Oxidative reactions of azines
5.* Ketodihydroxylation and coupling of 4-(γ-pyridyl)-1,2,5,6-tetrahydropyridines with acetone. Molecular and crystal structure of 3,4-dihydroxy-4-(γ-pyridyl)-1-ethylpiperidin-2-one

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Oxidative coupling of 1-alkyl(benzyl)-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridines with acetone in the presence of $KMnO_4$ follows two pathways and yields both 1-R-2-(acetylmethylene)tetrahydropyridines and 1-R-3,4-dihydroxypiperidin-2-ones. When acetonitrile is used instead of acetone, the reaction under similar conditions occurs as selective ketodihydroxylation of the starting piperideines yielding 1-R-3,4-dihydroxy-4-(γ-pyridyl)piperidin-2-ones. The molecular and crystal structures of one of these products (R = Et) was studied by X-ray diffraction analysis.

Key words: oxidative coupling, ketodihydroxylation, 1-R-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridines, 1-R-3,4-dihydroxy-4-(γ-pyridyl)piperidin-2-ones, 1-R-2-acetylmethylene-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridines; NMR, X-ray diffraction analysis; molecular and crystal structures.

Previously,[1,2] in a study dealing with modification of the Wagner oxidation, we discovered a new reaction, namely, oxidative C—C-coupling of α-methylketones with 4-aryltetrahydropyridines resulting in the formation of 2-acylmethylene derivatives of tetrahydropyridine. When acetone was used as the methyl-active component, 2-(acetylmethylene)tetrahydropyridines were isolated in yields of up to 70%.

This condensation was carried out in the presence of $KMnO_4$ under mild conditions (~25 °C) and could be complicated by dihydroxylation of the double bonds in the initial tetrahydropyridines. This was not observed in our experiments, which is in agreement with the data[3] that 4-phenyltetrahydropyridines are inert under conditions of the Wagner reaction. However, when we studied the possibility of coupling of acetonitrile with 4-aryltetrahydropyridines, we obtained 4-phenyl-3,4-dihydroxypiperidin-2-ones[4] in good yields and with high regioselectivity rather than the coupling products, and in the case of bulky 4-[2.2]paracyclophanyl substituent, the reaction yielded tetrahydropyridin-2-one.[5]

The present study dealing with the reaction of 4-heterylpiperideines was stimulated by the fact that the course and the extent of the oxidative transformations of 4-aryltetrahydropyridines in aqueous acetone and in aqueous acetonitrile in the presence of $KMnO_4$ are appreciably influenced by the nature of the methyl-active component, the temperature of the reaction, and the character of the substituent at C(4) in 3-piperideine. As the heterocyclic substituent, we chose the γ-pyridyl group, which increases both the polarization of the double bond and the CH-acidity of the methylene group in the allylamine fragment of the piperideine and is thus favorable for the formation of dihydroxylactams or for oxidative coupling. If these reactions occur by radical mechanisms, the pyridyl nucleus could inhibit oxidative processes, especially C—C-coupling. The transformations studied in this work are shown in Scheme 1. The following initial tetrahydropyridines were used: 1-methyl- (**5**), 1-ethyl- (**6**), and 1-benzyl-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridines (**7**). These compounds were synthesized by the reduction of 4-(γ-pyridyl)pyridinium quaternary salts (**2**—**4**) by $NaBH_4$; the salts were prepared from the corresponding haloalkanes and 4,4-dipyridine (**1**).

* For part 4, see Ref. 1

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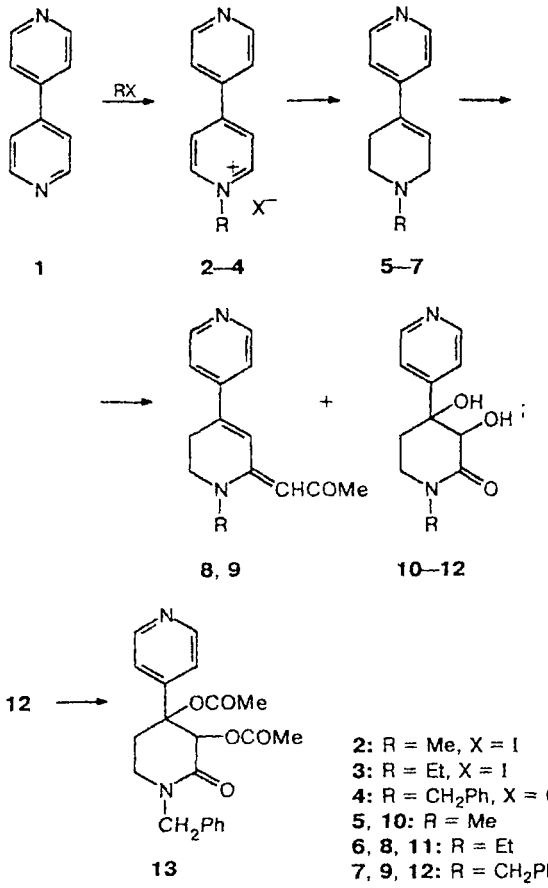
Scheme 1



First, we studied the possibility of the oxidative coupling of piperideines **5**—**7** with acetone. It was found that after the replacement of the aryl substituent at the C(4) atom by the pyridyl substituent, the rates of the competing reactions, coupling and ketodihydroxylation, become equal. The expected 2-(acetylmethylene)-tetrahydropyridines **8** and **9** were obtained in low yields, while the products of the parallel ketodihydroxylation, 3,4-dihydroxy-2-ketopiperidines (**10***—**12**), were isolated in 10, 21, and 7% yields, respectively. The structures of the products were confirmed by spectroscopy.

The IR spectra of derivatives **8** and **9** contain bands at 1729—1735 cm^{-1} corresponding to the carbonyl group and bands at 1598—1600 cm^{-1} due to the conjugated diene fragment. The ^1H NMR spectrum of compound **8** exhibits two singlets at 5.68 and 8.14 ppm, which are characteristic of the H(3) proton and the proton of the =CHC(O)— exocyclic group, respectively, as has been found previously[1] for analogous 2-(acetylmethylene)piperideines, whose structures were confirmed unambiguously by X-ray diffraction analysis. The ^{13}C NMR spectrum is also consistent with the structure of compound **8** (the signal of the carbonyl carbon atom is manifested at 197.7 ppm).

* Previously,[6] we have prepared lactamdiol **10** and confirmed its structure by NMR spectroscopy and X-ray diffraction analysis.

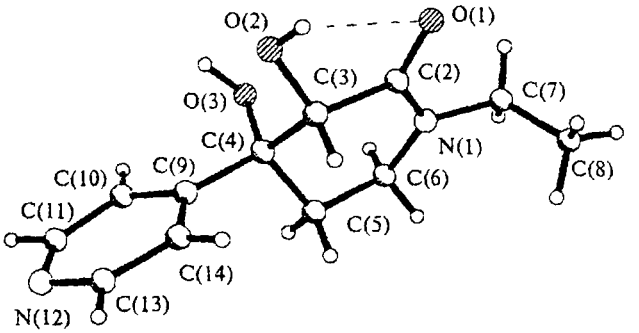


Fig. 1. Molecular structure of lactamdiol **11**.

The IR spectra of lactamdiols **11** and **12** contain absorption bands corresponding to the amide carbonyl groups (at 1620—1640 cm^{-1}) and bands for the hydroxyl groups at 3280—3453 cm^{-1}. Their structures were confirmed unambiguously by the data of ^1H and ^{13}C NMR spectra, and the structure of compound **11** was also determined by X-ray diffraction analysis.

The molecular structure of compound **11** is presented in Fig. 1. The molecule incorporates an intramolecular hydrogen bond, O(2)H...O(1), with the following parameters: O(2)...O(1) 2.695(4) Å, H...O(1) 2.40(4) Å, and the O(2)HO(1) angle is 115(2)°. The conformation of the piperideine ring is described most exactly as a flattened chair: the deviation from the plane drawn through the C(2), C(3), C(5), and C(6) atoms is 0.038 Å; the N(1) atom deviates from this plane by +0.195 Å, and the C(4) atom deflects from it by −0.733 Å. The pyridyl substituent occupies an equatorial position and is rotated with respect to the mean plane of the piperidine ring through an angle 61.2°. The OH group at C(3) is arranged equatorially and occupies a *cis*-position with respect to the axial OH(4)-group. The torsion angles characterizing the orientation of these substituents are the following: C(2)—C(3)—C(4)—C(9) 174.4°, C(2)—C(3)—C(4)—O(3) −60.2°, O(2)—C(3)—C(4)—O(3) 63.0°, and O(2)—C(3)—C(4)—C(9) −62.3°.

The molecules in the crystal are connected by two hydrogen bonds: O(2)—H...O'(3) (−1 + x, y, z) {the parameters: O(2)...O(3) 3.058(4) Å, H...O(3) 2.34(4), the O(2)HO(3) angle is 153(2)°} and O(2)H...O''(1) (−x, −0.5 + y, 1 − z) {the parameters: O(2)...O(1) 2.69(4) Å, H...O(1) 2.40 Å, the O(2)HO(1) angle is 104(2)°}.

To study the possibility of target-directed ketodihydroxylation, we carried out the oxidative reaction of 4-pyridylpiperideines **6** and **7** in acetonitrile. The replacement of acetone by acetonitrile results in the selective formation of only 3,4-dihydroxy-2-piperidines **11** and **12**, which were obtained in 81 and 68% yields, respectively.

In order to enhance its potential biological activity, lactamdiol **12** was converted into the corresponding diacetate (**13**), whose structure follows unambiguously from its IR and ^1H and ^{13}C NMR spectra; these spectra are presented in the Experimental.

Experimental

The compounds obtained were isolated and purified by chromatography on columns with L-60 silica gel (40/100). The reactions were monitored by TLC on Silufol UV-254 plates; elution was performed by a benzene—ether (2 : 1) mixture in the case of compounds **5**—**7**, by ether for compounds **8** and **9**, or by an ether—ethanol mixture (2 : 1) for compounds **10**—**12**. The plates were visualized by iodine vapor. The mass spectrum (EI) was obtained using an MX-1303 mass spectrometer (70 eV). The ^1H NMR spectra were recorded on Bruker WP-250 (250 MHz) and Bruker WM-400 (400 MHz) instruments in $CDCl_3$ (using tetramethylsilane as the internal standard).

X-ray diffraction study of lactamdiol (11). Crystals of **11** are monoclinic, space group $P2_1$; at 20 °C, a = 5.8315(9), b = 10.081(2), c = 9.635(2) Å, β = 90.52(1)°, M = 566.4(2) Å^3, Z = 2, d_{calc} = 1.385 g cm^{-3}. The unit cell parameters and the intensities of 1164 reflections were measured on a Siemens P3/PC automatic four-circle diffractometer (20 °C, Mo-Kα-radiation, graphite monochromator, $\theta/2\theta$-scanning, θ_{max} = 25°). The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were objectively localized in a differential Fourier synthesis and refined in the isotropic approximation. The final residual factors were R_1 = 0.037 over 1053 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.102 over 1057 independent reflections. All the calculations were carried out on an IBM PC/AT-486 computer using the SHELXTL PLUS and SHELXL-93 programs. The thermal parameters of the atoms and bond lengths and angles in molecule **11** will be reported in a separate communication.

Optical analysis of lactamdiol 11* was carried out using a Polam-P-113 polarization microscope. Compound **11** was obtained as well-formed transparent colorless quadrangular crystals: oblique rectangles. The crystals are optically anisotropic and possess very high interference colors. This points to dissimilar optical properties of polymorphic modifications. Refractive indices: n_D = 1.724±0.003 and n_D = 1.507±0.005.

Reduction of quaternary salts (2—4)

1-Methyl-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridine (5). At 20 °C, $NaBH_4$ (3 g, 80 mmol) was added portionwise with intense stirring to a solution of 4-pyridylpyridinium iodomethylate **2** (2.25 g, 8 mmol) in 60 mL of MeOH, and the mixture was kept for 0.5 h at 20 °C, refluxed for 1 h, and cooled. Water (20 mL) was added, and the product was extracted with benzene. The extract was concentrated *in vacuo* to a volume of 5 mL, and the precipitate was separated, washed with ether, and dried to give 0.7 g (48%) of colorless crystals, m.p. 42—43 °C, R_f 0.33. ^1H NMR, δ: 2.3 (s, 3 H, Me); 2.45 (br.s, 2 H, H(5)); 2.6 (t, 2 H, H(6), J = 5.8 Hz); 3.0 (dd, 2 H, H(2), J = 6.0 and 3.1); 6.2 (t, 1 H, H(3), J = 3.1 Hz); 7.1 and 8.4 (AA′XX′ type spectrum, 4 H, pyridyl H). ^{13}C NMR, δ: 26.8, 51.5, and 54.5 (CH_2); 45.2 (Me); 119.0 (2 CH_2) and 125.2 (CH); 149.5 (2 CH); 132.2 and 147.4 (C_{quat}). IR (ν/cm^{-1}): 1600 (C=C). MS, m/z (I_{rel} (%)): 174 $[M]^+$ (100), 173 (40), 159 $[M-Me]^{+\cdot}$ (4), 147 $[M-HCN]^{+\cdot}$ (8), 78 $[C_5H_4N]^{+\cdot}$ (8). Found (%): C, 75.4; H, 7.9; N, 16.1. $C_{11}H_{14}N_2$. M = 174. Calculated (%): C, 75.8; H, 8.0; N, 16.1.

1-Ethyl-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridine (6). A solution of pyridinium iodoethylate **3** (3.83 g, 10 mmol) in 20 mL of H_2O was added at 0 °C to a suspension of $NaBH_4$ (0.76 g, 20 mmol) in 70 mL of a 10% aqueous solution of Na_2CO_3, and the mixture was kept for 15 min at 0 °C and for 2 h at 20 °C. Water (40 mL) was added, and the product was extracted with $CHCl_3$. The extract was dried with $MgSO_4$, and the solvent was evaporated to give 1.9 g (82.6%) of compound **6** as a thick oil, R_f 0.34. ^1H NMR, δ: 1.1 (t, 3 H, Me, J = 7.2 Hz); 2.5 (m, 4 H, H(5) and N—$\underline{CH_2}$—Me); 2.68 (t, 2 H, H(6), J = 5.8 Hz); 3.14 (m, 2 H, H(2)); 6.27 (narrow.m, 1 H, H(3)); 7.2 and 8.48 (AA′XX′ type spectrum, 4 H, C_5H_4N). ^{13}C NMR, δ: 12.2 (Me); 27.3, 49.6, 51.9, and 52.7 (CH_2); 119.4 (2 CH) and 121.4 (CH); 149.8 (2 CH); 133.0 and 147.8 (C_{quat}). IR, ν/cm^{-1}: 1640 (C=C). MS, m/z (I_{rel} (%)): 188 $[M]^+$ (100). Found (%): C, 76.70; H, 8.62; N, 15.0. $C_{12}H_{16}N_2$. M = 188. Calculated (%): C, 76.59; H, 8.51; N, 14.89.

1-Benzyl-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridine (7) was prepared similarly to compound **6** from pyridylpyridinium chlorobenzylate (**4**) (4.39 g, 20 mmol) and $NaBH_4$ (1.13 g, 30 mmol). The product was obtained in a yield of 3.6 g (92%) as a thick oil, R_f 0.54. ^1H NMR, δ: 2.5 (br.s, 2 H, H(5)); 2.71 (t, 2 H, H(6), J = 5.9 Hz); 3.18 (m, 2 H, H(2)); 3.62 (s, 2 H, —N—CH_2—Ar); 6.28 (narrow m, 1 H, H(3)); 7.25 (m, 5 H, H_{arom}); 7.33 and 8.4 (AA′XX′ type spectrum, 4 H, C_5H_4N). ^{13}C NMR, δ: 27.1, 49.5, 53.1, and 62.5 (CH_2); 125.7 and 127.2 (CH); 119.3, 128.3, 129.1, and 149.8 (2 CH); 132.8, 138.0, and 147.8 (C_{quat}). IR, ν/cm^{-1}: 1651 (C=C). MS, m/z (I_{rel} (%)): 250 $[M]^+$ (100). Found (%): C, 81.0; H, 7.35; N, 11.0. $C_{17}H_{18}N_2$. M = 250. Calculated (%): C, 81.16; H, 7.2; N, 11.2.

Oxidation of tetrahydropyridines 5—7 in acetone. At 20 °C, finely powdered $KMnO_4$ (0.75 g, 4.8 mmol) was added in small portions over a period of 5 min to a solution of *N*-ethyltetrahydropyridine **6** (0.60 g, 3.2 mmol) in 10 mL of aqueous acetone. The mixture was stirred for 1.5 h, and the precipitate was separated and washed with hot acetone (3×10 mL). The filtrates were combined, the acetone was evaporated, and the residue was chromatographed on a column with silica gel (d = 2 cm, h = 30 cm); elution was carried out with hexane and then with ether. First, 3.75 g (5%) of **2-acetylmethylene-1-ethyl-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridine (8)** was isolated as an oil, R_f 0.35. ^1H NMR, δ: 1.2 (t) and 3.37 (m) (N—CH_2Me); 2.1 (s, 3 H, COMe); 2.3—2.6 (m, 2 H, H(5)); 3.5—3.7 (m, 2 H, H(6)); 5.68 (s, 1 H, H(3)); 7.68 and 8.7 (AA′XX′ type spectrum, 4 H, C_5H_4N); 8.14 (br.s, 1 H, CHCO). ^{13}C NMR, δ: 12.4 and 24.3 (Me); 41.3, 44.6 and 47.2 (CH_2); 95.0 and 121.0 (vinylic CH); 120.5 and 150.8 (2 CH_{arom}); 139.5, 148.2 and 150.0 (C_{quat}); 197.7 (CO). IR, ν/cm^{-1}: 1735 (CO); 1600 (C=C). MS, m/z (I_{rel} (%)): 242 $[M]^+$ (100). Found (%): C, 74.50; H, 7.42; N, 11.70. $C_{15}H_{18}N_2O$. M = 242. Calculated (%): C, 74.38; H, 7.43; N, 11.57.

After that, 0.16 g (21%) of **3,4-dihydroxy-1-ethyl-2-oxo-4-(γ-pyridyl)piperidine (11)** was obtained as colorless crystals, m.p. 170—172 °C, R_f 0.30. ^1H NMR (DMSO-d_6), δ: 1.07 (t, 3 H, Me, J = 7.3 Hz); 1.81 (ddd, 1 H, H(5e), $^2J_{5a,5e}$ = 12.0 Hz, $^3J_{5e,6a}$ = 4.8 Hz. $^3J_{5e,6e}$ = 2.0 Hz); 2.34 (dddd, H(5a), $^2J_{5a,5e}$ ≈ $^3J_{5a,6a}$ ≈ 12 Hz); 3.22 (ddd, H(6e), $^2J_{6e,6a}$ ≈ 12 Hz, $^3J_{5a,6e}$ ≈ 6.4 Hz, $^4J_{OH,5a}$ ≈ 1.5 Hz); 3.33 (q, 2 H, —N$\underline{CH_2}$Me, ^3J = 7.3 Hz); 3.52 (ddd, H(6a)); 4.28 (d, 1 H, H(3), $^3J_{OH(3)}$ = 3.8 Hz); 4.79 (d, 1 H, OH(3), $^3J_{OH(3)}$ = 3.8 Hz); 5.52 (d, 1 H, OH(4),

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$^4J_{OH,5a}$ = 1.5 Hz); 7.49 (d, 2 H, H(3′, 5′), ^3J = 6.0 Hz); 8.52 (d, 2 H, H(2′, 6′), ^3J = 6.0 Hz). ^{13}C NMR, δ: 12.1 (Me); 33.4, 42.3, and 43.4 (CH_2); 72.0 and 73.0 (C—OH); 120.2 and 150.1 (2 CH_{arom}); 131.6 and 154.0 (C_{quat}); 162.5 (CO). IR, ν/cm^{-1}: 1640 (C=O); 3400 (OH). MS, *m/z* (I_{rel} (%)): 236 $[M]^+$ (31), 58 (100). Found (%): C, 61.1; H, 6.9; N, 12.1. $C_{12}H_{16}N_2O_3$. *M* = 236. Calculated (%): C, 61.0; H, 6.8; N, 11.9.

Oxidation of 1-methyl-substituted tetrahydropyridine **5** (0.55 g, 3.2 mmol) carried out in a similar way gave 0.07 g (10%) of **3,4-dihydroxy-1-methyl-2-oxo-4-(γ-pyridyl)piperidine (10)** as colorless crystals. Judging from the melting point (220—222 °C), chromatographic mobility, and ^{1}H NMR and mass spectra, this sample was identical to that prepared previously by ketodihydroxylation of compound **5** in acetonitrile.[6] The corresponding product of condensation with compound **5** was not isolated.

Oxidation of 1-benzyl-substituted tetrahydropyridine **7** (0.8 g, 3.2 mmol) in acetone carried out in a similar way afforded, after chromatographic separation, 0.5 g (5%) of **2-acetylmethylene-1-benzyl-4-(γ-pyridyl)-1,2,5,6-tetrahydropyridine (9)** and 0.66 g (7%) of **1-benzyl-3,4-dihydroxy-2-oxo-4-(γ-pyridyl)piperidine (12)**. Compound **9** is a yellow oil, R_f 0.42. IR, ν/cm^{-1}: 1598 (C=C); 1729 (C=O). MS, *m/z* (I_{rel} (%)): 304 $[M]^+$ (15), 79 (70), 43 (40). Found (%): C, 79.0; H, 6.32; N, 9.0. $C_{20}H_{20}N_2O$. *M* = 304. Calculated (%): C, 78.94; H, 6.57; N, 9.21.

Lactamdiol **12** is a colorless crystalline solid, m.p. 210—212 °C, R_f 0.37. ^{1}H NMR (DMSO-d_6), δ: 1.77 (dd, H(5e), J = 13.7 and 4.0 Hz); 2.38 (ddd, H(5a), J = 13.7 and 5.8 Hz); 3.18 (dd, H(6e), J = 11.6 and 5.8 Hz); 3.4 (m, H(6a)); 4.42 (d, H(3), J = 4.0 Hz); 4.49 and 4.64 (both d, CH_2Ph, J = 15.2 Hz); 4.99 (d, 1 H, OH(3), J = 4.0 Hz); 5.69 (s, 1 H, OH(4)); 7.31 (m, 5 H, Ph); 7.51 and 8.5 (AA′XX′ type spectrum, 4 H, C_5H_4N). ^{13}C NMR (DMSO-d_6), δ: 43.5 and 49.4 (CH_2); 73.0 and 73.6 (C—OH); 120.9, 121.1, 127.5, 128.5, and 149.15 (CH_{arom}); 137.2 and 154.9 (C_{quat}); 171.0 (C=O). IR, ν/cm^{-1}: 1620 (C=O); 3280 and 3453 (OH). MS, *m/z* (I_{rel} (%)): 298 $[M]^+$ (100). Found (%): C, 68.6; H, 6.2; N, 9.7. $C_{17}H_{18}N_2O_3$. *M* = 298. Calculated (%): C, 68.5; H, 6.0; N, 9.4.

Oxidation of tetrahydropyridines 6 and 7 in acetonitrile. At 0 °C, $KMnO_4$ (1.13 g, 7.2 mmol) was added with intense stirring to a solution of 1-ethyltetrahydropyridine **6** (0.9 g, 4.8 mmol) in a mixture of 30 mL MeCN and 30 mL of H_2O; the mixture was kept for 1.5 h at ~20 °C. The precipitate of MnO_2 was separated and washed with $CHCl_3$ (5×10 mL). The filtrates were combined, the solvent was evaporated *in vacuo*, and the residue was purified on a column with silica gel to give 0.92 g (81.4%) of lactamdiol **11**.

A similar reaction involving 1-benzyltetrahydropyridine **7** (0.59 g, 3.8 mmol) gave 0.77 g (68%) of lactamdiol **12**.

3,4-Diacetoxy-1-benzyl-2-oxo-4-(γ-pyridyl)piperidine (13). Acetyl chloride (0.53 g, 6.71 mmol) and acetic anhydride (0.69 g, 6.71 mmol) were added to a solution of lactamdiol **12** (2.0 g, 6.71 mmol) in 20 mL of dry C_6H_6. The mixture was refluxed for 4 h, cooled to ~20 °C, and concentrated *in vacuo*. The residue was alkalified by a solution of NaOH up to pH 10—11. The free bases thus formed were extracted with $CHCl_3$ and dried with $MgSO_4$. The solvent was removed, and the residue was crystallized from ether to give 0.21 g (85%) of diester **13** as colorless crystals, m.p. 178—180 °C, R_f 0.70. ^{1}H NMR, δ: 1.8 (br.m, 1 H, H(5a)); 2.03 and 2.09 (both s, 2 Me); 2.70 (dd, 1 H, H(5e), J = 12.8 and 7.0 Hz); 3.15 (ddd, 1 H, H(6a), J = 12.8 and 7.0 Hz); 3.35 (dd, 1 H, H(6e), J = 11.5 and 7.0 Hz); 4.30 and 5.02 (AB spectrum, 2 H, N—CH_2—Ar, J = 14.6 Hz); 5.40 (s, H(3)); 7.17 and 8.60 (AA′XX′ type spectrum, 4 H, C_5H_4N); 7.33 (s, 5 H, Ph). ^{13}C NMR, δ: 20.3 and 21.1 (Me); 27.2, 42.3, and 50.4 (CH_2); 73.5 (CH(3)); 80.7 (C(4)); 120.0, 127.6, 127.9, 128.0, 128.2, 128.8, and 150.0 (CH_{arom}); 136.0 and 147.1 (C_{quat}); 164.5, 165.2, and 165.5 (C=O). IR, ν/cm^{-1}: 1640 (C=O); 1720 ($MeCO_2$). MS, *m/z* (I_{rel} (%)): 382 $[M]^+$ (100). Found (%): C, 66.01; H, 6.0; N, 7.40. $C_{21}H_{22}N_2O_5$. *M* = 382. Calculated (%): C, 65.96; H, 5.75; N, 7.32.

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