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Synthesis of Amides of 3-Hydroxy-2-naphthoic Acid: Derivatives of Benzimidazolone and Benzoxazolone

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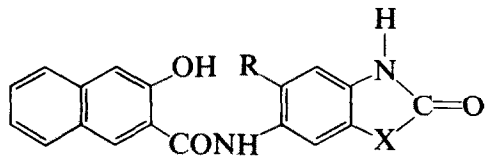
ABSTRACT

A method for the synthesis of N-*arylamides of 3-hydroxy-2-naphthoic acid, derived from 5-aminobenzimidazol-2-one and 6-aminobenzoxazol-2-one is presented. These compounds were synthesized by acylation of the corresponding amines with 3-hydroxy-2-naphthoyl chloride in glacial acetic acid,* N,N-*dimethylformamide or* N-*methylpyrrolidone in the presence of anhydrous sodium acetate.*

1 INTRODUCTION

N-Arylamides of 3-hydroxy-2-naphthoic acid, such as those derived from aniline, *o*- and *p*-toluidine, *p*-chloroaniline and other aromatic amines, have been widely used as coupling agents for naphthol dyes and in the synthesis of azo pigments. A conventional process for their synthesis consists of heating a mixture of 3-hydroxy-2-naphthoic acid and an aromatic amine in high-boiling organic solvents; e.g. xylene or chlorobenzene, in the presence of PCl_3 as condensing agent. It is assumed that 3-hydroxy-2-naphthoyl chloride or phosphine is an intermediate product in this reaction.[1]

In the 1960s, Hoechst introduced a range of high-performance organic pigments under the name Permanent H,[2] using in their synthesis a new coupling agent, namely 5-(3′-hydroxy-2′-napththoylamino)benzimidazol-2-one (**1**, X = NH, R = H).



X = NH, O
R = H, CH_3, Cl

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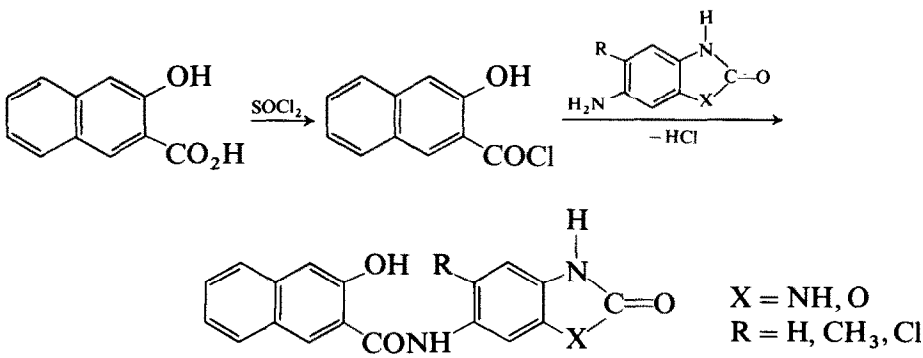
Our preliminary experiments on the synthesis of this amide and other derivatives of formula **1** by the conventional process above failed to give satisfactory results. Yields were very low and the products were heavily contaminated with products from side-reactions. Since there is no reference to the synthesis of these compounds in the literature, studies were undertaken to develop a suitable process to produce these compounds in high purity and good yield.[3]

2 EXPERIMENTAL

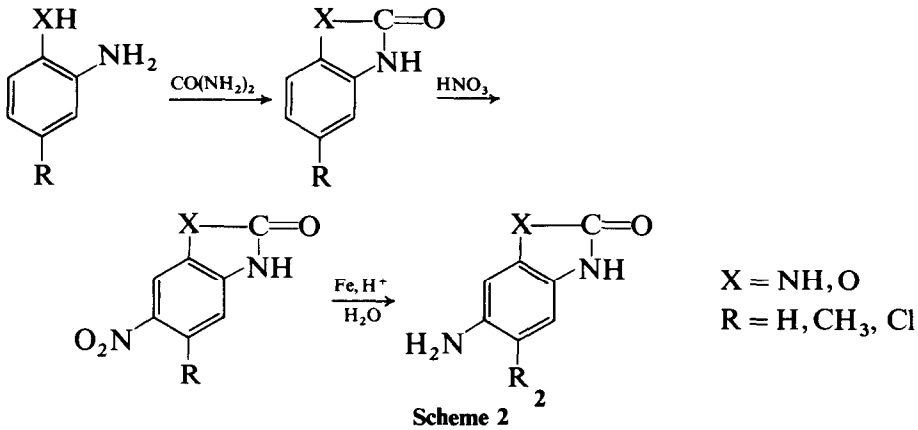
The synthesis of the amides was carried out according to the general Scheme 1.



X = NH, O
R = H, CH_3, Cl

Scheme 1

The 3-hydroxy-2-naphthoic acid used was prepared by acidifying the sodium salt isolated from a technical product. 3-Hydroxy-2-naphthoyl chloride was prepared by the treatment of a suspension of 3-hydroxy-2-naphthoic acid in carbon tetrachloride or chlorobenzene at 35–40°C with thionyl chloride in the presence of catalytic quantities of DMF. The solid product was isolated by crystallization from the post-reaction solution at 0–5°C and was used immediately after isolation since on storage solid 3-hydroxy-2-naphthoyl chloride is an unstable compound and it is converted to intermolecular esters of 3-hydroxynaphthoic acid. The acid chloride solution prepared in chlorobenzene was used in the synthesis of the amides directly after excess thionyl chloride was distilled off under vacuum.



Scheme 2

The amino derivatives of benzimidazolone and benzoxazolone used in the synthesis of amides were prepared by the method shown in Scheme 2. Benzimidazolone and its derivatives were prepared by melting 1,2-phenylenediamine or its derivatives with urea.[4,5] Nitration of these compounds was carried out by the method described by James & Turner,[6] using 63% nitric acid. The nitro compounds obtained were reduced to amines by the Béchamp method. In the same way, using 2-aminophenol and 4-chloro-2-aminophenol as starting compounds, amino derivatives of benzoxazolone (**2**, X = O; R = H, Cl) were obtained.[7–9] Commercial pure-grade reagents of POCh, Gliwice, were used in these syntheses.

The reaction between 3-hydroxy-2-naphthoyl chloride and the amino derivatives of benzimidazolone (**2**, X = NH) or benzoxazolone (**2**, X = O) was carried out in glacial acetic acid, DMF or *N*-methylpyrrolidone in the presence of a stoichiometric quantity of anhydrous sodium acetate.

The acylations in glacial acetic acid were performed at 30–35°C by adding solid 3-hydroxy-2-naphthoyl chloride to a solution of the appropriate amine and sodium acetate in glacial acetic acid. The precipitated amides were filtered after heating the mixture to 70–80°C. Acylations in DMF or *N*-methylpyrrolidone were carried out at 5–10°C by adding dropwise a chlorobenzene solution of 3-hydroxy-2-naphthoyl chloride to a solution of the appropriate amine in DMF or *N*-methylpyrrolidone in the presence of a stoichiometric quantity of sodium acetate. The precipitated amides were filtered after heating the reaction mixture to 50°C. For these acylation processes, commercial pure-grade acetic acid (POCh, Gliwice) was used and CCl_4, DMF, *N*-methylpyrrolidone and chlorobenzene were purified by distillation. The purity of the amides was assessed by paper chromatography, using paper Wh3 and a 25% NH_4OH–pyridine mixture (6:1) as developer. All the amides showed yellow–green fluorescence under UV light.

TABLE 1
Reaction Yield and Properties of Amides

Structure of amide		*Reaction medium*	*Yield (%)*	*Melting point (°C)*	R_f	*Elemental analysis (%)*								*Main absorption bands of IR spectra*	
X	*Z*					*C*		*H*		*N*		*Cl*		(cm^{-1})	
						Calcd	*Found*	*Calcd*	*Found*	*Calcd*	*Found*	*Calcd*	*Found*	*NH*	*C=O*
O	H	CH_3CO_2H	94·0[a]	335	0·306	67·5	67·5	3·8	3·8	8·75	8·75			3 250	1 640, 1 740, 1 780
O	Cl	CH_3CO_2H	89·3[a]	337	0·313	60·9	60·6	3·1	3·2	7·9	7·9	10·0	10·0	3 200	1 630, 1 680, 1 780
NH	H	CH_3CO_2H	96·1[a]	360	0·164	67·7	67·5	4·1	4·2	13·2	13·0			3 170	1 640, 1 710, 1 770
NH	CH_3	CH_3CO_2H	94·1[a]	360	0·173	68·5	68·1	4·5	4·8	12·6	12·5			3 200	1 630, 1 680
NH	Cl	CH_3CO_2H	96·3[a]	360	0·179	61·1	61·2	3·4	3·5	11·9	11·9	10·0	9·9	3 200	1 630, 1 665, 1775
NH	H	DMF	94·4[b]	360	0·164	67·7	67·4	4·1	4·2	13·2	13·1			3 170	1 640, 1 710, 1 770
NH	Cl	*N*-Methyl-pyrrolidone	87·4[b]	360	0·179	61·1	61·0	3·4	3·35	11·9	11·9	10·0	9·7	3 200	1 630, 1 665, 1 775

[a] Yield calculation based on 3-hydroxy-2-naphthoic chloride.
[b] Yield calculation based on 3-hydroxy-2-naphthoic acid.

The structure of the amides was confirmed by elemental analysis and IR spectra. Yields and other characterization data are given in Table 1. Melting points were determined with a Boetius HMPK apparatus. IR spectra were recorded on a Specord 71-IR (C. Zeiss, Jena).

The method developed is illustrated by the examples of synthesis of 5-(3′-hydroxy-2′-naphthoylamino)benzimidazol-2-one.

2.1 Example I

3-Hydroxy-2-naphthoic acid (37·6 g; 0·2 mol) was heated at 35–40°C in 150 cm^3 of CCl_4 containing 21 cm^3 of thionyl chloride and 0·5 cm^3 of DMF until the suspension was completely dissolved. The solution was left to crystallize for several hours at 0–5°C. The product was filtered, washed with 30 cm^3 of petroleum ether and dried in a vacuum desiccator; 35 g of 3-hydroxy-2-naphthoyl chloride (m.p. 90–92°C) was obtained in 84·7% yield. The product after recrystallization from ligroin had m.p. 93–96°C.

To the solution containing 4·47 g (0·03 mol) of 5-aminobenzimidazolone and 3 g of anhydrous sodium acetate in 100 cm^3 of glacial acetic acid, 6·2 g (0·031 mol of 3-hydroxy-2-naphthoyl chloride was added gradually at 36°C. Reaction was carried out at 35–40°C for 1 h, and the mixture was then heated for a short time to 90°C. The precipitate was filtered hot, washed with 30 cm^3 of glacial acetic acid and boiling water, and then dried, giving 9·2 g of amide (m.p. 360°C; yield 96·1%).

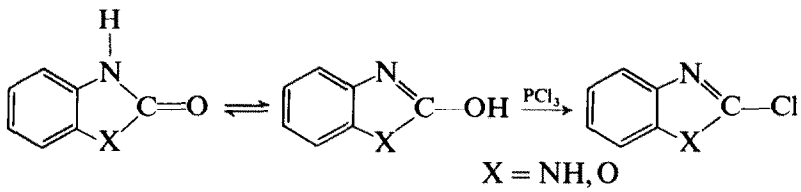
2.2 Example II

3-Hydroxy-2-naphthoic acid (9·9 g; 0·052 mol) was heated for 1·5 h at 35–40°C in 60 cm^3 of chlorobenzene containing 4·2 cm^3 of $SOCl_2$ and 0·1 cm^3 of DMF. When the reaction was complete, excess $SOCl_2$ was distilled off under vacuum and the solution then added dropwise over 0·5 h at 5–10°C to a solution containing 7·5 g (0·05 mol) of 5-aminobenzimidazol-2-one and 4·1 g of anhydrous sodium acetate in 70 cm^3 of DMF. The reaction mixture was stirred for 3 h at 20°C and then heated to 50°C and filtered. The product was washed with methanol and boiling water (13·5 g; 91·4%).

3 DISCUSSION OF RESULTS

Preliminary experiments showed that heating a mixture of 3-hydroxy-2-naphthoic acid with amines of general formula **2** in the presence of PCl_3 in high-boiling solvents such as toluene, xylene or chlorobenzene resulted in the formation of numerous impurities and reaction by-products, whilst the desired amide was only obtained in low quantities.

It was noted that the high temperatures necessary in this process and the low solubility of the amines in the solvent facilitated the formation of intermolecular esters of 3-hydroxy-2-naphthoic acid and of chlorination products of the heterocyclic rings of benzimidazolone and benzoxazolone (Scheme 3). Other compounds of similar structure, e.g. cyanuric acid, quinoxalino-2,3-dione, quinol-2-one, also show similar susceptibility to the chlorinating action of PCl_3.



Scheme 3

Further examination of the reaction between benzoyl chloride and amino derivatives of benzimidazolone and benzoxazolone showed that benzoylation of the amine group proceeds readily at 5–20°C, indicative of the high nucleophilicity of the amine group in these compounds. This led us to investigate the possible synthesis of amides of 3-hydroxy-2-naphthoic acid by acylation of amines with 3-hydroxy-2-naphthoyl chloride. The acylation process was carried out initially in xylene and chlorobenzene, giving formation of the amides in yields of 30–40%. It was found that under these conditions, 3-hydroxy-2-naphthoyl chloride forms large amounts of oligomeric esters, thus lowering the yield of amide in the reaction. Considerable improvement of the process yield and of purity of the amides was observed on changing the reaction system. The new system included glacial acetic acid, DMF or *N*-methylpyrrolidone and in presence of anhydrous sodium acetate as acid-binding agent. The use of these solvents significantly improved the solubility of the amines and the acylation process could be carried out at relatively low temperatures, i.e. 30–35°C in glacial acetic acid, and 5–10°C in DMF or *N*-methylpyrrolidone. This reduction in temperature ensured *N*-acylation of the amino group proceeded well and also inhibited side-reactions. Small amounts of unreacted materials and by-products were very soluble in the reaction system and were thus readily removed during filtration of the amide suspension.

The acylation of amines in glacial acetic acid with solid 3-hydroxy-2-naphthoyl chloride resulted in the formation of amides of high purity and high yields (89·3–96·3% based on the acid chloride), and allowed their use directly in the synthesis of pigments.

Taking into account that the use and recovery of glacial acetic acid in large quantities is troublesome under industrial conditions, in further

experiments DMF or *N*-methylpyrrolidone was used. The high polarity of these solvents made it possible to carry out the reaction in a homogeneous phase at low temperatures with 3-hydroxy-2-naphthoyl chloride in chlorobenzene. The presence of chlorobenzene in the reaction system (about 50% by vol.) did not detrimentally affect the yield and purity of the amides. The solution of acid chloride was obtained directly by treating 3-hydroxynaphthoic acid in chlorobenzene with thionyl chloride in the presence of catalytic quantities of DMF. Consequently, the stage of isolation of the solid chloride was eliminated, considerably simplifying the synthesis of the amides (87·4–91·4%, based on 3-hydroxy-2-naphthoic acid).

4 CONCLUSIONS

The use of solvents such as DMF and *N*-methylpyrrolidone in the synthesis of the amides **1** enabled the syntheses to be effected at relatively low temperatures and afforded **1** in high yield. The purity of **1** thus obtained was also high and sufficiently so for them to be used directly in the synthesis of pigments.

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