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Synthesis and Properties of Bis-Arylides of 3-Hydroxy-2-naphthoic Acid, Derivatives of 1,4-Phenylenediamines

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ABSTRACT

Bis arylides of 3-hydroxy-2-naphthoic acid were synthesised by heating a pyridine solution of 3-hydroxy-2-naphthoic acid and 1,4-phenylenediamine or its derivatives, in the presence of phosphorus trichloride. The suitability of chlorobenzene in this reaction was also demonstrated. © 1998 Elsevier Science Ltd

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INTRODUCTION

Considerable interest in bis-arylides of 3-hydroxy-2-naphthoic acid was observed during the third decade of this century. These compounds were expected to be very good passive components in ingrain dyestuffs. Benzidine and its derivatives [1] were mainly used in the synthesis, as well as 1,5-diaminonaphtalene [2], 3,8-diaminopyrene [3], 2,8-diaminochrysene [4] 1,4-diaminoanthraquinone [5] and other compounds [6–7].

Only two bis-arylides of 3-hydroxy-2-naphthoic acid have been employed in dye technology. These are derivatives of 3,3′-dimethylbenzidine (Naphtol AS-BM, CI 37570) and 3,3′-dimethoxybenzidine (Naphtol AS-BR CI. 37375). It was found, however, that these compounds did not afford good dyes for cotton—they had little resistance to sodium hypochlorite, and their

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production was short-lived. It was subsequently found that these arylides contained appreciable amounts of impurities which were the products of a unilateral condensation.

Interest in bis-arylides of 3-hydroxy-2-naphthoic acid emerged again, when new methods of synthesis of highly permanent pigments were developed. As a result of the presence of two carboxamide moities in a planar molecule, bis-arylides have become a potential passive component in the synthesis of such pigments. The synthesis of pigments by this method consisted in coupling diazotized aromatic amines with bis-arylides in aqueous medium and due to its simplicity could be competitive to the solvent method employed earlier in the synthesis of condensed pigments of the Cromophtal type. (CIBA-GEIGY). A prerequisite condition was the use of bis-arylides of new, inexpensive and non-toxic amines, in order to eliminate the use of carcinogenic benzidine and its derivatives. As a result of our preliminary investigations and experience gained therein during the syntheses of dis-azoic condensed pigments it was found that 1,4-phenylenediamine and its derivatives could be employed in the synthesis of bis-arylides.

The purpose of this work was to develop a process for obtaining bis-arylides of 3-hydroxy-2-naphthoic acid, using 1,4-phenylenediamine, 2-chloro- or 2,5-dichloro-1,4-phenylenediamine, and which would be distinguished by a very high degree of purity of the products obtained. The presence of impurities in such products is highly undesirable as they substantially deteriorate the properties of the resultant products.

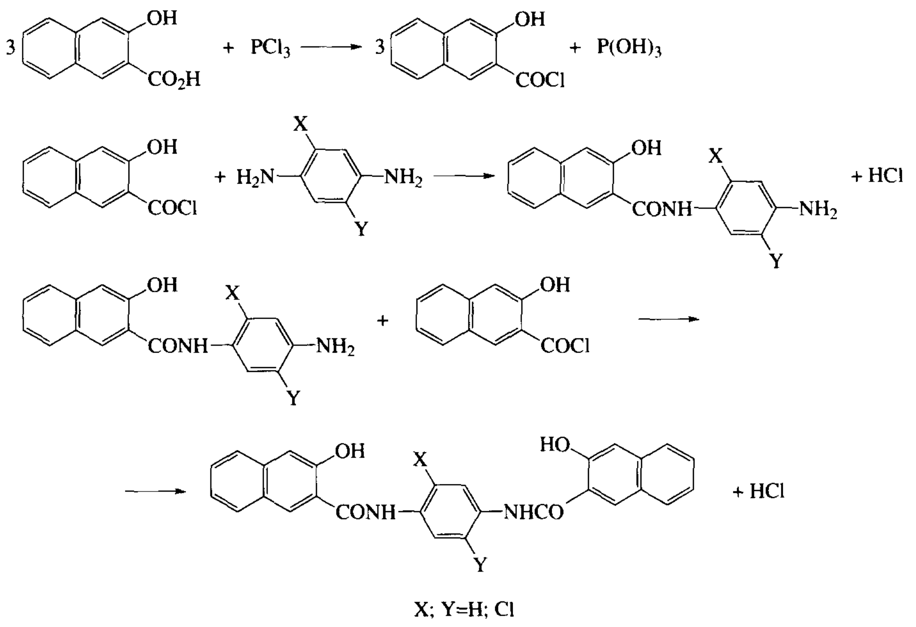
Only one preparative description [8] concerning the synthesis of this type of arylides has been found in the literature. In that method 3-hydroxy-2-naphthoic acid chloride was used for acylation of 1,4-phenylenediamine and 2,5-dichloro-1,4-phenylenediamine. It was shown, however, that the products of that reaction were highly contaminated by compounds resulting from a unilateral condensation.

Further investigation of the classical [9] method of bis-arylide synthesis, which consists in heating a mixture of 3-hydroxy-2-naphthoic acid and the appropriate diamine in a high-boiling solvent (xylene, chlorobenzene) gave different results. By acylation of 2,5-dichloro-1,4-phenylenediamine, the appropriate bis-arylide was obtained in satisfactory yield. After purification, the compound could be used for further syntheses.

The remaining reactions, which also involved 1,4-phenylenediamine and 2-chloro-1,4-phenylenediamine, gave low yields of highly impure products due to side-reactions. In order to increase the yield and the purity of the bis-arylides, different reaction media were investigated. Among the many solvents investigated, pyridine proved to be the most suitable, as in this solvent the side reactions proceeded very slowly and the separation of the pure products is much more facile.

EXPERIMENTAL

The synthesis of bis-arylides of 3-hydroxy-2-naphthoic acid involves three stages as outlined in Scheme 1.



Scheme 1

In the reaction purified 3-hydroxy-2-naphthoic acid was employed. It was obtained by acidifying the sodium salt isolated from a commercial product.

1.4-Phenylenediamine and 2-chloro-1,4-phenylenediamine (Fluka) were used as received 2,5 dichloro-1,4-phenylenediamine was obtained from commercially available 2,5-dichloroaniline through nitration of 2,5-dichloracetanilide and subsequent hydrolysis of the product and reduction of the resulting 2,5-dichloro-4-nitroaniline according to the Bechamp's [10] method. Other compounds were obtained from POCh (Poland) and were used as received. Pyridine and chlorobenzene were dried and distilled.

The course of the acylation reaction and its end point, as well as the purity of the bis-arylides obtained were controlled by paper chromatography using Wh3 paper and 25% ammonia–pyridine (6 : 2) as an eluent. The chromatograms were observed in UV Light and developed using a solution of the diazonium salt of 4-chloro-2-nitroaniline. The bis-arylides showed a yellow–green fluorescence in UV light, whereas the products of the unilateral condensation were blue–green. The condensation reaction was considered as completed when a minimum amount of residual 3-hydroxy-2-naphthoic acid was observed in the chromatogram of the reaction mixture.

The synthesis of the bis-arylides in pyridine was carried out by heating for a few hours a mixture of 3-hydroxy-2-naphthoic acid, the appropriate diamine and PCl_3 at reflux in pyridine. After completion of the reaction the mixture was left for several hours for crystallization. The evolved bis-arylides were filtered, washed with methanol and dried. The maximum yield product was obtained when a 40% excess of PCl_3, in relation to the stoichiometry given by the reaction Scheme 1, was employed.

The arylide derivative of 2,5-dichloro-1,4-phenylenediamine was obtained by heating the substrates in boiling chlorobenzene and filtering off the evolved product at elevated temperature. After washing with methanol, the product was heated for a few hours in boiling *N*,*N*-dimethylformamide, then filtered once more at elevated temperature and left to crystallize. The product was washed with methanol and dried. A 5% excess of 3-hydroxy-2-naphthoic acid and 10% excess of PCl_3 in relation to the stoichiometry given by eqn (1) were employed in this synthesis.

The structures of bis-arylides obtained were confirmed by elemental analysis of IR spectroscopy. The IR spectra were recorded on a Specord 71-IR (C. Zeiss-Jena). Melting points were determined on a Boetius HMPK apparatus. Some reaction parameters, physico-chemical parameters and the results of elemental analysis are given in Table 1. The synthetic method developed by us is illustrated by the following examples of synthesis:

2,5-Dichloro-1,4-phenylenediamine

A. 2,5-Dichloroacetanilide

To a solution of 2,5-dichloroaniline (40.5 g; 0.25 mol) in glacial acetic acid (150 ml) at 105–110°C was added dropwise 21 g of acetic anhydride. The mixture was stirred for 1 h then cooled down to 50–60°C and poured to 300 ml of ice-water. The liquor was filtered and the residue washed with water and dried at 70–80°C to give 45 g of product (89.8%). M.p.: 130–132°C.

B. 4-Nitro-2,5-dichloroacetanilide

40.8 g (0.2 mol) of 2,5-dichloroacetanilide was dissolved in 160 ml of conc. sulfuric acid. The solution was stirred at 5–10°C while a nitrating mixture (20 ml of 63% HNO_3 and 40 ml of conc. H_2SO_4 was added dropwise. After completion of the addition, the mixture was stirred for 1 h at room temperature and then poured into 600 ml of ice-water. The product was filtered washed with water, then with $NaHCO_3$ solution and then with water until

TABLE 1
Reaction Parameters and Properties of Bis-arylides of 3-Hydroxy-2-naphthoic Acid

Diamine		*1,4-phenylenediamine*		*2-Chloro-1,4-phenylenediamine*		*2,5-Dichloro-1,4-phenylenediamine*		
Reaction medium		Pyridine		Pyridine		Chlorobenzene		Pyridine
Reaction time (h)		3		4		8		5
Yield (%)		73.5		70		79.3		9
Melting point (°C)		366		347		> 370		> 370
R_f		0.36		0.42		0.50		0.50
		Calc'd	Found	Calc'd	Found	Calc'd	Found	
Elemental analysis (%)	C	75.0	74.7	69.6	69.5	65.0	65.0	—
	H	4.5	4.6	4.0	4.0	3.5	3.7	—
	N	6.3	6.3	5.8	5.7	5.4	5.5	—
	Cl	—	—	7.3	7.2	13.7	13.5	—
IR spectrum (cm^{-1})	NH	3270		3270		3240		3240
	CO	1615, 1630		1615, 1630		1620, 1640		1620, 1640

the eluate was neutral to Congo red. After drying at 60–70°C 46 g (92.4%) of the nitro compound was obtained. M.p.: 142–143°C.

C. 4-Nitro-2,5-dichloroaniline

37.4 g (0.15 mol) of 4-nitro-2,5-dichloracetanilide in 200 ml of 25% sulfuric acid was heated for 1 h at reflux. The mixture was diluted with 300 ml of water and then stirred for 1 h. The resulting product was filtered, washed with water and dried at 50–60°C to give 27 g (90.0%) of the nitro compound. M.p.: 150–153°C.

D 2,5-Dichloro-1,4-phenylenediamine

The nitro compound (20.7 g; 0.1 mol) was added in small portions to a boiling reducing mixture (25 g of Fe dust, 200 ml of ethanol, 100 ml of water, 0.5 ml of conc. HCl). After completion of the reduction process, the mixture was basified with a solution of Na_2CO_3 and filtered at elevated temperature using a heated Buchner funnel. The filtrate was left for a few hours to crystallize. The evolved amine was filtered, washed with water and dried at 90–100°C to give 14 g (79%) of the product. M.P.: 165–167°C.

Purification of 3-hydroxynaphthoic-2 acid

150 g of technical 3-hydroxy-2-naphthoic acid was dissolved in hot water (1500 ml) containing 80 ml of 30% NaOH. The solution obtained was filtered at elevated temperature after addition of activated charcoal. To the vigorously stirred filtrate was added 230 g of NaCl and stirring was continued for 1 h. The isolated sodium salt was filtered, washed with 15% brine, dissolved in 1500 ml of water and then 15% HCl was added dropwise until the mixture become acid to Congo red. After stirring 1h for the precipitated 3-hydroxy-2-naphthoic acid was filtered, washed with water and dried at 100°C to give 130 g of bright-yellow product. M.P.: 214–216°C. Paper chromatography (eluent: 25% NH_3-pyridine–water, 6 : 1 : 1; $R_f = 0.79$) did not show any impurities.

N,N' (2,5-Dichloro-1,4-phenylene)-bis(3-hydroxynaphthalene-2-carboxamide)

To a mixture of 17.gg (0.1 mol) of 2,5-dichloro-1,4-phenylenediamine and 39.5 g of 3-hydroxy-2-naphthoic acid in 400 ml of dry chlorobenzene was added 11.2 g of PCl_3 with vigorous stirring at 40–50°C; the mixture was then heated for 10 h at reflux. the isolated product was filtered hot (100–110°C), washed with methanol and then heated for 3 h in boiling DMF. The hot suspension was filtered and the residue washed with methanol and dried at 100°C to give 41 g (79.3%) of product.

N,N'-(1,4-phenylene)-bis(3-hydroxynaphthalene-2-carboxamide)

To a solution of 39.5 g of 3-hydroxy-2-naphthoic acid and 10.8 g (0.1 mol) of 1,4-phenylenediamine in 150 ml of pyridine was added dropwise 13.5 g of PCl_3 at 40–50°C and the resulting mixture was heated for 3 h at reflux. The mixture was then left for a few hours to crystallize. The product isolated was filtered, washed with methanol and dried at 100°C. 33 g of chromatographically pure bis-arylide was obtained. M.p.: 366°C.

DISCUSSION OF THE RESULTS AND CONCLUSION

As shown by the investigations, the synthesis of bis-arylides of 3-hydroxy-2-naphthoic acid is a complex process and each synthesis requires different conditions.

The acylation of aromatic diamines with 3-hydroxy-2-naphthoic acid occurs in two stages *viz*; in the first stage the product of the unilateral acylation is formed. In this reaction HCl is evolved, which reacts with the amino groups available in the reaction medium to form ammonium salts. In the reaction medium applied in this work, pyridine hydrochloride is formed, which leads to full unblocking of the amino groups of the diamines as well as the product of the monoacylation reaction. Therefore in the cases where 1,4-phenylenediamine and 2-chloro-1,4-phenylenediamine are used in the synthesis, the acylation reaction gives good yields of the products at the boiling point of pyridine. The free amino groups of the monoacylated product preserve the high nucleophilicity which makes the formation of the bis arylides faster than the formation of the undesirable intermolecular esters of 3-hydroxy-2-naphthoic acid.

During the acylation of 2,5-dichloro-1,4-phenylenediamine in the pyridine medium, the formation the monacylation product is initially observed, in addition to a small amount of the bis-arylide and a considerable amount of intermolecular esters, of 3-hydroxy-2-naphthoic acid. The esterification reaction is most probably accelerated by the basic pyridine medium, as well as by the weak nucleophilicity of the amino group of the monoacylated product caused by the presence of two Cl chloro substituents. In that case crystallization of pure bis-arylide from the reaction medium was not achieved.

The bis-arylide derived from 2,5-dichloro-1,4-phenylenediamine was obtained in chlorobenzene medium and was purified by heating in *N,N*-dimethylformamide.

The acylation reaction of diamines in the medium of aromatic hydrocarbons occurs in a different way to that in pyridine. The monoacylation product precipitates and the evolved HCl forms ammonium salts with the free amino groups, thus causing a significant change of the nucleophilic properties of the diamines and their basic properties. The latter factor would be related to differences in the electron donor and electron acceptor character of the substituent groups.

In the acylation reactions of the more basic diamines (1,4- and 2-chloro-1,4-phenylenediamine), relatively more stable ammonium salts are formed even for the products of monoacylation, which means that this formation of the bis-arylides is more difficult. Under such conditions a competitive reaction occurs leading to intermolecular esters of 3-hydroxy-2-naphthoic acid and yields of the desired bis-arylides are relatively low.

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