Synthesis of Substituted 3-Nitroso-2,4-pyridinediols for Use as Analytical Reagents

Robert E. Leard, III [1,2], John H. Bedenbaugh [3] and Angela O. Bedenbaugh

Department of Chemistry, University of Southern Mississippi,
Hattiesburg, Mississippi 39406-8466

Received February 9, 1983

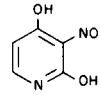
The 5-bromo, 5-iodo, and 5-nitro derivatives of 6-methyl-3-nitroso-2,4-pyridinediol were synthesized and shown to produce colored complexes with a number of Group VIII metal ions. Also synthesized were the 1-pentyl and 1-octyl esters of 4,6-dihydroxy-5-nitrosopyridine-3-carboxylic acid. These compounds showed potential as solvent extraction reagents for certain Group VIII metals.

J. Heterocyclic Chem., **20**, 1363 (1983).

Organic compounds which form highly-colored chelate complexes with metal ions have been used as colorimetric reagents for almost one hundred years. However, recent years have seen the development of refined procedures for isolating and characterizing metals. Specifically, the areas of solvent extraction and masking or interference obviation have received much attention [4]. Although these procedures also involve complexation of the metal ion with an organic compound, only rarely can the same complexing agent used in the colorimetric determination of a metal be used for solvent extraction or masking of the metal ion because the solubility requirements of the complex are different, depending upon the ultimate use of the complex. Thus standard colorimetric reagents known to have desirable complexing characteristics or known to form very stable complexes with a given metal ion usually cannot be considered for use in a solvent extraction procedure for that metal because the water solubility of the complex is not compatible with the requirement that the complex be extracted from water. Typically this situation requires the development of new reagents which will give complexes having the desired solubility characteristics, but frequently with less desirable complexing characteristics and/or less stability than the complex formed by the colorimetric reagent.

However, if a colorimetric reagent can be appropriately altered easily and economically only in the non-complexing region of the molecule so as not to affect significantly that area of the molecule involved in complexation, those characteristics which will impart the desired solubility behavior to the complex can thus be incorporated into a molecule which retains the desired complexing characteristics. The resulting reagent, a derivative of the colorimetric reagent, produces a colored complex which is an advantage (even if the ultimate analysis is noncolorimetric) because it enables the solvent extraction process, *etc.* to be followed visually. However, it is rare that such a molecular modification can be accomplished conveniently.

An exception is seen in the case of the 3-nitroso-2,4-pyridinediol system (**1**) which we have found to complex with certain Group VIII elements, but which is capable of considerable molecular modification without disturbing the complexing function. Numerous studies have shown that analytical reagents incorporating this system can be employed successfully in the spectrophotometric determination of such metals as iron, ruthenium, osmium, cobalt, and palladium [5-10].



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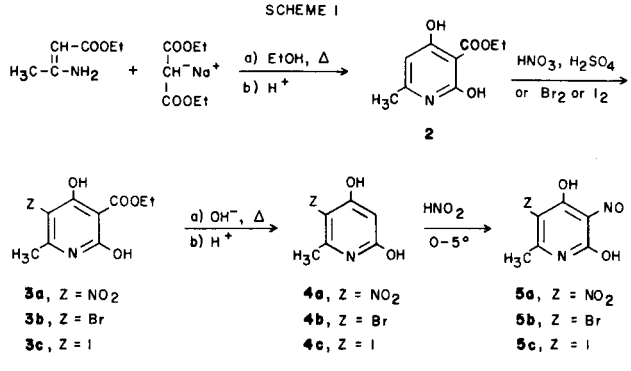
The purpose of this investigation was to synthesize derivatives of these analytical reagents having the same ion specificity as the original reagents but designed to form highly lipophilic complexes with approximately the same degree of stability as the complexes of the original reagents. These compounds would be tested for possible use in solvent extraction procedures. In order to be useful a reagent and its metal complex must both exhibit pronounced solubility in organic solvents. Concentration of the metal ion by extraction into a volatile organic solvent followed by evaporation of the solvent would permit the use of ultrasensitive analytical methods such as atomic absorption spectrometry in the determination of the metal.

The first compounds selected for synthesis and study were some 3-nitroso-6-methyl-5-substituted-2,4-pyridinediols. This system, incorporating the required chelating functionality, was chosen because the synthesis appeared

SCHEME I



straightforward and because substituents in the 5-position could be varied easily to modify solubility behavior. Thus, with the objective of increasing the solubility of the metal complex in organic solvents without altering the chelating function, various 5-substituted-6-methyl derivatives of 3-nitroso-2,4-pyridinediol were prepared by the route outlined in Scheme I.

Ethyl 2,4-dihydroxy-6-methyl-3-pyridinecarboxylate (**2**) was prepared by the condensation of equimolar quantities of ethyl β-aminocrotonate and diethyl malonate in the presence of sodium ethoxide according to the procedure of Klosa [11] who first demonstrated that the 5-position of **2** could be substituted with a halogen atom or a nitro group. He reported that the carbethoxy group of the resulting 5-iodo compound could be removed by saponification and decarboxylation. Our objective was to use Klosa's procedure to block the 3-position of **1**, then appropriately substitute the 5-position, next remove the blocking group, and finally nitrosate in the 3-position.

In a typical reaction sequence **2** was nitrated [12] with fuming nitric acid (d = 1.5) yielding ethyl 2,4-dihydroxy-6-methyl-5-nitro-3-pyridinecarboxylate **3a**. Saponification-decarboxylation of this material in one step gave 6-methyl-5-nitro-2,4-pyridinediol **4a**. A mixed solvent of *N,N*-dimethylacetamide and 20% hydrochloric acid was then used to dissolve **4a**. Treatment of the solution with 30% molar excess of sodium nitrite generated 6-methyl-5-nitro-3-nitroso-2,4-pyridinediol **5a** in a very pure state.

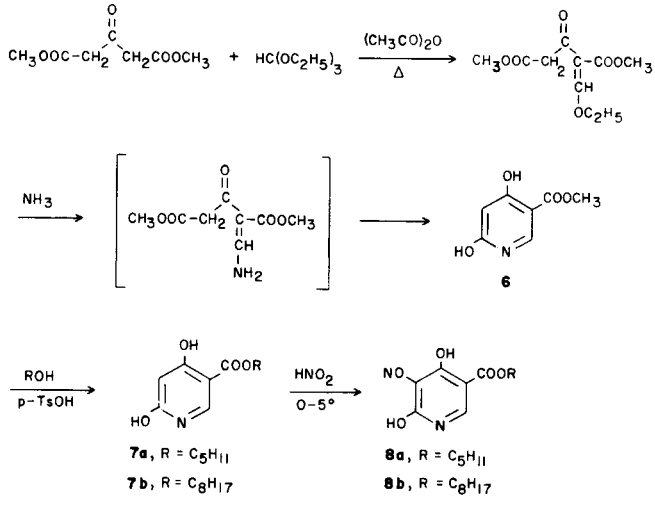
Analogous procedures originating with the bromination and iodination of **2** gave 5-bromo-6-methyl-3-nitroso-2,4-pyridinediol **5b** and 5-iodo-6-methyl-3-nitroso-2,4-pyridinediol **5c**, respectively, as the final products.

All of the 5-substituted-3-nitroso-2,4-pyridinediols prepared possessed good chelating properties but the complexes were only very slightly soluble in organic solvents.

In considering other ways to modify the basic system so as to enhance the lipophilicity of the complexes, it was noted that the solubility of the methyl ester analog of ethyl 4,6-dihydroxy-5-nitroso-3-pyridinecarboxylate previously made in this laboratory [7] was considerably different from that of the ethyl ester. This information prompted examination of the effect of increasing chain length of the carbalkoxy group on solubility. The 1-pentyl and 1-octyl esters were synthesized from the methyl ester *via* a Fischer-type transesterification [13] using *p*-toluenesulfonic acid as catalyst. The entire reaction sequence is given in Scheme II.

Methyl 4,6-dihydroxy-3-pyridinecarboxylate **6** was prepared by the method of Errera [14]. The condensation of equimolar quantities of ethyl orthoformate with dimethyl acetonedicarboxylate in the presence of acetic anhydride resulted in an intermediate which was treated with ammonia to give **6**. Transesterification of **6** produced the corresponding 1-pentyl 4,6-dihydroxy-5-nitroso-3-pyridinecarboxylate (**8a**) and 1-octyl 4,6-dihydroxy-5-nitroso-3-pyridinecarboxylate (**8b**).

SCHEME II



These compounds proved to be excellent chelating reagents. Their metal complexes were quite soluble in common organic solvents and in solvents currently in general use as extraction media for atomic absorption analysis, *e.g.*, methyl isobutyl ketone and ethyl propionate. Thus, long chain esters of 4,6-dihydroxy-5-nitroso-3-pyridinecarboxylic acid appear to have potential as analytical reagents where solvent extraction procedures are involved in the analysis of certain Group VIII metals. For example, **8a** has already been used in these laboratories to remove interfering ions by solvent extraction in new spectrophotometric procedures developed for the determination of osmium and ruthenium [15,16].

EXPERIMENTAL

Melting points and boiling points are reported uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating spectrometer, and nuclear magnetic resonance spectra were determined on a Varian model A-60D spectrometer with tetramethylsilane as an internal reference.

6-Methyl-5-nitro-2,4-pyridinediol (**4a**).

The saponification of ethyl 2,4-dihydroxy-5-nitro-6-methylpyridine-3-carboxylate [11] was acccomplished using a modification of a procedure by Knoevenegel and Fries [17]. The ester (18.0 g, 0.744 mole) was added to 500 ml of 3*N* potassium hydroxide and the mixture was refluxed for fifteen hours. The resulting solution was cooled to room temperature and acidified with 20% hydrochloric acid to *p*H 4 giving a precipitate. After cooling the mixture, the greenish-yellow precipitate was filtered off, washed with cold water, then with ether, and air dried. The yield was 9.50 g (75%) of **4a**. After recrystallization from water, the compound melted at 235-236° dec; ir (potassium bromide): ν max 3155 (m), 3040 (w), 3000 (w), 2940 (m), 2860 (s), 2770 (s), 1690 (vvs), 1625 (vvs), 1582 (vvs), 1536 (w), 1497 (vs), 1470 (vvs), 1422 (s), 1342 (vvs), 1328 (vvs), 1295 (vvs), 1211 (vs), 1190 (vvs), 1147 (vs), 1072 (vs), 1032 (s), 1007 (s), 962 (vs), 940 (m), 863 (vs), 856 (s), 770 (s), 745 (w), 718 (m) and 672 cm^{-1} (s); pmr (DMSO-d_6): τ 7.67 (s,

3H, -CH_3), 4.32 (s, 1H, aromatic proton), and 1.47 (broad s, 2H, -OH).

Anal. Calcd. for $C_6H_6N_2O_4$: C, 42.36; H, 3.56; N, 16.47. Found: C, 42.17; H, 3.37; N, 16.52.

6-Methyl-5-nitro-3-nitroso-2,4-pyridinediol (**5a**).

Compound **4a** (0.50 g, 2.9 mmoles) was added to 5.0 ml of 20% hydrochloric acid with stirring. Then sufficient *N,N*-dimethylacetamide (10-15 ml) was added to cause dissolution of the solid. After cooling the solution to 5° in an ice bath, a cold solution of 0.30 g (4.0 mmoles) sodium nitrite in 0.50 ml of water was added with stirring. The resulting amber solution was stirred for 45 minutes and then diluted with twice its volume of water resulting in the precipitation of a yellow solid which was filtered off, washed with ice water, and dried in a desiccator. Purification of **5a** was accomplished by digestion in ether for 15 minutes. The product (0.35 g, 60%) decomposed about 155°. This compound may explode if allowed to stand in air and then heated to the decomposition point; ir (potassium bromide): ν max 3515 (vs), 3445 (s), 3230 (vs), 3170 (vvs), 3100 (sh, vs), 2995 (vs), 2860 (s), 2540 (m), 1930 (vw), 1726 (sh, vvs), 1710 (vvs), 1665 (vvs), 1610 (vvs), 1515 (vvs), 1505 (vvs), 1464 (vs), 1435 (vvs), 1385 (s), 1350 (vvs), 1300 (vs), 1285 (sh, s), 1240 (vs), 1222 (vs), 1157 (vs), 1120 (vs), 1102 (m), 1075 (vs), 1064 (vs), 1022 (w), 939 (m), 903 (m), 819 (s), and 803 cm^{-1} (vs); pmr (DMSO-d_6): τ 7.72 (s, 3H, -CH_3) and 5.33 (broad s, 2H, -OH).

Anal. Calcd. for $C_6H_5N_3O_5$: C, 36.20; H, 2.51; N, 21.11. Found: C, 35.95; H, 2.80; N, 20.88.

5-Bromo-6-methyl-2,4-pyridinediol (**4b**).

The modification of the procedure of Knoevenagel and Fries [17] described above was also used to obtain 3.80 g (86%) of 5-bromo-6-methyl-2,4-pyridinediol (**4b**) from 6.00 g (0.0218 mole) of ethyl 5-bromo-2,4-dihydroxy-6-methylpyridine-3-carboxylate (**3b**). Compound **4b** melted at 236-237.5° dec; ir (potassium bromide): ν max 3260 (m), 3090 (vs), 3000 (vs), 2880 (vvs), 2675 (vs), 2590 (vs), 2482 (s), 1950 (br, m), 1655 (vvs), 1612 (vvs), 1580 (vvs), 1568 (sh, vvs), 1480 (vvs), 1423 (vvs), 1387 (sh, vvs), 1373 (vvs), 1340 (s), 1268 (vvs), 1256 (vvs), 1232 (vvs), 1062 (w), 1031 (w), 1003 (m), 977 (sh, w), 890 (s), 845 (s), 823 (m), 721 (vw) and 662 cm^{-1} (vs); pmr (DMSO-d_6): τ 7.72 (s, 3H, -CH_3), 4.34 (s, 1H, aromatic proton) and 4.53 (broad s, 2H, -OH).

Anal. Calcd. for $C_6H_6BrNO_2$: C, 35.31; H, 2.96; N, 6.89; Br, 39.15. Found: C, 35.09; H, 2.72; N, 6.62; Br, 38.94.

5-Bromo-6-methyl-3-nitroso-2,4-pyridinediol (**5b**).

Using a procedure similar to that used for **5a**, a solution of 0.816 g (4.00 mmoles) of **4b**, 10-12 ml of 20% hydrochloric acid and 8-10 ml of *N,N*-dimethylacetamide was treated with a cold solution of 0.420 g (6.09 mmoles) of sodium nitrite in 4 ml of water. Compound **5b** (0.780 g, 84%) was reddish orange, decomposed above 180°, but did not liquify below 350°; ir (potassium bromide): ν max 3245 (vvs), 3175 (vs), 3080 (s), 2940 (m), 2815 (w), 1695 (vvs), 1635 (vvs), 1588 (vvs), 1530 (s), 1475 (s), 1417 (s), 1380 (vw), 1332 (vs), 1288 (w), 1201 (vs), 1125 (vs), 1082 (s), 1056 (s), 852 (s) and 790 cm^{-1} (s); pmr (DMSO-d_6: τ 7.67 (s, 3H, -CH_3) and -1.32 (broad s, 2H, -OH).

Anal. Calcd. for $C_6H_5BrN_2O_3$: C, 30.93; H, 2.15; N, 12.02; Br, 34.30. Found: C, 31.00; H, 2.03; N, 12.08; Br, 34.09.

5-Bromo-6-methyl-3-nitroso-2,4-pyridinediol (**5b**).

Using a procedure similar to that used for **5a**, a solution of 0.816 g (4.00 mmoles) of **4b**, 10-12 ml of 20% hydrochloric acid and 8-10 ml of *N,N*-dimethylacetamide was treated with a cold solution of 0.420 g (6.09 mmoles) of sodium nitrite in 4 ml of water. Compound **5b** (0.780 g, 84%) was reddish orange, decomposed above 180°, but did not liquify below 350°; ir (potassium bromide): ν max 3245 (vvs), 3175 (vs), 3080 (s), 2940 (m), 2815 (w), 1695 (vvs), 1635 (vvs), 1588 (vvs), 1530 (s), 1475 (s), 1417 (s), 1380 (vw), 1332 (vs), 1288 (w), 1201 (vs), 1125 (vs), 1082 (s), 1056 (s), 852 (s) and 790 cm^{-1} (s); pmr (DMSO-d_6): τ 7.67 (s, 3H, -CH_3) and -1.32 (broad s, 2H, -OH).

Anal. Calcd. for $C_6H_5BrN_2O_3$: C, 30.93; H, 2.15; N, 12.02; Br, 34.30. Found: C, 31.00; H, 2.03; N, 12.08; Br, 34.09.

5-Iodo-6-methyl-3-nitroso-2,4-pyridinediol (**5c**).

Three 1.0 ml portions of *N,N*-dimethylacetamide were added to a stirred mixture of 0.90 g (3.6 mmoles) of 5-iodo-6-methyl-2,4-pyridinediol [11] in 5.0 ml of 20% hydrochloric acid to effect solution. The resulting yellow solution was cooled below 5° in an ice bath, and a cold solution of 0.36 g (4.8 mmoles) of sodium nitrite in 1.0 ml of water was added. The reddish-orange solution was kept cold for several minutes and then 30 ml of water was added. The mixture was refrigerated for 3-4 hours and the precipitate that formed was filtered off, washed with cold water then with small amounts of ethanol and ether. After drying in a desiccator, the red compound **5c** weighed 0.42 g (40%), mp 205° dec; ir (potassium bromide): ν max 3460 (vw), 3200 (w), 3120 (m), 3050 (w), 2960 (w), 1695 (vvs), 1617 (w), 1580 (s), 1532 (vs), 1470 (m), 1371 (vw), 1346 (m), 1300 (s), 1230 (w), 1142 (s), 1080 (w), 1050 (w) and 864 cm^{-1} (w); pmr (DMSO-d_6): τ 7.59 (s, 3H, -CH_3), and -1.46 (broad s, 2H, -OH).

Anal. Calcd. for $C_6H_5IN_2O_3$: C, 25.74; H, 1.80; N, 10.00; I, 45.32. Found: C, 25.55; H, 1.67; N, 9.99; I, 45.53.

Methyl 4,6-Dihydroxypyridine-3-carboxylate (**6**).

A stirred mixture of 150 g (0.860 mole) of dimethyl acetonedicarboxylate, 128 g (0.860 mole) of triethyl orthoformate, and 176 g (1.73 moles) of acetic anhydride was heated under reflux to 130° in an oil bath. The temperature was reduced to 120° over a one hour period, and then the red solution was allowed to cool to room temperature. After volatile materials were removed by distillation under aspirator vacuum, the residue was cooled in an ice bath and 24 ten-ml portions of concentrated ammonium hydroxide were added with swirling. After an hour the resultant precipitate was filtered off. The filtrate was acidified and the resultant precipitate filtered off and combined with the previously isolated solid. After washing the combined precipitates with water, the solid material was filtered off, air dried, boiled in benzene for one hour, filtered, and washed on the filter with cold 95% ethanol. The yield of **6** was 60.0 g (41%), mp 237-240° dec. An analytical sample was prepared by two recrystallizations of **6** from 50% methanol. Purified **6** melted at 236-237°; ir (potassium bromide): ν max 3030 (vs), 2680 (vs), 1957 (w), 1875 (vw), 1816 (vw), 1704 (vs), 1674 (vvs), 1640 (vvs), 1557 (vs), 1424 (vs), 1386 (w), 1356 (m), 1311 (vs), 1265 (s), 1214 (s), 1192 (s), 1103 (m), 1012 (vw), 987 (vw), 947 (w), 912 (w), 861 (vw) and 773 cm^{-1} (w); pmr (DMSO-d_6): τ 6.18 (s, 3H, -CH_3), 4.36 (s, 1H, aromatic proton), and 1.93 (s, 1H, aromatic proton).

Anal. Calcd. for $C_7H_7NO_4$: C, 49.70; H, 4.17; N, 8.28. Found: C, 49.93; H, 4.30; N, 8.22.

1-Pentyl 4,6-Dihydroxypyridine-3-carboxylate (**7a**).

Methyl 4,6-dihydroxypyridine-3-carboxylate (**6**) (5.0 g, 0.033 mole) was suspended in 130 ml of 1-pentanol in a one-neck, round-bottom flask equipped with Barrett trap, reflux condenser, magnetic stirrer, and heating mantle; and the mixture was heated to 140°. *p*-Toluenesulfonic acid monohydrate (0.50 g, 2.6 mmoles) was added cautiously. After heating for four days at low reflux, the mixture was darker in color and dissolution of some solid could be noted. An additional 0.20 g (1.5 mmoles) of *p*-toluenesulfonic acid monohydrate was added, and the heat was increased to 165°. Heating was discontinued after 24 hours at which time all solid had dissolved. Water (400 ml) was added, the mixture was shaken, and the solution was concentrated to a syrupy reddish-brown liquid using a rotary evaporator at 60°. To this liquid was added 150 ml of ligroine (bp 63-75°). The solid that formed when the mixture was cooled was allowed to stand several hours and filtered. Concentration of the filtrate and addition of ligroine produced more solid. The solids isolated were combined to give 2.8 g (41%) of **7a**. After recrystallization from ethyl acetate or benzene, **7a** melted at 144-146°; ir (potassium bromide): ν max 3155 (sh, m), 3060 (s), 2960 (vs), 2930 (s), 2872 (s), 2860 (s), 2355 (w), 1800 (vw), 1690 (sh, vvs), 1660 (vvs), 1613 (vs), 1570 (s), 1459 (vs), 1447 (vs), 1405 (s), 1380 (w), 1355 (m), 1328 (s), 1308 (vs), 1268 (vs), 1215 (vs), 1199 (sh, vs), 1151 (m), 1132 (m), 1105 (s), 1050 (w), 990 (vw), 950 (m), 937 (w), 912 (w), 876 (vw), 852 (w), 839 (w), 782 (m), 744 (vw) and 720 cm^{-1} (vw); pmr (DMSO-d_6): τ 8.63 (complex m, 9H, $>CH_2$ + -CH_3), 5.65 (t, 2H, -OCH_2-),

4.02 (s, 1H, aromatic proton), 1.76 (s, 1H, aromatic proton) and −2.24 (broad s, 2H, -OH).

Anal. Calcd. for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.71; H, 6.86; N, 6.13.

1-Octyl 4,6-Dihydroxypyridine-3-carboxylate (**7b**).

This procedure was similar to that used for the preparation of **7a**. Compound **6** (2.0 g, 12 mmoles) was suspended in 50 ml of 1-octanol. After the *p*-toluenesulfonic acid monohydrate (0.30 g, 1.6 mmoles) was added, the mixture was heated for five days at 130-140°. After cooling, the dark red solution was decanted from a small amount of undissolved material. Water (150 ml) was added to this solution and the mixture was concentrated by rotary evaporation at 60° to 10 ml. Ligroine (bp 63-75°) was added, and the mixture was refrigerated for several hours. The solid that formed was filtered off and washed with ligroine to produce 0.50 g (16%) of crude **7b**. After recrystallization from benzene, **7b** melted at 159.5-160°; ir (potassium bromide): ν max 3080 (m), 3057 (m), 2960 (s), 2930 (vs), 2900 (s), 2878 (s), 2860 (vs), 2812 (s), 2785 (m), 2745 (m), 2680 (m), 1725 (m), 1692 (vvs), 1687 (vvs), 1662 (vvs), 1619 (vvs), 1575 (vs), 1544 (vw), 1465 (vs), 1410 (vs), 1366 (m), 1345 (w), 1320 (vvs), 1304 (vs), 1280 (vvs), 1232 (vs), 1208 (vs), 1146 (w), 1132 (m), 1120 (s), 952 (s), 928 (m), 882 (vw), 800 (m), 792 (m), 756 (vw) and 722 cm^{-1} (vw); pmr (DMSO-d_6): τ 8.70 (complex m, 15H, $>CH_2$ + $-CH_3$), 5.72 (t, 2H, $-OCH_2-$), 4.32 (s, 1H, aromatic proton), 1.91 (s, 1H, aromatic proton) and −1.27 (broad s, 2H, -OH).

Anal. Calcd. for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.91; N, 5.23. Found: C, 62.91; H, 8.02; N, 5.21.

1-Pentyl 4,6-Dihydroxy-5-nitrosopyridine-3-carboxylate (**8a**).

Compound **7a** (0.25 g, 1.0 mmole) was added to 10 ml of 20% hydrochloric acid with stirring. *N,N*-Dimethylacetamide (3-4 ml) was added to effect solution (a small amount of residual **7a** had to be removed by filtration) and the solution was cooled. To this solution a cold solution of sodium nitrite (0.10 g, 1.4 mmoles) in 1.5 ml of water was added, producing a yellow precipitate. *N,N*-Dimethylacetamide (2.0 ml) was added; the solution was cooled in an ice bath for 20 minutes and then filtered. The precipitate **8a** was washed with cold water and air dried. The yield was 0.10 g (40%); mp 158-160° dec; ir (potassium bromide): ν max 3400 (vvw), 3200 (vs), 3082 (m), 2960 (s), 2935 (s), 2900 (m), 2866 (m), 2795 (w), 2610 (vw), 1725 (vvs), 1702 (vvs), 1640 (vs), 1605 (vvs), 1538 (w), 1495 (vs), 1428 (s), 1392 (w), 1372 (s), 1332 (vvs), 1282 (vs), 1221 (s), 1178 (vs), 1125 (m), 1058 (vs), 1000 (m), 930 (m), 840 (vw) and 810 cm^{-1} (m); pmr (DMSO-d_6): τ 8.72 (complex m, 9H, $>CH_2$ + $-CH_3$), 5.83 (t, 2H, $-OCH_2-$), 1.83 (s, 1H, aromatic proton), and −1.69 (broad s, 2H, -OH).

Anal. Calcd. for $C_{11}H_{14}N_2O_5$: C, 51.97; H, 5.55; N, 11.02. Found: C, 51.97; H, 5.54; N, 10.82.

1-Octyl 4,6-Dihydroxy-5-nitrosopyridine-3-carboxylate (**8b**).

Compound **7b** (0.90 g, 3.4 mmoles) was added with stirring to 15 ml of 20% hydrochloric acid. *N,N*-Dimethylacetamide (about 60 ml) was added in portions until solution occurred. The solution was cooled in an ice bath, and an ice-cold solution of sodium nitrite (0.28 g, 4.0 mmoles) in 1.5 ml of water was added. *N,N*-Dimethylacetamide (15 ml) was added to the turbid mixture which was warmed to 30° to effect solution. After refrigeration for 6 hours, the solution was diluted with water until turbid and refrigerated for four more hours. The yellow precipitate **8b** which formed was filtered off, washed with water, and air dried. After two recrystallizations from 95% ethanol, **8b** (0.30 g, 33%) melted at 150-152° dec; ir (potassium bromide): ν max 3195 (vvs), 3082 (s), 3028 (m), 2960 (vs), 2910 (vs), 2855 (s), 1722 (vvs), 1705 (vvs), 1638 (s), 1603 (vvs), 1578 (m), 1571 (w), 1557 (w), 1535 (w), 1490 (vs), 1475 (s), 1468 (m), 1456 (m), 1427 (s), 1395 (m), 1370 (s), 1330 (vvs), 1280 (vs), 1220 (s), 1180 (vs), 1125 (s), 1078 (w), 1052 (vs), 1023 (w), 988 (m), 922 (m), 842 (w), 810 (s), 750 (w) and 720 cm^{-1} (w); pmr (DMSO-d_6): τ 8.68 (complex m, 15H, $>CH_2$ + $-CH_3$), 5.83 (t, 2H, $-OCH_2-$) and 1.85 (s, 1H, aromatic proton).

Anal. Calcd. for $C_{14}H_{20}N_2O_5$: C, 56.75; H, 6.80; N, 9.45. Found: C, 56.94; H, 7.02; N, 9.32.

Acknowledgement.

The ir and nmr instruments used in this research were obtained through NSF research instrument grants. The authors also wish to express appreciation to the University of Southern Mississippi and the Mississippi Board of Trustees of Institutions of Higher Learning for partial financial support.

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[1] Research supported in part by an NSF traineeship awarded through the University of Southern Mississippi.

[2] Present Address: Department of Chemistry, Alcorn State University, Lorman, MS.

[3] Author to whom all correspondence should be addressed.

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