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A NOVEL METHOD FOR THE PREPARATION OF 3-AMINO-4-HYDROXYBENZENESULFONAMIDE PRECURSORS OF "ACID ALIZARIN VIOLET N" DERIVATIVES

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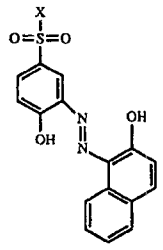
Abstract: Chlorosulfonation of 2-nitroanisole gave 4-methoxy-3-nitrobenzenesulfonyl chloride (**7**) which was converted with N-butyl(3-phenylpropyl)amine into benzenesulfonamide (**8**). Hydrolysis of the ether and reduction of the nitro group of **8** followed by diazotization and coupling with 2-naphthol gave N-Butyl-N-(3-phenylpropyl)-4-hydroxy-3-(2-hydroxy-1-naphthyl)azobenzenesulfonamide (**1d**).

Acid Alizarin Violet N (**1a**) is a commonly used cheap azo-dye with a number of applications. A derivative of this dye, sulfonamide **1b** is used in the form of its chromium[1-4] or cobalt[5-7] complexes in dyeing leather, wool and synthetic polyamide fibers. Chromium and cobalt complexes of **1b** found recent applications in the production of electrostatographic toners[8-13]. In this communication we report our findings during a search for a new route to 3-amino-



1a, X = O⁻ Na⁺

1b, X = NH_2

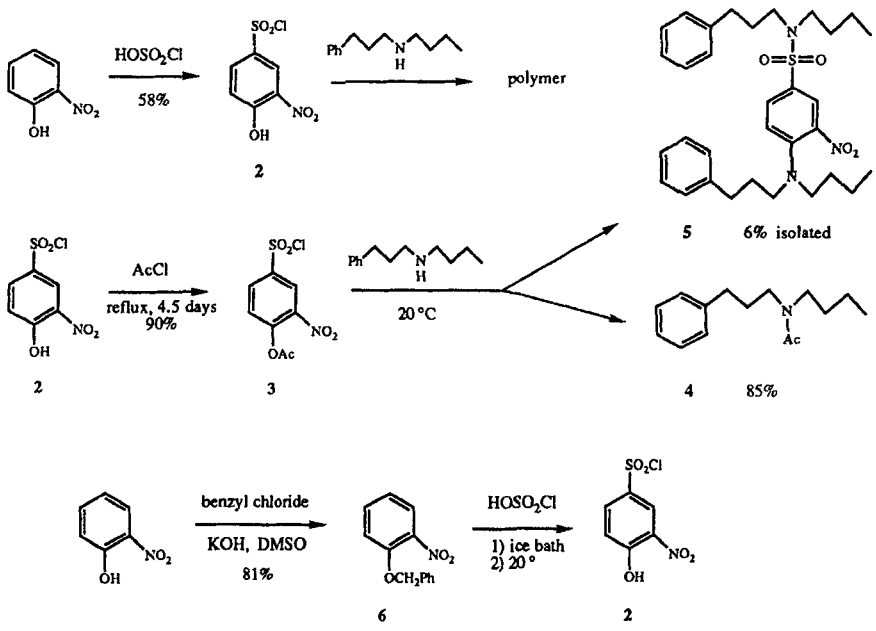
1c, X = NBu_2

1d, X = $PhCH_2CH_2CH_2NBu$

4-hydroxybenzenesulfonamides which resulted in preparation of dye **1d**. The classical method for the preparation of 3-amino-4-hydroxybenzenesulfonamide is a multistep process involving chlorosulfonation of 2-chloronitrobenzene, amination of the obtained sulfonyl chloride with ammonia, aromatic nucleophilic substitution of the chlorine atom with a hydroxy group and finally reduction of the nitro group[14].

To modify the properties of dye **1b**, a synthetic method for its N,N-dibutyl derivative **1c** has been elaborated in our laboratory[15]. The synthesis includes a Friedel-Crafts reaction of 2-nitrophenol with N,N-dibutylsulfamoyl chloride, reduction of the nitro group and diazotization and coupling of the amine with 2-naphthol. Several attempts to extend this method to sulfonamide **1d** and other dyes of this type with aralkyl substituents on the sulfonamide nitrogen atom failed because of preferential intramolecular Friedel-Crafts reactions of the sulfamoyl chlorides to the corresponding sultams[16].

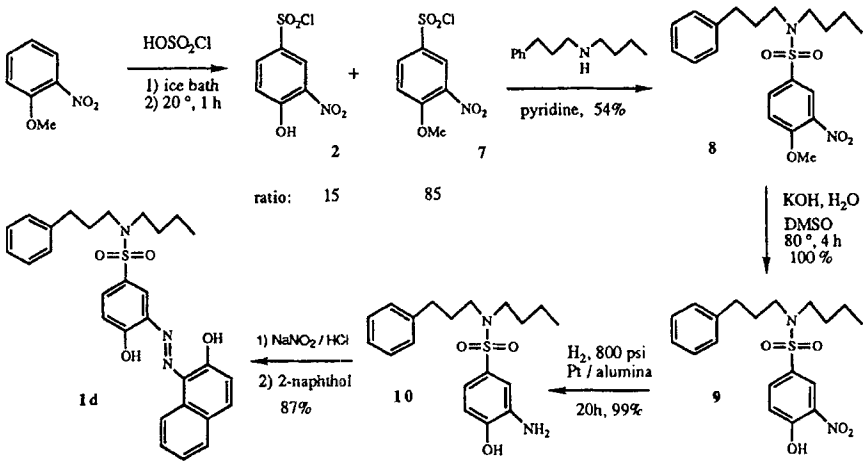
An obvious preparation route would involve 4-hydroxy-3-nitro-benzenesulfonyl chloride (**2**) which was readily synthesized from 2-nitrophenol (Scheme 1). However, reaction of **2** with N-(3-phenylpropyl)-N-butylamine with or without the presence of a base under various conditions gave only polymeric



Scheme 1

materials. We concluded that the hydroxy group of **2** needed protection. Sulfonyl chloride **2** was therefore converted into the acetyl derivative **3** in high yield. Unfortunately, the o-nitro and p-chlorosulfonyl groups were so strongly electron-withdrawing that the most electrophilic site of **3** became the carbonyl carbon instead of the sulfur atom, and reaction of **3** with the amine at room temperature gave the acetamide **4** as the main product (85%). A small amount (6%) of a diaminated by-product (**5**) was also isolated, arising from the substitution of the acetoxy group.

In another attempt, we benzylated the hydroxy group of 2-nitrophenol, obtaining compound **6** in 81% yield. However, when **6** was added very slowly to



Scheme 2

an excess of stirred chlorosulfonic acid in an ice-salt bath and the mixture was allowed to warm up overnight, only **2** was obtained, evidently benzyl is too easily cleaved.

These experiments indicated that methyl could be a suitable protecting group. Indeed, when 2-nitroanisole was treated with excess chlorosulfonic acid under mild conditions, a mixture of 4-methoxy-3-nitrobenzenesulfonyl chloride (**7**) and its demethylated product (**2**) was obtained (Scheme 2). The most favorable ratio achieved of these two products was 85:15. The mixture was treated directly with N-(3-phenylpropyl)-N-butylamine in the presence of pyridine to give sulfonamide **8**. In this reaction, compound **2** formed a polymer which could be removed easily. Analytically pure **8** was obtained by column chromatography. Compound **8** was successfully demethylated by treatment with KOH and water in dimethyl sulfoxide at 80 °C to give phenol **9**.

The nitro compound **9** was converted quantitatively to amine **10** by catalytic reduction with hydrogen under a pressure of 800 psi at room temperature. Amine **10** was diazotized and coupled with 2-naphthol under basic conditions to give the analytically pure azo compound, N-butyl-N-(3-phenylpropyl)-4-hydroxy-3-(2-hydroxy-1-naphthyl)azobenzenesulfonamide (**1d**) in high yield.[17]

EXPERIMENTAL

4-Hydroxy-3-nitrobenzenesulfonyl chloride (2). To stirred chlorosulfonic acid (6.0 mL, 90 mmol) cooled in an ice-water bath was added gradually 2-nitrophenol (4.17 g, 30 mmol) at a rate to keep the temperature below 10 °C. The mixture gradually turned brown, a precipitate formed and bubbling occurred. After the bubbling stopped, the mixture was heated in an oil bath at 60 °C for 20 minutes. The black mixture was poured onto ice (50 g), extracted with chloroform (50 mL, 3 X), washed with ice cold water (50 mL, 2 X), dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure at 20 °C to afford pure **2** as a brown solid (4.12 g, 17.3 mmol, 58% yield); mp 48.5-50.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (1H, d, J = 9.0 Hz), 8.22 (1H, dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz), 8.83 (1H, d, J = 2.4 Hz), 11.12 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 122.2, 125.8, 132.8 (q), 134.7, 135.9 (q), 159.3 (q); HR MS calcd. for $C_6H_4ClNO_5S$ (M^+): 236.9499. Found: 236.9500.

Anal. calcd. for $C_6H_4ClNO_5S$: C, 30.33; H, 1.70; N, 5.89.
Found: C, 30.13; H, 1.60; N, 5.78.

4-Acetoxy-3-nitrobenzenesulfonyl chloride (3). A mixture of 4-hydroxy-3-nitrobenzenesulfonyl chloride (**2**, 11.88 g, 50 mmol) and a large excess of acetyl chloride (20 mL) was refluxed in a round-bottom flask equipped with a Drierite drying tube. The reaction (monitored by NMR) took 4.5 days to complete. Excess acetyl chloride was removed by a rotary evaporator under reduced pressure and the residue was dried at 50 °C in a vacuum oven to afford **3** in a pure state as a dark brown solid (13.42 g, 45 mmol, 90% yield); 87.5-90 °C; ^{1}H NMR (300 mHz, $CDCl_3$): δ 2.44 (3H,s), 7.56 (1H, d, J = 8.7 Hz), 8.31 (1H, dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz), 8.75 (1H, d, J = 2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 125.3, 127.3, 132.6, 141.9 (q), 148.9 (q), 167.5 (q).

Anal. calcd. for $C_8H_6NClO_6S$: C, 34.36; H, 2.16; N, 5.01.

Found: C, 34.22; H, 2.03; N, 4.91.

N-Butyl-N-(3-phenylpropyl)acetamide (4) and N-butyl-N-(3-phenylpropyl)-4-[N-butyl-N-(3-phenylpropyl)amino]-3-nitrobenzenesulfonamide (5). To a stirred solution of 4-acetoxy-3-nitrobenzenesulfonyl chloride (**3**, 0.86 g, 3.08 mmol) in chloroform (5 mL) was added dropwise N-butyl-N-(3-phenylpropyl)amine (1.29 g, 6.77 mmol). The mixture became warm and a precipitate began to form. The mixture was stirred under nitrogen for 2 days and poured to water (50 mL), made basic (pH 9-10) with 40% K_2CO_3, and extracted with chloroform (40 mL, 2 X). The organic solution was washed with water (3 X), dried over anhydrous $MgSO_4$, filtered and concentrated to afford a yellow oil

(1.22 g). The oil was separated by column chromatography (silica gel/chloroform) to afford N-butyl-N-(3-phenylpropyl)-4-[N-butyl-N-(3-phenylpropyl)amino]-3-nitrobenzenesulfonamide (**5**, 0.14 g, 0.25 mmol, 8% yield) as a colorless oil; R_f 0.77 chloroform; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (3H, t, J = 7.9 Hz), 0.88 (3H, t, J = 7.9 Hz), 1.17-1.35 (4H, m), 1.43-1.58 (4H, m), 1.83-1.96 (4H, m), 2.57-2.64 (4H, m), 3.09-3.24 (8H, m), 7.00 (1H, d, J = 9.0 Hz), 7.10-7.28 (10H, m), 7.64 (1H, dd, J_1 = 9.0 Hz, J_2 = 2.3 Hz), 8.11 (1H, d, J = 2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7 (2 C), 19.8, 19.9, 28.8, 29.4, 30.3, 30.8, 32.7, 32.9, 47.8, 48.2, 50.7, 51.9, 120.1, 126.0, 126.1, 126.4, 128.26 (2 C), 128.29 (2 C), 128.36, 128.42 (2 C), 128.44 (2 C), 130.9, 139.1, 140.9, 141.1, 147.1.

Anal. calcd. for $C_{32}H_{43}N_3O_4S$: C, 67.93; H, 7.66; N, 7.43.
Found: C, 68.10; H, 7.75; N, 7.30.

The second fraction afforded N-butyl-N-(3-phenylpropyl)acetamide (**4**, 0.61 g, 2.61 mmol, 85%) as a colorless liquid (a mixture of two conformers); R_f 0.02 chloroform; ^{1}H NMR (mixture of two conformers) (300 MHz, $CDCl_3$): δ 0.90 (3H, t, J = 7.2 Hz), 0.93 (3H, t, J = 7.2 Hz), 1.24-1.38 (4H, m), 1.42-1.58 (4H, m), 1.81-1.98 (4H, m), 1.98 (3H, s), 2.07 (3H, s), 2.58-2.68 (4H, m), 3.10-3.40 (8H, m), 7.14-7.37 (10H, m); ^{13}C NMR (mixture of two conformers) (75 MHz, $CDCl_3$): δ 13.7, 13.8, 20.0, 20.1, 21.4, 21.5, 29.2, 29.8, 30.2, 31.0, 32.9, 33.2, 45.4 (2 C), 48.0, 48.6, 125.8, 126.1, 128.1, 128.2, 128.3, 128.5, 140.7 (q), 141.7 (q), 170.0, 170.1; HR MS calcd. for $C_{15}H_{23}NO$ (M^+) 233.1780. Found: 233.1775.

2-Nitrophenyl benzyl ether[18] **(6).** To a stirred mixture of 2-nitrophenol (13.91 g, 100 mmol) and DMSO (30 mL) was added KOH (6.17 g, 110 mmol) which dissolved quickly to give a hot red mixture. After cooling, benzyl chloride (11.51 ml, 100 mmol) was added and the mixture was stirred under nitrogen for 41 hours. The product was dissolved in diethyl ether, washed thoroughly with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to afford **6** as a colorless liquid (18.68 g, 81%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.18 (2H,s), 6.99 (1H, t, J = 8.4 Hz), 7.09 (1H, d, J = 8.7 Hz), 7.30-7.50 (6H, m), 7.80 (1H, d, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 70.9, 115.0, 120.5, 125.5, 126.8 (2 C), 128.1, 128.6 (2 C), 134.0, 135.5, 140.1, 151.7; HR MS calcd. for $C_{13}H_{11}NO_3$ (M^++1, CI): 230.0817. Found: 230.0812.

N-Butyl-N-(3′ -phenylpropyl)-4-methoxy-3-nitrobenzenesulfonamide (8). To stirred chlorosulfonic acid (5.32 mL, 80.0 mmol) cooled in an ice-water bath was added dropwise 2-nitroanisole (2.80 g, 18.3 mmol) at a rate to keep the temperature below 10 °C. After the addition, the ice bath was removed and the mixture was stirred at room temperature for 1 hour. The dark red mixture was poured very slowly into stirred ice/water, extracted with diethyl ether, washed with water (3 X), and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a mixture of 4-methoxy-3-nitrobenzenesulfonyl chloride (**7**) and 4-hydroxy-3-nitrobenzenesulfonyl chloride (**2**) (1.58 g, molar ratio 85:15) as a brown oil.

To a stirred mixture of the oil obtained above (1.51 g) and pyridine (5 mL) was added N-butyl-(3-phenylpropyl)amine (1.38 g, 7.20 mmol). The mixture was stirred for 30 hours, poured into water and extracted with chloroform (100 mL). After washing with water (100 mL, 6 X), drying over $MgSO_4$, and removal of the solvent, a red oil (1.95 g) was obtained. The oil was purified by column chromatography [silica gel/chloroform:hexane (1:1)] to give pure **8** (1.12 g, 2.76 mmol, 15% total yield) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, J = 7.3 Hz), 1.28 (2H, sextet, J = 7.6 Hz), 1.48 (2H, quintet, J = 7.6 Hz), 1.88 (2H, quintet, J = 7.6 Hz), 2.62 (2H, t, J = 7.6 Hz), 3.12 (2H, t, J = 6.5 Hz), 3.15 (2H, t, J = 6.5 Hz), 4.02 (3H, s), 7.13-7.25 (4H, m), 7.25-7.32 (2H, m), 7.91 (1H, dd, J_1 = 8.9 Hz, J_2 = 2.3 Hz), 8.22 (1H, d, J = 2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 19.8, 30.1, 30.6, 32.8, 47.6, 48.1, 57.0, 113.8, 124.8, 126.0, 128.2 (2 C), 128.4 (2 C), 132.2, 132.6, 139.1, 140.8, 155.3.

Anal. calcd. for $C_{20}H_{26}N_2O_5S$: C, 59.10; H, 6.45; N, 6.89.

Found: C, 59.16; H, 6.46; N, 6.85.

N-Butyl-N-(3′-phenylpropyl)-4-hydroxy-3-nitrobenzenesulfonamide (9). To a stirred solution of N-butyl-N-(3′-phenylpropyl)-4-methoxy-3-nitrobenzenesulfonamide (**8**, 0.73 g, 1.80 mmol) in DMSO (10 mL) was added 50% KOH (10 mL) and the mixture was stirred at 80 °C in an oil bath for 4 hours. The mixture was poured into water, acidified to pH 4-5 with 20% HCl, and extracted with $CHCl_3$. The organic solution was washed with water, dried over

$MgSO_4$, filtered, and concentrated to afford analytically pure **9** (0.71 g, 1.80 mmol, 100%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, J = 7.3 Hz), 1.12-1.35 (2H, m), 1.43-1.54 (2H, m), 1.81-1.95 (2H, m), 2.61 (2H, t, J = 7.6 Hz), 3.10-3.20 (4H, m), 7.10-7.32 (6H, m), 7.90 (1H, dd, J_1 = 8.9 Hz, J_2 = 2.3 Hz), 8.53 (1H, d, J = 2.3 Hz), 10.84 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 19.8, 30.1, 30.6, 32.8, 47.5, 48.0, 121.1, 124.8, 126.1, 128.2 (2 C), 128.4 (2 C), 132.5, 132.8, 135.1, 140.8, 157.3.

Anal. calcd. for $C_{19}H_{24}N_2O_5S$: C, 58.15; H, 6.16; N, 7.14.
Found: C, 57.96; H, 6.23; N, 7.09.

N-Butyl-N-(3′-phenylpropyl)-3-amino-4-hydroxybenzenesulfonamide (10). A mixture of N-butyl-N-(3′-phenylpropyl)-4-hydroxy-3-nitrobenzenesulfonamide (**9**, 13.16 g, 33.53 mmol), 1% platinum on alumina (2 g), and ethanol (200 mL) was stirred at room temperature for 22 hours in a bomb charged with 800 psi of hydrogen. The solution was filtered and concentrated to afford **10** as a colorless oil (12.02 g, 33.16 mmol, 99%); ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (3H, t, J = 7.3 Hz), 1.25 (2H, sextet, J = 7.5 Hz), 1.45 (2H, quintet, J = 7.1 Hz), 1.84 (2H, quintet, J = 7.3 Hz), 2.58 (2H, t, J = 7.6 Hz), 3.10-3.14 (4H, m), 4.2-5.4 (2H, broad, NH_2), 6.76 (1H, d, J = 8.1 Hz), 7.00 (1H, dd, J_1 = 8.3 Hz, J_2 = 2.2 Hz), 7.06 (1H, d, J = 2.2 Hz), 7.10-7.20 (4H, m), 7.21-7.30 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 19.8, 30.3, 30.8, 32.9, 47.9, 48.3, 114.1, 114.6, 118.7, 125.9, 128.28 (2 C), 128.35 (2 C), 130.5, 135.2, 141.2, 147.8; HR MS calcd. for $C_{19}H_{26}N_2O_3S$ (M^+): 362.1664. Found: 362.1664.

N-Butyl-N-(3-phenylpropyl)-4-hydroxy-3-(2-hydroxy-1-naphthyl)-azobenzenesulfonamide (1d). To a stirred solution of N-butyl-N-(3′-phenylpropyl)-3-amino-4-hydroxybenzenesulfonamide (**10**, 7.41 g, 20.4 mmol) in ethanol (30 mL) cooled in an ice-salt-water bath were added 37% HCl (5.6 ml, 56 mmol) and ice (20 g). The mixture was diazotized by dropwise addition of a solution of sodium nitrite (1.54 g, 22.3 mmol) in water (10 mL) to give a yellow suspension.

To a solution of 2-naphthol (2.94 g, 20.4 mmol) in ethanol (40 mL) were added a solution of sodium hydroxide (1.48 g, 37 mmol) in water (15 mL) and a solution of sodium acetate (4.11 g, 50.0 mmol) in water (20 mL). The mixture was cooled in an ice-salt bath to 0 °C and the diazonium salt prepared above was added dropwise. The mixture immediately turned violet, and soon changed to violet-blue, and finally to red during the addition. The mixture was allowed to warm up and was stirred at room temperature for 19 hours, diluted with water (200 mL) and stirred for 0.5 hour. The red precipitate was collected, washed thoroughly with water, and dried in a vacuum oven at 70 °C for 12 hours to give pure **1d** as a black powder (9.22 g, 17.8 mmol, 87% yield); mp 144-146 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (3H, t, J = 7.3 Hz), 1.32 (2H, sextet, J = 7.8 Hz), 1.49-1.55 (2H, m), 1.65 (broad, 2H), 1.89-1.94 (2H, m), 2.64 (2H, t, J = 7.6 Hz), 3.17 (2H, t, J = 6.8 Hz), 3.19 (2H, t, J = 6.8 Hz), &.14-7.22 (5H, m), 7.24-7.34 (2H, m), 7.50 (1H, dt, J = 8.0, 1.0 Hz), 7.64-7.69 (2H, m), 7.81 (1H, d, J = 7.1 Hz), 7.90 (1H, d, J = 9.0 Hz), 8.14 (1H, d, J = 2.3 Hz), 8.18 91H, d, J = 8.1 Hz); ^{13}C NMR (75 MHz, acetone-d_6): δ 14.0, 20.4, 31.1, 31.4, 33.5, 48.5, 48.7, 116.3,

117.2, 122.2, 126.0, 126.5, 127.0, 127.1, 128.9, 129.0 (2 C), 129.2 (2 C), 129.7, 130.0, 131.3, 132.7, 133.0, 133.9, 141.6, 142.3, 152.6, 175.0.

Anal. calcd. for $C_{29}H_{31}N_3O_4S$: C, 67.29; H, 6.04; N, 8.12.

Found: C, 67.47; H, 6.09; N, 7.83.

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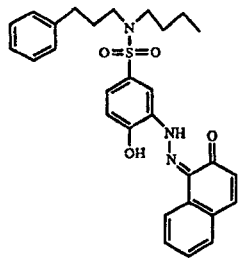

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