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Octahydro-7(1*H*)-quinolones. I. Stereochemistries of Catalytic Hydrogenation of 7-Hydroxyquinoline[1)]

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7-Hydroxyquinoline (X) was hydrogenated over 5% rhodium on alumina to give the *trans*-amino-alcohol (XIa) as a main product along with other possible diastereomeric isomers. Separation of four isomers from the row product was achieved after conversion to the *N*-benzyl derivatives, XIIIa, XIIIb, XIIIc and XIIId. Configurations of them were assigned from chemical and physical evidences. A possible mechanistic pathway to the *trans*-fused ring system on hydrogenation was also discussed.

Keywords——hydrogenation over 5% rhodium on alumina; 7-hydroxyquinoline; *trans*-octahydro-7(1*H*)-quinolone derivatives; *trans*-decahydro-7*β*-quinolinol; reaction mechanism; stereochemistry; intramolecular hydrogen bonding; ^{1}H-NMR

In 1967, Wiesner, *et al.*[3)] reported a synthesis of 12-epi-lycopodine (I) *via* the lactam (II) which was obtained by cyclization of the amide (III). Our previous effort to cyclize the amide (IV) to the lactam (V) was, however, unsuccessful[4)] under a similar condition to that for III. The difference in ring juncture of octahydro-7(1*H*)-quinolone system between III and IV seems to be responsible for these two results. However, in spite of its potential role as a key intermediate for the Lycopodium and Aspidosperma alkaloid syntheses,[3,5)] little is known of the chemical and physical properties of octahydro-7(1*H*)-quinolone system (VI). This paper describes stereochemistries of the catalytic hydrogenation of 7-hydroxyquinoline, a possible synthetic precursor of VI, over a rhodium catalyst.

In general, catalytic hydrogenation of quinolines to decahydroquinolines is known to be difficult.[6)] But a few reports concerning the hydrogenation of hydroxyquinolines have been presented,[6a,7)] and there have appeared a few reports concerning the stereochemistry of the products of the catalytic hydrogenation,[8)] since Hückel and Stepf[8a)] established the stereochemistry of *cis*- and *trans*-decahydroquinoline given by hydrogenation of quinoline itself. In Table I are summarized their results, indicating that hydrogenations over nickel catalysts give primarily the *trans*-isomer while those over platinum ones in acidic media

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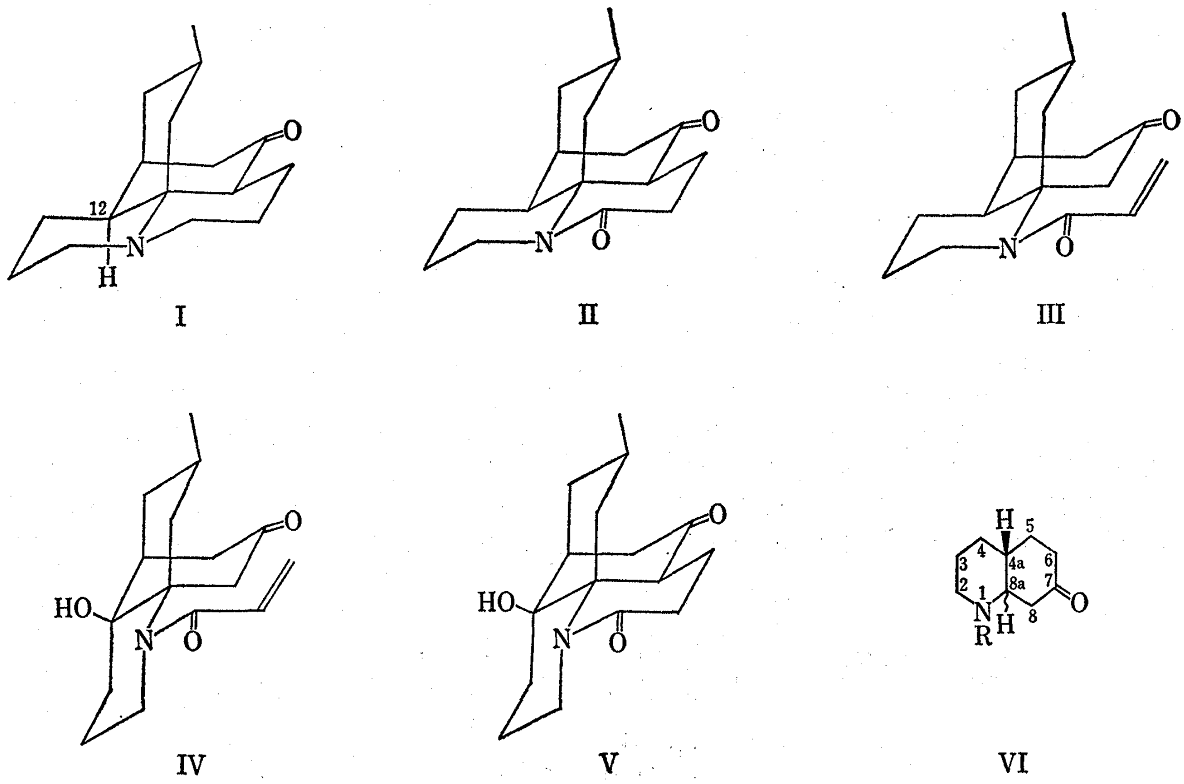

Chart 1

lead to predominance of the *cis*-isomer, and that the isomer ratio depends on the catalysts and conditions used for the reduction. A hydrogenation over rhodium catalysts available for the present study is expected[6a,9] to lead quinolines preferentially to the decahydroquinolines with *cis*-fused ring and not to be accompanied by hydrogenolysis.[10] Actually, hydrogenation of quinoline (VII) in ethanol at 80° and 70 atmospheric pressure over 5% rhodium on alumina yielded quantitatively *cis*-decahydroquinoline (VIII). Its benzoyl

TABLE I. Hydrogenation of Quinoline to Decahydroquinoline

Solvent	Catalyst	Temp. (°C)	Pressure (atm)	Time (hr)	Ratio *cis*	: *trans*	lit.
AcOH–H_2O	Pt	40	2—3	2	20	80	8*a*
AcOH–H_2O–HCl	Pt	40	2—3	1.5	65	35	8*a*
H_2O	Pt	40	2—3	3	tetrahydro compound		8*a*
H_2O (as oxalate)	Pt	40	2—3	3	10	90	8*a*
HCl–H_2O	Pt	r.t.	2	216	$\geqq$97		8*e*
—	Ni	210	70	7.5		$\geqq$98	8*d*
—	Ni	200	150—200	—	mixture		8*c*

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9) Several reports concerning the *cis*-hydrogenation of aromatics or enones over rhodium catalysts have appeared: H.S. Broadbent, E.L. Allred, L. Pendleton, and C.W. Whittle, *J. Am. Chem. Soc.*, **82**, 189 (1960); A.I. Meyers, W. Beverung, and G. Garcia-Munoz, *J. Org. Chem.*, **29**, 3427 (1964); Z. Horii, T. Imanishi, T. Tanaka, I. Mori, M. Hanaoka, and C. Iwata, *Chem. Pharm. Bull.* (Tokyo), **20**, 1768 (1972); M.R. Uskoković, D.C. Pruess, C.W. Despreausx, S. Shiuey, G. Pizzalato, and J. Gutzwiller, *Helv. Chim. Acta*, **56**, 2834 (1973).

10) Known to occur to a moderate extent in the reduction of alkoxy- or hydroxypyridines over nickel or platinum catalysts.[6a]

derivative (IX),[11] mp 95—98°, shows proton magnetic resonance (PMR) signals due to C_2 and C_{8a} protons at the low field (δ 2.5—5.0), the feature confirming its stereochemistry.[8e] The result is in accord with the general behavior[9] of rhodium catalysts in hydrogenation. Hydrogenation of 7-hydroxyquinoline (X)[12] over 5% rhodium on alumina under a similar condition to that for VII afforded a mixture of the isomeric amino-alcohols (XI), which gave on recrystallization a pure *trans*-amino-alcohol (XIa)[13] in 45% yield. A detailed examination of the hydrogenation product revealed that the mixture contained all of the four possible isomers (XIa—d), and that the all-*cis*-hydrogenated isomer (XId) was a minor component. Separation of the stereoisomers was successful with their *N*-benzyl derivatives (XIIIa, b, c, and d) which were derived from the crude hydrogenated mixture by benzoylation followed by lithium aluminum hydride reduction. A ratio of about 13: 1: 2: 8.5 for XIIIa: XIIIb: XIIIc: XIIId was obtained. Their stereochemistries were assigned as follows. In the infrared (IR) spectrum, merely one isomer (XIIId) displayed an intramolecular hydrogen bonding independent of concentration, the fact confirming the structure of XIIId as depicted. *N*-Benzoylation of XIa with benzoyl chloride in the presence of potassium carbonate followed by oxidation of the product (XIVa) with chromium trioxide in acetone gave the amide-

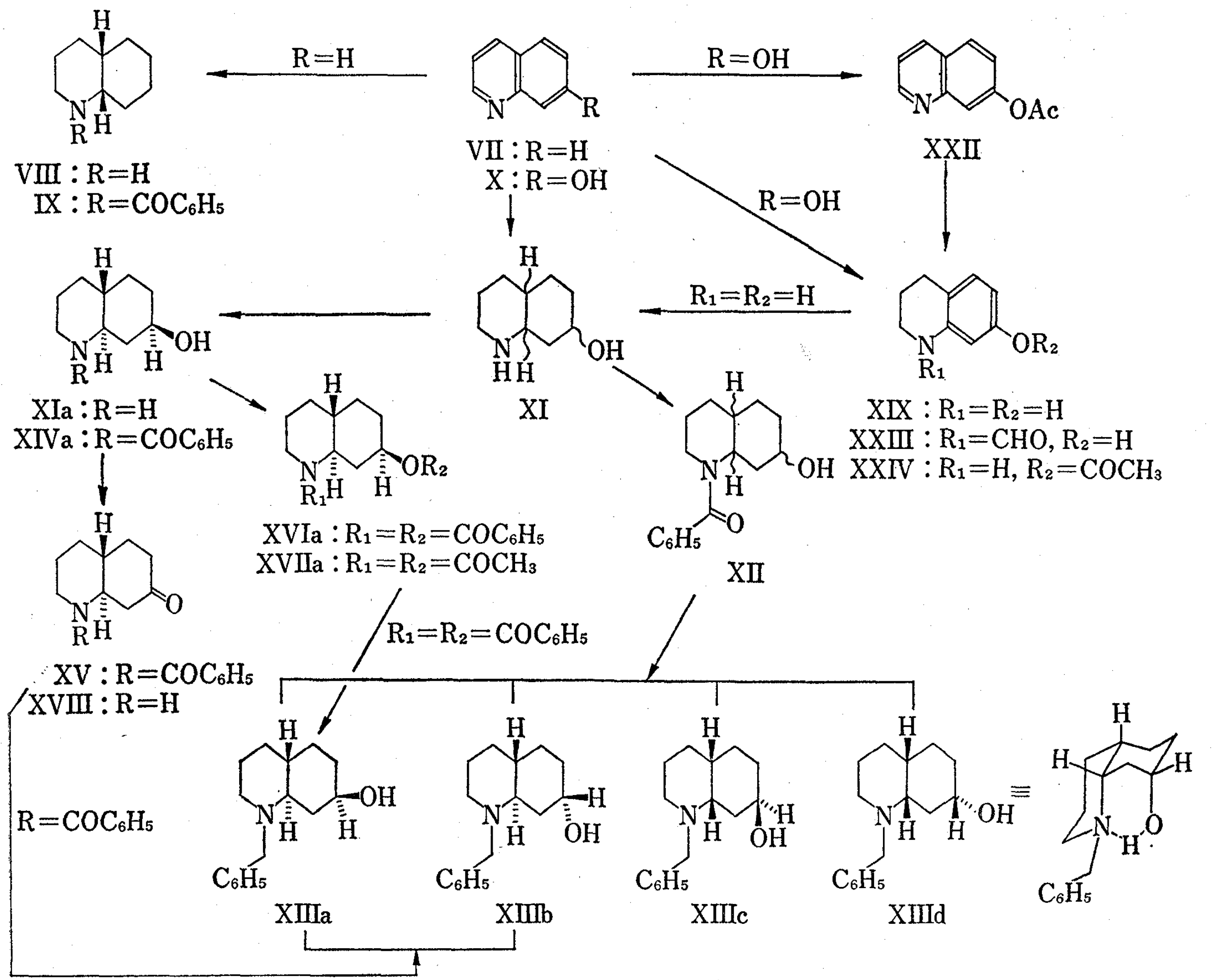

Chart 2

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[11] W.L.F. Armarego, *J. Chem. Soc.* (*C*), 377 (1967).

[12] *a*) E. Fujita, T. Saijoh, and N. Takao, *Yakugaku Zasshi*, **74**, 206 (1954); *b*) L. Bradford, T.J. Elliott, and F.M. Rowe, *J. Chem. Soc.*, 437 (1947).

[13] An alternative synthesis of XIa has been reported: see C.A. Grob and H.J. Wilkens, *Helv. Chim. Acta*, **48**, 808 (1965).

ketone (XV), which was reduced with lithium aluminum hydride in boiling ether to afford two isomeric amino-alcohols (XIIIa and b) with predominance of XIIIa. Since neither of them was identical with XIIId, it was concluded that both of these two isomers had a *trans* ring juncture. In addition, the PMR spectrum of the *N*,*O*-dibenzoyl derivative (XVIa) or the *N*,*O*-diacetyl derivative (XVIIa), given by treatment of XIVa with benzoyl chloride in pyridine or of XIa with acetic anhydride in pyridine, displays one proton signal due to the C_7 axial proton at 5.07 ppm ($W_{1/2}$=24 Hz) or 4.78 ppm ($W_{1/2}$=22 Hz). Furthermore, the benzoate (XVIa) gave only XIIIa on lithium aluminum hydride reduction. Thus, oxidation of XIa by the method of Grob, *et al.*[13] gave *trans*-octahydro-7(1*H*)-quinolone (XVIII), whose stereochemistry[14] was evident from the fact that its *N*-benzoylation gave XV in excellent yield.

It is of interest that the *trans*-isomers were formed preferentially on hydrogenation of X. Although the hydrogenation of X at *ca.* 150° gave unidentified products, that at room temperature gave only a 1,2,3,4-tetrahydro compound (XIX) in 75% yield, whose re-hydrogenation at 80° gave the products of isomer composition similar to that derived from the one-step hydrogenation of X described above. A vinylogous amide (XX)[13] was also hydrogenated at 80° to give the *trans*-isomers (XIa and b) more preferentially than the above run did. These results indicate that the vinylogous amide (XX) is perhaps a major intermediate[15] for the *trans*-isomers (XIa and b) in the hydrogenation of X, because an initial hydrogenation of the least hindered double bond at C_5–C_6 in XIX would give XX *via* an enol (XXI). And it seems likely that the synchronous, non-stepwise hydrogenation of X and/or XIX would occur to some extent to give the *cis*-isomer (XId).

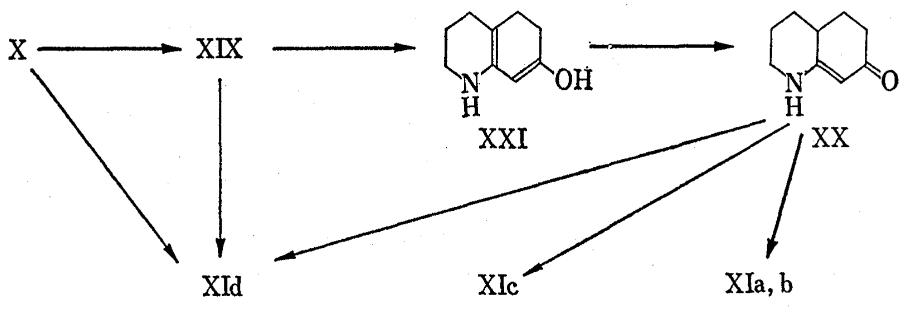

Chart 3

Attempted hydrogenation of 7-acetoxyquinoline (XXII) and a formamide (XXIII) in hopes of obtaining the *cis*-decahydroquinolines exclusively, because of their less possibility to form XX during the hydrogenation, was unsuccessful: XXII gave only a 1,2,3,4-tetrahydro compound (XXIV), and XXIII was unreactive.

Experimental

All melting points are uncorrected. IR spectra were taken on a Hitachi EPI-G3 grating spectrophotometer. PMR spectra were measured for solutions in $CDCl_3$ with a Hitachi R-20A (60 MHz) or R-22 (90 MHz) spectrometer using tetramethylsilane as an internal standard. Coupling constants (*J*) are given in Hz, and the following abbreviations are used; s=singlet, d=doublet, t=triplet, q=quartet, qn=quintet, m=multiplet, and dd=doublet of doublets. Mass spectra were taken on a Hitachi RMU-6E mass spectrometer. All the organic extracts were dried over anhydrous magnesium sulfate before evaporation. Column chro-

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[14] Independent elucidation of the stereochemistry has been described by Grob, *et al.*; ref. 13.

[15] A selective hydrogenation of XX into XIa over palladium or nickel catalyst was reported by Grob, *et al.*; ref. 13.

matography was performed on Merck Aluminiumoxid (Aktivitätsstufe II—III) or Mallinckrodt silicic acid. Thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 PF_{254} or Merck Aluminiumoxid PF_{254} (Typ T).

Hydrogenation of Quinoline (VII)——Quinoline (VII; 2.0 g) was hydrogenated over 5% rhodium on alumina (2.0 g) in abs. EtOH (20 ml) at 80° and 70 atmospheric pressure for 6 hr. The catalyst was filtered off, and the filtrate was evaporated under reduced pressure to give an oil (2.1 g), which was homogeneous on TLC and identical in its PMR spectrum with VIII reported by Armarego.[11)]

A suspension consisting of VIII (0.30 g), benzoyl chloride (0.30 ml), K_2CO_3 (0.70 g) and dry C_6H_6 (20 ml) was stirred at room temperature for 4.5 hr. The inorganic material was removed, and the organic solution was washed with 5% HCl, brine, satd. $NaHCO_3$ and brine, and evaporated under reduced pressure to give a solid, which was recrystallized from petr. ether to give 390 mg (74%) of IX, mp 95—98° (lit[11)] 95°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1609 (amide). PMR (60 MHz) δ: 2 5—5.0 (3H, m, C_2 and C_{8a} protons).

Hydrogenation of 7-Hydroxyquinoline (X)——a) 7β-Hydroxy-*trans*-decahydroquinoline (XIa): 7-Hydroxyquinoline (X; 4.6 g), mp 244—248° (lit[12a)] 234°), prepared by the method of Fujita, *et al.*,[12a)] was hydrogenated over 5% rhodium on alumina (4.6 g) in abs. EtOH (120 ml) at 80° and 70 atmospheric pressure for 6 hr. The catalyst was filtered off, and the filtrate was evaporated under reduced pressure to give a solid (4.9 g). Recrystallization from AcOEt gave 2.2 g (45%) of XIa as colorless needles, mp 169—171° (lit[13)] 170—171.5°). IR ν_{max}^{KBr} cm^{-1}: 3275 and 3125 (OH, NH). *Anal.* Calcd. for $C_9H_{17}ON$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.62; H, 11.13; N, 8.92.

b) *N*-Benzyl-7-hydroxydecahydroquinolines (XIIIa, XIIIb, XIIIc and XIIId): A suspension consisting of benzoyl chloride (0.50 g), K_2CO_3 (1.4 g), dry C_6H_6 (20 ml), and the crude decahydroquinolinol (0 50 g), obtained from the hydrogenation of X (0.47 g) over 5% rhodium on alumina in the same manner as that in a), was stirred at room temperature overnight. The reaction mixture was worked up as usual to give an oil (0.88 g), which was dissolved in dry ether (50 ml) and followed by addition of $LiAlH_4$ (0.88 g) and subsequent refluxing for 25 hr. After decomposing the excess reducing agent with AcOEt, an aqueous solution of sodium potassium tartrate was added to the reaction complex, and the supernatant was decanted. The precipitate was washed with ether. The combined ethereal layers were evaporated to give an oil (0.71 g), which was chromatographed on alumina in $CHCl_3$. The first fraction of the eluates gave 0.22 g (28%) of XIIId as an oil. The second one gave a mixture of XIIIb and XIIIc, which was separated by repeated preparative TLC on silica gel in ether to give 26 mg (3.3%) of XIIIb as an oil and 52 mg (6.6%) of XIIIc as colorless crystals. The third one gave 0.33 g (42%) of XIIIa as a solid.

XIIIa: mp 55—57° (crystallizable only from a large excess of non-dehydrated *n*-hexane). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3625 and 3360 (OH; 133 mM), 3625 (20 mM, 4 mM). Mass Spectrum *m/e*: 245 (M^+), 186, 91. *Anal.* Calcd. for $C_{16}H_{23}ON \cdot H_2O$: C, 72.96; H, 9.57; N, 5.32. Found: C, 72.95; H, 9.54; N, 5.54. Picrolonate: mp 185—189° (from EtOH). *Anal.* Calcd. for $C_{16}H_{23}ON \cdot C_{10}H_8O_5N_4$: C, 61.28; H, 6.13; N, 13.75. Found: C, 61.05; H, 6.17; N, 13.49.

XIIIb: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3625 and 3340 (OH; 133 mM), 3625 (20 mM, 4 mM). Mass Spectrum *m/e*: 245 (M^+), 186, 91. Picrolonate: mp 250—255° (from EtOH). *Anal.* Calcd. for $C_{26}H_{31}O_6N_5$: C, 61.28; H, 6.13; N, 13.75. Found: C, 61.26; H, 6.27; N, 13.49.

XIIIc: mp 87—90° (from *n*-hexane). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3625 and 3350 (OH; 133 mM), 3625 (20 mM, 4 mM). Mass Spectrum *m/e*: 245 (M^+), 186, 91. *Anal.* Calcd. for $C_{16}H_{23}ON$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.13; H, 9.49; N, 5.51.

XIIId: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3350 (OH; independent from the concentration, 4 mM, 20 mM, and 133 mM). Mass Spectrum *m/e*: 245 (M^+), 186, 91. Picrolonate: mp 228—231° (from EtOH). *Anal.* Calcd. for $C_{26}H_{31}O_6N_5$: C, 61.28; H, 6.13; N, 13.75. Found: C, 61.24; H, 6.18; N, 13.54.

7-Hydroxy-1,2,3,4-tetrahydroquinoline (XIX)——The quinoline (X; 350 mg) was hydrogenated over 5% rhodium on alumina in abs. EtOH (10 ml) at room temperature and an atmospheric pressure until the uptake of hydrogen ceased. After the catalyst was filtered off, the filtrate was evaporated under reduced pressure to give an oil (360 mg), which solidified on standing and was recrystallized from *n*-hexane to give 270 mg (75%) of XIX as colorless needles, mp 89—90°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3505 and 3300 (OH, NH), 1620 (C=C). PMR (90 MHz) δ: 1.88 (2H, qn, J=6, C_3-$\underline{H}_2$), 2.68 (2H, t, J=6, C_4-$\underline{H}_2$), 3.74 (2H, t, J=6, C_2-$\underline{H}_2$), 7.11—6.88 (1H, C_5-$\underline{H}$), 6.78—6.50 (2H, C_6-$\underline{H}$ and C_8-$\underline{H}$). *Anal.* Calcd. for $C_9H_{11}ON$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.43; H, 7.42; N, 9.24.

Hydrogenation of XIX——The tetrahydro compound (XIX; 0.50 g) was hydrogenated under a similar condition to that for XIa to afford a solid (460 mg) after a usual working up. Benzoylation of the crude decahydroquinolinol (460 mg) and subsequent reduction with $LiAlH_4$ in a manner similar to that described in b) for hydrogenation of X gave an oil (640 mg), which was worked up as described above to give 0.30 g (36%) of XIIIa, 17 mg (2.1%) of XIIIb, 39 mg (4.7%) of XIIIc, and 170 mg (21%) of XIIId.

Hydrogenation of 2,3,4,4a,5,6-Hexahydro-7(1*H*)-quinolone (XX)——The vinylogous amide (XX; 1.0 g) was hydrogenated over 5% rhodium on alumina (1.0 g) in abs. EtOH (100 ml) under a similar condition to that for XIa to afford a solid (0.50 g), benzoylation of which and subsequent reduction with $LiAlH_4$ in a similar manner to that described above gave an oil (1.3 g). Usual working up as described above gave 750 mg (46%) of XIIIa, 80 mg (5.0%) of XIIIb, 58 mg (3.5%) of XIIIc and 280 mg (17%) of XIIId.

7-Acetoxyquinoline (XXII)——A mixture of X (1.0 g) and Ac_2O (20 ml) was refluxed for 1 hr. After the solvent was evaporated under reduced pressure, the resulting residue was extracted with $CHCl_3$, and the extract was washed with satd. $NaHCO_3$ and brine. Evaporation of the extract gave a solid (1.3 g), which was recrystallized from *n*-hexane to afford 920 mg (71%) of XXII as pale yellow needles, mp 59—60°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1760 (ester). PMR (60 MHz) δ: 2.37 (3H, s, O–C$\underline{\mathrm{H}}_3$), 7.30 (1H, dd, $J=2$ and 9.5, C_6–$\underline{\mathrm{H}}$), 7.36 (1H, dd, $J=4$ and 8.5, C_3–$\underline{\mathrm{H}}$), 7.82 (1H, d, $J=2$, C_8–$\underline{\mathrm{H}}$), 7.82 (1H, d, $J=9.5$, C_5–$\underline{\mathrm{H}}$), 8.14 (1H, dd, $J=2$ and 8.5, C_4–$\underline{\mathrm{H}}$) 8.92 (1H, dd, $J=2$ and 4, C_2–$\underline{\mathrm{H}}$). *Anal.* Calcd. for $C_{11}H_{19}O_2N$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.86; H, 4.89; N, 7.77.

Attempted Hydrogenation of XXII——7-Acetoxyquinoline (XXII; 0.74 g) was hydrogenated over 5% rhodium on alumina (0.74 g) in abs. EtOH (70 ml) under a similar condition to that described for XIa. Usual working up afforded an oil (0.74 g), which was chromatographed on silica gel in $CHCl_3$ to give 0.40 g (53%) of XXIV as a colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1750 (ester). Mass Spectrum *m/e*: 191 (M^+). PMR (60 MHz) δ: 1.91 (2H, qn, $J=5.5$, C_3–$\underline{\mathrm{H}}_2$), 2.24 (3H, s, COC$\underline{\mathrm{H}}_3$), 2.71 (2H, t, $J=5.5$, C_4–$\underline{\mathrm{H}}_2$), 3.26 (2H, t, $J=5.5$, C_2–$\underline{\mathrm{H}}_2$), 3.62 (1H, m, N$\underline{\mathrm{H}}$), 7.00—6.81 (1H, C_5–$\underline{\mathrm{H}}$), 6.40—6.12 (2H, C_6–$\underline{\mathrm{H}}$ and C_8–$\underline{\mathrm{H}}$). Picrolonate: mp 167—169° EtOH). *Anal.* Calcd. for $C_{21}H_{21}O_7N_5$: C, 55.38; H, 4.65; N, 15.38. Found: C, 55.08; H, 4.65; N, 15.40.

***N*-Formyl-7-hydroxy-1,2,3,4-tetrahydroquinoline (XXIII)**——A mixture of XIX (0.26 g) and acetic-formic anhydride[16] (15 ml) was allowed to stand at room temperature overnight. After the solvent was removed under reduced pressure, the resulting residue was made alkaline with satd. $NaHCO_3$ and extracted with $CHCl_3$. The extract was evaporated, and the resulting residue (330 mg) was dissolved in MeOH (5 ml) and 28% aq. NH_3 (0.5 ml). The resulting mixture was stirred at room temperature for 2.5 hr and evaporated at room temperature under reduced pressure. The residue was extracted with $CHCl_3$, and the extract was evaporated to give 260 mg (85%) of XXIII as a solid, which was recrystallized from benzene–*n*-hexane to give an analytical sample, mp 120—121°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1660 (amide). Mass Spectrum *m/e*: 177 (M^+). PMR (60 MHz) δ: 1.90 (2H, qn, $J=6$, C_3–$\underline{\mathrm{H}}_2$), 2.69 (2H, t, $J=6$, C_4–$\underline{\mathrm{H}}_2$), 3.77 (2H, t, $J=6$, C_2–$\underline{\mathrm{H}}_2$), 7.10—6.86 (1H, C_5–$\underline{\mathrm{H}}$), 6.77—6.55 (2H, C_6–$\underline{\mathrm{H}}$, C_8–$\underline{\mathrm{H}}$), 8.72 (1H, s, N-C$\underline{\mathrm{H}}$O). *Anal.* Calcd. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26; N, 7.91. Found: C, 68.07; H, 6.47; N, 7.76.

Attempted Hydrogenation of XXIII——The formamide (XXIII; 230 mg) was hydrogenated over 5% rhodium on alumina (230 mg) in abs. EtOH (30 ml) under a similar condition to that for XIa. Usual working up resulted in a recovery of the starting material.

***trans*-Octahydro-7(1*H*)-quinolone (XVIII)**——According to the procedure of Grob, *et al.*,[13] the aminoketone (XVIII) was synthesized from the amino alcohol (XIa) in 60% yield. Recrystallization from *n*-hexane gave colorless needles, mp 90—93° (lit[13] 91—93°). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1710 (CO). Mass Spectrum *m/e*: 153 (M^+). *Anal.* Calcd. for $C_9H_{15}ON$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.59; H, 9.87; N, 9.30.

***N*-Benzoyl-7β-hydroxy-*trans*-decahydroquinoline (XIVa)**——A suspension consisting of XIa (0.25 g), benzoyl chloride (0.30 g), K_2CO_3 (0.70 g) and dry C_6H_6 (20 ml) was stirred at room temperature overnight. The reaction mixture was worked up as usual to give an oil (0.50 g), which was chromatographed on alumina in $CHCl_3$ to afford 340 mg (81%) of XIVa as a solid. Recrystallization from benzene gave an analytical sample as colorless plates, mp 185—187°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3390 (OH), 1605 (amide). *Anal.* Calcd. for $C_{16}H_{21}O_2N$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.04; H, 8.12; N, 5.31.

***N*-Benzoyl-*trans*-octahydro-7(1*H*)-quinolone (XV)**——a) To a stirred solution of XIVa (160 mg) in acetone was added dropwise a slight excess of Jones reagent at 0—2°, and stirring was continued at the same temperature for 5 min and at room temperature for 30 min. An excess of the reagent was decomposed with MeOH, and the reaction complex was extracted with $CHCl_3$. Evaporation of the extract gave a solid (150 mg), which was recrystallized from *n*-hexane to afford 0.10 g (63%) of XV as fine colorless needles, mp 106—108°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1711 (CO), 1619 (amide). Mass Spectrum *m/e*: 257 (M^+), 105. PMR (90 MHz) δ: 3.28—3.85 (3H, m, C_2–H_2 and C_{8a}–$\underline{\mathrm{H}}$), 7.36 (5H, s, $C_6\underline{\mathrm{H}}_5$). *Anal.* Calcd. for $C_{16}H_{19}O_2N$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.50; H, 7.36; N, 5.39.

b) A suspension consisting of XVIII (130 mg), benzoyl chloride (160 mg), K_2CO_3 (350 mg) and dry C_6H_6 (10 ml) was stirred at room temperature overnight. The reaction mixture was worked up as usual to give an oil (250 mg), which was chromatographed on silica gel in $CHCl_3$ to give 170 mg (78%) of XV as colorless crystals. The IR spectrum of this product was identical with that obtained in a).

***N*-Acetyl-7β-acetoxy-*trans*-decahydroquinoline (XVIIa)**——A mixture of XIa (0.050 g), Ac_2O (2 ml) and dry pyridine (2 ml) was allowed to stand at room temperature overnight, and evaporated under reduced pressure. The resulting residue was extracted with $CHCl_3$, and the extract was washed with satd. $NaHCO_3$, brine, 5% HCl and brine, and evaporated to give 77 mg of XVIIa as a solid. Recrystallization from *n*-hexane gave an analytical sample as colorless needles, mp 80—82°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1725 (CO), 1625 (amide).

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16) L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, 1967, p. 4.

PMR (90 MHz) δ: 1.97 (3H, s, N-COC$\underline{H}_3$), 2.03 (3H, s, O-COC$\underline{H}_3$), 4.78 (1H, m, $W_{1/2}=22$, $\underline{H}$C-OAc). *Anal.* Calcd. for $C_{13}H_{21}O_3N$: C, 65.24; H, 8.84; N, 5.85. Found: C, 65.35; H, 8.84; N, 5.85.

***N*-Benzoyl-7*β*-benzoyloxy-*trans*-decahydroquinoline (XVIa)**——A mixture of XIVa (0.20 g), benzoyl chloride (140 mg) and dry pyridine (10 ml) was allowed to stand at room temperature overnight. The mixture was poured into 5% HCl-ice and extracted with $CHCl_3$. The extract was washed with H_2O and evaporated to give an oil, which was chromatographed on silica gel in $CHCl_3$ to give 230 mg (82%) of XVIa. Recrystallization from *n*-hexane gave an analytical sample as colorless plates, mp 118—119°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1710 (ester), 1620 (amide). PMR (90 MHz) δ: 5.07 (1H, m, $W_{1/2}=24$, $\underline{H}$C-OCOC_6H_5), 7.20—7.56 (8H, aromatic protons), 7.90—8.19 (2H, aromatic protons). *Anal.* Calcd. for $C_{23}H_{25}O_3N$: C, 76.00; H, 6.93; N, 3.85. Found: C, 75.76; H, 6.93; N, 3.92.

Reduction of XVIa——A suspension consisting of XVIa (0.090 g), $LiAlH_4$ (90 mg) and abs. ether (20 ml) was refluxed for 17 hr. The mixture was worked up as usual to afford 0.050 g of an oil, which was chromatographed on alumina in $CHCl_3$ to give 37 mg (55%) of XIIIa as colorless crystals. This product was identical with an authentic sample in comparison of the IR spectra and in TLC.

Reduction of XV——A mixture of XV (53 mg), $LiAlH_4$ (150 mg) and abs. ether was refluxed for 8 hr. The mixture was worked up as usual to afford an oil (45 mg), which was chromatographed on alumina in $CHCl_3$ to give 35 mg (69%) of XIIIa and 5.5 mg (11%) of XIIIb. These products were identical with authentic samples in comparison of the IR spectra and in TLC.