[Chem. Pharm. Bull. 25(7)1797—1802(1977)]

UDC 547.831.7.04 : 541.63.03

Octahydro-7(1*H*)-quinolones. II.[1] A Stereoselective Synthesis of *cis*-Octahydro-7(1*H*)-quinolone

Takefumi Momose, Shuji Uchida, Masahiko Kinoshita, and Takeshi Imanishi

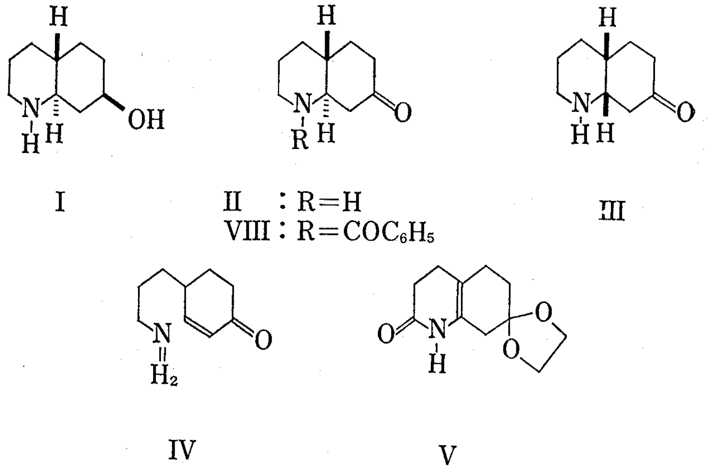
Faculty of Pharmaceutical Sciences, Osaka University[2]

(Received March 31, 1977)

cis-Octahydro-7(1*H*)-quinolone (III) was synthesized stereoselectively by two different routes, one *via* intramolecular Michael addition of an amino enone (IV) and the other *via* catalytic hydrogenation of a bicyclic lactam (V). Detailed examinations of hydrogenation products in the latter was also described.

Keywords——*cis*-octahydro-7(1*H*)-quinolone; stereoselective synthesis; intramolecular Michael addition; hydrogenation of a bicyclic lactam; vinylogous imide; double bond migration; PMR

In a preceding paper,[1] we described the catalytic hydrogenation of 7-hydroxyquinoline which resulted, unexpectedly, in predominant formation of 7β-hydroxy-*trans*-decahydroquinoline (I) and served as a novel route to *trans*-octahydro-7(1*H*)-quinolone (II). Although decahydroquinolin-7-ols of *cis*-fused ring juncture were contained as additional components in the hydrogenation products, neither of them could be isolated intact. This paper deals with two stereoselective routes to the elaboration of *cis*-octahydro-7(1*H*)-quinolone (III), one *via* intramolecular Michael addition of an amino enone (IV) and the other *via* hydrogenation of a bicyclic lactam (V), and with a new alternative method for the preparation of *trans*-octahydro-7(1*H*)-quinolone.



I

II : R=H
VIII : $R=COC_6H_5$

III

IV

V

Chart 1

The route similar to that used for the conversion[3] of 8-(3-aminopropyl)-8-ethyl-1,4-dioxaspiro[4,5]dec-6-ene into 4a-ethyl-*cis*-octahydro-7(1*H*)-quinolone was first applied to our purpose. Birch reduction of 3-(*p*-methoxyphenyl)propylamine (VI)[4] afforded the dihydro derivative (VII) in 77% yield. Its infrared (IR) spectrum showed an ethylenic band at 1660 cm^{-1}, and the proton magnetic resonance (PMR) spectrum exhibited two olefinic proton signals at 4.62 and 5.38 ppm.[5] On treatment of the enol ether (VII) with boiling 2N sulfuric

---

[1] Part I: T. Momose, S. Uchida, N. Yamaashi, and T. Imanishi, *Chem. Pharm. Bull.* (Tokyo), **25**, 1436 (1977).

[2] Location: *133-1, Yamada-Kami, Suita, Osaka, 565, Japan.*

[3] G. Stork and J.E. Dolfini, *J. Am. Chem. Soc.*, **85**, 2872 (1963). The stereochemistry was established by Y. Ban, I. Iijima, I. Inoue, M. Akagi, and T. Oishi, *Tetrahedron Lett.*, **1969**, 2067.

[4] A.W. Fort and J.D. Roberts, *J. Am. Chem. Soc.*, **78**, 584 (1956).

[5] *cf.* J.B. Hendrickson, R.W. Alder, D.R. Dalton, and D.G. Hey, *J. Org. Chem.*, **34**, 2667 (1969).

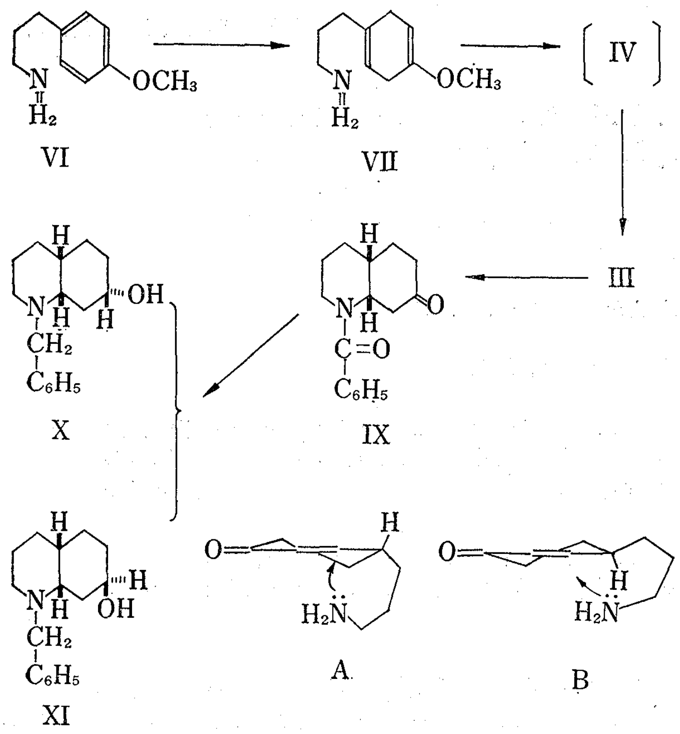


Chart 2

acid, hydrolysis and cyclization were effected to give *cis*-octahydro-7(1*H*)-quinolone (III), mp 68.5—70.5°, probably *via* an amino enone (IV). *N*-Benzoylation[6] of the row cyclization products and subsequent examination of the thin-layer chromatography (TLC) revealed that no *trans*-isomer was formed in the above cyclization. The stereochemistry of the *N*-benzoyl derivative (IX) was previously assigned from the chemical shifts of the two deshielded proton singnals due to those attached equatorially to C-2 and C-8a in the PMR spectrum.[7] The same conclusion was also obtained by the following chemical conversion. Lithium aluminum hydride reduction of IX afforded two known *cis*-isomers of *N*-benzyldecahydroquinoline-7-ols (X and XI)[1] in 63% and 12% yields, respectively.

High stereoselectivity in the intramolecular Michael addition step was well interpreted as a result of very severe stereoelectronic requirements for the cyclization. Namely, in the "pre-*cis*" attack (A), the nitrogen (N-1) is easily able to approach perpendicularly to the β-position of the enone system, and in the "pre-*trans*" one (B), on the contrary, the nitrogen is situated too far from the enone system to furnish perpendicular approach. The yield from VII to III was, however, markedly influenced by the reaction conditions used (maximum 75% yield), and sometimes the desired ketone (III) was hardly obtained in a pure state, probably owing to its instability.

To exploit an alternative, stereoselective, and elegant route to III, hydrogenation of a readily available vinylogous imide (XII)[8] and its derivative was then examined as a starting

Table I. Hydrogenation of V

Conditions				Products (%)			
Catalyst	Pressure of H_2	Solvent	Temperature	V	XIV	XV	XVI
5% Pd-C	1 atm	EtOH	r.t.		62	30	Trace
PtO_2	1 atm	EtOH	r.t.		67	19	11
5% $Rh-Al_2O_3$	1 atm	EtOH	r.t.	41	47		
5% $Rh-Al_2O_3$	4—5 atm	EtOH	r.t.	Trace	91		
5% $Rh-Al_2O_3$	45 atm	EtOH	r.t.		99		

r.t.: room temperature.

---

6) In spite of different behavior of two isomeric octahydro-7(1*H*)-quinolones (II and III) in IR and PMR spectra, they had the same *Rf* values on TLC in many solvent systems. But, a good separation was obtained for their *N*-benzoyl derivatives (VIII and IX) on TLC using silica gel in ether.

7) T. Momose, S. Uchida, N. Yamaashi, and T. Imanishi, *Heterocycles*, 3, 713 (1975).

8) C.F. Koelsch and H.M. Walker, *J. Am. Chem. Soc.*, 72, 346 (1950).

reaction. Ketalization[9] of XII resulted in migration[10] of the double bond at C_8–C_{8a} to the most stable position (C_{4a}–C_{8a}) to give an unsaturated lactam (V) in high yield. The non-migrated ketal (XIII) could not be obtained. The structure of V was assigned from its PMR and mass spectra. Thus, the PMR spectrum exhibited no olefinic proton signal, and the mass spectrum showed a base peak due to a retro-Diels-Alder fragmentation at m/e 86. Hydrogenation of V under various conditions was carried out, and the results are summarized in Table I. The hydrogenation over palladium on carbon or platinum oxide gave the desired saturated *cis*-lactam (XIV) along with a moderate amount of over-reduced products (XV and XVI). The PMR spectrum of XIV exhibited one proton signal due to the C-8a proton at 3.52—3.82 ppm with a half width ($W_{1/2}$) of 15 Hz characteristic of a *cis*-fused ring system.[11] The hydrogenolyzed products (XV and XVI), it is assumed, would be formed from XIII through an initial isomerization[12] of the double bond to C_8–C_{8a} and subsequent allylic hydrogenolysis. On the other hand, hydrogenation of V over rhodium on alumina afforded XIV as a sole product without accompanying any over-reduced products. Treatment of XIV with 1N hydrochloric acid gave *cis*-decahydroquinoline-2,7-dione (XVII), quantitatively.

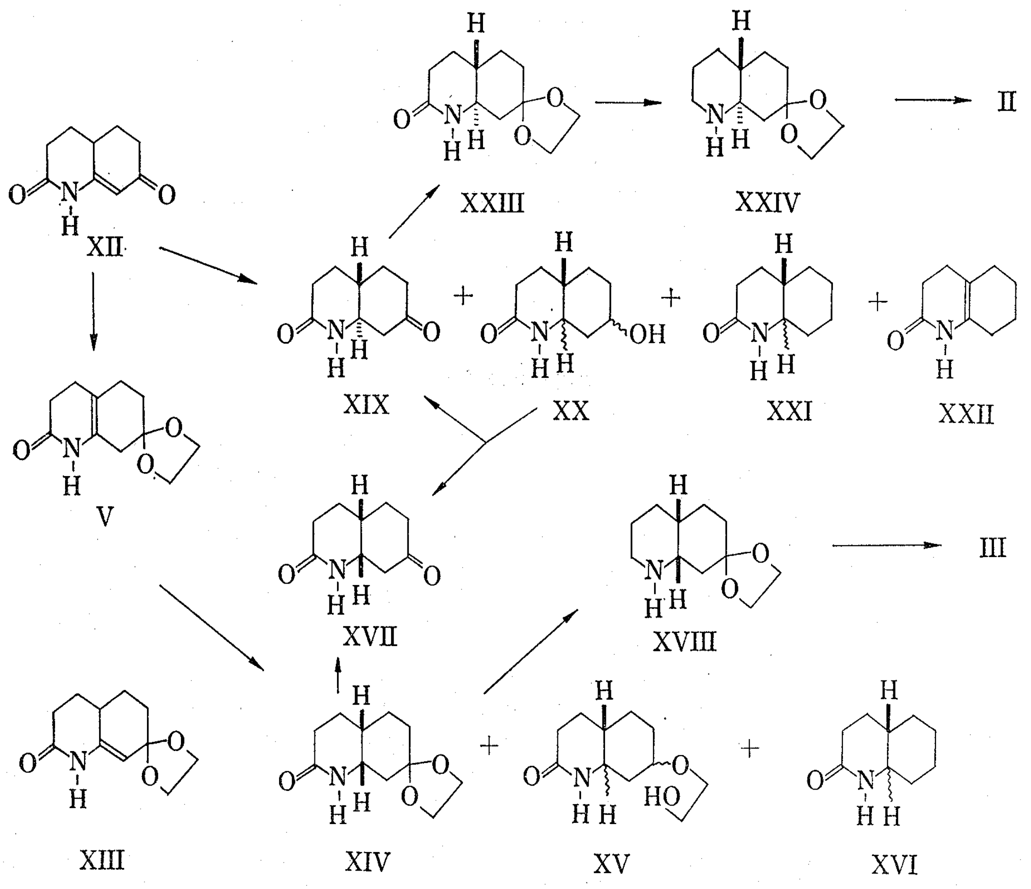


Chart 3

---

9) Carried out for protection of the rather reactive carbonyl: Vinylogous imides analogous to XII were reported to react with hydroxylamine. See Y. Tamura, Y. Kita, and J. Uraoka, *Chem. Pharm. Bull.* (Tokyo), **20**, 876 (1972).

10) A ketalization accompanied by migration of a double bond has been described in many literatures. See, for example, C. Djerassi, "Steroid Reactions: An Outline for Organic Chemists," Holden-Day, Inc., San Francisco, 1963, pp. 3—16.

11) T. Ibuka, N. Masaki, I. Saji, K. Tanaka, and Y. Inubushi, *Chem. Pharm. Bull.* (Tokyo), **23**, 2779 (1975).

12) Examples of isomerization of double bond during catalytic hydrogenation have been described in J.B. Bream, D.C. Eaton, and H.B. Henbest, *J. Chem. Soc.*, **1957**, 1974; J.F. Sauvage, R.H. Baker, and A.S. Hussey, *J. Am. Chem. Soc.*, **83**, 3874 (1961).

Its PMR spectrum exhibited a C-8a proton signal at 3.84—4.07 ppm ($W_{1/2}=9$ Hz). The saturated lactam ketal (XIV) was reduced with lithium aluminum hydride in boiling ether and subsequently deketalized with 1N hydrochloric acid to afford *cis*-octahydro-7(1*H*)-quinolone (III) in 60—70% yield from XIV with constant reproducibility. Here, we have established a highly stereoselective route to *cis*-octahydro-7(1*H*)-quinolone.

Finally, we examined hydrogenation of the vinylogous imide itself (XII). Hydrogenation of substituted vinylogous imides analogous to XII was reported[13] to yield a mixture of saturated alcohols isomeric in ring juncture with predominance of the *trans*-isomers. Actually, hydrogenation of XII over 5% palladium on carbon in water afforded the *trans*-amide ketone (XIX) in 33% yield, a poorly separable mixture of isomeric amido alcohols (XX) in 22% yield, and the hydrogenolyzed products, XXI (28%) and XXII (trace). Oxidation of XX with chromium trioxide in aqueous acetic acid gave a mixture of XIX and its isomer (XVII) in a ratio of 2: 1. The PMR spectrum of XIX exhibited one proton signal due to C-8a proton at 3.10—3.50 ppm ($W_{1/2}=27$ Hz). Its value is consistent with the fact[11,14] that C-8a proton signals for *cis*-isomers of perhydroquinoline-2-one analogs appear at the field lower than those for *trans*-isomers do in PMR spectra. The above ratio for XIX and XVII in the oxidation mixture of XX was determined from the ratio of integration for C-8a protons. Similarly, the *cis-trans* ratio in the hydrogenolyzed product (XXI) was determined as 7: 2 with predominance of the *cis*-isomer. On the other hand, hydrogenation of XII over 5% rhodium on alumina under 70 atmospheric pressure furnished no ketonic compounds but a mixture of alcohols (XX), which was oxidized to a mixture of isomeric ketones (XVII and XIX) with a *cis-trans* ratio of 5: 4. The unsaturated lactam (XXII) was identical with an authentic sample[15] prepared from cyclohexanone and acrylonitrile. *trans*-Octahydro-7(1*H*)-quinolone (II) was obtained from XIX *via* the ketal (XXIII) in 60% overall yield, in a sequence (XXIII→XXIV→II) analogous to that for the *cis*-isomer (III).

Experimental

All melting points and boiling 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. Half widths ($W_{1/2}$) are given in Hz, and the following abbreviations are used; s=singlet and m=multiplet. Mass spectra (MS) were taken on a Hitachi RMU-6E mass spectrometer. All organic extracts were dried over anhydrous magnesium sulfate before evaporation. Column chromatography 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).

4-(3-Aminopropyl)-1-methoxy-1,4-cyclohexadiene (VII)——To a stirred solution of 3-(*p*-methoxyphenyl)-propylamine[4] (VI; 10.0 g) in abs. MeOH (50 ml) and liq. NH_3 (600 ml) was added metallic Na (9.0 g) portionwise over a period of 3 hr at −50°. After Na had been consumed, the reaction mixture was quenched with NH_4Cl (30 g) and evaporated at room temperature. The resulting residue was extracted with $CHCl_3$, and the extract was evaporated to give an oil (11 g), which was distilled under reduced pressure to give 7.7 g (77%) of VII as a colorless oil, bp 97—100° (2 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 (C=C). MS *m/e*: 167 (M^+). PMR (90 MHz) δ: 3.53 (3H, s, O–C$\underline{H}_3$), 4.62 and 5.38 (each 1H, each broad s, olefinic protons).

1,2,3,4,5,6,7,8-Octahydroquinoline-2,7-dione 7-Ethylene Ketal (V)——A mixture of the vinylogous imide (XII[8]; 1.6 g), ethylene glycol (6.5 ml), *p*-TsOH (100 mg), and C_6H_6 (250 ml) was heated under reflux with stirring using a Dean-Stark water separator for 40 hr. After the solvent was removed under reduced pressure, the resulting residue was extracted with $CHCl_3$. The extract was washed with satd. $NaHCO_3$ and brine, and evaporated to give a solid (2.60 g), which was chromatographed on alumina. Elution first with C_6H_6 and subsequently with C_6H_6–EtOH (50: 1) gave 1.43 g (71%) of V as colorless needles (from C_6H_6–hexane), mp 147.5—148.5°. IR ν_{max}^{KBr} cm^{-1}: 1682 (lactam). MS *m/e*: 209 (M^+), 86. PMR (60 MHz) δ: 4.00

---

13) I. Inoue and Y. Ban, *J. Chem. Soc.* (*C*), **1970**, 602; Y. Ban, Y. Sato, I. Inoue, M. Nagai, T. Oishi, M. Terashima, O. Yonemitsu, and Y. Kanaoka, *Tetrahedron Lett.*, **1965**, 2261; G. Metz and G. Schwenker, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, **305**, 918 (1972).

14) J. Fedière, E. Guy, and F. Winternitz, *Ann. Chim.*, **10**, 337 (1975).

15) J.J. Vill, T.R. Steadman, and J.J. Godfrey, *J. Org. Chem.*, **29**, 2780 (1964).

(4H, s, O–C$\underline{H}_2$C$\underline{H}_2$–O), 7.90 (1H, broad s, N$\underline{H}$). *Anal.* Calcd. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.95; H, 7.37; N, 6.69. Elution with C_6H_6–EtOH (10: 1) recovered the starting material (XII, 0.47 g).

Catalytic Hydrogenation of V——a) Over 5% Pd–C: The ketal (V; 0.43 g) was hydrogenated over 5% Pd–C (0.13 g) in EtOH (22 ml) at room temperature and an atmospheric pressure for 15 hr. The catalyst was filtered off, and the filtrate was evaporated under reduced pressure to give a solid (0.51 g), which was chromatographed on silica gel. The first fraction eluted with $CHCl_3$ gave 10 mg (3.2%) of XVI as colorless crystals (from hexane), mp 105—109°. IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1650 (lactam). MS *m/e*: 153 (M$^+$). The second fraction eluted with $CHCl_3$ gave 0.26 g (60%) of XIV as colorless crystals (from C_6H_6–hexane), mp 172.5—173.5°. IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1668 (lactam). PMR (90 MHz) δ: 3.52—3.82 (1H, m, $W_{1/2}=15$, C_{8a}–$\underline{H}$), 3.94 (4H, s, O–C$\underline{H}_2$C$\underline{H}_2$–O), 6.85 (1H, broad s, N$\underline{H}$). MS *m/e*: 211 (M$^+$), 99. *Anal.* Calcd. for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.71; H, 8.09; N, 6.75. Elution with $CHCl_3$–EtOH (10: 1) gave 0.14 g (32%) of XV as colorless crystals (from AcOEt), mp 160—164°. IR $\nu_{\max}^{KCl}$ cm^{-1}: 1646 (lactam). MS *m/e*: 213 (M$^+$), 153, 110. *Anal.* Calcd. for $C_{11}H_{19}NO_3$: C, 61.94; H, 8.98; N, 6.57. Found: C, 61.65; H, 9.23; N, 6.54.

b) Over PtO_2: The ketal (V; 0.10 g) was hydrogenated over PtO_2 (30 mg) in EtOH (10 ml) at room temperature and an atmospheric pressure for 10 hr. Working up as described in a) gave 69 mg (67%) of XIV, 19 mg (19%) of XV, and 8 mg (11%) of XVI.

c) Over 5% Rh-Al_2O_3 under an Atmospheric Pressure: The ketal (V; 105 mg) was hydrogenated over 5% Rh-Al_2O_3 (95 mg) in EtOH (10 ml) at room temperature and an atmospheric pressure for 8 hr to afford a solid (100 mg), which was worked up as described in a) to give 50 mg (47%) of XIV and 43 mg (41%) of the starting material.

d) Over 5% Rh-Al_2O_3 under 4—5 Atmospheric Pressure: The ketal (V; 107 mg) was hydrogenated over 5% Rh–Al_2O_3 (110 mg) in EtOH (10 ml) at room temperature and 4—5 atmospheric pressure for 10 hr to give a solid (110 mg), which was worked up as described in a) to give 98 mg (91%) of XIV and a trace of the starting material.

e) Over 5% Rh–Al_2O_3 under 45 Atmospheric Pressure: The ketal (V; 0.63 g) was hydrogenated over 5% Rh–Al_2O_3 (0.55 g) in EtOH (30 ml) at room temperature and 45 atmospheric pressure for 5 hr to give a solid (0.69 g), which was homogeneous on TLC and was recrystallized from C_6H_6–hexane to afford 0.63 g (99%) of XIV.

***cis*-Decahydroquinoline-2,7-dione (XVII)**——A mixture of XIV (160 mg) and 1 N HCl (5 ml) was allowed to stand at room temperature for 24 hr. After cooling, the reaction mixture was made alkaline with K_2CO_3 and evaporated under reduced pressure. The resulting residue was extracted with $CHCl_3$. The extract was washed with brine and evaporated to give a solid (130 mg), which was homogeneous on TLC and was recrystallized from AcOEt to give 90 mg (71%) of the ketone (XVII) as colorless plates, mp 174.5—175.5°. IR $\nu_{\max}^{KCl}$ cm^{-1}: 1711 (CO), 1673 (lactam). MS *m/e*: 167 (M$^+$). PMR (90 MHz) δ: 3.84—4.07 (1H, m, $W_{1/2}=9$, C_{8a}–$\underline{H}$), 7.15 (1H, broad s, N$\underline{H}$). *Anal.* Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.65; H, 7.80; N, 8.38.

***cis*-Octahydro-7(1*H*)-quinolone 7-Ethylene Ketal (XVIII)**——A suspension consisting of the ketal (XIV; 0.49 g), $LiAlH_4$ (0.49 g), and abs. ether (50 ml) was heated under reflux for 15 hr. The mixture was worked up as usual to afford an oil (0.40 g), which was distilled under reduced pressure to give 0.37 g (80%) of XVIII as a colorless oil, bp 130—140° (3 mmHg) (bath temperature). IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3350 (NH). MS *m/e*: 197 (M$^+$). The picrolonate: mp 213—216° (from EtOH). *Anal.* Calcd. for $C_{11}H_{19}NO_2 \cdot C_{10}H_8N_4O_5$: C, 54.65; H, 5.90; N, 15.18. Found: C, 54.65; H, 5.93; N, 15.24.

***cis*-Octahydro-7(1*H*)-quinolone (III)**——a) From VII: A mixture of VII (2.6 g) and 2 N H_2SO_4 (72 ml) was refluxed for 2.5 hr under nitrogen. The reaction mixture was made alkaline with K_2CO_3 and extracted with ether. The ethereal layer was evaporated to give 1.8 g (75%) of the product which was pure enough for subsequent experiments. Recrystallization from hexane gave 0.86 g of III as colorless needles, mp 68.5—70.5°. IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1710 (CO). MS *m/e*: 153 (M$^+$), 96. *Anal.* Calcd. for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.52; H, 9.89; N, 9.40.

b) From XVIII: A mixture of the ketal (XVIII; 146 mg) and 1 N HCl (2 ml) was allowed to stand at room temperature under nitrogen for 4 days. The resulting mixture was made alkaline with K_2CO_3 and extracted with $CHCl_3$. Removal of the solvent gave a solid (120 mg), which was recrystallized from hexane to afford 79 mg (70%) of III as colorless needles, mp 62—66°. Its IR spectrum was identical with that of III obtained from VII. The mother liquor was chromatographed on alumina in AcOEt to give additional III (10 mg; 9%) and 7 mg of the starting material.

***N*-Benzoyl-*cis*-octahydro-7(1*H*)-quinolone (IX)**——A suspension consisting of III (0.20 g), benzoyl chloride (0.30 g), and dry C_6H_6 (10 ml) was stirred at room temperature overnight. 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 an oil, which was chromatographed on silica gel in $CHCl_3$ to afford 240 mg (71%) of IX as colorless plates (from hexane), mp 117—118°. IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1714 (CO), 1620 (amide). MS *m/e*: 257 (M$^+$). PMR (90 MHz) δ: 3.60—5.10 (2H, m, C_{8a}–$\underline{H}$ and equatorial C_2–$\underline{H}$). *Anal.* Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.86; H, 7.44; N, 5.41.

_N_-Benzyl-7α- and -7β-hydroxy-_cis_-decahydroquinoline (X and XI)——A suspension consisting of IX (53 mg), $LiAlH_4$ (150 mg) and abs. ether (20 ml) was heated under reflux for 7 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 (49 mg), which was chromatographed on alumina in $CHCl_3$ to give 33 mg (63%) of X and 6.0 mg (12%) of XI. These products were identical with authentic samples[7] in comparison of IR and TLC.

Catalytic Hydrogenation of 1,2,3,4,4a,5,6,7-Octahydroquinoline-2,7-dione (XII)——a) Over 5% Pd–C: The vinylogous imide (XII; 5.0 g) was hydrogenated over 5% Pd–C (1.0 g) in EtOH (100 ml) at room temperature and 7 atmospheric pressure for 20 hr. The catalyst was filtered off, and the filtrate was evaporated under reduced pressure to give a solid (5.1 g), which was chromatographed on alumina. The first fraction eluted with C_6H_6 gave 1,2,3,4,5,6,7,8-octahydroquinoline-2-one (XXII; 70 mg; 1.5%) as crystals (from hexane), mp 139—143°. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1670 (lactam). MS _m/e_: 151 (M^+). This product was identical with an authentic sample obtained by the method of Vill, _et al._[15] in comparison of IR, TLC and mixed mp. The second fraction eluted with C_6H_6 gave 1.25 g (28%) of a mixture of _cis_- and _trans_-octahydro-2(1_H_)-quinolone (XXI) as colorless crystals (from hexane), mp 115—117°. IR $\nu_{\max}^{\text{KCl}}$ cm^{-1}: 1660 (lactam). MS _m/e_: 153 (M^+). PMR (90 MHz) δ: 2.60—3.10 (2/9H, m, C_{8a}–$\underline{H}$ for the _trans_-isomer), 3.40—3.62 (7/9H, m, C_{8a}–$\underline{H}$ for the _cis_-isomer). Elution with C_6H_6–EtOH (50: 1) gave 1.7 g (33%) of _trans_-decahydroquinoline-2,7-dione (XIX) as colorless crystals (from C_6H_6), mp 192—193°. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1710 (CO), 1660 (amide). MS _m/e_: 167 (M^+). PMR (90 MHz) δ: 3.10—3.50 (1H, m, $W_{1/2}=27$, C_{8a}–$\underline{H}$), 7.15 (1H, broad s, N$\underline{H}$). _Anal._ Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.57; H, 7.82; N, 8.43. Elution with C_6H_6–EtOH (10: 1) gave 1.1 g (22%) of a mixture of 7-hydroxy-_cis_- and -_trans_-octahydro-2(1_H_)-quinolone (XX) as colorless crystals (from C_6H_6–EtOH), mp 182—187°. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1650 (lactam). MS _m/e_: 169 (M^+). _Anal._ Calcd. for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.73; H, 8.97; N, 8.38. To a stirred solution of XX (0.19 g) in AcOH (0.53 ml) and H_2O (0.07 ml) was added CrO_3 (0.41 g) portionwise under ice-cooling. The mixture was stirred for 8 hr under cooling and extracted with $CHCl_3$. The extract was washed with satd. $NaHCO_3$ and H_2O, and evaporated to give an oil, which was chromatographed on alumina. Elution with $CHCl_3$ gave 95 mg (51%) of a mixture of _cis_- and _trans_-decahydroquinoline-2,7-dione (XVII and XIX), which showed two spots on TLC. PMR (90 MHz) δ: 3.10—3.50 (2/3H, m, C_{8a}–$\underline{H}$ for XIX), 3.84—4.07 (1/3H, m, C_{8a}–$\underline{H}$ for XVII).

b) Over 5% Rh–Al_2O_3: The vinylogous imide (XII; 0.95 g) was hydrogenated over 5% Rh–Al_2O_3 (0.72 g) in EtOH (50 ml) at room temperature and 70 atmospheric pressure for 8 hr. Usual working up afforded a solid (0.98 g), which was recrystallized from C_6H_6–EtOH to give 0.94 g (97%) of a mixture of the alcohols (XX), mp 220—225°. The alcohols (XX; 0.19 g) was oxidized in a similar manner to that in a) to give 92 mg (48%) of a mixture of XVII and XIX. PMR (90 MHz) δ: 3.10—3.50 (4/9H, m, C_{8a}–$\underline{H}$ for XIX), 3.84—4.07 (5/9 H, m, C_{8a}–$\underline{H}$ for XVII).

trans-Decahydroquinoline-2,7-dione 7-Ethylene Ketal (XXIII)——A mixture of XIX (1.06 g), ethylene glycol (2.0 ml), _p_-TsOH (47 mg) and C_6H_6 (100 ml) was heated under reflux using a Dean-Stark water separator for 5 hr. The solvent was removed under reduced pressure, and the resulting residue was extracted with $CHCl_3$. The extract was washed with satd. $NaHCO_3$ and brine, and evaporated to give a solid (1.53 g), which was recrystallized from C_6H_6–hexane to afford 1.31 g (98%) of the ketal (XXIII) as colorless needles, mp 192—193°. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1655 (lactam). MS _m/e_: 211 (M^+). PMR (90 MHz) δ: 3.01—3.38 (1H, m, $W_{1/2}=25$, C_{8a}–$\underline{H}$), 3.96 (4H, s, O–C$\underline{H}_2$C$\underline{H}_2$–O), 6.75 (1H, broad s, N$\underline{H}$). _Anal._ Calcd. for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.37; H, 8.06; N, 6.56.

trans-Octahydro-7(1_H_)-quinolone 7-Ethylene Ketal (XXIV)——A suspension consisting of the lactam ketal (XXIII; 0.34 g), $LiAlH_4$ (0.34 g) and abs. ether (50 ml) was heated under reflux for 14 hr. The reaction mixture was worked up as usual to afford a colorless oil (275 mg), which was distilled under reduced pressure to give 0.24 g (74%) of XXIV, bp 85—90° (1 mmHg) (bath temperature). IR $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3320 (NH). PMR (90 MHz) δ: 3.95 (4H, s, O–C$\underline{H}_2$C$\underline{H}_2$–O). The picrolonate: mp 244—246° (dec.). _Anal._ Calcd. for $C_{11}H_{19}NO_2 \cdot C_{10}H_8N_4O_5$: C, 54.65; H, 5.90; N, 15.18. Found: C, 54.54; H, 5.95; N, 15.37.

trans-Octahydro-7(1_H_)-quinolone (II)——A mixture of the ketal (XXIV; 145 mg) and 1 N HCl (2 ml) was allowed to stand at room temperature under nitrogen for 24 hr. After making alkaline with K_2CO_3, the mixture was extracted with $CHCl_3$. Removal of the solvent afforded a solid (113 mg), which was recrystallized from hexane to give 92 mg (82%) of the _trans_-ketone (II) as colorless needles, mp 92—94°. The product was identical with an authentic sample[1] in comparison of IR, TLC and mixed mp.