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Improved Synthesis of Several Methoxynitronaphthalenes****

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Summary. An improved procedure for the synthesis of several isomeric methoxynitronaphthalenes is described. The key intermediates in the synthesis are the respective nitronaphthylamines and nitronaphthols. The syntheses of 1-methoxy-3-nitronaphthalene (**1**), 1-methoxy-5-nitronaphthalene (**2**), and 2-methoxy-5-nitronaphthalene (**3**) are reported.

Keywords. Methoxynitronaphthalenes; Nitronaphthylamines; Nitronaphthols.

Eine verbesserte Synthese für einige Methoxynitronaphthalinverbindungen

Zusammenfassung. Es wird eine verbesserte Arbeitsvorschrift für einige isomere Methoxynitronaphthaline angegeben. Die Schlüsselverbindungen dazu sind die entsprechenden Nitronaphthylamine und Nitronaphthole. Es wird die Synthese von 1-Methoxy-3-nitronaphthalin (**1**), 1-Methoxy-5-nitronaphthalin (**2**) und 2-Methoxy-5-nitronaphthalin (**3**) beschrieben.

Introduction

For a number of years, we have been interested in studies of excited-state physical properties of aromatic and heteroaromatic compounds and their photochemical reactivity. In the latter area, photosubstitution reactions seemed especially intriguing because they represent a somewhat less popular, albeit a difficult and interesting group of photoreactions [1 – 5].

Methoxynitronaphthalenes are one of the groups of compounds we studied. We investigated their photohydrolysis in an alkaline medium which, in most cases, led to the formation of the corresponding nitronaphthols. In addition to our investigation of the photochemical behavior of methoxynitronaphthalenes, we studied their electronic absorption and phosphorescence spectra and phosphorescence life-

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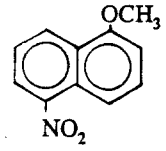
times, and we also carried out PPP (LCI-SCF-MO) calculations on these compounds [4, 6–9]. Similar studies were reported by two other groups [10–16].

More recently, we have become interested in the ground- and excited-state dipole moments of methoxynitronaphthalenes. In addition to their electronic absorption and phosphorescence spectra, we have measured their fluorescence spectra and we have worked on an improvement of the PPP calculations of these compounds, with a new set of parameters for the nitro group [17].



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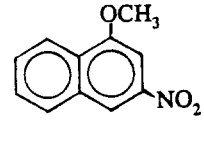

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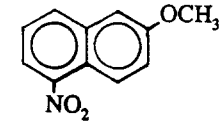

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Out of the fourteen possible isomeric methoxynitronaphthalenes, ten were experimentally studied in our, Havinga's, and Letsinger's groups.

In connection with the above work, we have modified and improved the synthetic procedures leading to 1-methoxy-3-nitronaphthalene (**1**), 1-methoxy-5-nitronaphthalene (**2**), and 2-methoxy-5-nitronaphthalene (**3**).

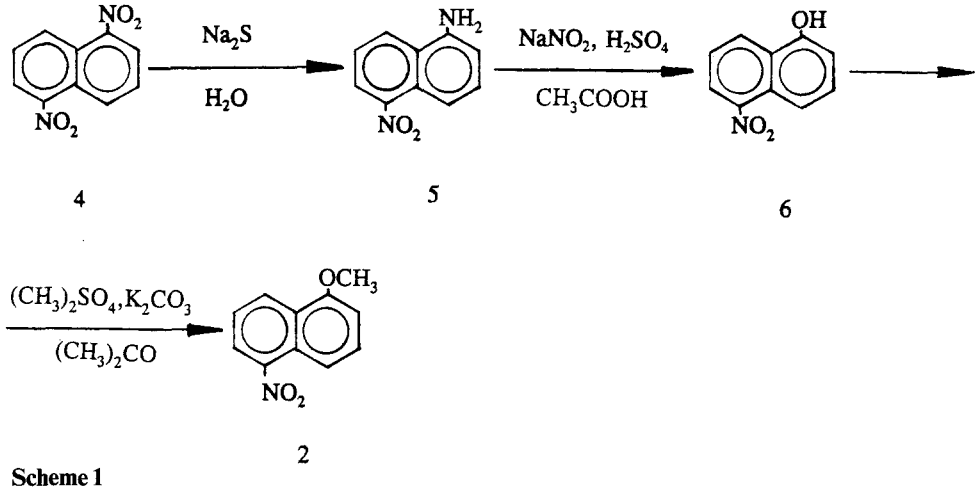
These improved syntheses are described in the present contribution. Among the remaining isomeric methoxynitronaphthalenes, 1-methoxy-4-nitronaphthalene is commercially available [18, 19] and 1-methoxy-2-nitronaphthalene and 2-methoxy-1-nitronaphthalene are readily obtained by methylation of 2-nitro-1-naphthol [18, 19] and 1-nitro-2-naphthol [20], respectively. The syntheses of these isomers, in some case using starting materials different from the commercial products described above, were reported elsewhere [6, 7], with the corresponding procedures taken from the literature. 2-Methoxy-6-nitronaphthalene was obtained as a minor product in the preparation of 2-methoxy-1-nitronaphthalene by nitration of 2-methoxynaphthalene [6].

Results and Discussion

The first synthesis of 1-methoxy-5-nitronaphthalene (**2**) was described by Fichter and Kühnel [21] by methylation of 5-nitro-1-naphthol (**6**) which was obtained by diazotization of an amino derivative [22]. However, our results indicate that the described procedure is not very satisfactory. Similarly, our attempts to synthesize 5-nitro-1-naphthylamine (**5**) by monoreduction of 1,5-dinitronaphthalene (**4**) using the procedure developed by Hodgson and Birtwell [23] yielded only traces of the desired product **5**. Equally unsatisfying were the attempts to employ the catalytic method of Veselý and Rein [24]. Partial reduction of 1,5-dinitronaphthalene (**4**) with sodium hydrogen sulfide [25] or hydrazine hydrate [26] afforded very low amounts of 5-nitro-1-naphthylamine (**5**) and an extensive purification of the product was required.

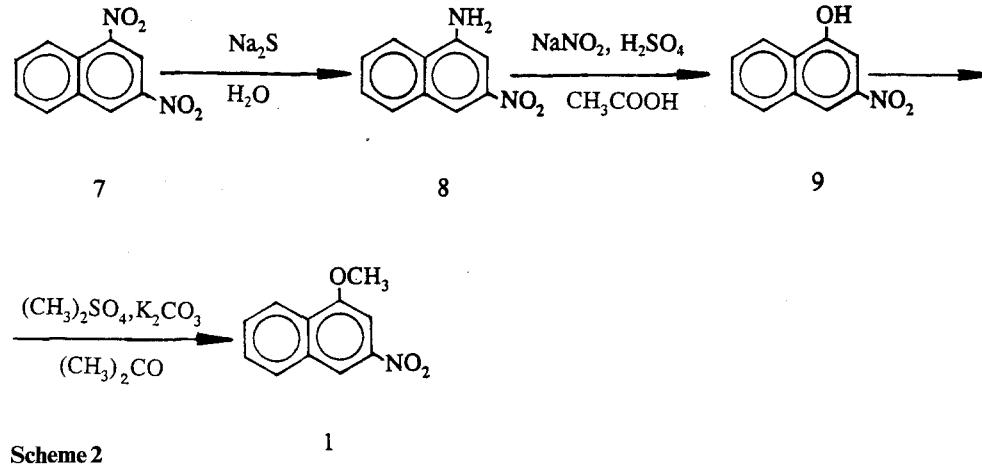
Because we have found the above procedures cumbersome and not quite adequate, we have developed a new, improved method for the synthesis of 5-nitro-1-naphthylamine (**5**) described herein. To a warm suspension of 1,5-dinitronaphthalene (**4**) in water, an aqueous solution of sodium sulfide was added dropwise and the mixture was stirred at 80°C. The precipitated reduction product, 5-nitro-

1-naphthylamine (**5**), was washed with cold water, dissolved in hydrochloric acid, and reprecipitated with ammonium hydroxide. The purified product, crystallized from a mixture of water and ethanol, formed red needles. 5-Nitro-1-naphthol (**6**) was then obtained by slow diazotization of **5** at a low temperature (below 5°C) followed by decomposition of the resulting diazonium salt in boiling sulfuric acid. Finally, methylation of 5-nitro-1-naphthol (**6**) with dimethyl sulfate in boiling acetone in the presence of potassium carbonate afforded 1-methoxy-5-nitronaphthalene (**2**) (Scheme 1).



Scheme 1

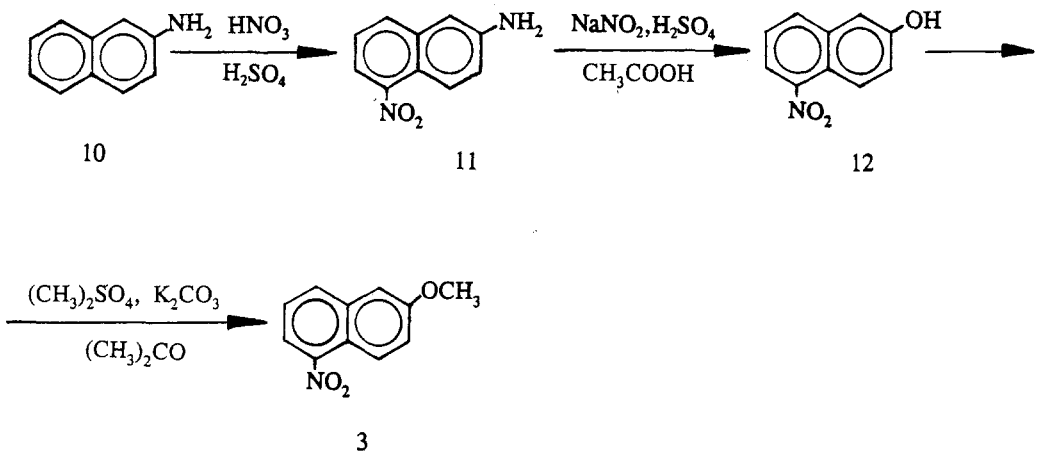
The same procedures as described above, but with 1,3-dinitronaphthalene (**7**) as the substrate, gave 3-nitro-1-naphthylamine (**8**) which was subsequently converted into 3-nitro-1-naphthol (**9**) and then into 1-methoxy-3-nitronaphthalene (**1**) (Scheme 2) . Rosenblatt, Nachlas, and Seligman reported the synthesis of 3-nitro-1-naphthol (**9**) by heating of **8** in a sealed tube in the presence of hydrochloric acid at 160 – 165°C [27].



Scheme 2

The third isomer, 2-methoxy-5-nitronaphthalene (**3**), was obtained in a similar fashion, with 2-naphthylamine (**10**) as the starting material. 2-Naphthylamine (**10**) was converted into 5-nitro-2-naphthylamine (**11**) by nitration in the presence of

urea and **11** was subsequently diazotized, the diazonium salt was decomposed in boiling sulfuric acid, and the resulting 5-nitro-2-naphthol (**12**) was methylated to 2-methoxy-5-nitronaphthalene (**3**) (Scheme 3).



10 11 12

3

Scheme 3

As shown in the Experimental Part, the three methoxynitronaphthalenes and the intermediates in their synthesis gave satisfactory elemental analyses and possessed sharp, well-defined melting points. Their ^{1}H-NMR, ^{13}C-NMR, IR, and UV-spectra were in a good agreement with their expected structures.

The ^{1}H-NMR spectra indicate the presence of an amino group in the nitronaphthylamines **5** (δ 5.5 ppm), **8** (5.8 ppm), and **11** (5.6 ppm). Similarly, the presence of a hydroxyl in the nitronaphthols is clearly indicated in their ^{1}H-NMR spectra: **6** (δ 3.6 ppm), **9** (4.1 ppm), and **12** (3.4 ppm). The methoxynitronaphthalenes contain a methyl group in the methoxy group which can be easily identified in their ^{1}H-NMR spectrum: **1** (δ 4.07 ppm), **2** (4.0 ppm), and **3** (3.92 ppm). The assignments of the chemical shifts in the ^{13}C-NMR spectra were made in the standard fashion [28, 29] and, for the methyl group carbon, they are: **1** (δ 55.6 ppm), **2** (55.5 ppm), and **3** (54.7 ppm). In the IR spectra, the hydroxyl group exhibits a strong band at 3 360 – 3 450 cm^{-1}, and the amino group shows a strong band at 3 340 – 3 400 cm^{-1} and a moderately strong band at 1 620 – 1 650 cm^{-1}.

In summary, an improved procedure for the synthesis of several isomeric methoxynitronaphthalenes has been developed. It was used to obtain 1-methoxy-3-nitronaphthalene (**1**), 1-methoxy-5-nitronaphthalene (**2**), and 2-methoxy-5-nitronaphthalene (**3**). The key steps involve monoreduction of the respective dinitronaphthalene (with the exception of the synthesis of **3**), followed by diazotization of the resulting nitronaphthylamine, thermal decomposition of the diazonium salt to a nitronaphthol, and methylation of the nitronaphthol to the desired methoxynitronaphthalene.

Experimental Part

All melting points were determined on a Mel-Temp II capillary melting point apparatus and are uncorrected. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a General Electric QE 300 (300 MHz) spectrometer. The IR spectra were measured with a Mattson Model 4020 (Galaxy) FT infrared spectrometer (intensity of the absorption: s = strong, m = medium, w = weak). The UV ab-

sorption spectra were obtained on a Varian Cary 3 UV-visible spectrophotometer. The purity of all compounds was checked by thin-layer chromatography (*TLC*) on silica gel 60-F-254 precoated plates and the spots were located in the UV light or by iodine vapor. Elemental microanalyses were carried out by Desert Analytics, Tucson, AZ. Most of the starting materials were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. Commercial reagents were used without further purification. All solvents used were reagent grade except the methanol used for spectroscopic measurements (spectrophotometric grade).

5-Nitro-1-naphthylamine (**5**)

The procedure described in the literature was modified for the monoreduction of 1,5-dinitronaphthalene (**4**). To a warm suspension of **4** (15.0 g, 69 mmol) in water (400 ml), a solution of sodium sulfide (11.0 g, 141 mmol) in water (50 ml) was added dropwise. Immediately upon the addition of sodium sulfide, the suspension became dark and turned clear when the addition had been completed. The mixture was stirred for 2.5 h at 80°C. After cooling to room temperature, the precipitated product **5** was filtered off with suction and washed three times with cold water. The solid material was extracted four times with hot 2 *N* hydrochloric acid (total, 3 l), and the extract was left to cool at room temperature. After addition of ammonium hydroxide, the basified solution was then cooled in an ice-water bath for 24 h. The cold mixture was filtered to obtain **5** (5.6 g, 43.1% yield), m.p. 114 – 116°C. Crystallization from water-ethanol (10 : 1) afforded the pure product as red needles, m.p. 117 – 118°C (lit. [30] gives 119°C). ^{1}H-NMR (acetone-d_6): δ 5.50 (s, 2 H, NH_2), 6.95, 7.46, 7.54, 7.58, 8.10, 8.45 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 108.8, 109.5, 110.4, 120.8, 121.3, 122.4, 123.6, 125.4, 127.9, 204.8 ppm; IR (potassium bromide): $\tilde{\nu}$ 3410 (m, NH_2), 3000 – 3330 (m, C=N), 1630 (m, NH_2), 1570 (m), 1520 (s, NO_2), 1510 (s), 1460 (m), 1320 (s, NO_2), 1280 (m), 780 (s). Anal. calcd. for $C_{10}H_8N_2O_2$ (188.2): C 63.83, H 4.28, N 14.89; found: C 63.95, H 4.18, N 14.79.

5-Nitro-1-naphthol (**6**)

5-Nitro-1-naphthylamine (**5**, 4.0 g, 21 mmol) was dissolved in acetic acid (20 ml). A solution of sulfuric acid (50% concd. sulfuric acid and 50% water, vol.) was added to the mixture resulting in the formation of a dark-brown paste. The mixture was diazotized with a solution of sodium nitrite prepared by dissolving sodium nitrite (5.2 g, 75 mmol) in distilled water (15 ml). Diazotization was carried out slowly in an ice-water bath (below 5°C, in the dark). After the sodium nitrite solution had been added, urea (0.2 g, 3.3 mmol) was added to the dark but clear solution. The diazotization was completed in about 4 h. The diazonium salt was decomposed by slow addition of this mixture to a stirred boiling solution of sulfuric acid (400 ml, 7%, vol.). The mixture was heated with stirring for another 30 min (some black precipitate began to form on the surface of the solution), and then the hot aqueous solution was filtered with suction. The cooled mixture gave the crude product **6** which was repeatedly extracted with boiling 5% sulfuric acid until no more **6** could be obtained from the resulting filtrate (total 3 l). The combined filtrates were cooled in an ice-water bath for 24 h, and then filtered with suction (1.2 g, 30% yield), m.p. 168 – 169°C. Crystallization from water-ethanol (10 : 1) afforded the pure product as yellow crystals, m.p. 170 – 171°C (lit. [21, 22] gives 171°C). ^{1}H-NMR (acetone-d_6): δ 3.6 (m, 1 H, OH), 7.09, 7.52, 7.58, 7.83, 8.39, 8.59 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 109.4, 112.5, 122.3, 123.6, 125.6, 125.9, 126.4, 126.9, 153.3, 205.7 ppm; IR (potassium bromide): $\tilde{\nu}$ 450 (s, OH), 1580 (s), 1500 (s, NO_2), 1330 (s, NO_2), 1250 (s), 1110 (m), 780 (s), 740 (m) cm^{-1}. Anal. calcd. for $C_{10}H_7NO_3$ (189.2): C 63.49, H 3.73, N 7.40; found: C 63.36, H 3.56, N 7.34.

1-Methoxy-5-nitronaphthalene (**2**)

Dimethyl sulfate (0.80 g, 6.3 mmol) was added to a mixture containing acetone (10 ml), anhydrous potassium carbonate (1.2 g, 8.7 mmol), and 5-nitro-1-naphthol (**6**, 0.5 g, 2.6 mmol). The mixture was refluxed for 4 h, during which time the initially red-brown dark solution became noticeably lighter.

Water (50 ml) was added and acetone was distilled off on a steam bath. The mixture containing a yellow precipitate was then cooled in an ice-water bath and the crude product was filtered off. Crystallization from water-ethanol (10 : 1) afforded the pure **2** as yellow needles (0.48 g , 90% yield), m.p. 90 – 91°C (lit. [21, 22] gives 91°C). ^{1}H-NMR (acetone-d_6): δ 4.0 (s, 3 H, OCH_3), 7.08, 7.59, 7.65, 7.87, 8.20, 8.56 ppm (m, 6 H, naphthyl); ^{13}C-NMR (acetone-d_6): δ 55.5 (OCH_3), 104.9, 110.2, 122.3, 123.8, 124.2, 127.8, 127.9, 128.4, 157.5, 204.8 ppm; IR (potassium bromide): $\tilde{\nu}$ 2900 – 3300 (w, OCH_3), 1580 (m), 1520 (s, NO_2), 1460 (m), 1330 (m, NO_2), 1270 (s), 1130 (m), 1020 (m), 780 (s), 740 (m) cm^{-1}; UV (methanol): λ_{max} (log ε): 268 (3.89), 325 (sh) (3.47), 370 nm (3.70). Anal. calcd. for $C_{11}H_9NO_3$ (203.2): C 65.02, H 4.46, N 6.90; found: C 64.87, H 4.37, N 6.89.

3-Nitro-1-naphthylamine (**8**) [31]

To a hot suspension of 1,3-dinitronaphthalene (**7**, 12.0 g, 55 mmole) in water (300 ml), a solution of crystallized sodium sulfide (10.0 g, 128 mmole) in water (50 ml) was added dropwise. The mixture became dark and turned clear later on. The solution was stirred for 3 h at 90°C and then it was left to cool to room temperature. The precipitated crude **8** was filtered off with suction and washed with cold water several times. The dark crude **8** was repeatedly extracted with hot 2 *N* hydrochloric acid (total 3 l), the combined extract was left to cool to room temperature, and was basified with ammonium hydroxide. Immediately upon the addition of ammonium hydroxide, an orange-yellow precipitate was formed. The basified solution was cooled in an ice bath for 24 h and the cold mixture was filtered to give **8** (4.5 g, 43.5% yield). Crystallization from water-ethanol (5 : 1) afforded the pure product **8** as orange-yellow needles, m. p. 135 – 136°C (lit. [32, 33] gives 136 – 137°C). ^{1}H-NMR (acetone-d_6): δ 5.84 (m, 2 H, NH_2), 7.49, 7.61, 7.67, 8.05, 8.09, 8.17 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 99.14, 106.11, 111.80, 121.87, 127.46, 130.14, 132.93, 146.06, 205.16 ppm; IR (potassium bromide): $\tilde{\nu}$ 3410 (s, NH_2), 2990 – 3340 (w-m), 1650 (m, NH_2), 1580 (m), 1530 (s, NO_2), 1500 (s), 1440 (s), 1340 (s, NO_2), 1280 (m), 870 (m), 760 (s), 690 (s) cm^{-1}. Anal. calcd. for $C_{10}H_8N_2O_2$ (188.2); C 63.83, H 4.28, N 14.89; found: C 63.78, H 4.15, N 14.68.

3-Nitro-1-naphthol (**9**)

Finely ground 3-nitro-1-naphthylamine (**8**, 2.0 g, 10.6 mmol) was dissolved in acetic acid (8 ml) and added dropwise to a stirred aqueous solution of sulfuric acid (50 ml, 50% concd. sulfuric acid and 50% water, vol.). The resulting dark-brown paste was diazotized with a solution of sodium nitrite prepared by dissolving sodium nitrite (2.5 g, 36 mmol) in distilled water (10 ml). Diazotization was carried out slowly in an ice bath (below 5°C in the dark). After the addition of sodium nitrite solution had been completed, urea (0.1 g, 1.7 mmol) was added to the dark but clear solution which was then stirred for an additional 2 h on an ice bath. The diazonium salt was decomposed by slow addition of this mixture to a stirred boiling solution of sulfuric acid (300 ml, 7%, vol.). The mixture was heated for another 30 min until a dark precipitate began to form on the surface of the boiling sulfuric acid solution. Then the hot solution was filtered under suction. Crystals of **9** began to form in the filtrate upon cooling. The mixture was left to stand overnight and the crude product was filtered off. Collected material was repeatedly extracted with boiling sulfuric acid (5%, vol.) until no more **9** could be obtained from the resulting filtrate upon cooling. The combined filtrates were cooled in an ice bath for 24 h and then filtered, giving the crude **9** (1.2 g, 60% yield). Crystallization from water-ethanol (5 : 1) afforded the pure product as yellow needles, m.p. 168 – 169°C (lit. [33, 34] gives 169 – 170°C). ^{1}H-NMR (acetone-d_6): δ 4.1 (m, 1 H, OH), 7.60, 7.67, 8.08, 8.27, 8.34 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 100.62, 115.30, 122.24, 127.33, 128.07, 129.64, 132.74, 154.13, 205.36 ppm; IR (potassium bromide): $\tilde{\nu}$ 3390 (s, OH), 1580 (s), 1510 (s, NO_2), 1330 (s, NO_2), 1250 (s), 1230 (s), 1090 (s), 790 (s), 760 (s) cm^{-1}. Anal. calcd. for $C_{10}H_7NO_3$ (189.2): C 63.49, H 3.73, N 7.40; found: C 63.56, H 3.55, N 7.38.

1-Methoxy-3-nitronaphthalene (**1**)

To a mixture of dimethyl sulfate (0.80 g, 6.3 mmol), acetone (10 ml), and anhydrous potassium carbonate (1.3 g, 9.4 mmol), 3-nitro-1-naphthol (**9**, 0.5 g, 2.6 mmol) prepared by the above procedure was added. The mixture was refluxed for 4 h on a steam bath, during which time the initially deep brown-red solution became noticeably lighter. Water (50 ml) was added, the acetone was removed on a steam bath with stirring, and additional water (50 ml) was added. A yellow precipitate was formed. The mixture was allowed to cool in an ice-water bath for 24 h and then the precipitate was filtered off with suction. The crude product was purified by crystallization from water-ethanol (5 : 1), giving yellow needles (0.47 g, 89% yield), m.p. 103 – 104°C (lit. [33, 34] gives 104 – 104.5°C). ^{1}H-NMR (acetone-d_6): δ 4.07 (s, 3 H, OCH_3), 7.47, 7.63, 7.67, 8.04, 8.16, 8.33 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 55.57 (OCH_3), 96.96, 116.37, 121.74, 127.59, 128.15, 128.77, 129.53, 132.13, 145.69, 156.02, 205.05 ppm; IR (potassium bromide): $\tilde{\nu}$ 2 850 – 3 100 (m, OCH_3), 1 590 (s), 1 530 (s, NO_2), 1 500 (s), 1 430 (s), 1 380 (s), 1 350 (s, NO_2), 1 280 (s), 1 240 (s), 1 100 (s), 890 (m), 760 (m) cm^{-1}; UV (methanol): λ_{max} (log ε): 264 (3.97), 304 (3.95), 311 (sh), (3.89), 372 (3.81) nm. Anal. calcd. for $C_{11}H_9NO_3$ (203.2): C 65.02, H 4.46, N 6.90; found: C 65.22, H 4.25, N 6.79.

5-Nitro-2-naphthylamine (**11**)

2-Naphthylamine (**10**, 30.0 g, 210 mmol) was added to a boiling solution containing water (250 ml), concentrated nitric acid (20 ml), and urea (0.6 g, 10 mmol). The resulting nitrate was filtered off and dried. The finely ground nitrate was slowly added to concentrated sulfuric acid (300 ml) while maintaining the temperature between 0 – 5°C. This mixture was then carefully poured into water (1.5 l). The solution was boiled and then filtered hot. Upon cooling the filtrate in a refrigerator for about 24 h, the sulfate was precipitated. The filtered-off sulfate was then added to a boiling solution of water (75 ml) and concentrated ammonium hydroxide (80 ml). A red solid formed which was recrystallized three times from ethanol (charcoal). The yield was 6.5 g (16.4%), m.p. 141 – 143°C (lit. [30] gives 144.5°C). ^{1}H-NMR (acetone-d_6): δ 5.6 (s, 2 H, NH_2), 7.08, 7.25, 7.42, 7.80, 7.88, 8.17 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 106.62, 118.56, 121.15, 123.3, 124.1, 131.63, 136.55, 147.48, 205.13 ppm; IR (potassium bromide): $\tilde{\nu}$ 3 430 (m, NH_2), 3 320 (m), 3 210 (m), 1 630 (s, NH_2), 1 510 (s, NO_2), 1 470 (m), 1 330 (s, NO_2), 1 250 (s), 840 (m), 790 (m), 730 (m) cm^{-1}. Anal. calcd. for $C_{10}H_8N_2O_2$ (188.2): C 63.83, H 4.28, N 14.89; found: C 63.78, H 4.15, N 15.02.

5-Nitro-2-naphthol (**12**)

Finely ground 5-nitro-2-naphthylamine (**11**, 4.0 g, 21.3 mmol) was dissolved in acetic acid (15 ml) and added dropwise to a solution of sulfuric acid (100 ml, 50% concd. sulfuric acid and 50% water, vol.) below 5°C using an ice-salt bath. The mixture was diazotized with a solution of sodium nitrite which was prepared by dissolving sodium nitrite (5.0 g, 72 mmol) in distilled water (15 ml). Diazotization was carried out slowly in an ice-salt bath (below 5°C, in the dark). When the addition of sodium nitrite solution had been completed, urea (0.2 g, 3.3 mmol) was added to the dark but clear solution and the mixture was being stirred in an ice bath for more than 1.5 h. The hydroxylation was accomplished by slow addition of this mixture, with stirring, to a boiling diluted sulfuric acid solution (400 ml, 5% concd. sulfuric acid, vol.). The hot aqueous solution was filtered with suction and the crude product **12** began to form in the filtrate upon cooling. The filtered residue was repeatedly extracted with boiling 5% sulfuric acid until no more **12** could be obtained from the resulting filtrate (total 3 l). The combined filtrates were cooled in an ice bath for 24 h, giving yellow platelets of **12** (1.3 g, 32% yield). Crystallization from water afforded the pure **12**, m.p. 148 – 149°C (lit. [30] gives 147 – 149°C). ^{1}H-NMR (acetone-d_6): δ 3.4 (m, 1 H, OH), 7.37, 7.53, 7.99, 8.02, 8.05, 8.30 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 109.65, 119.03, 120.35, 121.37, 124.26, 132.42, 136.18, 146.67, 156.10, 205.3 ppm; IR (potassium bromide): $\tilde{\nu}$ 3 360 (s, OH), 3 310 (s), 1 610 (s), 1 510 (s, NO_2), 1 460 (s), 1 390 (m), 1 330 (s, NO_2), 1 250 (s), 860 (s), 730 (s) cm^{-1}. Anal. calcd. for $C_{10}H_7NO_3$ (189.2): C 63.49, H 3.73, N 7.40; found: C 63.58, H 3.85, N 7.25.

2-Methoxy-5-nitronaphthalene (**3**)

To a mixture of dimethyl sulfate (0.80 g, 6.3 mmol), acetone (10 ml), and anhydrous potassium carbonate (1.4 g, 10 mmol), 5-nitro-2-naphthol (**12**, 0.6 g, 3.2 mmol) was added. The mixture was refluxed for 4 h on a steam bath, during which time the initially dark red-brown solution became noticeably lighter. Water (50 ml) was added, the acetone was removed on a steam bath, and more water (50 ml) was added. After 24 h in an ice bath, a golden-yellow precipitate was obtained. The product was filtered off and crystallized from water ethanol (10 : 1). Golden-yellow needles (0.60 g, 92% yield), m.p. 74 – 75°C (lit. [30] gives 74.5 – 75.5°C). ^{1}H-NMR (acetone-d_6): δ 3.92 (s, 3 H, OCH_3), 7.35, 7.44, 7.56, 8.04, 8.12, 8.32 ppm (m, 6 H, aromatic); ^{13}C-NMR (acetone-d_6): δ 54.7 (OCH_3), 106.29, 119.67, 120.81, 121.65, 123.88, 124.70, 132.95, 135.95, 158.19, 205.02 ppm; IR (potassium bromide): $\tilde{\nu}$ 2840 – 3090 (m, OCH_3), 1630 (s), 1610 (s), 1510 (s, NO_2), 1470 (s), 1325 (s, NO_2), 1270 (s), 1245 (s), 1180 (s), 1030 (s), 860 (s), 800 (s), 735 (m) cm^{-1}; UV (methanol): λ_{max} (log ε): 260 (3.13), 333 (3.07), 370 (sh) (3.49) nm. Anal. calcd. for $C_{11}H_9NO_3$ (203.2): C 65.02, H 4.46, N 6.90; found: C 64.94, H 4.28, N 6.77.

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