Naphth[1,2-*d*]oxazole Intermediates in the Preparation of 3-Hydroxy-4-(1-alkyl-3-methyl-5-hydroxy-4-pyrazolyl)-azo-1-naphthalenesulfonamide Dyes

Alan R. Katritzky*, Bogumila Rachwal and Stanislaw Rachwal

Center for Heterocyclic Compounds,
Department of Chemistry, University of Florida,
Gainesville, FL 32611-2046

David Macomber and Terrance P. Smith

3M Company, Graphics Sector Laboratory,
3M Center, Hudson Road,
St. Paul, MN 55144-1000

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Acylation of 4-amino-3-hydroxy-1-naphthalenesulfonic acid (**3**) with benzoyl chloride in pyridine gave pyridinium 3-hydroxy-4-(*N*-benzoylamino)-1-naphthalenesulfonate (**12**) which was converted by thionyl chloride followed by diethylamine into *N,N*-diethyl-2-phenylnaphth[1,2-*d*]oxazole-5-sulfonamide (**14**). The naphthoxazole moiety was hydrolyzed with potassium hydroxide and the resulting *N,N*-diethyl-4-amino-3-hydroxy-1-naphthalenesulfonamide (**11**) coupled with 1-alkyl-3-methyl-5-pyrazolones. The 2-phenylnaphth[1,2-*d*]oxazole intermediates and various by-products were investigated.

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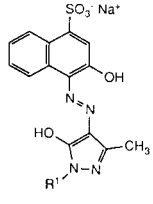
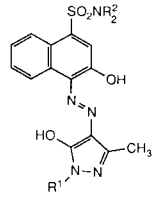
Due to its chelation ability and intense color, Eriochrome Red B, (**1a**) has found applications in the analysis of several metals, *e.g.*, berylium [1], cadmium [2], copper [2], gallium [3], nickel [4], titanium [5,6], vanadium [6,7] and zinc [8,9]. Chromium co-complexes of Eriochrome Red B and a second ligand, usually another azo dye, are valuable in dyeing wool, polyamide fibers and leather [10-19]. To improve solubility of the dye in organic solvents, we converted **1a** into sulfonamide **2a** [20] modifying the literature method [21] for the preparation of a dimethylsulfonamide derivative **2b**. To investigate the influence of the substituents on the pyrazole ring on the properties of the dye, we required several alkyl derivatives of Eriochrome Red B (**1b**) and their sulfonamide derivatives **2c**. A literature survey revealed that dyes of types **1b** and **2c** were unknown. As a result of our research, we report here a general synthetic method for dyes of type **2c**.



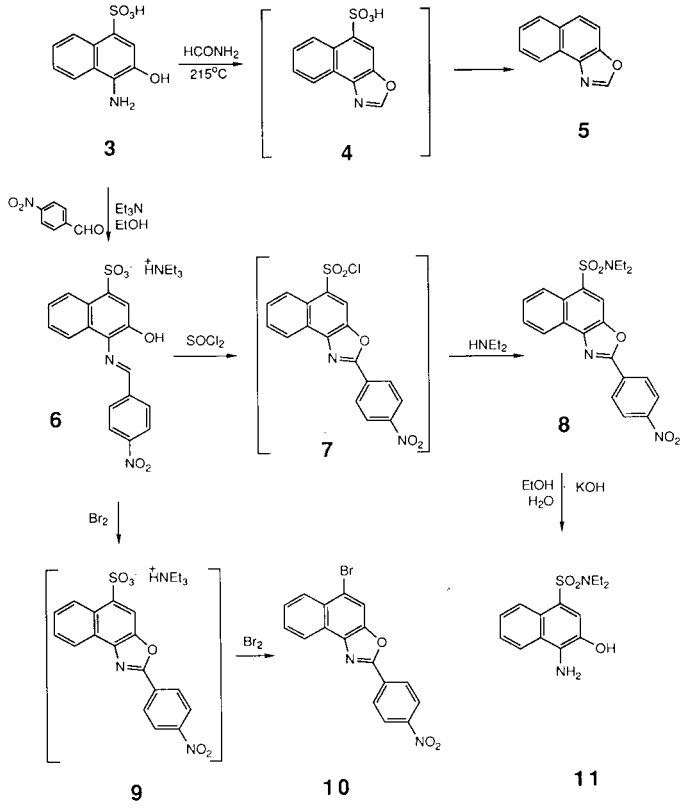


1 a, R^1 = Ph (Eriochrome Red B)
b, R^1 = alkyl

2 a, R^1 = Ph, R^2 = Bu
b, R^1 = Ph, R^2 = Me
c, R^1 = alkyl, R^2 = alkyl

Our attempts to prepare alkyl analogs of Eriochrome Red B by coupling diazotized 4-amino-3-hydroxy-1-naphthalenesulfonic acid (**3**) with 1-alkyl-3-methyl-5-pyrazolones failed. Knowing that we could not expect high yields in the further transformation, from **1b** to **2c** (**1a** has been converted to **2a** with an overall yield of 40% [20]), we decided to convert the sulfonic acid group of **3** to a sulfonamido function as the first step. As this conversion was expected to give the lowest yield in the whole sequence, it would allow us to conserve the 1-alkylpyrazolones which had to be prepared and give a convergent synthesis. Since it would be necessary to make a sulfonyl chloride, the

Scheme 1



amino and hydroxy groups of **3** had first to be protected.

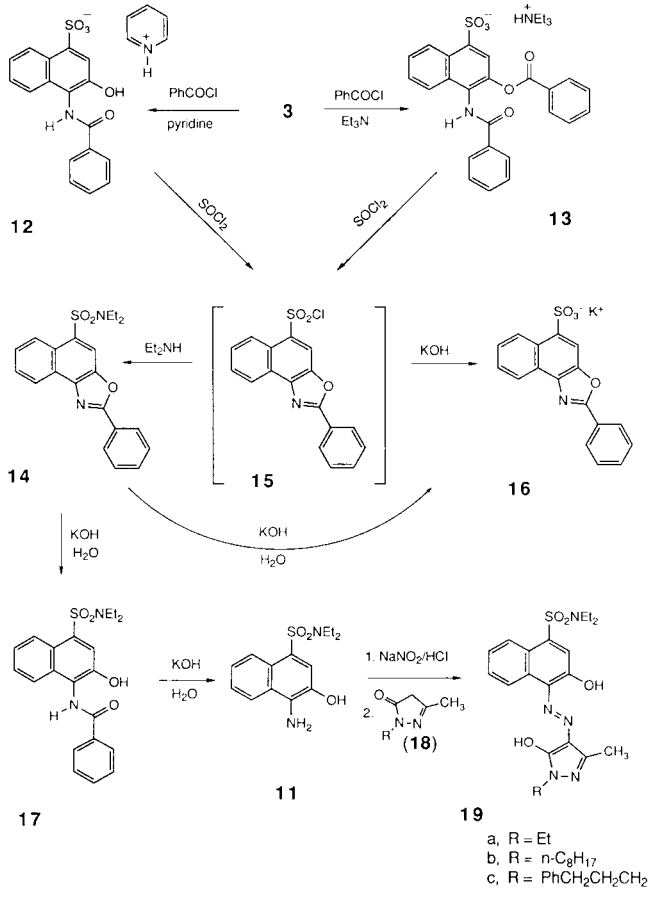
The best method for this protection [22] seemed to be cyclocondensation of **3** with formamide to give the reported naphth[1,2-*d*]oxazole-5-sulfonic acid (**4**) (Scheme 1). However, when we performed the reaction under the published conditions [22], the product was not the sulfonic acid **4** but unsubstituted naphth[1,2-*d*]oxazole (**5**). The reported properties of the compound previously claimed to be **4** (mp 68-69°, soluble in benzene-petroleum ether) are in agreement with our data and with the data previously reported for **5** [23]. Unfortunately, the nmr data for the product claimed to be **4** were not reported [22].

We had to consider other methods to protect the amino and hydroxy groups of **3** under milder conditions which would not cause elimination of the sulfonic group. The first choice was formation of a Schiff base with 4-nitrobenzaldehyde. The nitro group was expected to decrease the solubility of the product making possible its higher recovery from the reaction mixture. When **3** was treated with 4-nitrobenzaldehyde in the presence of triethylamine (to neutralize the acidity of the sulfonic acid group), the Schiff base as its triethylammonium salt **6** was obtained in a nearly quantitative yield. We hoped that oxidation of **6** would cause formation of an oxazole ring **9**. However, treatment with bromine gave a product in which the new ring had formed, but the sulfonic group had been substituted by a bromine atom giving 5-bromonaphth[1,2-*d*]oxazole (**10**).

Refluxing thionyl chloride converted the Schiff base **6** to the sulfonyl chloride **7**. Here, thionyl chloride acted as both a mild oxidant and a chlorinating agent. The sulfonyl chloride **7** could not be isolated, but was converted to sulfonamide **8** by treatment of the crude reaction mixture with diethylamine (13% yield from **6**). Hydrolysis of the protective oxazole ring of **8** to give amine **11** appeared to be difficult.

At this point, it was decided to investigate the simpler 2-phenyl oxazole ring as a protection system for **3**. A classical method for the preparation of 2-phenylbenzoxazole [24] requires heating a mixture of 2-aminophenol with benzoic and polyphosphoric acids to 250°. To avoid such severe conditions which might affect the sulfonic group, **3** was treated with benzoyl chloride in the presence of a base. In the presence of pyridine, the benzamide **12** was separated (Scheme 2). In the presence of the stronger base triethylamine, the hydroxy group of **3** was also benzoylated to give the amido-ester **13** in good yield.

Scheme 2



Both benzamides, **12** and **13**, were converted smoothly to the ring closed sulfonyl chloride **15** in refluxing thionyl chloride. Attempted isolation of **15** by aqueous work-up resulted in hydrolysis of the chlorosulfonyl group. Neutralization of the reaction mixture with potassium hydroxide allowed the separation the sulfonic acid as its potassium salt **16**. Direct treatment of the crude **15** with diethylamine converted it into sulfonamide **14**.

Several attempts were made to hydrolyze the oxazole ring of **14**. Heating with hydrochloric or sulfuric acid did not cause its hydrolysis. Compound **14** also appeared to be inert towards sodium borohydride. Heating **14** with lithium aluminum hydride gave a complex mixture. Finally we have found that upon treatment with potassium hydroxide, the oxazole ring of **14** was relatively easily opened to give benzamide **17**. Unfortunately, hydrolysis of the sulfonamide group of **14** competed to some degree with ring opening as the sulfonate **16** was also separated from the reaction mixture (9% yield). Prolonged heating with a solution of potassium hydroxide converted **14** to the completely deprotected amine **11**. Amine **11** appeared to be very sensitive to air being oxidized within hours (turning black) when exposed to the atmosphere. Because its CHN analysis did not give satisfactory results, **11** was characterized by hrms.

Aminonaphthol **11** was diazotized and coupled with 1-ethyl- (**18a**), 1-octyl- (**18b**) and 1-(3-phenylpropyl)-3-methyl-5-pyrazolone (**18c**) in basic solutions to give azo dyes **19a**, **19b** and **19c**, respectively. Overall yields of the syntheses

from **3** were: 15%, 16% and 21%, for **19a, 19b** and **19c**, respectively.

EXPERIMENTAL

The ^1H and ^{13}C nmr spectra were obtained for the deuteriochloroform solutions (except when stated otherwise) on a Varian VXR-300 spectrometer, at 300 MHz and 75 MHz, respectively. Chemical shifts are reported in ppm relative to tetramethylsilane in deuteriochloroform as the solvent, except when specified otherwise. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Column chromatography was run on silica gel 230-400 Mesh.

Naphth[1,2-*d*]oxazole (**5**).

A mixture of **3** (83.74 g, 350 mmoles) and formamide (31.52 g, 700 mmoles) was heated in an oil bath at 210-215° for 2 hours. After cooling, the product was removed by steam distillation (2 hours). The distilate was set aside for a few hours and the precipitate collected and dried in a vacuum oven to give **5** (1.1 g, 2%), mp 65° (lit [23] mp 68°); ^1H nmr: δ 7.52 (t, J = 6.9 Hz, 1H), 7.65 (m, 2H), 7.77 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 8.19 (s, 1H), 8.51 (d, J = 8.1 Hz, 1H); ^{13}C nmr: δ 110.9, 122.0, 125.4, 126.5, 126.6, 127.2, 128.5, 131.1, 135.4, 147.4, 151.5.

Triethylammonium 3-hydroxy-4-(4-nitrobenzylidene)amino-1-naphthalenesulfonate (**6**).

A solution of **3** (2.39 g, 10 mmoles), *p*-nitrobenzaldehyde (1.51 g, 10 mmoles) and triethylamine (2.0 ml, 20 mmoles) in absolute ethanol (10 ml) was refluxed for 1 hour. Evaporation of the solvent gave crude **6** (5.12 g, 100%) as an orange solid. An analytical sample was prepared by recrystallization from methanol, orange needles, mp 222-223°; ^1H nmr: δ 1.23 (t, J = 7.3 Hz, 9H, Et), 3.05 (q, J = 7.4 Hz, 6H, Et), 3.60 (bs, 1H), 7.40 (m, 2H), 8.08 (s, 1H), 8.21 (m, 1H), 8.22 (d, J = 8.6 Hz, 2H), 8.34 (d, J = 8.5 Hz, 2H), 8.80 (d, J = 8.1 Hz, 1H), 9.15 (s, 1H); ^{13}C nmr: δ 8.3 (3C, Et), 45.8 (3C, Et), 118.7, 122.8, 123.1, 123.5 (2C), 123.8, 125.6, 126.4, 128.7 (2C), 131.1, 140.1, 142.3, 142.4, 148.5, 161.17, 161.20.

Anal. Calcd. for $C_{23}H_{27}N_3O_6S$: C, 58.28; H, 5.75; N, 8.87. Found: C, 58.01; H, 5.67; N, 8.78.

N,N-Diethyl-2-(4-nitrophenyl)naphth[1,2-*d*]oxazole-5-sulfonamide (**8**).

A solution of **6** (2.40 g, 5 mmoles) in thionyl chloride (5 ml) was refluxed for 1 hour. Toluene (20 ml) was added and the excess thionyl chloride was evaporated under reduced pressure to give sulfonyl chloride **7** (2.86 g). To a stirred solution of **7** in chloroform (10 ml) diethylamine (5 ml) was added in 1 ml portions within 15 minutes. Evolution of heat was observed. The reaction mixture was stirred for an additional 15 minutes, poured into ice-water (50 ml) and extracted with chloroform (50 ml). The organic layer was separated, washed with water (2 x 50 ml) and dried over sodium sulfate. Evaporation of the solvent gave an oily product that was subjected to column chromatography (chloroform) to give **8** as a crystalline product (0.54 g, 13%). Recrystallization from toluene gave greenish needles, mp 203-204°; ^1H nmr: δ 1.21 (t, J = 7.1 Hz, 6H, Et), 3.42 (q, J = 7.1 Hz, 4H, Et), 7.71 (m, 2H), 8.35 (m, 4H), 8.52 (s, 1H), 8.57 (d, J = 8.6 Hz, 1H), 8.71 (d, J = 8.7 Hz, 1H); ^{13}C nmr: δ 13.6 (2C, Et), 40.9 (2C, Et), 115.0, 122.9, 124.2 (2C), 125.9, 127.0, 127.4, 128.0, 128.3 (2C), 131.89, 131.92, 134.4, 141.5, 145.9, 149.4, 162.4.

Anal. Calcd. for $C_{21}H_{19}N_3O_5S$: C, 59.25; H, 4.54; N, 9.87. Found: C, 58.86; H, 4.41; N, 9.61.

5-Bromo-2-(4-nitrophenyl)naphth[1,2-*d*]oxazole (**10**).

Bromine (0.5 ml, 10 mmoles) was added portionwise to a stirred suspension of **6** (3.25 g, 7 mmoles) in chloroform (30 ml) and stirring continued at room temperature for 2 hours. The starting material dissolved as the bromine was added, and after 2 hours a new precipitate had formed. Thionyl chloride (4.3 ml, 50 mmoles) was added and the mixture refluxed for 30 minutes. Toluene (20 ml) was added and evaporated under reduced pressure to remove excess thionyl chloride. The solid residue was dissolved in chloroform (30 ml) and diethylamine (5 ml, 50 mmoles) added portionwise. Work up with water, evaporation of the solvent and column chromatography (chloroform) gave **10** (1.27 g, 49%) as a brown-yellow solid practically insoluble in organic solvents, mp 218-220°.

Anal. Calcd. for $C_{17}H_9BrN_2O_3$: C, 55.31; H, 2.45; N, 7.59. Found: C, 55.61; H, 2.58; N, 7.68.

Pyridinium 3-hydroxy-4-(*N*-benzoylamino)-1-naphthalenesulfonate (**12**).

Benzoyl chloride (1.8 ml, 15 mmoles) was added portionwise to a vigorously stirred suspension of 4-amino-3-hydroxy-1-naphthalenesulfonic acid (**3**) (2.39 g, 10 mmoles) in a mixture of pyridine (50 ml) and water (20 ml) kept in an ice bath. The mixture was stirred for 2 hours at room temperature. The solid product was collected and washed with 10 ml of ice-cold water. Drying in a vacuum oven gave crude **12** (2.55 g, 60%); an analytical sample was prepared by recrystallization from a mixture of THF and water (9:1), mp 225°; ^1H nmr (DMSO): δ 7.28 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.52 (m, 3H), 7.79 (m, 3H), 7.91 (s, 1H), 8.15 (d, J = 7.3 Hz, 2H), 8.31 (t, J = 8.1 Hz, 1H), 8.78 (m, 3H), 9.2-9.5 (bs, 2H), 9.95 (s, 1H); ^{13}C nmr (DMSO): δ 116.2, 116.4, 120.3, 120.9, 122.4, 124.1, 124.5 (2C), 125.7, 126.2 (2C), 126.4 (2C), 129.6, 130.7, 132.6, 141.5, 141.9, 142.1 (2C), 147.6, 164.6.

Anal. Calcd. for $C_{22}H_{16}N_2O_5S$: C, 62.55; H, 4.29; N, 6.63. Found: C, 62.53; H, 4.22; N, 6.66.

Triethylammonium 3-benzoyloxy-4-(*N*-benzoylamino)-1-naphthalenesulfonate (**13**).

Benzoyl chloride (36 ml, 300 mmoles) was added portionwise to a stirred suspension of 3-hydroxy-4-amino-1-naphthalenesulfonic acid (**3**) (2.39 g, 10 mmoles) in chloroform (200 ml) and triethylamine (80 ml). Heat was evolved and the reactants dissolved. The reaction mixture was left at room temperature for 5 hours and the precipitate collected, washed with 95% ethanol and dried *in vacuo* to give **13** (28.1 g, 51%) of high purity (nmr). An analytical sample was prepared by recrystallization (DMSO, water, 3:2) mp 244°; ^1H nmr: δ 1.18 (t, J = 7.1 Hz, 9H, Et), 3.05 (q, J = 7.1 Hz, 6H, Et), 3.40 (bs, 1H), 7.41-7.64 (m, 9H), 7.96 (d, J = 8.0 Hz, 2H), 8.04-8.09 (m, 3H), 8.98 (d, J = 8.0 Hz, 1H), 10.39 (s, 1H); ^{13}C nmr: 8.6 (3C), 45.9 (3C), 120.9, 123.4, 125.6, 125.9, 126.3, 127.6 (2C), 128.2 (2C), 128.6 (2C), 129.1, 129.6 (2C), 130.2, 131.4, 131.5, 133.7, 134.1, 134.9, 142.8, 143.4, 164.0, 166.1.

Anal. Calcd. for $C_{30}H_{32}N_2O_6S$: C, 65.67; H, 5.87; N, 5.10. Found: C, 65.58; H, 5.90; N, 5.01.

N,N-Diethyl-2-phenylnaphth[1,2-*d*]oxazole-5-sulfonamide (**14**).

A mixture of **12** (3.43 g, 8 mmoles) and thionyl chloride (10 ml) was refluxed for 3.5 hours. Toluene (20 ml) was added and the excess thionyl chloride was distilled off with toluene under reduced pressure. The solid residue was dissolved in methylene chloride (50 ml) and diethylamine (10 ml) was added portionwise while stirring. After 30 minutes the reaction mixture was poured into ice-water (100 ml) and extracted with dichloromethane (100 ml). The organic phase was separated, washed with water and dried over sodium sulfate. Evaporation of the solvent gave **14** (2.52 g, 82%) of high purity, by nmr. Recrystallization from 95% ethanol gave an analytical sample, mp 157°; ^{1}H nmr: δ 1.09 (t, J = 7.0 Hz, 6H, Et), 3.97 (q, J = 7.0 Hz, 4H, Et), 7.53 (m, 3H), 7.70 (m, 2H), 8.30 (m, 2H), 8.55 (s, 1H), 8.65 (d, J = 7.8 Hz, 1H), 8.72 (d, J = 8.2 Hz, 1H); ^{13}C nmr: δ 13.6 (2C), 40.8 (2C), 115.2, 123.0, 125.8, 126.6, 126.8, 127.0, 127.3, 127.5, 127.7 (2C), 129.0 (2C), 131.9, 132.8, 141.8, 145.5, 165.0.

Anal. Calcd. for $C_{21}H_{20}N_2O_3S$: C, 66.29; H, 5.29; N, 7.36. Found: C, 66.27, H, 5.23; N, 7.21.

Hydrolysis of **14** with Potassium Hydroxide.

A solution of potassium hydroxide (3 g) in water (12 ml) was added portionwise to a suspension of **14** (3.81 g, 10 mmoles) in 95% ethanol (18 ml) and the mixture stirred and refluxed for 2 hours. After cooling to 25°, the precipitate was collected and recrystallized (THF/water, 10:1) to give potassium 2-phenylnaphth-[1,2-*d*]oxazole-5-sulfonate **16** (0.33 g, 9%); ^{1}H nmr (DMSO): δ 7.60 (m, 4H), 7.71 (t, J = 8.0 Hz, 1H), 8.30 (m, 2H), 8.42 (s, 1H), 8.50 (d, J = 8.1 Hz, 1H), 9.07 (d, J = 8.3 Hz, 1H); ^{13}C nmr (DMSO): δ 110.0, 121.4, 125.1, 126.0, 126.6, 126.8, 126.9 (2C), 127.0, 127.2, 128.6, 129.0 (2C), 131.3, 137.7, 142.4, 145.9.

Anal. Calcd. for $C_{17}H_{10}NO_4KS$: C, 56.18; H, 2.77; N, 3.85. Found: C, 56.11; H, 2.73; N, 3.81.

The alkaline water-alcohol solution obtained (after separation of **16**) was poured into ice-water, neutralized with acetic acid and extracted with chloroform. The chloroform solution was washed with water, dried (sodium sulfate) and evaporated. The residue was subjected to column chromatography (chloroform) to give **17** (2.58 g, 62%). Recrystallization from acetic acid gave needles of **17** monohydrate, mp 200-201°; ^{1}H nmr: δ 1.21 (t, J = 7.1 Hz, 6H, Et), 2.69 (bs, 2H), 3.38 (q, J = 7.1 Hz, 4H, Et), 7.52 (m, 5H), 7.96 (s, 1H), 8.00 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 7.3 Hz, 2H), 8.52 (d, J = 8.3 Hz, 1H), 9.46 (bs, 1H, NH), 10.01 (bs, 1H, OH); ^{13}C nmr (DMSO): δ 13.2 (2C, Et), 40.4 (2C, Et), 121.5, 122.4, 122.6, 123.2, 124.3, 126.2, 127.5 (2C), 127.70, 127.75 (2C), 131.2, 131.4, 132.8, 134.3, 147.8, 167.8.

Anal. Calcd. for $C_{21}H_{24}N_2O_5S$: C, 60.56; H, 5.80; N, 6.73. Found: C, 60.60; H, 5.84; N, 6.67.

N,N-Diethyl-4-amino-3-hydroxy-1-napthalenesullfonamide **11**.

A mixture of **14** (38.1 g, 100 mmoles), 20% potassium hydroxide (140 ml) and ethanol (180 ml) was refluxed for 24 hours under nitrogen and the product was extracted with ethyl acetate (3 x 500 ml). The combined extracts were dried over sodium sulfate and the solvent evaporated to give crude **11** as a black sticky oil (45.4 g, 50% pure by nmr). An analytical sample was prepared by column chromatography (chloroform) to give pure **11** as a glassy material which upon trituration with ether gave a black solid, mp 120-122°; ^{1}H nmr: δ 1.00 (t, J = 7.1 Hz, 6H, Et), 3.27 (q, J = 7.0 Hz, 4H, Et), 5.1-5.4 (bs, 2H, NH_2), 7.38 (m, 2H), 7.77 (m, 1H), 8.00 (s, 1H), 8.42 (m, 1H), 9.3-9.5 (bs, 1H, OH); ^{13}C nmr: δ 13.3 (2C), 40.4 (2C), 120.7, 121.0, 122.1, 123.7, 124.9, 125.0, 125.1, 126.1, 134.5, 136.8; hrms: Calcd. for $C_{14}H_{18}N_2O_3S$: 294.1038. Found: 294.1028.

2,4-Dihydro-2-ethyl-5-methyl-3*H*-pyrazol-3-one (**18a**).

A mixture of 3-methyl-3-pyrazolin-5-one (49 g, 0.50 mole) and bromoethane (60.00 g, 0.55 mole) was sealed in a glass pressure tube and heated in an oil bath at 130° for 40 hours. After cooling, the tube was opened and the contents were poured to ice-water (200 g). Sodium bicarbonate (42.00 g, 0.50 mole) was added in small portions with stirring. The resulting mixture was stirred and heated to 100° for 1 hour, cooled to room temperature and extracted with chloroform (10 x 50 ml). The combined extracts were dried over calcium chloride, evaporated under reduced pressure and the residue recrystallized from ethanol to give **18a** (20.10 g, 31%) as colorless prisms, mp 112-113° (lit [25] mp 109°); ^{1}H nmr: δ 1.26 (t, J = 7.2 Hz, 3H, Et), 2.10 (s, 3H, Me), 3.20 (s, 2H, pyrazole), 3.68 (q, J = 7.2 Hz, 2H, Et); ^{13}C nmr: δ 13.5, 16.9, 38.7, 41.8, 155.4, 171.7.

2,4-Dihydro-5-methyl-2-octyl-3*H*-pyrazol-3-one (**18b**).

A mixture of 3-methyl-3-pyrazolin-5-one (19.63 g, 0.20 mole) and 1-bromooctane (42.40 g, 0.22 mole) was stirred and heated at 135° for 50 hours. After cooling, the reaction mixture was triturated with water (200 ml), treated with sodium bicarbonate (17.00 g, 0.20 mole, in small portions) and heated at 100° for 1 hour. After cooling, the mixture was extracted with chloroform (3 x 100 ml). The combined extracts were dried (calcium chloride), the solvent evaporated and the oily residue crystallized from hexane (at −5°) to give **18b** (17.50 g, 42%) as white plates, mp 59° (lit [26] mp 57-59°); ^{1}H nmr: δ 0.87 (t, J = 6.5 Hz, 3H, octyl), 1.29 (m, 10H), 1.66 (m, J = 6.5 Hz, 2H, octyl), 2.10 (s, 3H, Me), 3.20 (s, 2H, pyrazol), 3.61 (t, J = 7.2 Hz, 2H, octyl); ^{13}C nmr: δ 13.9 (Me, octyl), 16.7 (Me, pyrazol), 22.4, 26.5, 28.2, 29.0 (2C), 31.6, 41.6, 43.8, 155.2, 171.9.

2,4-Dihydro-5-methyl-2-(3-phenylpropyl)-3*H*-pyrazol-3-one (**18c**).

By a procedure similar to that for **18b**, starting from 3-methyl-3-pyrazolin-5-one (19.63 g, 0.20 mole) and 1-bromo-3-phenylpropane (39.80 g, 0.20 mole), pyrazolone **18c** (29.40 g, 69%) was obtained as colorless needles, mp 103-105°; ^{1}H nmr: δ 2.00 (quintet, J = 7.3 Hz, 2H), 2.05 (s, 3H, Me), 2.64 (t, J = 7.8 Hz, 2H), 3.11 (s, 2H, pyrazol), 3.67 (t, J = 6.8 Hz, 2H), 7.16-7.28 (m, 5H, Ph); ^{13}C nmr: δ 16.9 (Me), 29.7, 33.0, 41.7, 43.6, 125.9, 128.3 (2C), 128.4 (2C), 141.3, 155.4, 172.1.

Anal. Calcd. for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 71.87; H, 7.50; N, 12.76.

N,N-Diethyl-3-hydroxy-4-(1-ethyl-5-hydroxy-3-methyl-1*H*-pyrazol-4-yl)azo-1-naphthalenesulfonamide (**19a**).

N,N-Diethyl-3-hydroxy-4-amino-1-naphthalenesulfonamide **11** (2.94 g, 10 mmoles) was dissolved in ethanol (10 ml) and 10 g of ice added. The reaction mixture was cooled in an ice bath to keep the temperature below 5°. Hydrochloric acid (37%, 3 ml) was added, followed by dropwise addition of a solution of sodium nitrite (0.83 g, 12 mmoles) in water (2 ml) and stirring was continued for 30 minutes. In a separate flask, to a solution of 2,4-dihydro-2-ethyl-5-methyl-3*H*-pyrazol-3-one (**18a**) (1.26 g, 10 mmoles) in ethanol (10 ml), 20% sodium acetate (11 ml) followed by 10% sodium hydroxide (9 ml) were added, while the temperature was maintained below 5°. The diazonium salt (as a suspension) was then added portionwise to the stirred solution of **18a** at 5° and the resulting mixture stirred for 30 minutes at room temperature.

The product was extracted with chloroform (100 ml), and the organic layer washed with 5% formic acid and water, dried over anhydrous sodium sulfate and the solvent evaporated to give crude **19a** (3.25 g). The product was subjected to column chromatography (toluene) to give pure **19a** (2.55 g, 59%) which was recrystallized from methanol to give dark red prisms, mp 174-175°; ^{1}H nmr: δ 1.11 (t, J = 7.1 Hz, 6H, Et), 1.37 (t, J = 7.2 Hz, 3H, Et-pyrazole), 2.30 (s, 3H), 3.38 (q, J = 7.1 Hz, 4H, Et), 3.85 (q, J = 7.1 Hz, 2H, Et-pyrazole), 7.50 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.88 (s, 1H), 8.60 (d, J = 8.3 Hz, 1H), 10.25 (bs, 2H, 2OH); ^{13}C nmr: δ 11.5, 13.66, 13.72 (2C), 39.2, 41.0 (2C), 118.6, 121.0, 123.1, 123.8, 124.5, 125.6, 125.9, 128.1, 128.2, 133.5, 143.7, 144.9, 158.5.

Anal. Calcd. for $C_{20}H_{25}N_5O_4S$: C, 55.67; H, 5.84; N, 16.23. Found: C, 55.29; H, 5.86; N, 16.14.

N,N-Diethyl-3-hydroxy-4-(5-hydroxy-3-methyl-1-octyl-1*H*-pyrazol-4-yl)azo-1-naphthalenesulfonamide (**19b**).

From octyl pyrazole (**18b**, 2.10 g, 10 mmoles) by the above procedure was obtained **19b** (2.10 g, 41%). Recrystallization from ether/hexane gave analytically pure **18b**, mp 104-105°; ^{1}H nmr: δ 0.87 (t, J = 6.8 Hz, 3H), 1.11 (t, J = 7.1 Hz, 6H, Et), 1.27 (m, 10H, octyl), 1.75 (m, 2H, octyl), 2.28 (s, Me), 3.38 (q, J = 7.0 Hz, 4H, Et), 3.80 (q, 2H, J = 6.9 Hz, octyl), 7.48 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 6.8 Hz, 1H), 7.84 (d, 1H, J = 8.4 Hz), 7.86 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 10.17 (bs, 2H); ^{13}C nmr: δ 11.6, 13.7 (2C), 13.9, 22.5, 26.6, 28.3, 29.0 (2C), 31.6, 41.0 (2C), 44.3, 118.6, 121.0, 123.0, 123.7, 124.4, 125.5, 125.9, 128.0, 128.1, 133.5, 143.7, 144.8, 158.7.

Anal. Calcd. for $C_{26}H_{37}N_5O_4S$: C, 60.56; H, 7.23; N, 13.58. Found: C, 60.36; H, 7.30; N, 13.47.

N,N-Diethyl-3-hydroxy-4-(5-hydroxy-3-methyl-1-(3-phenylpropyl)-1*H*-pyrazol-4-yl)azo-1-naphthalenesulfonamide (**19c**).

From **18c** (2.16 g, 10 mmoles) by the above procedure was obtained 4.7 g of a dark red oil which after column chromatography (toluene) gave **19c** (2.75 g, 53%). Recrystallization from methanol gave an analytical sample, mp 122-123°; ^{1}H nmr: δ 1.08 (t, J = 7.0 Hz, 6H, Et), 2.12 (t, J = 7.3 Hz, 2H, CH_2), 2.25 (s, 3H, Me), 2.70 (t, J = 7.3 Hz, 2H, Et), 3.36 (quartet, J = 7.1 Hz, 4H, Et), 3.84 (t, J = 7.0 Hz, 2H, CH_2), 7.22 (m, 5H), 7.48 (t, 1H, J = 7.0 Hz), 7.59 (t, 1H, J = 8.2 Hz), 7.87 (m, 2H), 8.60 (d, J = 8.4 Hz, 1H); ^{13}C nmr: δ 11.6, 13.7 (2C), 29.7, 32.9, 41.0 (2C), 43.9, 118.6, 121.0, 123.0, 123.8, 124.4, 125.6, 125.9 (2C), 128.1, 128.21 (2C), 128.25 (2C), 131.5, 140.9, 143.7, 144.9, 158.8.

Anal. Calcd. for $C_{27}H_{31}N_5O_4S$: C, 62.17; H, 5.99; N, 13.43. Found: C, 62.24; H, 5.98; N, 13.16.

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