back to -78 °C, and then ethyl acetate (18.4 g, 0.21 mol) was added to the enolate solution over 15 min. The reaction mixture was kept at -78 °C for 10 min and at -78 to -20 °C for 0.5 h, quenched with pH 6.4 buffer (4 mL), and then concentrated in vacuo. The concentrate was diluted with ether (300 mL), washed with cold water (2 × 50 mL), filtered through $MgSO_4$, and evaporated to leave 27.1 g of faint yellow liquid, which was subjected to Kugelrohr distillation to give pure product **6b** (20.4 g, 75.8% yield), after ca. 3 g of impure forerun: bp 120 °C (0.2 mmHg) (Kugelrohr); R_t = 4.74 min; ^{1}H NMR ($CDCl_3$) 0.09 (s, 9 H), 2.33 (s, 3 H), 3.97 (s, 2 H), 7.40-7.94 (m, 5 H). Anal. Calcd for $C_{12}H_{19}N_1O_2S_1Si_1$: C, 53.49; H, 7.10. Found: C, 53.49; H, 7.06.

***S*-(2-Methoxy-2-oxoethyl)-*S*-phenyl-*N*-(trimethylsilyl)-sulfoximine (6c).** To a 100-mL, three-necked flask equipped with a magnetic stirbar and a rubber septum was added tetramethylpiperidine (3.38 g, 24 mmol) and THF (10 mL). To this mixture was added *n*-butyllithium (2.7 M in hexane, 7.4 mL, 20 mmol) at 0 °C via syringe over 3 min. The resulting solution was stirred 10 min at 0 °C and then cooled to -78 °C, and to it was added dropwise via syringe a solution of compound **5** (2.27 g, 10 mmol) in THF (5 mL). The reaction mixture was stirred at -78 °C for 10 min and at -78 to -10 °C for 0.5 h and was then recooled to -78 °C followed by addition of methyl chloroformate (2.26 g, 24 mmol) over 5 min. The yellow mixture was kept at -78 °C for 1 h and at -78 to -10 °C for 10 min, quenched with aqueous NH_4Cl (1 mL), and then concentrated in vacuo. The residue was taken up in ether (100 mL), washed with cold water (2 × 15 mL) and brine (1 × 20 mL) filtered through $MgSO_4$, and evaporated to leave 3.70 g of crude compound. Kugelrohr distillation of the crude product gave pure **6c** (2.08 g, 80.0% yield) after ca. 1.5 g of impure forerun: bp 130 °C (0.1 mmHg) (Kugelrohr); R_t = 5.17 min; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 3.67 (s, 3 H), 4.00 (s, 2 H), 7.61 (m, 3 H), 8.00 (m, 2 H); IR (NaCl, film) 1760 cm^{-1}. Anal. Calcd for $C_{12}H_{19}N_1O_3S_1Si_1$: C, 50.49; H, 6.70. Found: C, 51.16; H, 6.70. Inverse addition of the anion of **5** to a solution of methyl chloroformate gave the same result as reported here.

3-[*S*-Phenyl-*N*-(trimethylsilyl)sulfonimidoyl]-1-propanol (6d). The procedure is described in the preparation of **7d**.

1-(*S*-Phenylsulfonimidoyl)-2-propanone (7b). A solution of compound **6b** (9.6 g, 35.5 mmol) in methanol/water (10:1, 15 mL) was treated with cesium fluoride (0.5 g, 3.3 mmol) at 25 °C. The reaction mixture was heated at ca. 50 °C for 10 min. GC and TLC analysis after 10 min indicated reaction was complete. The reaction mixture was concentrated in vacuo, taken up in ethyl acetate (50 mL), and washed with water (1 × 20 mL). The water wash was extracted with CH_2Cl_2 (5 × 10 mL). The CH_2Cl_2 extracts were combined with the ethyl acetate solution, and the resulting mixture was dried ($MgSO_4$) and evaporated in vacuo to give crude product (7.2 g). Purification by flash column chromatography eluting with 60% EtOAc/hexane gave **7b** (6.9 g, 98.5% yield) as pale yellow liquid: R_t = 4.52 min; R_f (60% EtOAc/hexane) 0.33; ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 2.80 (br, 1 H), 4.09 (s, 2 H), 7.50-8.03 (m, 5 H). Anal. Calcd for $C_9H_{11}S_1N_1O_2$: C, 54.80; H, 5.62. Found: C, 54.70; H, 5.63.

(Phenylsulfonimidoyl)acetic Acid, Methyl Ester (7c). From the same procedure as for **7b**, **7c** was obtained in quantitative yield: R_t = 5.04 min; R_f (60% EtOAc/hexane) 0.40; ^{1}H NMR ($CDCl_3$) δ 3.47 (m, 1 H), 3.67 (s, 3 H), 4.15 (s, 2 H), 7.50-8.12 (m, 5 H). Anal. Calcd for $C_9H_{11}N_1O_2S_1$: C, 50.68; H, 5.20. Found: C, 49.65; H, 5.38.

3-(*S*-Phenylsulfonimidoyl)-1-propanol (7d). To a solution of **5** (22.7 g, 0.10 mol) in THF (100 mL) was added *n*-butyllithium (2.58 M in hexane, 29.5 mL, 0.10 mol) over a 5 min at -78 °C under argon atmosphere. The reaction mixture was stirred at -78 to -20 °C for 15 min and at 0 °C for 20 min and recooled to -78 °C. Ethylene oxide (4.84 g, 0.11 mol), dried over sodium hydride, was bubbled through the reaction mixture, which was then allowed to warm to 20 °C. After stirring for 0.5 h at 20 °C, the reaction mixture was quenched with saturated NH_4Cl solution (3 mL), concentrated in vacuo, diluted with ether (200 mL), and washed with cold water (2 × 30 mL). The aqueous washings were further extracted with ether (1 × 20 mL). The combined ether solution was dried ($MgSO_4$) and evaporated to afford **6d** (30.0 g) as a colorless liquid, R_t = 6.51 min. Without purification, compound **6d** was desilylated by the same procedure as described for the preparation of **7b**. Purification of the crude product by flash column chromatography, eluting with ethyl acetate, gave free sulfoximine **7d** (14.8 g, 74.4% overall yield) as a white powder: mp 61.0-61.5 °C; R_t = 6.01 min; R_f (EtOAc) 0.21; ^{1}H NMR ($CDCl_3$) δ 1.96 (m, 2 H), 3.24 (br t, 4 H, including OH and =NH), 3.67 (t, J = 7.0 Hz, 2 H), 7.67 (m, 3 H), 7.94 (m, 2 H). Anal. Calcd for $Cl9H_{13}N_1O_2Si$: C, 54.24; H, 6.58. Found: C, 54.19; H, 6.62.

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Registry No. **4**, 4381-25-3; **5**, 89902-44-3; **6a**, 99531-75-6; **6b**, 99531-76-7; **6c**, 99531-77-8; **6d**, 99531-78-9; **7b**, 99531-79-0; **7c**, 99531-80-3; **7d**, 99531-81-4; bromoacetaldehyde dimethyl acetal, 7252-83-7; ethyl acetate, 141-78-6; methyl chloroformate, 79-22-1; ethylene oxide, 75-21-8.

Unusual "Hydrolysis" of 2-Nitrosopyridines: Formation of 1-(2-Pyridyl)-2(1*H*)-pyridones[1]

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We have recently described[2] a simple procedure for the conversion of primary heterocyclic (and aromatic) amino groups to nitroso groups by *m*-chloroperbenzoic acid oxidation of intermediate *S*,*S*-dimethylsulfilimines. During an investigation of the chemistry of these new nitroso-substituted heterocycles, it was observed that 2-nitrosopyridine (**1a**) and its 3-(**1b**) and 4-methyl (**1c**) derivatives were irreversibly transformed into new, colorless compounds in high yield upon heating with water. We describe in this paper the structures of these hydrolysis products and comment upon their possible mechanism of formation.

Stirring a suspension of powdered 2-nitrosopyridine (**1a**) in water at room temperature resulted in gradual dissolution and a change in the color of the solution from pale green to light yellow. TLC showed that the starting 2-nitrosopyridine had been completely consumed and that only one major product had been formed. The aqueous solution was extracted with methylene chloride, and the extracts were dried and evaporated to give a colorless crystalline solid, mp 55.5-56 °C, which was shown by microanalysis and by mass spectroscopy to have the empirical formula $C_{10}H_8N_2O$. The product contained one carbonyl group (IR 1667 cm^{-1}), which was confirmed by its ^{13}C NMR spectrum (see the Experimental Section). This compound was positively identified as 1-(2-pyridyl)-2(1*H*)-pyridone (**2a**) by comparison with an authentic sample prepared by the reaction of 2-pyridone with 2-bromopyridine in the presence of copper.[3]

Since the conversion of **1a** to **2a** by stirring in water accelerated with time, and the aqueous reaction solution became acidic over time, it was apparent that the reaction was probably acid catalyzed. This was confirmed by the observation that addition of one drop of concentrated sulfuric acid to a 25% dioxane/water solution of **1a** led to complete conversion to **2a** within $2^1/_2$ h; this contrasts with the 27-30 h required, in the same solvent mixture, in the absence of added acid. No reaction whatsoever took

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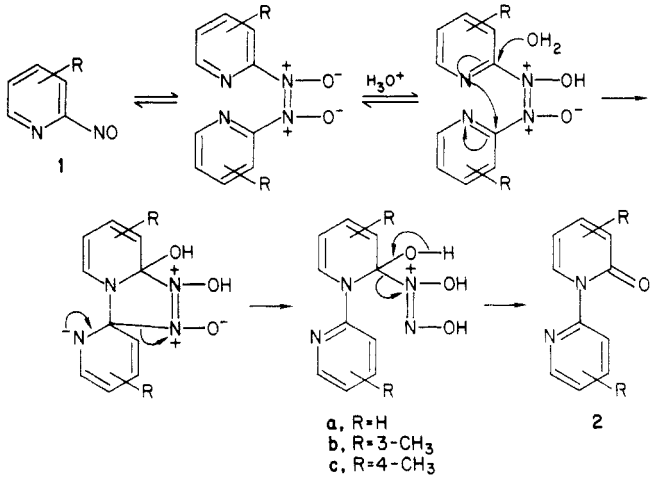
Scheme I



place upon stirring **1a** in 25% dioxane/aqueous phosphate buffer (pH 7.5–8.0) for 7 days; under these conditions, unchanged starting material was recovered in 80% yield.

Analogous transformations of 3-methyl-2-nitrosopyridine (**1b**) and 4-methyl-2-nitrosopyridine (**1c**) to **2b** and **2c**, respectively, proceeded more slowly. For example, no reaction was observed upon stirring aqueous suspensions of **1b** and **1c** in water for 15 days at room temperature. However, refluxing of these aqueous suspensions resulted in slow dissolution and the formation of the 1-(2-pyridyl)-2(1*H*)-pyridones **2b** and **2c**, respectively. In the latter case a small amount of 4-methyl-2(1*H*)-pyridone was also isolated. Once again, the rate of transformation of these methyl-substituted 2-nitrosopyridines to **2b,c** was markedly enhanced by acid. Thus, the addition of one drop of concentrated sulfuric acid to an aqueous solution of the above 2-nitrosopyridines at room temperature resulted in the formation of **2b** and **2c**, respectively, in excellent yield within a matter of 1–2 h.

We suggest that these dimeric "hydrolysis" products are formed by ipso attack of water at the 2-position of the nitrosopyridine dimers[4] as depicted in Scheme I. The electrophilicity of C-2 in these dimers would clearly be enhanced by protonation (presumably on oxygen). 4-Methyl-2(1*H*)-pyridone presumably arises by direct hydrolysis of the monomer **2c**. A possible alternative mechanism for the formation of **2a–c** involving hydrolysis of some of the monomeric 2-nitrosopyridine to the corresponding 2(1*H*)-pyridone, followed by nucleophilic addition of the oxygen of an unchanged molecule of the 2-nitrosopyridine to the lactam carbonyl of the 2(1*H*)-pyridone, was eliminated by the observation that an aqueous acidic solution of a mixture of 2(1*H*)-pyridone and 4-methyl-2-nitrosopyridine gave only **2c**; no trace of a mixed pyridylpyridone could be detected.

Experimental Section

1-(2-Pyridyl)-2(1*H*)-pyridone (2a). A suspension of 0.245 g of recrystallized and powdered 2-nitrosopyridine[2] in 25 mL of water was stirred at room temperature. As the solid slowly dissolved, the solution became first pale green and then yellow. The course of the reaction was monitored by TLC (10% methanol/chloroform); all starting material had disappeared after 8 h of stirring at room temperature. The reaction mixture was extracted with methylene chloride, the extracts were dried ($MgSO_4$) and evaporated, and the residual thick gum was dissolved in ether/petroleum ether (1:1) and passed over silica gel. Evaporation of the eluate gave 0.13 g (66%) of 1-(2-pyridyl)-2-(1*H*)-pyridone. The product can be readily purified either by sublimation (51 °C (0.2 mm)) or by rapid column chromatography on silica gel with 1:1 petroleum ether/ether, followed by recrystallization from petroleum ether: white needles, mp 55.5–56 °C (lit.[3] mp 55–56 °C); IR ($CHCl_3$) 1667, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.30 (t, 1 H), 6.65 (d, 1 H), 7.35 (m, 2 H), 7.90 (m, 3 H), 8.59 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 162.1, 151.9, 148.9, 140.2, 137.7, 136.1, 123.1, 122.0, 121.4, 106.2. Anal. Calcd for $C_{10}H_8N_2O$: C, 69.76; H, 4.68; N, 16.27. Found: C, 69.55; H, 4.48; N, 16.00.

Hydrolysis of **1a** in water at 62 °C was complete after 2 h (69%), in 25% aqueous dioxane at room temperature after 30 h (79%), and in 25% aqueous dioxane at room temperature with one drop of concentrated sulfuric acid added, after $2^1/_2$ h (72%).

3-Methyl-2-nitrosopyridine (1b). To a cold (0 °C) solution of 13.67 g (0.0794 mol, 80–90%) of *m*-chloroperbenzoic acid in 200 mL of dry methylene chloride was added, all at once, a solution of 7.8 g (0.0464 mol) of *S,S*-dimethyl-*N*-(3-methyl-2-pyridyl)-sulfilimine[5] in 75 mL of methylene chloride. The reaction mixture was stirred at 0–5 °C for 90 min, and then 3 mL of dimethyl sulfide was added. Stirring was continued for an additional 30 min and 300 mL of saturated sodium carbonate added. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated to give a yellow solid that was recrystallized from methanol; yield 3.0 g (55%); mp 169–170 °C; ^1H NMR ($CDCl_3$) δ 2.55 (s, 3 H), 7.12, 7.20 (dd, J = 4, 8 Hz, 1 H), 7.65 (d, J = 8 Hz, 1 H), 7.90 (d, J = 4 Hz, 1 H). Anal. Calcd for $C_6H_6N_2O$: C, 59.00; H, 4.91; N, 22.95. Found: C, 58.94; H, 4.89; N, 22.96.

1-(3-Methyl-2-pyridyl)-3-methyl-2(1*H*)-pyridone (2b) was prepared by refluxing 0.2 g of 3-methyl-2-nitrosopyridine in 10 mL of water for 6 h, followed by work-up as described above; yield 55%; mp 87–89 °C (from hexane); IR (KBr) 1645, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (s, 3 H), 2.20 (s, 3 H), 6.18 (m, 1 H), 7.26 (m, 3 H), 7.66 (d, J = 6.5 Hz, 1 H), 8.39 (d, J = 3.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 162.0, 152.7, 146.9, 139.8, 137.3, 134.1, 131.0, 130.6, 124.2, 105.7, 17.3, 17.0. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.98. Found: C, 71.81; H, 6.09; N, 13.81.

1-(4-Methyl-2-pyridyl)-4-methyl-2(1*H*)-pyridone (2c) was prepared analogously by aqueous hydrolysis of 4-methyl-2-nitrosopyridine;[2] yield 46% of light cream-colored crystals; mp 87–88 °C (from hexane); IR (KBr) 1660, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 2.43 (s, 3 H), 6.15 (d, J = 8 Hz, 1 H), 6.48 (s, 1 H), 7.12 (d, J = 5 Hz, 1 H), 7.75 (m, 2 H), 8.43 (d, J = 5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 162.1, 152.0, 151.8, 149.1, 148.4, 135.1, 124.1, 121.9, 120.0, 108.8, 21.2, 21.1. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.98. Found: C, 71.98; H, 6.01; N, 13.86.

Further elution of the silica gel column with ether/methanol (10:1) gave a small amount (10%) of 4-methyl-2(1*H*)-pyridone, mp 126–128 °C (lit.[6] mp 130 °C).

Registry No. **1a**, 79917-37-6; **1b**, 99548-31-9; **1c**, 79917-38-7; **2a**, 3480-65-7; **2b**, 99548-29-5; **2c**, 99548-30-8; *S,S*-dimethyl-*N*-(3-methyl-2-pyridyl)sulfilimine, 62135-45-9.

(4) The observation that the rate of hydrolysis decreases markedly with decreasing polarity of the aqueous medium (i.e., upon addition of dioxane) supports the suggestion that the nitroso dimer is the reacting species.

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Preparation of *N*-(2-Naphthyl)-2-amino Acids and Esters of High Enantiomeric Purity

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Enantiomers of *N*-(2-naphthyl)-2-amino esters and amides show an unusually high degree of chiral recognition when chromatographed on chiral stationary phases (CSPs) derived from *N*-(3,5-dinitrobenzoyl)-2-amino acids.[1] As

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