

ARYL ESTERS AND ARYLAMIDES OF 2-HYDROXY-3-NAPHTHOIC ACID AND 1-BROMO-2-HYDROXY-3-NAPHTHOIC ACID

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THE aryl esters of the acids are prepared by heating the respective phenol and the acid in presence of phosphorus oxy-chloride at 130–140° C. The esters of the bromo acid and *o*-anisidide and *o*-toluidide of the bromo acid are also obtained by the bromination of the esters and the corresponding arylamides of the simple hydroxy acid.

The method for the preparation of arylamides of 2-hydroxy-3-naphthoic acid are either covered by patents or are very tedious,¹ probably because the preparation of its acid chloride is very tedious.² Now it is found that these arylamides can be easily prepared by heating the mixture of the acid and the amine with excess of phosphorus trichloride.

In the case of 1-bromo-2-hydroxy-3-naphthoic acid, however, as the acid chloride can be easily prepared by the action of phosphorus pentachloride on the acid in presence of dry benzene, its arylamides are prepared by the interaction of the acid chloride and the respective amine in presence of dry benzene at room temperature.

Experimental

Preparation of aryl esters.—

The acid and the phenol were taken in equal weights and phosphorus oxychloride whose volume was equal to half the weight of the acid was added to the mixture. The mixture was heated at 130–40°, until a clear solution was obtained. When cold, the reaction mixture was diluted with water and separated solid was washed completely. All the substances are crystallised from acetic acid. They are described in Table I.

2-Hydroxy-3-naphth-o-toluidide.—A mixture of the acid (4 g.) and freshly distilled *o*-toluidine (5 g.) was heated to melt the acid and then phosphorus trichloride (10 c.c.) was added through the top of the condenser and the mixture was heated at 160–70° for two hours. When cold, the mixture was titrated with dilute hydrochloric acid and washed with water. It

TABLE I

Substance	Crystalline shape	M.P.	Formula	Found	Required	Yield %
<i>o</i> -Cresyl-2-hydroxy-3-naphthoate	Yellow needles	119-20°	C ₁₈ H ₁₄ O ₃	C, 77.4 ; H 5.0;	C, 77.7 H, 5.0	85
<i>m</i> -Cresyl-2-hydroxy-3-naphthoate	Pale yellow needles	94.5°	C ₁₈ H ₁₄ O ₃	C, 77.7 ; H, 4.4;	C, 77.7 H, 5.0	80
*Phenyl-1-bromo-2-hydroxy-3-naphthoate	Pale yellow needles	131-2°	C ₁₇ H ₁₁ O ₃ Br.	Br, 23.0;	Br, 23.3	75
* <i>o</i> -Cresyl-1-bromo-2-hydroxy-3-naphthoate	Yellow needles	163-4°	C ₁₈ H ₁₃ O ₃ Br.	Br, 22.4 ;	Br, 22.4	75
* <i>m</i> -Cresyl 1-bromo-2-hydroxy-3-naphthoate	Pale yellow needles	146-7°	C ₁₈ H ₁₃ O ₃ Br.	Br, 22.7 ;	Br, 22.4	75

crystallised from acetic acid in small white needles, m.p. 192-3°. Yield 35%. (D.R.P. 293,897 gave m.p. 195-6°). (Found: N, 4.8; C₁₈H₁₅O₂N requires N, 5.1 per cent.)

2-Hydroxy-3-naph-m-toluidide.—A mixture of the acid (5 g.), *m*-toluidine (6 g.) and phosphorus trichloride (20 c.c.) was heated under reflux at 170-80° for two hours and then worked up as above. It crystallised from acetic acid in shining plates, m.p. 213-14°. Yield 80%. Found: N, 4.9; C₁₈H₁₅O₂N requires N, 5.1 per cent.)

2-Hydroxy-3-naphth-o-anisidide.—A mixture of the acid (5 g.), *o*-anisidine (7 g.) and phosphorus trichloride (20 c.c.) was heated under reflux at 170-90° for two and a half hours and then worked up as before. It crystallised from acetic acid in small needles, m.p. 162-4°. Yield 20%. (D.R.P. 293, 897 gave m.p. 167-8°.) (Found: N, 4.5; C₁₈H₁₅O₂N requires N, 4.8 per cent.)

1-Bromo-2-hydroxy-3-naphthoyl chloride.—A mixture of the acid (3 g.) and phosphorus pentachloride (3 g.) and dry benzene (10 c.c.) was heated gently on a water-bath until a clear orange solution was obtained. On cooling the solution, yellow needles of the acid chloride separated out. The solid was washed with dry petroleum ether and dried in vacuum over phosphorus pentoxide, m.p. 145-6°. (Found: Cl, 12.2; ; Br, 27.6; C₁₁H₈O₂ClBr requires Cl, 12.4; Br, 28.0 per cent.)

Arylamides of 1-bromo-2-hydroxy-3-naphthoic acid.—The acid chloride prepared from a certain weight of the acid was dissolved in sufficient quantity of dry benzene (10 times in vol. of the weight taken) and to it the amine, whose volume was equal to the weight of the acid taken, dissolved in a little dry benzene was added and the mixture was left at room temperature for one hour. The solid obtained after the removal of the solvent was treated with dilute hydrochloric acid, washed with water and then crystallised from acetic acid. The substances are described in Table II.

TABLE II

Substance	Crystalline shape	M.P.	Formula	Found	Required	Yield %
1-Bromo-2-hydroxy-3-naphth-anilide	Pale yellow needles	165-6°	C ₁₇ H ₁₂ O ₂ NBr	Br, 23.1	Br, 23.4	60
*1-Bromo-2-hydroxy-3-naphth- <i>o</i> -toluidide	Yellow needles	234-5°	C ₁₈ H ₁₄ O ₂ NBr	Br, 22.3	Br, 22.5	56
1-Bromo-2-hydroxy-3-naphth- <i>m</i> -toluidide	Yellow plates	171-2°	C ₁₈ H ₁₄ O ₂ NBr	Br, 22.9	Br, 22.5	75
1-Bromo-2-hydroxy-3-naphth- <i>p</i> -toluidide	Pale yellow needles	201-2°	C ₁₈ H ₁₄ O ₂ NBr	Br, 22.6	Br, 22.5	70
*1-Bromo-2-hydroxy-3-naphth- <i>o</i> -anisidide	Yellow needles	191-2°	C ₁₈ H ₁₄ O ₃ NBr	Br, 21.9	Br, 21.5	60
1-Bromo-2-hydroxy-3-naphth- <i>p</i> -anisidide	Yellow plates	173-4°	C ₁₈ H ₁₄ O ₃ NBr	Br, 21.2	Br, 21.5	60

Substances marked * are prepared by direct condensation as well as by the bromination of the corresponding derivatives of the 2-hydroxy-3-naphthoic acid.

(The preparation of *o*- and *m*-cresyl esters of 2-hydroxy-3-naphthoic acid and *o*- and *m*-toluidides and *o*-anisidide of the same acid as well as phenyl, *o*- and *m*-cresyl esters and anilide, *o*-, *m*- and *p*-toluidides and *o*- and *p*-anisidides of 1-bromo-2-hydroxy-3-naphthoic acid is described. The esters and *o*-toluidide and *o*-anisidide of 1-bromo-2-hydroxy-3-naphthoic acid are also; prepared by the bromination of the corresponding derivatives of the 2-hydroxy-3-naphthoic acid.)

Bromination of the phenyl, o-, and m-cresyl esters and o-toluidide and o-anisidide of 2-hydroxy-3-naphthoic acid.—

The requisite ester (2 g.) was mixed with dry chloroform (10 c.c.) and the solution of bromine in the same solvent (14 c.c. of 10% solution) was gradually added to it. The reaction mixture was left at room temperature for half an hour and then the solvent was removed. The bromo-derivative was crystallised from acetic acid and mixed melting point with the authentic specimen described in Table I was taken, when no lowering in melting point was observed.

In the bromination of *o*-toluidide and *o*-anisidide the same method was used, but they being less soluble, more solvent was used, the proportion of the reactants being 1:1. These products also were crystallised from acetic acid and mixed melting points with authentic specimens described in Table II showed no lowering.

REFERENCES

- Schoff .. *Ber.*, 1892, 25, 2743; Brit. patent 289037; U. S. patent 1,733, 468 of 1937; Jap. patent 95038 of 1932; D. R. P. 289027, 293897, 294799 of 1916.
- Meyer .. *M.* 1901, 22, 791.
- Fries .. *Ber.*, 1925, 58, 2848; French patent 632,767 (1927); U. S. patent 1,684,273 (1927); *J. Gen. Chem.* (U. S. S. R.), 1938, 8, 557-64.