2	7·1	7·1	$C_{25}H_{28}O_3N_2$	74·2	6·9	6·9
Ph	Black	109—110	Dil. EtOH	6300	76·5	5·6	6·7	$C_{27}H_{24}O_3N_2$	76·4	5·7	6·6
CH_2Ph	Dark blue-green	67—68	,,	6430	76·6	6·0	6·3	$C_{28}H_{26}O_3N_2$	76·7	5·9	6·4

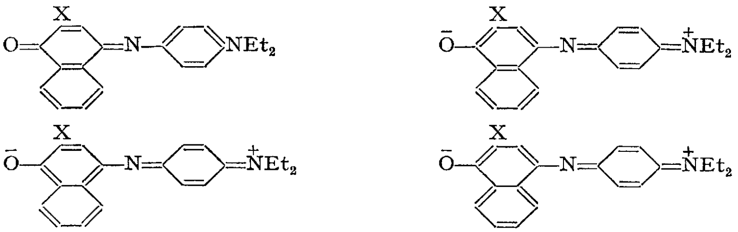
(I.)



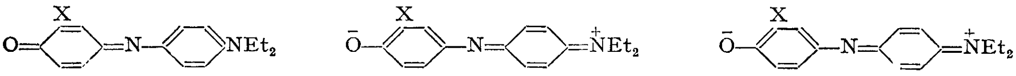
Derivatives of α-naphthol-blue were obtained from a dilute alcoholic solution of an ester and diethyl-*p*-phenylenediamine in alkaline medium by oxidising it with either (*a*) potassium persulphate or (*b*) silver halide by the action of light.

Only method (*a*) could be used for preparing the dyes of esters of salicylic acid, but these could not be isolated because of their instability (cf. Vittum and Brown, *J. Amer. Chem. Soc.*, 1946, **68**, 2236). The greater stability of the dyes obtained from the esters of 1-hydroxy-2-naphthoic acid could be explained by their ability to exhibit more resonance, thereby facilitating the dispersion of the negative charge of the polarised phenolic oxygen.

The possible resonance forms for the naphthol-blue *dyes* are (X = H or CO_2R) :



whereas those for phenol blue dyes are :



EXPERIMENTAL.

(M. p.s are uncorrected.)

1-*Hydroxy*-2-*naphthoyl Chloride*.—10 G. of the acid were refluxed with 12 c.c. of thionyl chloride in 50 c.c. of light petroleum (b. p. 60—80°) until an orange solution resulted. On evaporation under reduced pressure, yellow needles were obtained, m. p. 84°.

Esterification. The acid chloride was refluxed for 2 hrs. with 4 times its weight of the appropriate alcohol. On cooling in a freezing mixture, the ester crystallised. If crystallisation did not set in, the alcohol was distilled off on the water-bath, and the residual oil under reduced pressure. The following 1-hydroxy-2-naphthoates were prepared : methyl, buff needles from alcohol, m. p. 76° (Schmidt and Burkhardt, *Ber*., 1887, **20**, 2700; Cohen and Dudley, *J*., 1910, **97**, 1747; Kaufmann and Egner, *Ber*., 1913, **46**, 3782); ethyl, fine pale pink needles from alcohol, m. p. 46° (Schmidt and Burkhardt, *loc. cit.*; Lassar-Cohn and Loewenstein, *loc. cit.*); *propyl*, buff needles from alcohol, m. p. 63° (Found : C, 73·0; H, 6·1. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%); iso*propyl*, buff platelets from alcohol, m. p. 51° (Found : C, 73·0; H, 6·1%); *butyl*, yellowish needles from alcohol, m. p. 40° (Found : C, 73·8; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%); iso*butyl*, oil which distilled at 208°/45 mm. and solidified to a mass of yellowish needles from alcohol, m. p. 62° (Found : C, 73·8; H, 6·5%); *benzyl*, long white needles from alcohol, m. p. 72° (Found : C, 77·7; H, 5·0. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%).

Hexyl ester. This ester could not be obtained by the previous method, so the following procedure was adopted. To 8·8 g. of 1-hydroxy-2-naphthoyl chloride was added a cold solution of sodium hexyloxide in benzene, prepared by refluxing a mixture of 9·5 c.c. of *n*-hexyl alcohol and 1 g. of finely divided sodium in 200 c.c. of dry benzene for 10 hr.; the mixture was refluxed for 2 hr., the benzene distilled off, and the residual oil poured into crushed ice with stirring. The yellow precipitate so obtained was collected, and recrystallised from alcohol; white short needles, m. p. 43° (Found : C, 75·0; H, 7·4. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3%).

Phenyl ester. A modification of Jusa and von Janovitch's method (*Monatsh*., 1938, **71**, 205) was adopted. 3·78 G. of the acid and 0·55 c.c. of phosphorus oxychloride were added in three separate and equal portions to 1·88 g. of phenol at intervals of 30 mins. at a temperature of 110°. The mixture was maintained at this temperature until no more hydrogen chloride was evolved. To the cold mixture a little water was added. The resulting hard mass was broken up, washed until neutral, and then made alkaline (litmus) by addition of sodium carbonate solution. The precipitate was filtered off, washed till neutral, dried at 50°, stirred with methanol at 30°, and dried at 50°; m. p. 91°.

Naphthol-blue Dyes.—(a) *By oxidation with potassium persulphate*. 1 G. of the ester was dissolved in a small amount of ethanol to which was added 1 g. of diethyl-*p*-phenylenediamine hydrochloride. To the warm solution were added 2·5 g. of potassium persulphate and a few drops of 3N-sodium hydroxide The blue-green dye was precipitated by water; in some cases it solidified only on cooling in a freezing mixture. The dye was filtered off, washed well with water, dried, and recrystallised.

(b) *By oxidation with silver halide exposed to light*. 0·5 G. of the ester, dissolved in 10 c.c. of ethanol, was added to 20 c.c. of a silver halide emulsion containing 10% of gelatin and 1·5% of calsolene oil (I.C.I.) in the dark. This emulsion was coated on a glass plate, dried, exposed to light for a few seconds, and developed in an alkaline solution of diethyl-*p*-phenylenediamine hydrochloride. The silver and silver halide were then removed, leaving a blue-green image.

Spectrophotometric Measurements.—All these were carried out on a Hilger spectrophotometer.

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