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Studies on Indenopyridine Derivatives and Related Compounds. III.[1] Stereochemistry of 1-Substituted 4,9-Dihydroxy-9-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridines

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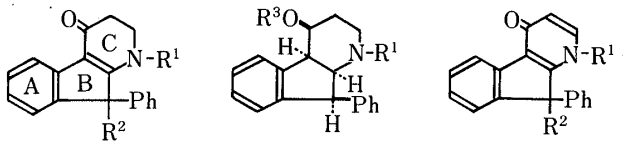
Reaction of 1-methyl- or 1-benzyl-9-phenyl-1,2,3,4-tetrahydro-9*H*-indeno[2,1-*b*]pyridin-4-ones (**1a** and **1b**) with potassium hydroxide in 1-propanol gave the 9-hydroxy derivatives (**4a** and **4b**) in good yield. Sodium borohydride reduction of **4a** gave the B/C-*cis*-4,9-dihydroxy-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (**8**) stereospecifically. On the other hand, **4b** gave the B/C-*trans*-4,9-dihydroxy-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (**10**) and its C-9 isomer (**11**). Treatment of **11** with acetic anhydride in pyridine gave the corresponding monoacetate **13**. However, acetylation of **10** afforded the B/C-*cis* monoacetate **12** with isomerization at B/C ring juncture. The structure and stereochemistry of these compounds is discussed.

Keywords——vinylogous lactam; hexahydro-9*H*-indeno[2,1-*b*]pyridine; sodium borohydride reduction; autoxidation; stereochemistry

In a previous paper,[1] we reported the synthesis of 1-methyl- or 1-benzyl-9-phenyl-1,2,3,4-tetrahydro-9*H*-indeno[2,1-*b*]pyridin-4-ones (**1a** and **1b**) and their reduction to give the hexahydroalcohols (**2a** and **2b**), which gave the corresponding acetate (**3a** and **3b**) upon treatment with acetic anhydride and pyridine. The stereochemistries of **2** and **3** were deduced from the proton nuclear magnetic resonance (^{1}H-NMR) spectra, which firmly established the axial configuration of the C-4 hydroxyl group in a stable B/C *cis*-fused form[2] of **2** in which the C_{4a}–C_{4b} bond is equatorial with respect to the piperidine ring, whereas **3** has the C-4 acetoxyl group equatorial in an unstable B/C *cis*-fused system in which the C_{4a}–C_{4b} bond is axial with respect to the piperidine ring. As a continuation of our studies on indenopyridines, we describe the synthesis and reduction of the 9-hydroxy derivatives (**4a** and **4b**) of **2**, from which we could obtain the B/C-*trans*-hexahydro-9*H*-indeno[2,1-*b*]pyridines **10** and **11**.



1a, b: R^2=H **4a, b**: R^2=OH **6b**: R^2=OAc

2a, b: R^3=H **3a, b**: R^3=Ac

5a, b: R^2=OAc **7a**: R^2=OH

a: R^1=Me; **b**: R^1=CH_2Ph

Chart 1

When a solution of **1a** and an equivalent amount of potassium hydroxide (KOH) in 1-propanol was boiled under reflux for 10 h, 1-methyl-9-hydroxy-9-phenyl-1,2,3,4-tetrahydro-9*H*-indeno[2,1-*b*]pyridin-4-one (**4a**) was obtained in 92% yield. The reaction under a continuous argon stream resulted in recovery of **1a**, so **4a** is presumably formed by

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autoxidation. It is well known that 9-alkylfluorenes are oxidized smoothly by oxygen to 9-hydroperoxy-9-alkylfluorenes and 9-alkylfluorenols in pyridine in the presence of benzyltrimethylammonium hydroxide.[3] Triphenylmethane and diphenylmethane also react with oxygen in a mixture of *tert*-butyl alcohol and dimethylsulfoxide in the presence of potassium *tert*-butoxide to give the corresponding carbinols.[4] The structure of **4a** was elucidated from the elemental analysis data, and the following spectral data: OH band at 3200 cm^{-1} in the infrared (IR) spectrum, molecular ion peak at *m/e* 291 in the mass spectrum (MS), ultraviolet (UV) absorption maxima at 245, 290 and 378 nm ascribable to the vinylogous lactam chromophore[5] and, in particular, the disappearance of a signal due to H-9 in **1a** (4.51 ppm) in the ^{1}H-NMR spectrum. Treatment of **4a** with acetic anhydride in pyridine at 80 °C gave 9-acetoxy-1-methyl-9-phenyl-1,4-dihydro-9*H*-indeno[2,1-*b*]pyridin-4-one (**5a**) in 65% yield. Treatment of **1a** with acetic anhydride in refluxing pyridine resulted in autoxidation, acetylation and dehydrogenation to give **5a** in 55% yield. The ^{1}H-NMR spectrum of **5a** revealed a pair of doublet (J=8 Hz) at 6.30 and 7.60 ppm. The IR spectrum showed characteristic absorption bands at 1765 cm^{-1} ($OCOCH_3$), and at 1635 and 1600 cm^{-1} ascribable to the γ-pyridone.[6] Hydrolysis of **5a** with KOH in ethanol afforded **7a** in good yield. In the same manner as with **1a**, **1b** was autoxidized to **4b**, which was then treated with acetic anhydride and pyridine to give **5b** in 52% yield, together with 9-acetoxy-1-benzyl-9-phenyl-1,2,3,4-tetrahydro-9*H*-indeno[2,1-*b*]pyridin-4-one (**6b**) in 17% yield. The structure of **6b** was confirmed by comparison of its IR, UV and ^{1}H-NMR spectra with those of **4b**.

Next, reductions of **4a** and **4b** with sodium borohydride ($NaBH_4$) were examined. A single product, namely 4,9-dihydroxy-1-methyl-9-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (**8**), was produced in excellent yield, indicating that the reduction takes place stereospecifically. Catalytic hydrogenation of **4a** over platinum oxide (PtO_2) in ethanol at atmospheric pressure gave **8** in 94% yield. Acetylation of **8** with acetic anhydride and pyridine gave the monoacetate **9** in 83% yield. The ^{1}H-NMR spectral data, shown in the table, for H-4, H-4a and H-9a clearly showed that both compounds (**8** and **9**) have the B/C *cis*-fused form with the C-4 hydroxyl group axial in **8** and the C-4 acetoxyl group equatorial in **9**. Thus, conformational change occurs during the acetylation, presumably because of the bulkiness of the acetoxyl group. In the reduction of the vinylogous lactam **4a**, either chemically or catalytically, the approach of the hydride (or catalyst) from the side opposite to the large C-9 phenyl ring appears to be preferred.[7] Therefore, a stable *cis*-B/C ring fusion for **8** and an unstable *cis*-B/C ring fusion for **9** were assigned.[8] These results were in good agreement with those of the previous paper.[1] Further evidence supporting these stereochemical assignments is provided by the abnormal high-field shift of the *N*-methyl resonance (1.60 ppm) of **9**, since the C-9 phenyl ring shields the *N*-methyl protons in the unstable B/C-*cis* form.[9] The products of $NaBH_4$ reduction of **4b** were separated by column chromatography on alumina to give the diol **10** (76%) accompanied by the diol **11** (11%). The ^{1}H-NMR spectra of both diols showed a doublet due to H-9a [2.92 ppm (J=13.8 Hz) in **10**; 2.97 ppm (J=13.2 Hz) in **11**] which led us to assign the B/C *trans*-fused structure. The signals of H-4a appeared as a doublet at 4.27 ppm (J=13.8 Hz) in **10** and at 4.69 ppm (J=13.2 Hz) in **11**, showing no coupling with H-4. The signals of H-4, shown in the table, also support the axial orientation of C-4 hydroxyl groups in both diols. The two compounds (**10** and **11**) are therefore epimeric at C-9. The fact that only the *trans*-B/C ring forms could be isolated is surprising, since the closely related 9-phenyl-hexahydro-1*H*-indeno[2,1-*c*]pyridine[9,10] and 5-phenyl-hexahydro-1*H*-indeno[1,2-*b*]-pyridines,[7] are reported to be in the B/C-*cis* forms, and our previous results[1] also established B/C-*cis* stereochemistry for several compounds.

Finally, the stereochemistry of the C-9 hydroxyl group in the diols (**10** and **11**) was supported to be α in **10** and β in **11** for the following reasons. The MS of **10** exhibited no molecular ion peak but gave a base peak at *m/e* 336 [$M^+ - (H_2O$ and OH)], while **11** showed

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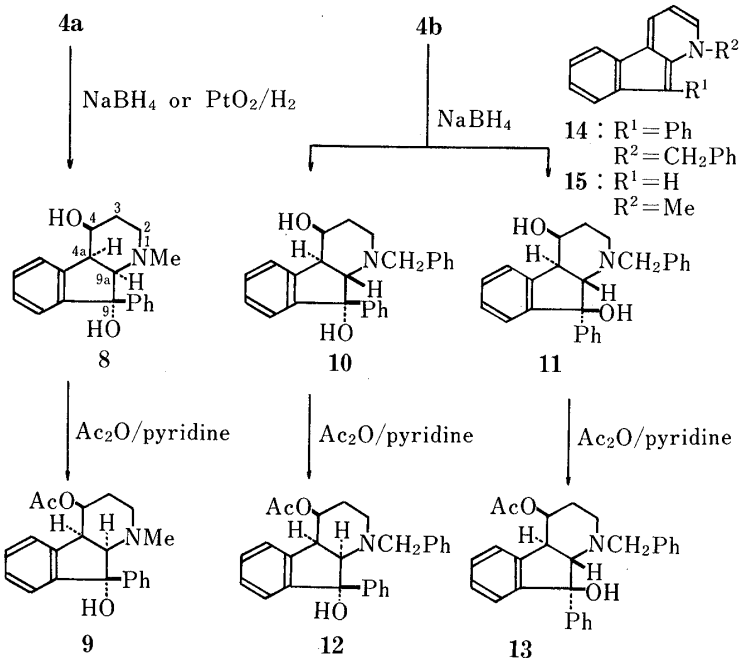

Chart 2

TABLE I. ^{1}H-NMR Data for Hexahydro-9*H*-indeno[2,1-*b*]pyridines in $CDCl_3$ (300 MHz)[a]

Compound	H-4	H-4a	H-9a
8	4.20 br d J=3.3 Hz	3.61 dd J=7.9, 3.3 Hz	3.20 d J=7.9 Hz
9	5.30 br dd J=9.0, 5.3 Hz	4.13 t J=5.3 Hz	3.19 d J=5.3 Hz
10	4.23 br t J=2.0 Hz	4.27 d J=13.8 Hz	2.92 d J=13.8 Hz
11	4.70 q J=2.7 Hz	4.69 d J=13.2 Hz	2.97 d J=13.2 Hz
12	5.48 br dd J=10.6, 5.9 Hz	3.88 dd J=7.9, 5.9 Hz	3.70 d J=7.9 Hz
13	5.82 q J=2.7 Hz	4.73 d J=13.2 Hz	2.98 d J=13.2 Hz

a) Chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard.

the molecular ion peak at *m/e* 371. Heating of **10** in acetic acid gave 1-benzyl-9-phenyl-1*H*-indeno[2,1-*b*]pyridine (**14**) in 33% yield, accompanied by a large amount of tarry materials, while **11** was recovered unchanged under the same conditions. This significant difference might be due to the ease of *trans*-elimination between the C-9 hydroxyl group and adjacent C-9a hydrogen atom. The formation of the Δ^9-double bond would facilitate dehydration of the C-4 hydroxyl group and ultimately give **14** by subsequent dehydrogenation. The structure of **14**, red-violet crystals, was substantiated by its spectral properties. The UV spectrum (see Experimental) was very similar to that of 1-methyl-1*H*-indeno[2,1-*b*]pyridine (**15**), which can be prepared by methylation of 1-azafluorene followed by treatment with KOH.[11] The ^{1}H-NMR spectrum showed signals due to H-2 (dd, J=7 and 1 Hz) and H-4 (br d, J=7 Hz) at 8.23 and 8.19 ppm, respectively, together with the signal due to H-3 (t, J=7 Hz) at 6.48 ppm; these signals closely resemble those of **15**. Acetylation in pyridine at 40 °C converted **10** to the

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monoacetate **12** in 83% yield, accompanied by some tarry materials, while **11** yielded **13** in 95% yield. The ^{1}H-NMR spectral data for H-4, H-4a and H-9a, shown in the Table I, indicated that **13** has a *trans*-B/C ring fusion and an axially oriented acetoxyl group at C-4. On the other hand, the ^{1}H-NMR spectrum of **12** showed signals due to H-9a (d, $J=7.9$ Hz) at 3.70 ppm and H-4 (br dd, $J=10.6$ and 5.9 Hz) at 5.48 ppm, indicating a *cis*-B/C ring fusion and equatorial orientation of the acetoxyl group. Further evidence of the ring transformation was provided by the following chemical means. Catalytic hydrogenation of **12** over 10% palladium on carbon (Pd–C) in ethanol in the presence of acetic acid, followed by *N*-methylation with formaldehyde,[12] gave **9**, whose identity was verified by direct comparison of the IR and ^{1}H-NMR spectra with those of authentic **9**. The mechanism of this ring transformation is not clear at present.

Consequently, we have synthesized two B/C-*trans*-hexahydro-9*H*-indeno[2,1-*b*]pyridines by $NaBH_4$ reduction of **4b**.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrometer, UV spectra were determined on JASCO UVIDEC-505 spectrometer in 95% EtOH, and ^{1}H-NMR spectra were recorded with Hitachi R-24A (90 MHz) and Varian XL-300 (300 MHz) spectrometers with tetramethylsilane as an internal standard. MS were recorded with a Hitachi RMU-7L spectrometer.

9-Hydroxy-1-methyl-9-phenyl-1,2,3,4-tetrahydro-9*H*-indeno[2,1-*b*]pyridin-4-one (4a)——The vinylogous lactam (**1a**) (2.75 g, 0.01 mol) was dissolved in a solution of KOH (0.4 g, 0.01 mol) in 1-propanol (50 ml) and the mixture was boiled under reflux for 10 h, then allowed to cool. The resulting precipitate was filtered off, washed with cold MeOH and dried to give pale yellow crystals of **4a** (2.68 g, 92%). Recrystallization from MeOH gave an analytical sample, mp 300 °C (dec.). IR ν (KBr) cm^{-1}: 3200 (OH), 1618, 1606 (N–C=C–CO). UV λ_{max}^{EtOH} nm (log ε): 245 (4.00), 290 (4.19), 378 (3.83). ^{1}H-NMR (DMSO-d_6) δ: 2.92 (3H, s, NCH_3), 3.65 (2H, m, H-2), 6.75 (1H, s, OH), 6.80—7.50 (8H, m, Ar-H), 7.70 (1H, dd, $J=8$ and 3 Hz, H-5). MS *m/e*: 291 (M^+). *Anal.* Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.49; H, 6.03; N, 4.71.

1-Benzyl-9-hydroxy-9-phenyl-1,2,3,4-tetrahydro-9*H*-indeno[2,1-*b*]pyridin-4-one (4b)——A solution of **4b** (3.67 g, 0.01 mol) and KOH (0.4 g, 0.01 mol) in 1-propanol (50 ml) was worked up in the same manner as described for the synthesis of **4a** to give pale yellow crystals of **4b** (3.16 g, 82%), which were recrystallized from MeOH to give an analytical sample, mp 294—296 °C (dec.). IR ν (KBr) cm^{-1}: 3200 (OH), 1620, 1610 (N–C=C–CO). UV λ_{max}^{EtOH} nm (log ε): 250 (4.13), 287 (4.26), 378 (3.95). ^{1}H-NMR (DMSO-d_6) δ: 3.62 (2H, m, H-2), 4.55 (2H, br s, NCH_2Ar), 6.72 (1H, s, OH), 6.70—7.50 (13H, m, Ar-H), 7.70 (1H, dd, $J=8$ and 3 Hz, H-5). *Anal.* Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.94; H, 5.97; N, 3.92.

9-Acetoxy-1-methyl-9-phenyl-1,4-dihydro-9*H*-indeno[2,1-*b*]pyridin-4-one (5a)——a) From **4a**: A suspension of **4a** (291 mg, 1 mmol) in acetic anhydride (20 ml) and pyridine (20 ml) was heated at 80 °C until all the **4a** had dissolved. After evaporation of the acetic anhydride and pyridine *in vacuo*, the residue was recrystallized from MeOH to give pale yellow crystals of **5a** (217 mg, 65%), mp 300 °C. IR ν (KBr) cm^{-1}: 1765 (CO), 1635, 1600 (γ-pyridone). UV λ_{max}^{EtOH} nm (log ε): 230 (4.53), 273 (3.90), 283 (4.02), 304 (4.05). ^{1}H-NMR (DMSO-d_6) δ: 2.22 (3H, s, $OCOCH_3$), 3.38 (3H, s, NCH_3), 6.30 and 7.60 (each 1H, each d, $J=8$ Hz, N–CH=CH–CO), 6.85—7.75 (4H, m, Ar-H). MS *m/e*: 331 (M^+). *Anal.* Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23. Found: C, 76.43; H, 5.41; N, 3.93.

b) From **1a**: A suspension of **1a** (275 mg, 1 mmol) in acetic anhydride (20 ml) and pyridine (20 ml) was worked up in the same manner as described above to give **5a** (183 mg, 55%), which was identical with an authentic sample (IR spectral comparison).

Acetoxylation of 4b——A mixture of **4b** (0.7 g, 2 mmol) in acetic anhydride (20 ml) and pyridine (20 ml) was worked up in the same manner as described for the acetoxylation of **4a** to give a crude solid, which was recrystallized from MeOH to give **5b** from the more soluble fractions and **6b** from the less soluble fractions.

9-Acetoxy-1-benzyl-9-phenyl-1,4-dihydro-9*H*-indeno[2,1-*b*]pyridin-4-one (5b)——Yield 52%, mp 241—243 °C. IR ν (KBr) cm^{-1}: 1760 (CO), 1640, 1605, 1600 (γ-pyridone). UV λ_{max}^{EtOH} nm (log ε): 231 (4.49), 275 (3.92), 285 (4.05), 306 (4.10). ^{1}H-NMR (DMSO-d_6) δ: 1.60 (3H, s, $OCOCH_3$), 5.0 (2H, s, NCH_2Ar), 6.40 and 7.55 (each 1H, each d, $J=8$ Hz, N–CH=CH–CO), 6.80—7.66 (9H, m, Ar-H). *Anal.* Calcd for $C_{27}H_{21}NO_3$: C, 79.59; H, 5.20; N, 3.44. Found: C, 79.65; H, 5.41; N, 3.52.

9-Acetoxy-1-benzyl-9-phenyl-1,2,3,4-tetrahydro-9*H*-indeno[2,1-*b*]pyridin-4-one (6b)——Yield 17%, mp 204—206 °C. IR ν (KBr) cm^{-1}: 1760 (CO), 1630, 1590 (γ-pyridone). UV λ_{max}^{EtOH} nm (log ε): 290 (4.18), 380 (3.86). ^{1}H-NMR (DMSO-d_6) δ: 2.0 (3H, s, $OCOCH_3$), 4.45 (2H, s, NCH_2Ar), 7.70 (1H, dd, $J=8$ and 3 Hz, H-5), 6.45—7.53 (9H, m,

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Ar-H). *Anal.* Calcd for $C_{27}H_{23}NO_3$: C, 79.19; H, 5.66; N, 3.42. Found: C, 79.11; H, 5.85; N, 3.53.

9-Hydroxy-1-methyl-9-phenyl-1,4-dihydro-9*H*-indeno[2,1-*b*]pyridin-4-one (7a)——A solution of **5a** (331 mg, 1 mmol) and KOH (40 mg, 1 mmol) in MeOH (50 ml) was allowed to stand overnight, then neutralized with AcOH. The solvent was evaporated off *in vacuo*. The residue was recrystallized from MeOH to give **7a** as yellow crystals (277 mg, 94%), mp 300 °C. IR ν (KBr) cm^{-1}: 3300 (OH), 1620, 1600 (γ-pyridone). UV λ_{max}^{EtOH} nm (log ε): 270 (3.90), 280 (4.04), 304 (4.07). ^{1}H-NMR (DMSO-d_6) δ: 3.25 (3H, s, NCH_3), 6.23 and 7.53 (each 1H, each d, J=8 Hz, N–CH=CH–CO), 6.90 (1H, s, OH), 6.86—7.23 (4H, m, Ar-H). *Anal.* Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.58; H, 5.44; N, 4.84.

Reduction of 4a with $NaBH_4$——A suspension of **4a** (2.91 g, 0.01 mol) and $NaBH_4$ (1.79 g, 0.05 mol) in EtOH (200 ml) was stirred at 60 °C for 5 h. After evaporation of the solvent, the residue was neutralized with aq. AcOH under ice cooling, and extracted with EtOAc. The extract was washed with sat. aq. $NaHCO_3$, and H_2O, then dried over Na_2SO_4. Removal of the solvent gave an oil, which was chromatographed on a column of Al_2O_3 with benzene–MeOH (10:1) to afford 4,9-dihydroxy-1-methyl-9-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (**8**) (2.72 g, 92%) as a viscous oil. IR ν ($CHCl_3$) cm^{-1}: 3650 (OH). ^{1}H-NMR ($CDCl_3$) δ: 1.97 (3H, s, NCH_3), 2.40 (1H, br s, OH), 3.20 (1H, d, J=7.9 Hz, H-9a), 3.61 (1H, dd, J=7.9 and 3.3 Hz, H-4a), 4.20 (1H, br d, J=3.3 Hz, H-4), 7.0—7.50 (9H, m, Ar-H). MS *m/e*: 295 (M^+). The perchlorate of **8** was recrystallized from EtOH–Et_2O to give colorless crystals, mp 195—197 °C. *Anal.* Calcd for $C_{19}H_{22}ClNO_6$: C, 57.64; H, 5.60; N, 3.53. Found: C, 57.84; H, 5.63; N, 3.83.

Hydrogenation of 4a with PtO_2 Catalyst——A solution of **4a** (291 mg, 1 mmol) in EtOH (15 ml) was hydrogenated over PtO_2 (30 mg) under atmospheric pressure. The catalyst was removed by filtration and removal of the solvent gave an oil, which was purified by column chromatography on Al_2O_3. Elution with benzene–MeOH (10:1) gave **8** (275 mg, 94%), which was identical with an authentic sample by comparison of their ^{1}H-NMR spectra.

Reduction of 4b with $NaBH_4$——A suspension of **4b** (3.67 g, 0.01 mol) and $NaBH_4$ (1.79 g, 0.05 mol) in EtOH (200 ml) was worked up as described for the reduction of **4a** to give an oil. This was subjected to column chromatography on Al_2O_3, and elution with benzene–MeOH (10:1) afforded 1-benzyl-4,9-dihydroxy-9-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (**10**) (2.67 g, 76%) from former fractions. Recrystallization from *n*-hexane gave colorless crystals, mp 138—139 °C. IR ν (KBr) cm^{-1}: 3400 (OH). ^{1}H-NMR ($CDCl_3$) δ: 2.92 (1H, d, J=13.8 Hz, H-9a), 3.54 (2H, q, J=8 Hz, NCH_2Ar), 4.23 (1H, br t, J=2.0 Hz, H-4), 4.27 (1H, d, J=13.8 Hz, H-4a), 6.60—7.50 (14H, m, Ar-H). MS *m/e*: 336 $M^+-(H_2O$ and OH). *Anal.* Calcd for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.72; H, 6.94; N, 3.68. The later fractions yielded the diol **11** (0.41 g, 11%). Recrystallization of the product from benzene–*n*-hexane gave colorless crystals, mp 182—186 °C. IR ν (KBr) cm^{-1}: 3400 (OH). ^{1}H-NMR ($CDCl_3$) δ: 1.60 (1H, s, OH), 2.97 (1H, d, J=13.2 Hz, H-9a), 3.21 and 3.37 (each 1H, each d, J=10 Hz, NCH_2Ar), 4.69 (1H, d, J=13.2 Hz, H-4a), 4.70 (1H, q, J=2.7 Hz, H-4), 7.0—7.50 (14H, m, Ar-H). MS *m/e*: 371 (M^+). *Anal.* Calcd for $C_{25}H_{25}NO_3$: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.79; H, 6.78; N, 3.71.

General Procedure for Acetylation of Compounds 8, 10 and 11——A solution of a diol (**8**, **10** or **11**) (1 mmol) in acetic anhydride (10 ml) and pyridine (1 ml) was allowed to stand at 40 °C for 48 h. The mixture was poured into ice water, made alkaline with $NaHCO_3$, and extracted with EtOAc. The extract was washed with H_2O, and dried over Na_2SO_4. Removal of the solvent gave an oil, which was purified by column chromatography (Al_2O_3, $CHCl_3$).

4-Acetoxy-9-hydroxy-1-methyl-9-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (9)——Yield 83%, mp 121—122 °C (ligroin). IR ν (KBr) cm^{-1}: 3450 (OH), 1750 (CO). ^{1}H-NMR ($CDCl_3$) δ: 1.60 (3H, s, NCH_3), 2.10 (3H, s, $OCOCH_3$), 3.20 (1H, d, J=5.3 Hz, H-9a), 4.13 (1H, t, J=5.3 Hz, H-4a), 5.30 (1H, br dd, J=9.0 and 5.3 Hz, H-4), 7.10—7.70 (9H, m, Ar-H). MS *m/e*: 347 (M^+). *Anal.* Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.65; H, 7.06; N, 4.28.

4-Acetoxy-1-benzyl-9-hydroxy-9-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (12)——Yield 83%, mp 93—94 °C (*n*-hexane). IR ν (KBr) cm^{-1}: 3500 (OH), 1730 (CO). ^{1}H-NMR ($CDCl_3$) δ: 1.90 (3H, s, $OCOCH_3$), 3.60 (2H, q, J=14 Hz, NCH_2Ar), 3.70 (1H, d, J=7.9 Hz, H-9a), 3.88 (1H, dd, J=7.9 and 5.9 Hz, H-4a), 5.48 (1H, br dd, J=10.6 and 5.9 Hz, H-4), 7.10—7.60 (9H, m, Ar-H). MS *m/e*: 413 (M^+). *Anal.* Calcd for $C_{27}H_{27}NO_3$: C, 78.42; H, 6.58; N, 3.39. Found: C, 78.52; H, 6.76; N, 3.69.

4-Acetoxy-1-benzyl-9-hydroxy-9-phenyl-1,2,3,4,4a,9a-hexahydro-9*H*-indeno[2,1-*b*]pyridine (13)——Yield 95%, mp 181—182 °C (petr. ether). IR ν (KBr) cm^{-1}: 3500 (OH), 1730 (CO). ^{1}H-NMR ($CDCl_3$) δ: 2.0 (3H, s, $OCOCH_3$), 2.47 (1H, s, OH), 2.98 (1H, d, J=13.2 Hz, H-9a), 3.30 (2H, q, J=13 Hz, NCH_2Ar), 4.73 (1H, d, J=13.2 Hz, H-4a), 5.82 (1H, q, J=2.7 Hz, H-4), 6.95—7.40 (9H, m, Ar-H). MS *m/e*: 413 (M^+). *Anal.* Calcd for $C_{27}H_{27}NO_3$: C, 78.42; H, 6.58; N, 3.39. Found: C, 78.37; H, 6.51; N, 3.23.

Conversion of 12 to 9——A solution of **12** (82 mg, 0.02 mol) in EtOH (20 ml) containing AcOH (2 ml) was hydrogenated for 5 h over 10% Pd–C (50 mg) under atmospheric pressure. After the usual work-up, a mixture of the residual oil thus obtained and 37% HCHO (200 mg) in MeOH (20 ml) was hydrogenated over 10% Pd–C (50 mg) for 2 h. The catalyst was removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was dissolved in EtOAc, and the solution was washed with H_2O, then dried over Na_2SO_4. Removal of the solvent gave an oil, which was purified by column chromatography (Al_2O_3, $CHCl_3$) to give **9** (18 mg). This product was identical with an authentic sample (IR and ^{1}H-NMR spectral comparisons).

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1-Benzyl-9-phenyl-1*H*-indeno[2,1-*b*]pyridine (14)——A solution of **10** (371 mg, 1 mmol) in AcOH (10 ml) was heated at 100—110 °C for 2 h. After evaporation of the AcOH *in vacuo*, the residue was neutralized with sat. aq. $NaHCO_3$, and extracted with EtOAc. The extract was dried over Na_2SO_4. Removal of the solvent afforded a red-violet oil, which was triturated with EtOAc under ice cooling. The resulting solid was recrystallized from EtOAc to give **14** (109 mg, 33%) as red-violet crystals, mp 144—146 °C. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 255 (4.21), 305 (4.32), 335 sh (4.10), 345 sh (3.84), 520 (3.24), 565 sh (3.18). ^{1}H-NMR ($CDCl_3$) δ: 5.30 (2H, s, NCH_2Ar), 6.48 (1H, t, J=7 Hz, H-3), 7.10—7.40 (14H, m, Ar-H), 8.19 (1H, br d, J=7 Hz, H-4), 8.23 (1H, dd, J=7 and 1 Hz, H-2). MS *m/e*: 333 (M^+). *Anal.* Calcd for $C_{25}H_{19}N$: C, 90.09; H, 5.71; N, 4.20. Found: C, 89.85; H, 5.43; N, 4.49.

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