

1-NITRO-2-HYDROXY-3-NAPHTHOIC ACID AND ITS DERIVATIVES

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6-NITRO-2-HYDROXY-3-NAPHTHOIC acid is obtained by the nitration of 1-amino-2-hydroxy-3-naphthoic acid or its diazo-oxide and subsequent elimination of the amino or diazo group (*I. G. Farbenind. A. G.*, Ger. 623496; General Aniline Works, U.S. 2040587; *I. G. Farbenind. A. G.*, Brit. 445278). This 1-amino-2-hydroxy-3-naphthoic acid has been prepared by various indirect methods (Mohlau, *Ber.*, 1893, **26**, 3066; Mohlau and Kriebel, *Ber.*, 1895, **28**, 3091; Weil and Heerdt, *Ber.*, 1922, **55**, 226). Robertson (*J. pr. ch.*, 1893, (2), **48**, 534), however, claims to have obtained it by the reduction of 1-nitro-2-hydroxy-3-naphthoic acid which in its turn is obtained by the nitration of 2-hydroxy-3-naphthoic acid, but no experimental details are available and the melting point of the nitro acid given by this author is 233–38° which is quite different from the one described here (246–48°) and therefore his nitro acid may not be pure.

Later Gradenwitz (*Ber.*, 1894, **27**, 2623) nitrated methyl 2-hydroxy-3-naphthoic acid and got simple phthalic acid by the oxidation of the nitro derivative obtained. He thus proved isonuclear positions of –OH, –COOH and –NO₂ groups, but he did not definitely name the substance. But the only possible position taken up by the nitro group, according to the directing influences of –OH and –COOH groups, is 1 only. His nitro derivative must, therefore, be methyl 1-nitro-2-hydroxy-3-naphthoate.

In the present work the methyl and ethyl esters of 2-hydroxy-3-naphthoic acid are nitrated according to Gradenwitz (*loc. cit.*) and free acid is obtained by hydrolysis with alcoholic potassium hydroxide. 1-Nitro-2-hydroxy-3-naphthoic acid melts at 246–48°.

The ethyl ester of the nitro acid has the melting point 155–56°, identical with that described by Meisenheimer, Theilcker and Beißwenger (*Ann.*, 1932, **495**, 275) who have not given experimental details.

The acid chloride of 1-nitro-2-hydroxy-3-naphthoic acid is easily obtained. From this acid chloride, some derivatives like ethyl esters and arylamides are prepared from aniline, *o*-, *m*-, and *p*-toluidines and *o*-, *p*-, anisidines.

EXPERIMENTAL

1-Nitro-2-hydroxy-3-naphthoic acid.—A mixture of methyl 1-nitro-2-hydroxy-3-naphthoate (or the ethyl ester) (10 g.), rectified spirit (50 c.c.) and potassium hydroxide (100 c.c. of 2 N) was refluxed on boiling water-bath for about two hours. The acid, that separated on acidification, was crystallised from dilute alcohol in shining yellow needles, m.p. 246–48°. (Found: N, 6.0%; $C_{11}H_7O_5N$ requires N, 6.0%.)

1-Nitro-2-hydroxy-3-naphthoyl chloride.—A mixture of 1-nitro-2-hydroxy-3-naphthoic acid (1 g.), phosphorous pentachloride (2 g.) and dry chloroform (25 c.c.) was refluxed on boiling water-bath until a clear solution was obtained. On cooling the reaction mixture, the acid chloride separated in brownish yellow needles, which were filtered and washed with dry petroleum ether and dried under vacuum over phosphorous pentoxide, m.p. 168–70° (Found: Cl, 14.2%. $C_{11}H_6O_4NCl$ requires Cl, 14.1%.)

Phenyl-1-nitro-2-hydroxy-3-naphthoate.—It is prepared by heating together a mixture of acid (2 g.), phosphorous oxychloride (1 c.c.) and phenol (2 g.) at 140–50° until effervescence ceases. The mixture is cooled, diluted with water and washed.

TABLE I
Derivatives of 1-nitro-2-hydroxy-3-naphthoic acid

Name	Formula	Appearance	Melting point	Nitrogen	
				Found	Required
1 Phenyl-1-nitro-2-hydroxy-3-naphthoate	$C_{17}H_{11}O_5N$	Thick flat needles	170–71°	4.7%	4.5%
2 Ethyl-1-nitro-2-hydroxy-3-naphthoate	$C_{13}H_{11}O_5N$	Yellow needles	155–56°	5.1%	5.4%
3 1-Nitro-2-hydroxy-3-naphth-anilide	$C_{17}H_{12}O_4N_2$	Small yellow needles	188–89°	9.5%	9.1%
4 1-Nitro-2-hydroxy-3-naphth- <i>o</i> -toulidide	$C_{18}H_{14}O_4N_2$	Orange needles	190–91°	9.2%	8.7%
5 1-Nitro-2-hydroxy-3-naphth- <i>m</i> -toulidide	$C_{18}H_{14}O_4N_2$	Pale yellow needles	196–97°	9.0%	8.7%
6 1-Nitro-2-hydroxy-3-naphth- <i>p</i> -toulidide	$C_{18}H_{14}O_4N_2$	Long pale yellow needles	199–200°	9.3%	8.7%
7 1-Nitro-2-hydroxy-3-naphth- <i>o</i> -anisidide	$C_{18}H_{14}O_5N_2$	Yellow flat needles	224–25°	8.4%	8.3%
8 1-Nitro-2-hydroxy-3-naphth- <i>p</i> -anisidide	$C_{18}H_{14}O_5N_2$	Yellow needles	210–11°	8.9%	8.3%

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The arylamides are prepared by leaving the mixture of the amine and acid chloride in presence of dry benzene for an hour and washing the solid obtained with dilute hydrochloric acid after the removal of the solvent. They are crystallised from glacial acetic acid. They are described in Table I.

SUMMARY

Free 1-nitro-2-hydroxy-3-naphthoic acid is isolated, its acid chloride, phenyl ester and anilide, *o*-, *m*-, *p*-toulidides and *o*- and *p*-anisidides are prepared.