Novel Pyranopyridine Derivatives from an Enaminone

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Received June 7, 1994

The pyranopyridine derivatives **2** and **15B** were synthesized from enaminone **1** and hydroxylamine in the presence of 2*N* and 1*N* aqueous sodium hydroxide solutions, and consecutive reactions with these compounds are described.

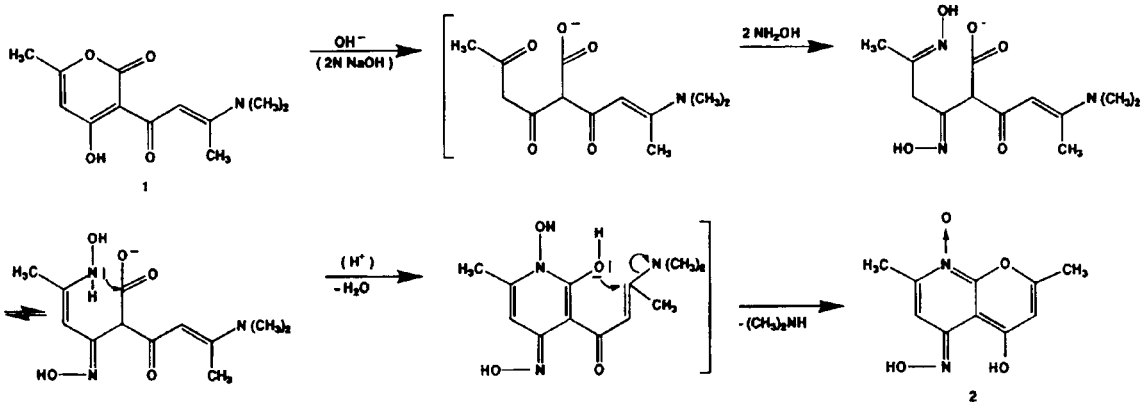
J. Heterocyclic Chem., **31**, 1577 (1994).

Enaminone **1** [1], easily prepared from dehydroacetic acid and *N,N*-dimethylacetamide acetal by an improved method [2], was found to be a suitable reagent, in particular to prepare novel heterocyclic systems. Two structural elements of the enaminone **1**, namely its lactone ring and its enaminone function, play a decisive role in these reactions.

First, the enaminone **1** was dissolved in 2*N* sodium hydroxide solution, and an aqueous solution of hydroxylamine hydrochloride was added. After this solution had been acidified, the *E*-oxime of the pyranopyridine **2** was preferentially isolated [1,3].

Alkaline opening of the lactone ring of the enaminone **1** occurs in the course of this reaction. Next, two molecules of hydroxylamine react with the two carbonyl groups of the open lactone ring to form dioxime. After acidification the 1,4-dihydropyridine ring closes under elimination of water, followed by closure of the pyran ring after elimination of dimethylamine (Scheme 1).

Scheme 1



The pyranopyridine **2** can be alkylated with an excess of methyl iodide. Basically only two compounds, the bisalkyl products **3** and **4**, can be formed (Scheme 2). The argument for the compound **4** as compared to compound **2** is that its H-3 proton exhibits a downfield shift from δ = 5.87 to 6.36 ppm in the ^{1}H-nmr spectrum. The resonance signal of the C-2 methyl protons of **4** is also shifted downfield by 0.2 ppm to 2.46 ppm. The two methoxy signals appear at 3.90 and 3.97 ppm. A marked carbonyl stretching vibration occurs at 1660 cm^{-1} in the ir spectrum, which can be attributed to a 4-pyrone. However, this is overshadowed by a C=N stretching vibration, which appears as a broad band. The absence of the usual marked *N*-oxide absorption at 1190 cm^{-1} is an additional argument for the presence of the bisalkyl product **4**.

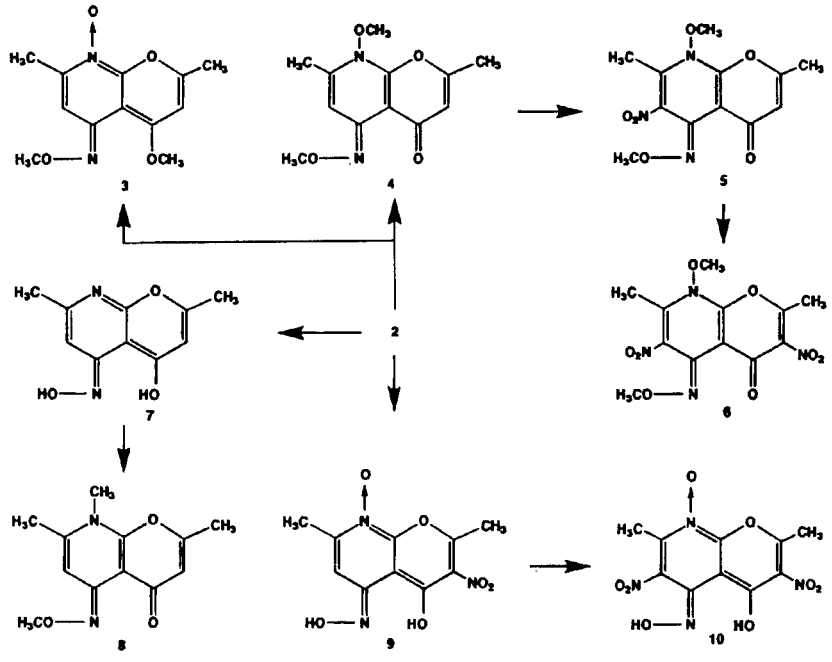
Using triethylphosphite, the pyranopyridine **2** can be deoxygenated to pyranopyridine **7**. The structure of compound **7** is substantiated by the absence of *N*-oxide bands in the ir spectrum. Furthermore, the values of 5.84 and 6.64 ppm for the H-3 and the H-6 protons in ^{1}H-nmr spectrum, respectively, are comparable to those of the compound **2**.

Reacting the deoxygenated compound **7** with an excess of methyl iodide gives the bisalkylation product **8**, assuming double alkylation occurs. The four methyl resonance signals at 2.26, 2.42, and 3.85 ppm (6H) in the ^{1}H-nmr spectrum (which correlate well with those of the compound **4**) prove the presence of the compound **8**.

Nitration of pyranopyridine **2** is also interesting. With this *N*-oxide, mononitration first occurs in the pyran ring to produce the compound **9**, which undergoes a second nitration in the pyridine part to form the bisnitro product **10**.

In the case of the bisalkyl product **4**, a 6-nitro compound **5** is first formed due to the enamine structure in the

Scheme 2



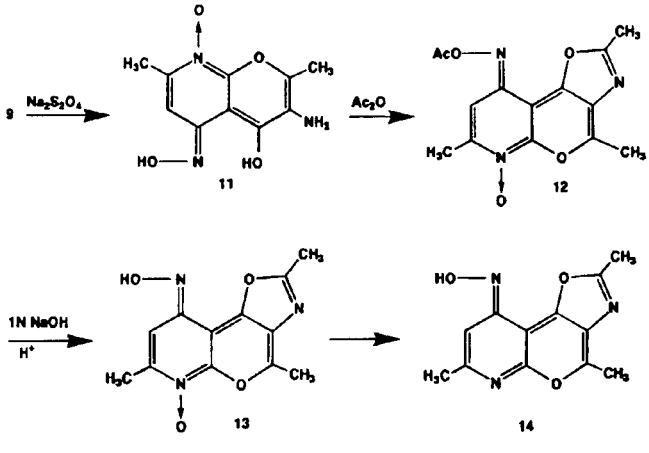
pyridine ring. This can then be converted to the bisnitro compound **6** under different reaction conditions.

The structure of the mononitro product **9** is proven by the disappearance of the H-3 signal in the ^{1}H-nmr spectrum, which appears at 5.87 ppm in the compound **2**. The H-6 proton appears at 6.62 ppm. In the case of the mononitro compound **5**, the H-6 signal that occurs at 6.62 ppm in the compound **4** does not occur. The H-3 proton now appears at $\delta = 6.49$ ppm.

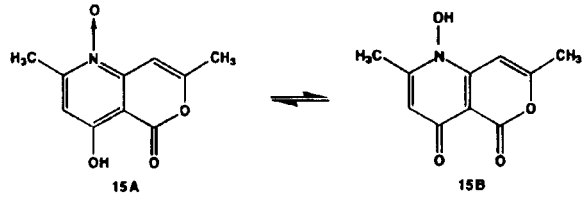
Using sodium dithionite, the nitro compound **9** can be reduced to form the amine **11**. With the help of its 4-hydroxyl group, the compound **11** can then be cyclized with acetic anhydride to form annelated oxazole **12**. In the process, the oxime group is also converted to an oxime ester. Using 1*N* sodium hydroxide solution, the compound can be hydrolyzed to oxime **13**. Lastly, the *N*-oxide group of the compound **13** is deoxygenated to the tricyclus **14** (Scheme 3).

Recrystallization of the compound **14** with *N,N*-dimethylformamide, dimethyl sulfoxide and glacial acetic acid produced violet fluorescence of the entire solution. This characteristic is even more pronounced in thin-layer chromatograms. At higher wavelengths (360 nm), the compound **14** fluoresces bright blue. At shorter wavelengths, a brilliant bright blue fluorescence can be observed.

Scheme 3



Scheme 4

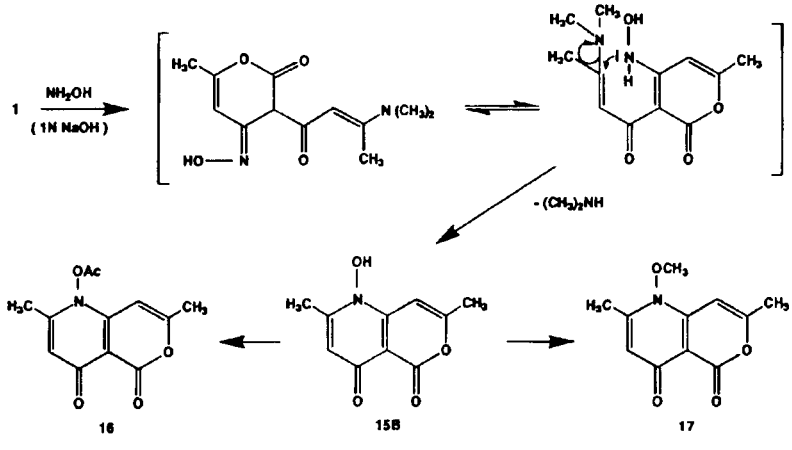


After it had been shown that one can obtain the bicycle **2** by reacting the enaminone **1** with hydroxylamine in the presence of 2*N* sodium hydroxide solution, we wanted to determine how such a corresponding conversion of the compound **1** in the presence of 1*N* sodium hydroxide solution would proceed. Our elemental analyses and mass spectrum studies revealed that, after acidification, a substance containing only a single nitrogen atom was formed. In view of these results, one would expect that

the resulting compound has one of the following structures (**15A** ⇌ **15B**) (Scheme 4).

The lactone band that occurs at 1710 cm^{-1} in the ir spectrum is a striking finding. Another carbonyl stretching vibration occurs at 1650 cm^{-1}. In the ^{1}H-nmr spectrum the signals for the H-3 and H-8 protons occurred at 6.57 and 6.20 ppm, respectively. The characteristic M-16 fragment for *N*-oxides was absent in the mass spectrum. These findings are indicative of the presence of the structure **15B**. In order for the compound **15B** to be produced by the enaminone **1**, the lactone ring must remain closed in the 1*N* sodium hydroxide solution. The reaction occurs only after the aqueous hydroxylamine hydrochloride solution has been added. The hydroxylamine reacts with the 4-carbonyl group of the compound **1**, thereby producing an oxime that is at tautomeric equilibrium with the hydroxylamine group. Next, the hydroxylamine group adds to the enamine double bond. After elimination of a dimethylamine molecule, the new heterocycle **15B** is formed (Scheme 5).

Scheme 5



The compound **15B** can be alkylated with methyl iodide. The exclusive product of this reaction is the ether **17**, the structure of which was confirmed by spectral comparison with **15B**. Acylation of the compound **15B** by reacting it with acetic anhydride is also attributable to the hydroxylamine group. This is supported by the fact that, in addition to the lactone bands at 1730 cm^{-1}, an additional carbonyl band appears at 1760 cm^{-1} in the ir spectrum of compound **16**. This absorption pattern is characteristic of hydroxylamine-*O*-esters.

EXPERIMENTAL

4-Hydroxy-6-methyl-3-(3-dimethylaminocrotonyl)-2*H*-pyran-2-one (**1**).

A solution of dehydroacetic acid (1.65 g, 10 mmoles) and *N,N*-dimethylacetamide dimethyl-acetal (1.46 g, 11 mmoles) in dry xylole (60 ml) was refluxed for 15 minutes. The solid obtained upon cooling was recrystallized from ethanol to yield **1** (1.7 g, 72%) as yellow crystals, mp 170°, lit [1] 171°.

4-Hydroxy-5-oximino-2,7-dimethyl-5*H*-pyrano[2,3-*b*]pyridine 8-Oxide (**2**).

A solution of **1** (2.37 g, 10 mmoles) and hydroxylamine hydrochloride (2.5 g) in 2*N* aqueous sodium hydroxide (80 ml) was stirred at room temperature for 12 hours. The reaction mixture was acidified using 2*N* aqueous hydrochloric acid. The solid separated was filtered, washed with water, dried and recrystallized from ethanol to yield **2** (1.85 g, 83%) as colorless crystals, mp 230°, lit [1] 229°.

5,8-Dihydro-5-methoximino-8-methoxy-2,7-dimethyl-4*H*-pyrano-[2,3-*b*]pyridin-4-one (**4**).

To a well stirred solution of **2** (0.5 g, 2.25 mmoles) in dry *N,N*-dimethylformamide (20 ml) was added potassium carbonate (1.0 g) and methyl iodide (0.5 ml) at room temperature. Stirring was continued for an additional 4 hours. After removal of the insoluble material by filtration, the filtrate was concentrated under reduced pressure to a volume of about 10 ml. Thereafter the filtrate was treated with aqueous sodium thiosulfate solution (0.6 g/100 ml) and the solid obtained was collected by filtration and recrystallized from ethanol and petroleum benzine (1:1) to give 0.32 g (57%) of **4** as colorless needles, mp 105°; ir (potassium bromide): ν 1660 cm^{-1}; ms: m/z 250 (M^+); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.25 (s, 3H, 6-CH_3), 2.46 (s, 3H, 2-CH_3), 3.90 (s, 3H, O-CH_3), 3.97 (s, 3H, O-CH_3), 6.36 (s, 1H, H-3), 6.62 (s, 1H, H-6).

Anal. Calcd. for $C_{12}H_{14}N_2O_4$: C, 57.53; H, 5.64; N, 11.18. Found: C, 57.42; H, 5.60; N, 11.30.

5,8-Dihydro-5-methoxmino-8-methoxy-2,7-dimethyl-6-nitro-4*H*-pyrano[2,3-*b*]-pyridin-4-one (**5**).

A solution of **4** (0.15 g, 0.6 mmoles) in a mixture of glacial acetic acid (2 ml) and 100% nitric acid (10 drops) was refluxed for 5 minutes. The mixture was poured into ice-water (50 ml) to give a yellow solid, which on recrystallization from ethanol and petroleum benzine (1:1) afforded the pure yellow crystalline material (0.12 g, 58%) of **5**, mp 178° dec; ir (potassium bromide): ν 1655 , 1510, 1360 cm^{-1}; ms: m/z 295 (M^+); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.50 (s, 6H, 7-CH_3, 2-CH_3), 3.91 (s,

3H, H_3C-O-N-), 3.97 (s, 3H, CH_3, oxime ether), 6.49 (s, 1H, H-3); ^{13}C-nmr (dimethyl sulfoxide-d_6): δ 10.98 (7-CH_3), 17.35 (2-CH_3), 57.22 (CH_3, oxime ether), 63.71 (H_3C-O-N-), 93.18 (C-3), 96.86 (C-4a), 130.79 (C-6), 152.08 (C-2), 155.21 (C-8a), 155.37 (C-7), 164.11 (C-4), 165.82 (C-5).

Anal. Calcd. for $C_{12}H_{13}N_3O_6$: C, 48.76; H, 4.44; N, 14.22. Found: C, 48.53; H, 4.35; N, 14.27.

5,8-Dihydro-5-methoximino-8-methoxy-2,7-dimethyl-3,6-dinitro-4*H*-pyrano[2,3-*b*]pyridine-4-one (**6**).

A solution of **4** (0.15 g , 0.6 mmole) in a mixture of glacial acetic acid (2 ml) and 100% nitric acid (1 ml) was refluxed for 5 minutes. The mixture was poured into ice-water to give a pale yellow solid. Recrystallization of this solid from ethanol and petroleum ether afforded pale yellow crystals (0.12 g, 62%) of **6**, mp 202° dec; ir (potassium bromide): ν 2940, 1660, 1520, 1525, 1355, 1365 cm^{-1}; ms: m/z 340 (M$^+$); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.57 (s, 3H, 7-CH_3), 2.60 (s, 3H, 2-CH_3), 3.71 (s, 3H, CH_3, oxime ether), 4.05 (s, 3H, H_3C-O-N-).

Anal. Calcd. for $C_{12}H_{12}N_4O_8$: C, 42.31; H, 3.56; N, 16.45. Found: C, 42.50; H, 3.48; N, 16.42.

2,7-Dimethyl-4-hydroxy-5-oximo-5*H*-pyrano[2,3-*b*]pyridine (**7**).

A well stirred solution of **2** (0.3 g, 1.35 mmoles) in triethyl phosphite (50 ml) was refluxed for 3 hours. Upon cooling the reaction mixture was concentrated *in vacuo*. The residue was treated with water (100 ml) and allowed to stand at room temperature for 5 days. The solid obtained was filtered, dried and recrystallized from *N,N*-dimethylformamide and ethanol (1:1) to give **7** (0.066 g, 24%) as colorless crystals, mp 290° dec; ir (potassium bromide): ν 3300, 1630, 1610 cm^{-1}; ms: m/z 206 (M$^+$);^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.14 (s, 3H, 2-CH_3), 2.22 (s, 3H, 7-CH_3), 5.84 (s, 1H, H-3), 6.64 (s, 1H, H-6), 11.19 (s, 1H, =NOH, exchangeable), 11.43 (s, 1H, OH, exchangeable).

Anal. Calcd. for $C_{10}H_{10}N_2O_3$: C, 58.19; H, 4.90; N, 13.57. Found: C, 57.91; H, 5.00; N, 13.50.

5,8-Dihydro-2,7,8-trimethyl-5-methoximino-8-methyl-4*H*-pyrano-[2,3-*b*]pyridin-4-one (**8**).

A solution of **7** (0.2 g, 0.96 mmole) in dry *N,N*-dimethylformamide (40 ml) was treated with methyl iodide (0.5 ml) in the presence of potassium carbonate (1 g) and the mixture was heated under reflux for 6 hours. Thereafter potassium carbonate was filtered off, the solid was washed with with *N,N*-dimethylformamide (20 ml) and the combined solutions were concentrated under reduced pressure to a small volume (about 20 ml). The dark solution was extracted with ether (3 x 10 ml). The combined organic phases were washed with 10% sodium bicarbonate solution (20 ml) and evaporated under reduced pressure to give the crude dialkyl derivative **8** (0.086 g, 38%) as colorless, analytical pure crystals, mp 78°; ir (potassium bromide): ν 2980, 2900, 1650 cm^{-1}; ms: m/z 234 (M$^+$); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.26 (s, 3H, 7-CH_3), 2.42 (s, 3H, 2-CH_3), 3.85 (s, 6H, O-CH_3, N-CH_3), 6.47 (s, 1H, H-3), 6.82 (s, 1H, H-6).

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.48; H, 6.03; N, 11.96. Found: C, 61.55; H, 6.31; N, 11.10.

4-Hydroxy-2,7-dimethyl-3-nitro-5-oximino-5*H*-pyrano[2,3-*b*]-pyridine 8-Oxide (**9**).

To a stirred suspension of **2** (1.0 g, 4.5 mmoles) in glacial acetic acid was added a mixture of 100% nitric acid and glacial acetic acid (5/45, 5 ml). Stirring was continued only for 1 minute. Thereafter the reaction mixture was poured onto ice water (50 ml). The insoluble solid which separated was filtered, washed with water and dried. Recrystallization from ethanol yielded **9** (1.06 g, 83%) as pale yellow needles, mp 239° dec; ir (potassium bromide): ν 3440-2600, 1645, 1520, 1335 cm^{-1}; ms: m/z 267 (M$^+$); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.25 (s, 3H, 7-CH_3), 2.43 (s, 3H, 2-CH_3), 6.62 (s, 1H, H-6).

Anal. Calcd. for $C_{10}H_9N_3O_6$: C, 44.91; H, 3.39; N, 15.71. Found: C, 45.11; H, 3.30; N, 15.77.

4-Hydroxy-2,7-dimethyl-3,6-dinitro-5-oximino-5*H*-pyrano[2,3-*b*]-pyridine 8-Oxide (**10**).

Compound **10** was prepared by the method described for **9**. The only difference is heating of the reaction mixture for 2 minutes. The solid obtained was recrystallized from ethanol to yield **10** (1.1 g, 79%) as pale yellow crystals, mp 176-178° dec; ir (potassium bromide): ν 1655, 1510, 1370, 1360 cm^{-1}; ms: m/z 312 (M$^+$); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.46 (s, 3H, 2-CH_3), 2.54 (s, 3H, 7-CH_3), 5.0-6.5 (br, s, 2 OH).

Anal. Calcd. for $C_{10}H_8N_4O_8$: C, 38.43; H, 2.58; N, 17.93. Found: C, 38.70; H, 2.42; N, 18.00.

3-Amino-4-hydroxy-2,7-dimethyl-5-oximino-5*H*-pyrano[2,3-*b*]-pyridine 8-Oxide (**11**).

To a well stirred suspension of **9** (1.0 g, 3.74 mmoles) in water (20 ml) was added a mixture of sodium dithionite (5.0 g) in water (20 ml) and the resulting mixture was stirred for additional 2 hours. The solids were collected by filtration, washed sequentially with water and ethanol and dried to give **11** (0.75 g, 84%) as beige, analytically pure crystals, mp >340° dec; ir (potassium bromide): ν 3340, 3220, 1655 cm^{-1}; ms: m/z 237 (M$^+$); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.26 (s, 3H, 7-CH_3), 2.31 (s, 3H, 2-CH_3), 6.71 (s, 1H, H-6), 4.4-5.9 (br, 2 OH).

Anal. Calcd. for $C_{10}H_{11}N_3O_4$: C, 50.61; H, 4.67; N, 17.71. Found: C, 50.45; H, 4.63; N, 17.55.

Acetyl Derivative of 9-Hydroximino-2,4,7-trimethyl-9*H*-pyridino[2,3-*b*]-pyrano[3,4-*d*]oxazole 6-Oxide (**12**).

A stirred mixture of **11** (0.5 g, 2.11 mmoles), acetic anhydride (30 ml) and acetyl chloride (30 ml) was heated under reflux for 2 hours. Unchanged compound **11** was removed immediately by filtration and the filtrate concentrated to dryness under reduced pressure. The solid residue was treated with ethanol (20 ml) then allowed to stand at room temperature overnight. The solid was collected and recrystallized from *N,N*-dimethylformamide and ethanol (1:1) to afford **12** (0.32 g, 50%) as pink crystals, mp 198° dec; ir (potassium bromide): ν 1805, 1675 cm^{-1}; ms: m/z 303 (M$^+$); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.29 (s, 3H, 7-CH_3), 2.46 (s, 3H, CO-CH_3), 2.56 (s, 3H, 4-CH_3), 2.61 (s, 3H, 2-CH_3), 6.90 (s, 1H, H-8).

Anal. Calcd. for $C_{14}H_{13}N_3O_5$: C, 55.43; H, 4.32; N, 13.86. Found: C, 55.10; H, 4.11; N, 13.52.

9-Hydroximino-2,4,7-trimethyl-9*H*-pyridino[2,3-*b*]pyrano[3,4-*d*]-oxazole 6-Oxide (**13**).

A solution of **12** (0.5 g, 1.65 mmoles) in 1*N* aqueous sodium hydroxide (20 ml) was stirred at room temperature for 1 hour. The reaction mixture was acidified with 5% sulfuric acid (*p*H 5). The solid separated was filtered immediately, washed with water, dried and recrystallized from *N,N*-dimethylformamide and methanol (1:1) to yield **13** (0.42 g, 98%) as pink crystals, mp >300° dec; ir (potassium bromide): ν 3300-2500, 1665

cm^{-1}; ms: m/z 261 (M^+); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.27 (s, 3H, 7-CH_3), 2.56 (s, 3H, 4-CH_3), 2.59 (s, 3H, 2-CH_3), 6.93 (s, 1H, H-8).

Anal. Calcd. for $C_{12}H_{11}N_3O_4$: C, 55.13; H, 4.24; N, 16.08. Found: C, 54.91; H, 4.06; N,16.01.

9-Hydroximino-2,4,7-trimethyl-9*H*-pyridino[2,3-*b*]pyrano[3,4-*d*]-oxazol (**14**).

A mixture of **13** (0.5 g ,1.92 mmoles) in triethyl phosphite (20 ml) was refluxed for 24 hours. The unchanged compound **13** was removed by filtration and the filtrate was allowed to stand in a refrigerator at 5° for 7 days. The solid was collected and recrystallized from *N,N*-dimethylformamide and methanol (1:1) to give **14** (0.14 g, 57%) as pale yellow crystals, mp >340° dec; ir (potassium bromide): ν 3060-2040, 1665 cm^{-1}; ms: m/z 245 (M^+); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.33 (s, 3H, 7-CH_3), 2.53 (s, 3H, 4-CH_3), 2.64 (s, 3H, 2-CH_3), 7.00 (s, 1H, H-8).

Anal. Calcd. for $C_{12}H_{11}N_3O_3$: C, 58.75; H, 4.52; N, 17.14. Found: C, 58.52; H, 4.24; N, 16.95.

1,4-Dihydro–1-hydroxy-2,7-dimethyl-5*H*-pyrano[4,3-*b*]pyridine-4,5-dione (**15B**).

To a well stirred solution of **1** [1] (5.0 g, 21.1 mmoles) in 1*N* aqueous sodium hydroxide (50 ml) was added dropwise a solution of hydroxylamine hydrochloride (5.0 g) in water (7.5 ml). Stirring was continued for an additional 12 hours. The reaction mixture was acidified using 2*N* aqueous hydrochloric acid. The solid separated was filtered, washed with water, dried and recrystallized from *N,N*-dimethylformamide and ethanol (1:1) to yield **15B** (0.8 g, 46%) as colorless crystals, mp 148°; ir (potassium bromide): ν 3400, 1710, 1650 cm^{-1}; ms: m/z 207 (M^+); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.24 (s, 6H, 2-CH_3, 7-CH_3), 6.20 (s. 1H, H-8), 6.57 (s, 1H, H-3); ^{13}C-nmr (dimethyl sulfoxide-d_6): δ 10.78 (CH_3-2), 19.46 (CH_3-7), 90.93 (C-8a), 99.89 (C-3), 104.19 (C-8) 158.59 (C-7), 160.60 (C-4a), 163.30 (C-2), 163.66 (C-5), 168.09 (C-4).

Anal. Calcd. for $C_{10}H_9NO_4$: C, 57.94; H, 4.37; N, 6.76. Found: C, 57.81; H, 4.35; N, 6.92.

1,4-Dihydro-1-acetoxy-2,7-dimethyl-5*H*-pyrano[4,3-*b*]pyridine-4,5-dione (**16**).

A solution of **15B** (0.3 g, 1.45 mmoles) and acetic anhydride (40 ml) was refluxed for 1 hour. The reaction mixture was concentrated under reduced pressure and the solid obtained was recrystallized from ethanol to yield **16** (0.1 g, 28%) as colorless crystals, mp 125°; ir (potassium bromide): ν 1760, 1730, 1640 cm^{-1}; ms: m/z 249 (M^+); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.27 (s, 3H, 7-CH_3), 2.26 (s. 3H, 2-CH_3-), 2.32 (s, 3H, CO-CH_3), 6.55 (s, 1H, H-8); 6.88 (s, 1H, H-3).

Anal. Calcd. for $C_{12}H_{11}NO_5$: C, 57.78; H, 4.40; N, 5.62. Found: C, 57.72; H; 4.39; N, 5.52.

1,4-Dihydro-1-methoxy-2,7-dimethyl-5*H*-pyrano[4,3-*b*]pyridine-4,5-dione (**17**).

To a well stirred mixture of **15B** (0.3 g, 1.45 mmoles), dry *N,N*-dimethylformamide (40 ml) and potassium carbonate (1.5 g) was added dropwise methyl iodide (1 ml). Stirring was continued for an additional 7 hours. Thereafter the reaction mixture was concentrated to a volume of about 20 ml and treated with aqueous sodium thiosulfate solution (0.6 g/100 ml). The mixture was extracted twice with chloroform (2 x 20 ml). The extracts were washed with water, dried (magnesium sulfate), filtered and the solvent removed under reduced pressure to yield **17** (0.11 g, 35%) as analytically pure colorless crystals, mp 132° ; ir (potassium bromide): ν 1730, 1640 cm^{-1}; ms: m/z 221 (M^+); ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 2.24 (s, 3H, 7-CH_3), 2.33 (s. 3H, 2-CH_3), 4.02 (s, 3H, -O-CH_3), 6.59 (s, 1H, H-8); 6.77 (s, 1H, H-3).

Anal. Calcd. for $C_{11}H_{11}NO_4$: C, 59.67; H, 5.00; N, 6.33. Found: C, 59.78; H, 5.06; N, 6.31.

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