Recl. Trav. Chim. Pays-Bas 112, 552-556 (1993) 0165-0513/93/10552-05$6.00

Preparation of dyes derived from Eriochrome Red B and Acid Alizarin Violet N soluble in organic solvents

Alan R. Katritzky [#], Bogumila Rachwal [#], Stanislaw Rachwal [#], Terrance P. Smith [§] and David W. Macomber [§]

[#] *Department of Chemistry, University of Florida Gainesville, FL 32611-2046, USA*
[§] *Graphic Research Laboratory, 3M, St. Paul, MN 55144-1000, U.S.A.*
(Revised manuscript received February 9, 1993)

Abstract. Both hydroxy groups of Eriochrome Red B are protected by acetylation and the sulfonic acid group is converted to the sulfonyl chloride with phosphorus pentachloride. Reaction with dibutylamine or *N*-butylbenzeneethanamine followed by the deprotection gives red azo dyes **7a** or **7b**, readily soluble in chloroform and toluene. A similar procedure applied to Acid Alizarin Violet N gives only a multicomponent mixture. Friedel-Crafts reaction between dibutylsulfamoyl chloride and 2-nitrophenol gives *N,N*-dibutyl-4-hydroxy-3-nitrobenzenesulfonamide (**11**). Reduction of the nitro group gives amine **14** which is diazotized and coupled with 2-naphthol to give the required dye **13** giving deep-red solutions in methanol, chloroform and acetone.

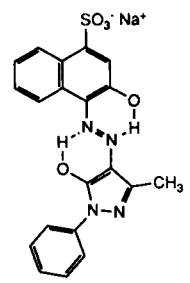
Introduction

Sodium 3-hydroxy-4-(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-ylazo)-1-naphthalenesulfonate **1** (Eriochrome Red B, Superchrome Red), sodium 4-hydroxy-3-(2-hydroxy-1-naphthylazo)benzenesulfonate (**2**) (Acid Alizarin Violet N), and the well known sulfonamide **3** of **2** form very stable chelates **4** with chromium, cobalt and several other transition metal cations[1].

Due to its intense color, **1** has found applications in the analysis of several metals, *e.g.*, berylium[2], cadmium[3], copper[3], gallium[4], nickel[5], titanium[6,7], vanadium[7,8] and zinc[9,10]. Chromium co-complexes of Eriochrome Red B and a second ligand, usually another azo dye, are valuable in dyeing wool, polyamide fibers and leather[11-20]. Sulfonamide **3** is also a frequently used dye of this type. Its chromium[21-24] and cobalt[25-27] complexes are used in dyeing leather, wool and synthetic polyamide fibers and have found recent application in the production of electrostatographic toners[28-33].

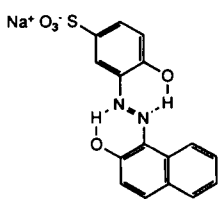
Most of the applications for metallized azos have involved aqueous-based systems. In fact very little work has been done on organic compatible derivatives. A survey of all the solvent dyes identified as either metal-azo or acid-basic dye complexes in the third edition, and subsequent supplements, of the Colour Index[34] reveals that very few metal-azo dyes possess significant solubility in hydrocarbon media. Of the 152 dyes identified as metal-azo dyes or acid-basic dye complexes only sixty-six had any solubility data for hydrocarbon solvents (turpentine, white spirits and mineral oil); of these, sixty dyes are listed as insoluble to very slightly soluble, five are listed as slightly soluble to soluble and only one entry is listed as very soluble. Metal-azo dyes are also known to form insoluble lakes[35]. The superior light, heat, and chemical stability of metal-azo dyes make them potentially attractive materials for many applications, particularly, as colorants in high technology applications such as electrography, thermal-dye-diffusion transfer, and other advanced imaging systems. However, many of these applications require significant changes in the physical properties (*i.e.* melting point, organic solubility, compatibility with polymers). The preparation of metal-azo dyes with greater organic compatibility requires the preparation of more organic soluble azo ligands.

The methodology for preparing of organic soluble dyes based on two common azo chromophores, Eriochrome



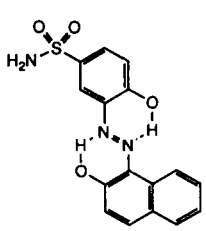
Eriochrome Red B

1

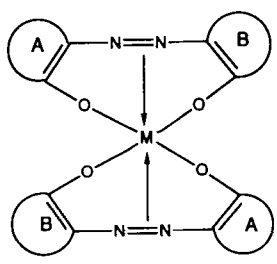


Acid Alizarin Violet N

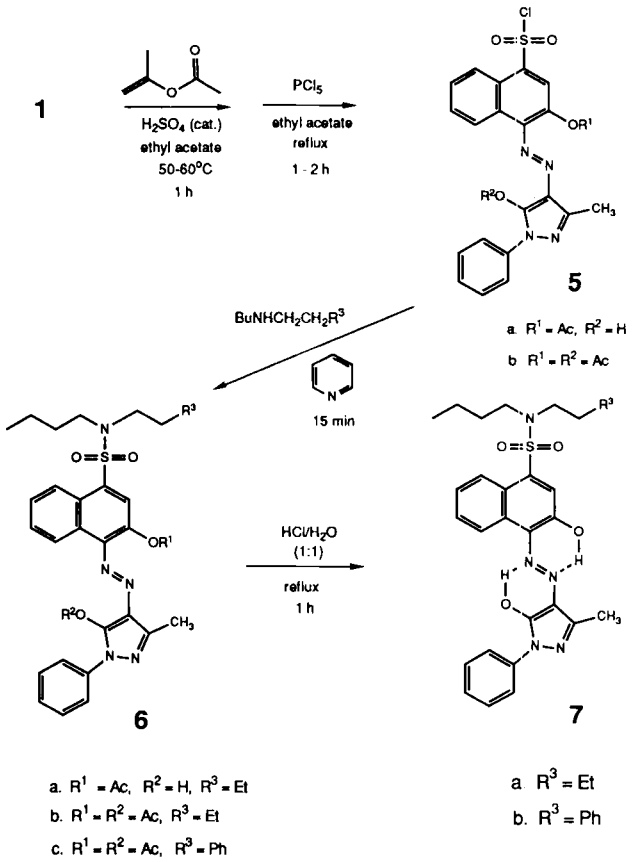
2



3



4



Scheme 1.

Red and Acid Alizarin Violet, have been investigated. The only conversion of Eriochrome Red B into a more soluble derivative that we have located is to the *N,N*-dimethylsulfonamide via the sulfonyl chloride[36]. However, this sulfonamide has a relatively high melting point (232°C) and could be recrystallized only from methyl cellosolve. The goal of the present work was the preparation of soluble derivatives of Eriochrome Red B and Acid Alizarin Violet N by transformation of their sulfonic acid functions into sulfonamido with the nitrogen atoms bearing large alkyl or arylalkyl substituents.

Results and discussion

Derivatives of Eriochrome Red B

Following the literature method[36] for the synthesis of the *N,N*-dimethylsulfonamide from Eriochrome Red B, the naphthyl hydroxy group was acetylated using isopropylidene acetate and the sulfonic acid function was then transformed into the sulfonyl chloride by reaction with phosphorus pentachloride (Scheme 1). The crude sulfonyl chloride **5a** was purified by Soxhlet extraction with ethyl acetate and then reacted with dibutylamine to give the corresponding sulfonamide (**6a**) from which, after deprotection, the desired sulfonamide **7a** was obtained. Unfortunately, the overall yield from Eriochrome Red B was lower than 10% and the material obtained was of low purity.

The whole multi-step process was therefore optimized by means of the following modifications. In the first step, the mixture of Eriochrome Red B, ethyl acetate, isopropenyl acetate and sulfuric acid was heated at 60°C for $1\frac{1}{2}$ h (instead of stirring at 20°C). The reaction with phosphorus pentachloride was then carried out under conditions similar to those described in the literature[36] (reflux in ethyl acetate), but extraction with ethyl acetate in a Soxhlet extractor was now unnecessary as the product was pure enough to use in the next stage. The NMR spectra of the product **5b** showed both hydroxyl groups acetylated, whereas under the milder literature conditions[36] only the naphthol group was acetylated (**5a**).

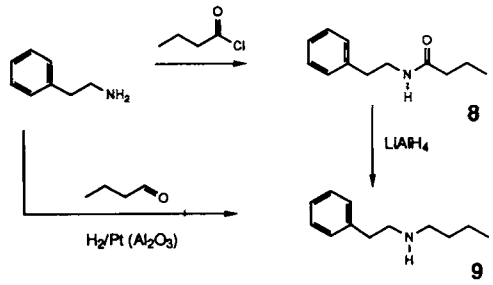
When sulfonyl chloride **5b** was added directly to an excess of dibutylamine, the reaction was strongly exothermic and the heavy precipitate inhibited stirring and caused local overheating. After work-up with 20% HCl, only a low purity product **6** was obtained. However, added pyridine served both as a good solvent for the starting material and as a base to neutralize evolved hydrogen chloride. After the reaction was accomplished, the pyridine and excess dibutylamine were easily washed out with 20% HCl, giving essentially pure **6b**. The final product **7a** was obtained by refluxing in 20% HCl to deprotect the hydroxy groups. The overall yield was raised to 40% and purity of the crude **7a** was greater than 95% (by NMR).

The *N*-butylbenzeneethanamine derivative **7b** was obtained from sulfonyl chloride **5b** in essentially the same manner as **7a** but work-up was more difficult and gave a final product of lower purity. One of the reasons was the difficulty of washing out the excess amine with hydrochloric acid (a very sticky glassy material was obtained). Another reason may be the lower stability of the sulfonamide function with its nitrogen atom substituted by a phenethyl group due to possible cleavage of the phenethyl C–N bond with elimination of styrene[37]. Both derivatives of Eriochrome Red B (**7a** and **7b**) were found to be readily soluble in toluene, chloroform and acetone giving orange-red colors in diluted solutions.

Because *N*-butylbenzeneethanamine (**9**) needed for the synthesis of **7b** is not available commercially, it was prepared by the acylation of benzeneethanamine with butanoyl chloride and reduction of the obtained amide **8** with lithium aluminum hydride (Scheme 2) in an overall yield of 37%. In an alternative synthesis, platinum-catalyzed hydrogenation of an equimolar mixture of benzeneethanamine and butyraldehyde at a pressure of 1300 psi gave **9** almost quantitatively. A similar reaction catalyzed by activated nickel was reported to give **9** in 36% yield[38,39].

Derivatives of Acid Alizarin Violet N

The first attempt to synthesize *N,N*-dibutyl-4-hydroxy-3-(2-hydroxy-1-naphthylazo)benzenesulfonamide (**13**), following a similar procedure to that used for the synthesis of **6** (successive treatment of Acid Alizarin Violet N with isopropenyl acetate, phosphorus pentachloride, dibutylamine and final hydrolysis of the acetoxy groups with hydrochloric acid) gave only an insoluble black tar. Several other attempts to prepare the sulfonyl chloride derivative of Acid Alizarin Violet N using different reaction conditions (solvents, temperature, reaction time, separation of the intermediate, $SOCl_2$ instead of PCl_5) also failed. Investigation of the NMR spectra (^1H and ^{13}C) of the reaction mixtures led to the conclusion that on treatment with PCl_5 or $SOCl_2$ the N=N bond is cleaved.



Scheme 2.

Because of these difficulties we decided on total synthesis of **13**. Azo sulfonamide **3** is produced by diazotization of 3-amino-4-hydroxybenzenesulfonamide followed by coupling with 2-naphthol[40]. One of the methods for the preparation of 3-amino-4-hydroxybenzenesulfonamide (and its *N*-alkylated derivatives) is a multi-step process involving chlorosulfonation of 2-chloronitrobenzene, amidation of the obtained sulfonyl chloride with ammonia (or an amine), aromatic nucleophilic substitution of the chlorine atom with a hydroxy group and finally reduction of the nitro group[41]. According to another method for compounds of this type, *N*,*N*-dimethyl-4-hydroxybenzenesulfonamide was nitrated and the nitro group reduced (H_2/Pd) to give *N*,*N*-dimethyl-3-amino-4-hydroxybenzenesulfonamide[42].

Modification of the literature method for the synthesis of dialkylsulfamoyl chlorides[43,44] allowed for the preparation of pure dibutylsulfamoyl chloride (**10**) in relatively good yield and with no need for distillation of the crude product. Several attempts to react **10** with phenol catalyzed by aluminum chloride gave only complex mixtures, but quite good results were obtained with the less reactive 2-nitrophenol (Scheme 3). The strongly predominant isomer (yield 59%) appeared to be that with the sulfonamido group *para* to the hydroxy group (**11**). Traces of isomer **12** (less than 10%) were detected by NMR in the crude product. Because separation of **11** from its *ortho* isomer **12** was difficult, the reaction mixture was used for the next step.

Attempted catalytic reduction of **11** with formic acid over palladium[45] gave **14** of low purity. Catalytic reduction of the mixture of nitrophenols over platinum on alumina proved to be a good method for the preparation of aminophenol **14**. Due to the *ortho* orientation of the hydroxy and amino groups, **14** appeared to be very sensitive to oxygen, especially in the light, being oxidized to dark material. This made it necessary to perform all operations under nitrogen atmospheres and to minimize any exposure of **14** to the air. Attempted distillation of **14** under a pressure of 0.05 mm Hg gave only polymeric material making its purification by column chromatography necessary. The first fraction from the column was *N*,*N*-dibutyl-3-amino-2-hydroxybenzenesulfonamide (**15**) obtained in 6% yield. The second fraction was pure **14** in 86% yield.

In the first approach to the coupling of diazotized **14** with 2-naphthol, 2-naphthol in ethanol was added to an acidic solution of the diazonium salt **17** to give a complex mixture from which dye **13** was isolated by column chromatography in low yield. Progress in this step was achieved by diazotization of a mixture of amine **14** with 2-naphthol. Column chromatography of the crude product obtained from such a reaction gave dye **13** in 28% yield. The second fraction appeared to be 6-diazo-4-(dibutylsulfonamido)-2,4-cyclohexadien-1-one (**18**, or its 1,2,3-benzoxadiazole isomer[46]). Treatment of **18** with 2-naphthol under neutral conditions gave analytically pure **13**. This proved that an acidic solution is not suitable for coupling diazotized amine **14** with 2-naphthol. Indeed, addition of a solution of diazonium salt **17** to a basic solution of 2-naphthol afforded dye **13** in high yield and high purity. Dye **13** was found to be soluble in methanol, chloroform and acetone giving intense deep red colors on dilution.

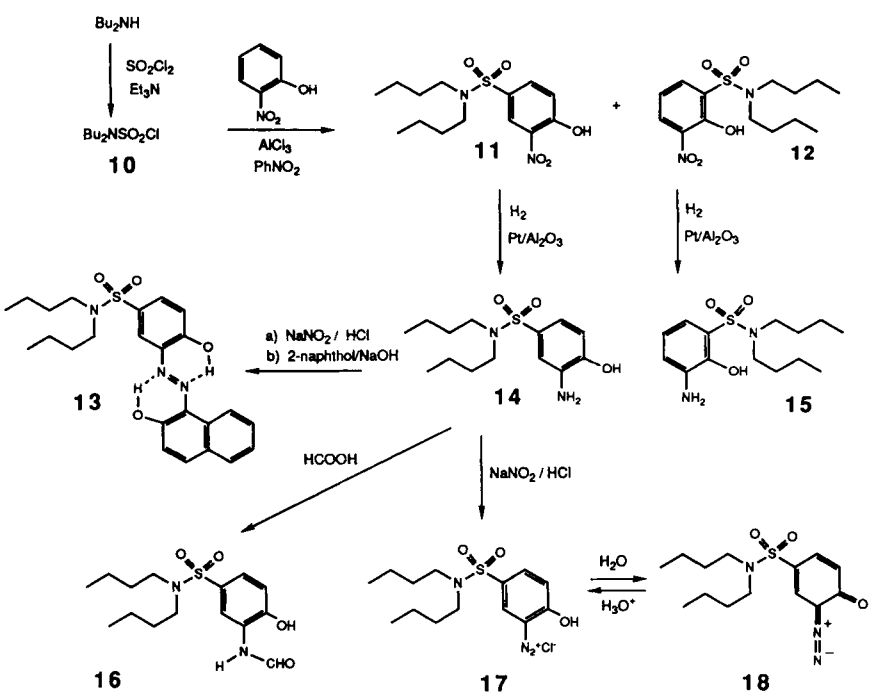
Summary

General methodology for the preparation of lower melting derivatives of Eriochrome Red B and Acid Alizarin Violet N have been developed. The new derivatives are substantially more soluble in organic solvents than previously prepared derivatives.

Experimental

Melting points were determined using a Thomas–Hoover capillary melting point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian VXR-300 (300 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. Chemical shifts (δ) are given in ppm. Elemental analyses were determined in the Department of Chemistry under the supervision of Dr. R.W. King.

Dry ethyl acetate was obtained by storage of the commercial solvent over molecular sieves 4 Å for a period of at least 3 days.



Scheme 3.

3-Acetoxy-4-(5-acetoxy-3-methyl-1-phenyl-1H-pyrazol-4-ylazo)-1-naphthalenesulfonyl chloride (**5b**)

A mixture of Eriochrome Red B (10.0 g, 22 mmol), ethyl acetate (100 ml), isopropenyl acetate (10.0 ml, 90 mmol) and concentrated H_2SO_4 (1.2 ml) was stirred at 60°C for 1½ h. A heavy precipitate formed making the stirring difficult. Then PCl_5 (10.00 g, 48 mmol) was added in a few portions. The mixture became hot and the evolution of HCl was observed as the precipitate dissolved. After the addition was complete, stirring under reflux was continued for 2 h. Again a heavy precipitate was formed and the stirring had to be very vigorous to avoid overheating and adherance of the precipitate to the flask walls. After cooling, the obtained precipitate was filtered off, quickly washed with ice-cold ethyl acetate to reduce its exposure to the atmosphere and used in the next step without purification.

N,N-Dibutyl-3-hydroxy-4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-ylazo)-1-naphthalenesulfonamide (**7a**)

A mixture of crude **5** from the above reaction (total product), dibutylamine (2.34 g, 30 mmol) and pyridine (20 ml) was stirred at 25°C for 15 min. 20% HCl (30 ml) was then added in portions to the reaction mixture. Slowly an oily fraction separated from the solution. The sticky oil obtained (product **6b**) was separated from the reaction mixture by decantation of the aqueous fraction, the oil was triturated with water, again separated by decantation and after addition of 20% HCl (60 ml), the mixture was stirred and refluxed for 1 h. The oil slowly became a crystalline material. After cooling to room temperature, the crystals were filtered off, washed with water and dried in a vacuum oven. The crude **7a** was dissolved in $CHCl_3$ (150 ml) and the solution washed with water (3×100 ml) and dried over $MgSO_4$. Evaporation of the solvent gave **7a** (4.71 g, 40%) of purity 95% (by NMR). A small sample of the product was recrystallized from methanol/THF (1:1) to give red needles; m.p. 173–174°C. ^{1}H NMR, δ: 0.83, t, 6H, *J* 7.2 Hz; 1.21, sextet, 4H, *J* 7.3 Hz; 1.48, m, 4H; 2.32, s, 3H, Me; 3.28, t, 4H, *J* 7.5 Hz; 7.19, t, 1H, *J* 7.4 Hz; 7.46, m, 3H; 7.62, t, 1H; 7.94, m, 4H; 8.60, d, 1H, *J* 8.5 Hz; 10.3, s, 1H, OH. ^{13}C NMR ($CDCl_3$), δ: 11.7; 13.6, 2C; 19.8, 2C; 30.2, 2C; 46.5, 2C; 118.4, 2C; 123.7; 123.2; 123.9; 124.5; 125.6; 125.7; 126.1; 127.9; 128.3; 128.8; 129.0, 2C; 134.0; 137.5; 144.1; 146.4; 158.1. Anal. calcd. for $C_{28}H_{33}N_5O_4S$: C 62.78, H 6.21, N 13.07; found: C 63.03; H 6.30; N 13.15%.

N-Butyl-N-phenethyl-3-hydroxyl-4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-ylazo)-1-naphthalenesulfonamide (**7b**)

N-Butylbenzeneethanamine (10.8 g, 60 mmol) was added dropwise to a stirred solution of crude sulfonyl chloride **5b** (obtained from 40 mmol of Eriochrome Red B) in pyridine (20 ml). During the addition, the temperature rose to 100°C. After the addition was complete, the mixture was stirred for an additional 15 min and 20% HCl (100 ml) was added portionwise. Soon, an oily layer formed on the flask bottom. The oil was separated by decantation, triturated with water and again separated. Finally 15% HCl (100 ml) was added to the oil and the obtained mixture was stirred and refluxed for 1 h. After cooling to room temperature, the glassy precipitate formed was separated by filtration. The solid was dissolved in $CHCl_3$ (100 ml) and the solution washed with water (2×100 ml). The organic layer was separated, dried ($MgSO_4$) and the solvent evaporated under reduced pressure to give a glassy substance. The glass was triturated with hexane, the hexane was decanted off and the residue, dissolved in a small amount of $CHCl_3$, was subjected to dry column chromatography (silica gel, $CHCl_3$) to give **7b** (9.10 g, 39%), purity 90% (by NMR). An analytical sample was obtained by careful column rechromatography (silica gel/toluene) and final recrystallization from toluene to give red needles; m.p. 192°C. ^{1}H NMR, δ: 0.82, t, 3H, *J* 7.5 Hz; 1.26, m, 2H; 1.51, m, 2H; 2.38, s, 3H, Me; 2.80, t, 2H, *J* 7.8 Hz; 3.33, t, 2H, *J* 7.5 Hz; 3.52, t, 2H, *J* 7.8 Hz; 7.07, d, 2H, *J* 7.8 Hz; 7.20, m, 5H; 7.45, m, 3H; 7.65, m, 1H; 7.93, m, 3H; 8.58, d, 1H, *J* 8.5 Hz; 10.2, s, 1H, OH. ^{13}C NMR, δ: 11.7; 13.5; 19.7; 30.1, 35.1; 47.1; 48.5; 118.5, 2C; 120.9; 123.2, 123.8, 124.5, 125.6, 125.8, 126.0, 126.4, 128.0, 128.3, 128.4, 2C; 128.5, 2C; 128.7, 128.9, 2C; 133.7, 137.4, 138.1, 144.0, 146.4, 158.0. Anal. calcd. for $C_{32}H_{33}N_5O_4S$: C 65.85, H 5.70, N 12.00; found C 66.12, H 5.61, N 12.04%.

N-*Butylbenzeneethanamine*

Method A. To a solution of butanoyl chloride (52 ml, 0.5 mol) in benzene (200 ml) was added dropwise a solution of benzeneethanamine (63.1 ml, 0.50 mol) in benzene (200 ml). The reaction was exothermic. After the addition was complete, the mixture was stirred at reflux for 1 h. The product was poured into ice–water. The organic layer was separated, washed with 10% Na_2CO_3 followed by water, dried over $MgSO_4$ and the solvent evaporated to give amide **8**. The amide was dissolved in THF (100 ml) and added dropwise to a suspension of $LiAlH_4$ (18.98 g, 0.5 mol) in THF (200 ml) at a rate to maintain a gentle reflux and refluxing was continued for 1 h, after the addition was complete. The reaction mixture was poured onto ice (300 g), extracted with $CHCl_3$ (200 ml) and the $CHCl_3$ solution dried over Na_2CO_3. Evaporation of the solvent gave the crude product which was purified by fractional distillation to give pure *N*-butylbenzeneethanamine **9** (32.5 g, 36.7%) as a fraction distilling at 73–74°C/0.5 mm Hg (Lit.[39] b.p. 85°C/8 mm Hg).

Method B. Butanal (17.7 ml, 200 mmol) was added portionwise to a solution of benzeneethanamine (24.5 ml, 200 mmol) in methanol (300 ml) cooled to 0°C. The reaction mixture was placed in an autoclave, 1 g of a platinum catalyst (1% Pt on Al_2O_3) added, the autoclave charged with H_2 to a pressure of 1300 psi and the reduction was allowed to proceed overnight at room temperature. The catalyst was filtered off and the solvent evaporated under reduced pressure to give 34.30 g (97%) of pure *N*-butylbenzeneethanamine.

Dibutylsulfamoyl chloride (**10**)

To a stirred solution of $SOCl_2$ (60.6 ml, 2 mol) in $CHCl_3$ (1000 ml) in a round bottom flask equipped with a dropping funnel, a thermometer and a magnetic stirrer and immersed in an ice–water bath, was added dropwise a mixture of triethylamine (139.4 ml, 1 mol) and dibutylamine (168.5 ml, 1 mol) at a rate to keep the temperature within a range of 15–20°C. After the addition was complete, the reaction mixture was stirred without cooling for an additional 1 h and poured into iced water (2000 ml). The $CHCl_3$ phase was separated and washed with 10% HCl (1000 ml) followed by ice cold water. The solution was dried and the solvent evaporated to give pure **10** (147.7 g, 64.8%) as a colorless oil. ^{1}H NMR, δ: 0.96, t, 6H, *J* 7.3 Hz, Me; 1.39, sextet, 4H, *J* 7.5 Hz, CH_2-Me; 1.68, quintet, 4H, *J* 7.5 Hz, CH_2; 3.30, t, 4H, *J* 7.5 Hz, CH_2N. ^{13}C NMR, δ: 13.5, 2C, Me; 19.5, 2C, CH_2; 29.4, 2C, CH_2; 50.8, 2C, CH_2N. Anal. calcd. for $C_8H_{18}ClNO_2S$: C 42.19, H 7.97, N 6.15; found: C 42.38, H 7.88, N 6.25%.

N,N-*Dibutyl-4-hydroxy-3-nitrobenzenesulfonamide* (**11**)

Anhydrous $AlCl_3$ (176.6 g, 1.32 mol) was added portionwise to a stirred mixture of **10** (136.2 g, 600 mmol) and 2-nitrophenol (83.4 g, 600 mmol) in nitrobenzene (125 ml). During the addition, the mixture was warmed on an oil bath and after the addition was complete, it was heated at 85–90°C for 4 h. Progress of the reaction was monitored by TLC. The crude oily product was poured into ice–water (1000 ml) and extracted with ether. The organic layer was separated, washed with water and dried over $MgSO_4$. Evaporation of the ether under reduced pressure and distillation of the nitrobenzene at 2 mm Hg afforded crude **11** as a yellow-green oil (129.6 g, 59%). ^{1}H NMR, δ: 0.91, t, 6H, *J* 7.6 Hz, Me; 1.30, sextet, 4H, *J* 7.2 Hz, CH_2; 1.52, quintet, 4H, *J* 7.0 Hz CH_2; 3.14, t, 4H, *J* 7.6 Hz, CH_2; 7.3, d, 1H, *J* 9.0 Hz; 7.97, dd, 1H, *J* 8.8 and 2.2 Hz; 8.57, d, 1H, *J* 2.4 Hz; 10.8, s, 1H, OH. ^{13}C NMR, δ: 13.7, 2C, Me; 19.9, 2C, CH_2Me, 30.7, 2C, CH_2, 47.9, 2C, CH_2N, 121.2, 124.8, 132.9, 2C, 135.2, 157.3. Exact mass calcd. for $C_{14}H_{22}N_2O_5S$: 330.1250; found 330.1257.

N,N-*Dibutyl-3-amino-4-hydroxysulfonamide* (**14**)

To a solution of crude **11** (12.2 g, 37 mmol) in ethanol (200 ml) was added 2 g of a platinum catalyst (1% Pt on alumina). The reaction mixture was placed in a reactor which was charged with hydrogen at 750 psi. The reduction was carried out at 25° over 20 h. After filtration and evaporation of the solvent, a high purity mixture of **14** and **15** (11.30 g, 100%) was obtained. Column chromatography of the crude product (silica gel/$CHCl_3$) afforded, as the first fraction, pure *N,N*-dibutyl-3-amino-2-hydroxybenzenesulfonamide (**15**) (0.67 g, 6%). ^{1}H NMR, δ: 0.90, t, 6H, *J* 7.3 Hz, Me; 1.30, sextet, 4H, *J* 7.6 Hz, CH_2Me; 1.51, quintet, 4H, *J* 7.7 Hz, CH_2; 3.14, t, 4H, *J* 7.6 Hz, CH_2N; 3.98, bs, 2H, NH_2; 6.80, t, 1H, *J* 7.8 Hz; 6.83, d, 1H, *J* 7.7 Hz; 6.90, d, 1H, *J* 7.8 Hz; 9.10, s, 1H, OH. ^{13}C NMR, δ: 13.6, 2C, Me; 19.8, 2C, CH_2, 30.5, 2C, CH_2, 47.9, 2C, CH_2N, 116.4, 118.7, 120.2, 122.2, 136.8, 142.9. Exact mass calcd. for $C_{14}H_{24}N_2O_3S$: 300.1507; found: 300.1499.

As the second fraction, **14** (9.72 g, 86%) was obtained. ^{1}H NMR, δ: 0.87, t, 6H, *J* 7.5 Hz, Me; 1.27, sextet, 4H, *J* 7.4 Hz, CH_2Me; 1.47, quintet, 4H, *J* 8.1 Hz, CH_2; 3.05, t, 4H, *J* 7.5 Hz, CH_2-N; 5.35, bs, 3H, NH_2 + OH; 6.79, d, 1H, *J* 8.3 Hz; 7.02, dd, 1H, *J* 8.3 Hz and 2.0

Hz; 7.10, d, 1H, *J* 2.2 Hz. ^{13}C NMR, δ: 13.7, 2C, Me, 19.9, 2C, CH_2Me, 30.8, 2C, CH_2, 48.2, 2C, CH_2N, 114.1, 114.7, 118.8, 130.3, 135.3, 148.4. The product was characterized as its solid derivative **16** obtained by heating **14** with 100% formic acid. Recrystallization of the crude product from ethanol gave pure formamide **16** as yellowish prisms, mp. 156°C. ^{1}H NMR: δ 0.89, t, 6H, *J* 7.3 Hz, Me; 1.29, sextet, 4H, *J* 7.3 Hz, CH_2Me; 1.49, m, 4H, CH_2; 3.09, t, 4H, *J* 7.5 Hz, CH_2-N; 6.99, d, 1H, *J* 8.4 Hz, H-5; 7.38, d, d, 1H, *J* 8.4 Hz and 2.1 Hz, H-6; 8.41, d, 1H, *J* 1.7 Hz, CH=O; 8.54, d, 1H, *J* 2.1 Hz, H-2; 9.10, bs, 1H, NH; 10.51, bs, 1H, OH. ^{13}C NMR: δ 13.7, 2C, 19.9, 2C, 30.7, 2C, 48.0, 2C, 115.6, 119.9, 124.2, 126.1, 130.3, 150.3; 159.9, NCH=O. Anal. calcd. for $C_{15}H_{24}N_2SO_4$: C 54.86, H 7.36, N 8.53; found: C 54.78, H 7.41, N 8.36%.

Coupling of **14** *with 2-naphthol under acidic conditions*

Crude **14** (6.0 g, 20 mmol) and 2-naphthol (2.88 g, 20 mmol) were dissolved in ethanol (80 ml) and added dropwise to a stirred solution of $NaNO_2$ (1.54 g, 24 mmol) and concentrated HCl (60 ml) in ice and water (200 ml). After about 30 min, a heavy, oily fraction started to separate. After further 30 min, the water layer was decanted off and the oily residue was dissolved in $CHCl_3$ (200 ml) and washed twice with cold water. The $CHCl_3$ solution was dried ($CaCl_2$) and the solvent was evaporated to give the crude dye (7.35 g) as a sticky dark brown-violet oil of 40% purity (by NMR). Column chromatography of the crude dye using silica gel (dry column) and ethyl-acetate/toluene (1:4) as the eluent gave **13** (2.57 g, 28%) as the first fraction (orange-brown crystalline product); m.p. 162–163°C. ^{1}H NMR, δ: 0.92, t, 6H, *J* 7.3 Hz, Me; 1.34, sextet, 4H, *J* 7.6 Hz, CH_2Me; 1.56, quintet, 4H, *J* 7.2 Hz, CH_2; 3.17, t, 4H, *J* 7.6, CH_2N; 7.17, d, 2H, *J* 8.8 Hz; 7.48, t, 1H, *J* 7.6 Hz; 7.65, t, 1H, *J* 8.1 Hz; 7.72, dd, 1H, *J* 8.6 and 2.1 Hz; 7.79, d, 1H, *J* 8.0 Hz; 7.88, d, 1H, *J* 9.3 Hz; 8.17, m, 2H. ^{13}C NMR, δ: 13.8, 2C, Me; 20.0, 2C, CH_2Me, 30.8, 2C, CH_2, 48.0, 2C, CH_2-N, 119.1, 120.1, 120.8, 125.4, 127.7, 128.1, 128.5, 129.1, 129.3, 129.7, 131.1, 132.2, 133.3, 137.6; 155.1; 158.0. Anal. calcd. for $C_{24}H_{29}N_3O_4S$: C 63.27, H 6.42, N 8.22; found: C 63.42, H 6.73, N 8.07%.

The second fraction (0.56 g, 9%) was identified as **18**, yellow prisms; m.p. 67–68°C. ^{1}H NMR, δ: 0.91, t, *J* 7.2 Hz, 6 H, Me; 1.29, sextet, *J* 7.6 Hz, 4H, CH_2-Me; 1.52, m, 4H, CH_2; 3.13, t, *J* 7.6 Hz, 4H, CH_2N; 6.72, d, *J* 9.8 Hz, 1H; 7.50, dd, *J* 9.8 and 2.5 Hz, 1H; 7.94, d, *J* 2.5 Hz, 1H. ^{13}C NMR, δ: 13.7, 2C, Me; 20.0, 2C, CH_2, 30.8, 2C, CH_2, 47.8, 2C, CH_2N, 87.0, 125.7, 125.8, 128.0, 135.3, 176.6, C=O. Anal. calcd. for $C_{14}H_{21}N_3O_3S$: C 54.00, H 6.79, N 13.49; found: C 53.6 H 6.81 N 13.34%.

Coupling of **14** *with 2-naphthol under basic conditions*

To the cooled solution of **14** (3.30 g, 11 mmol) in 95% ethanol (10 ml) stirred in an ice–salt bath, 37% HCl (3 ml, 30 mmol) was added in one portion. After the temperature had reached −5°C, ice (10 g) and a solution of $NaNO_2$ (0.83 g, 12 mmol) in water (2 ml) was added. The temperature raised to +5°C, but because the reaction mixture was still cooled, soon fell again to −5°C. In the meantime, 2-naphthol (1.59 g, 11 mmol) was dissolved in a mixture of ethanol (10 ml) and 10% NaOH (9 ml, 20 mmol) and 20% solution of CH_3COONa (11 ml) was added. To this solution, cooled until its temperature reached −10°C, the diazonium salt was added portionwise with stirring. Formation of a strong violet color was observed. The reaction mixture was stirred at room temperature for 1 h and poured onto ice. The obtained precipitate was filtered off, washed with water and dried in a vacuum oven to give black crystalline product (4.90 g) which appeared to be the sodium salt of **13**. To get back the neutral form, the crystals were dissolved in $CHCl_3$ and washed twice with 10% HCl followed by water. Drying over $MgSO_4$ and evaporation of the solvent gave analytically pure **13** (4.15 g, 83%).

References

[1] *G. Schetty*, Helv. Chim. Acta **53**, 1437 (1970).

[2] *C. Perez Conde, J.A. Perez-Bustamante* and *F. Burriel Marti*, Anal. Chim. Acta **73**, 191 (1974).

[3] *E. Norkus*, Liet. TSR Mokslu Akad. Darb., Ser. B, 53 (1981); Chem. Abstr. **95**, 143509v (1981).

[4] *M.C. Perez Conde, R. Gallego Andreu* and *J.A. Perez-Bustamante Monasterio*, Afinidad **40**, 69 (1983); Chem. Abstr. **99**, 32367k (1983).

[5] *M.C. Perez Conde, A.M. Gutierrez Carreras, M.C. Rodriguez de Miguel* and *L.M. Polo Diez*, Quim. Anal. (Barcelona) **5**, 67 (1986); Chem. Abstr. **106**, 148528f (1987).

[6] *I.A. Tserkovnitskaya* and *V.V. Pereroshchikova*, Instrum. Khim. Metody Anal. 95 (1973); Chem. Abstr. **82**, 38236n (1975).

[7] *I.A. Tserkovnitskaya* and *V.V. Pereroshchikova*, Zh. Anal. Khim. **27**, 1111 (1972); Chem. Abstr. **77**, 121834y (1972).

[8] *M.N. Gordeeva, A.M. Ryndina* and *T.V. Stanevich*, Vestn. Leningr. Univ., Fiz., Khim. 117 (1976); Chem. Abstr. **86**, 50206t (1977).

[9] *Yu.K. Tselinskii, E.D. Kuchkina* and *A.B. Nikolaevskaya*, Zh. Prikl. Khim. (Leningrad) **47**, 1035 (1974); Chem. Abstr. **81**, 57807v (1974).

[10] *N.L. Shestidesyatnaya, L.I. Kotelyanskaya* and *V.V. Semenyuk*, Zh. Anal. Khim. **33**, 303 (1978); Chem. Abstr. **89**, 52780m (1978).

[11] *F. Beffa, A. Buehler, P. Donath, H.U. Shuetz* and *G. Back*, Ger. Pat. 2,363,635 (1974); Chem. Abstr. **81**, 107363v (1974).

[12] *C. Brouard* and *P. Ficht*, Ger. Pat. 2,409,435 (1974); Chem. Abstr. **82**, 45023u (1975).

[13] *H.U. Shuetz, G. Back* and *F. Beffa*, Ger. Pat. 2,500,550 (1975); Chem. Abstr. **83**, 195218w (1975).

[14] *A. Breda* and *C. Brouard*, Ger. Pat. 2,504,787 (1975); Chem. Abstr. **83**, 195221s (1975).

[15] *A. Breda, L.J. Georges* and *J. Roussel*, Eur. Pat. 44,767 (1982); Chem. Abstr. **96**, 219267h (1982).

[16] *W. Scholl*, Eur. Pat. 72,516 (1983); Chem. Abstr. **99**, 24010y (1983).

[17] BASF A.-G., Jpn. Pat. 59,159,855 (1984); Chem. Abstr. **102**, 47328c (1085).

[18] *H. Salathe, H. Flensberg* and *H. Schaetzer*, Eur. Pat. 135,198 (1985); Chem. Abstr. **103**, 143308n (1985).

[19] *W. Iff, D. Parisot* and *H. Shaller*, Eur. Pat. 157,733 (1985); Chem. Abstr. **104**, 150782m (1986).

[20] *W. Mennicke*, Ger. Pat. 3,433,980 (1986); Chem. Abstr. **106**, 51680m (1987).

[21] *S. Salagacki, J. Osinski, W. Cieslak* and *T. Kilanski*, Pol. Pat. 104,025 (1979); Chem. Abstr. **92**, 95627w (1980).

[22] *Z. Olszewski, M. Kazmierska, M. Nalewajko* and *Z. Zaremba*, Pol. Pat. 112,419 (1982); Chem. Abstr. **96**, 182681k (1982).

[23] Ciba-Geigy A.-G., Jpn. Pat. 60 40,157 (1985); Chem. Abstr. **103**, 55386f (1985).

[24] *S. Kawasaki, A. Hirano, H. Kawashita, H. Yamaguchi* and *Y. Takamatsu*, Jpn. Pat. 77 63,223 (1977); Chem. Abstr. **87**, 119238v (1977).

[25] *E. Bialkowski, J. Majcher, Z. Olszewski, W. Sekula, W. Cieslak, R. Salagacki* and *K. Gawlinski*, Pol. Pat. 124,569 (1985); Chem. Abstr. **104**, 70664j (1986).

[26] *J. Dore*, Belg. Pat. 841,482 (1976); Chem. Abstr. **87**, 40733u (1977).

[27] Ciba-Geigy A.-G., Jpn. Pat. 59,140,264 (1984); Chem. Abstr. **101**, 231888r (1984).

[28] Orient Chemical Industries, Ltd., Jpn. Pat, 57,167,033 (1982); Chem. Abstr. **100**, 59585f (1984).

[29] Hodogaya Chemical Co., Ltd., Jpn. Pat. 59 78,361 (1984); Chem. Abstr. **101**, 81652t (1984).

[30] Nippon Kayaku Co., Ltd., Jpn. Pat. 59 93,547 (1984); Chem. Abstr. **101**, 181170c (1984).

[31] *P. Bamfield, P. Gregory* and *K.L. Birkett*, Eur. Pat. 162,632 (1985); *Chem. Abstr.* **104**, 139294h (1986).

[32] Konishiroku Photo Industry Co., Ltd., Jpn. Pat. 59,188,660 (1984); Chem. Abstr. **102**, 195096r (1985).

[33] *S. Shindo, M. Torigoe* and *Y. Ishizaka*, Jpn. Pat. 63,216,061 (1988); Chem. Abstr. **111**, 87374g (1989).

[34] Colour Index, 3rd Edition, The Society of Dyers and Colourists, Bradford, Yorkshire, England, 1971.

[35] *H.D.K. Drew* and *R.E. Fairbairn*, J. Chem. Soc. 823–835 (1939).

[36] *M. Idelson, I.R. Karady, B.H. Mark, D.O. Rickter* and *V.H. Hooper*, Inorg. Chem. **6**, 450 (1967).

[37] *R. Brettle, N.A. Hilton* and *S.M. Shibib*, J. Chem. Res. (S), 379 (1984).

[38] *C.F. Winans* and *H. Adkins*, J. Am. Chem. Soc. **54**, 306 (1932).

[39] *E.J. Schwoegler* and *H. Adkins*, J. Am. Chem. Soc. **61**, 3499 (1939).

[40] *C. Przybylski, J. Gmaj* and *Z. Zaremba*, Pol. Pat. 136,769 (1987); Chem. Abstr. **110**, 77488n (1989).

[41] *G. Schetty* and *E. Steiner*, Helv. Chim. Acta **55**, 1509 (1972).

[42] *R.E. Ford, P. Knowles, E. Lunt, S.M. Marshall, A.J. Penrose, C.A. Ramsden, A.J.H. Summers, J.L. Walker* and *D.E. Wright*, J. Med. Chem. **29**, 538 (1986).

[43] *S.K. Gupta*, Synthesis 39 (1977).

[44] *J.C. Warner, M. Nakajima* and *J.P. Anselme*, Bull. Soc. Chim. Belg. **93**, 919 (1984).

[45] *N.A. Cortese* and *R.F. Heck*, J. Org. Chem. **42**, 3491 (1977).

[46] *R. Schulz* and *A. Schweig*, Angew. Chem. **96**, 494 (1984); Angew. Chem. Int. Ed. Engl. **23**, 509 (1984).