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Studies on 1-Azabicyclo Compounds. XXVII.[1] Synthesis of Ten-membered Ring Amines from 1-Oxo-, 9a-Benzyl-, and 9a-Benzyl-1-oxo-quinolizidine[2]

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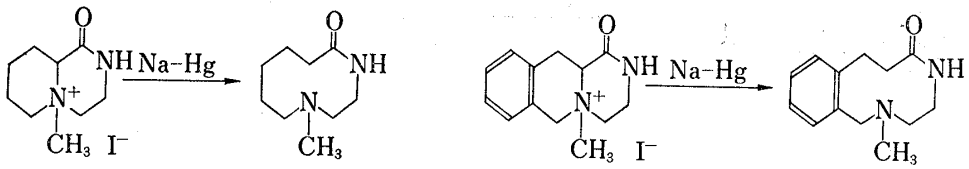
The Stevens rearrangement of the N-benzyl bromide (VII), derived from 1-oxoquinolizidine (V), afforded 9a-benzyl-1-oxoquinolizidine (VIII). Reduction of the methiodides (VI and IX) of V and VIII with sodium amalgam gave the ten-membered aminoketones (XII and XIII), respectively. The yield of XIII was much more excellent than that of XII, because of the influence of the C_{9a}-benzyl substituent in IX. The C_{9a}-benzyl substituent, however, produced little effect on the reductive cleavage in the Birch reduction of IX leading to XIII and XV in comparison with that of VI leading to XIV, though 9a-benzylquinolizidine methiodides (XIa and XIb) furnished the ten-membered amine (XVI) in considerable yields.

In the previous papers[4,5] of this series, it has been reported that, on treatment with sodium amalgam (Na–Hg) in ethanol, the methiodides (I and III) gave the ten-membered ring amines (II and IV), respectively, and that the yield of IV was much more excellent than that of II. As the structure of III can be regarded as a kind of C_{9a}-benzyl derivative of I, the presence of a C_{9a}-benzyl substituent in the quinolizidines would facilitate this reductive cleavage reaction. On the above assumption, it is of interest to study such a reaction of 1-oxoquinolizidine[6] (V) in comparison with that of its 9a-benzyl derivative (VIII) as well as 9a-benzylquinolizidine[7] (X).



I II III IV

Chart 1

Quaternization of V with methyl iodide afforded the methiodide (VI), which was shown to be a mixture of the *cis*- and *trans*-isomer by the appearance of two N^+-methyl signals at 6.99 and 6.86 τ in its nuclear magnetic resonance (NMR) spectrum. Attempts to separate two isomers were unsuccessful. Treatment of the N-benzyl bromide (VII), derived from V,

1) Part XXVI: Y. Arata, M. Hanaoka, H. Kato, E. Koshinaka, and T. Nishikawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 2381 (1975).
2) Presented at the 94th Annual Meeting of the Pharmaceutical Society of Japan, Sendai, April 1974.
3) Location: *13-1, Takara-machi, Kanazawa, 920, Japan.*
4) Y. Arata and Y. Nakagawa, *Chem. Pharm. Bull.* (Tokyo), **21**, 1248 (1973).
5) H. Kato, E. Koshinaka, Y. Arata, and M. Hanaoka, *Chem. Pharm. Bull.* (Tokyo), **21**, 2039 (1973).
6) *a*) G.R. Clemo and G.R. Ramage, *J. Chem. Soc.*, **1931**, 437; *b*) N.J. Leonard, S. Swann Jr., and J. Figuras Jr., *J. Am. Chem. Soc.*, **74**, 4620 (1952); *c*) S.F. Mason, K. Schofield, and R.J. Wells, *J. Chem. Soc.* (C), **1967**, 626.
7) *a*) N.J. Leonard and A.S. Hay, *J. Am. Chem. Soc.*, **78**, 1984 (1956); *b*) A.J. Sisti and D.L. Lohner, *J. Org. Chem.*, **32**, 2026 (1967).

with sodium hydride in dimethyl sulfoxide effected the Stevens rearrangement[8] to give 9a-benzyl-1-oxoquinolizidine (VIII), mp 109.5—111°, *m/e* 243 (M^+), in 39% yield. The product showed the bands at 2750 (Bohlmann band) and 1705 cm^{-1} (C=O) in its infrared (IR) spectrum. The rearrangement product (VIII) was synthesized more conveniently by treatment of VII with potassium hydroxide in ethanol in 64% yield. The methiodide (IX) of VIII exhibited the single N^+-methyl signal at 6.58 τ in its NMR spectrum.

The product obtained by quaternization of X with methyl iodide was fractionally recrystallized to give two isomeric methiodides[9] in the 2:1 ratio: the major methiodide (XIb), mp 286—287° (decomp.), NMRτ: 6.72 (N^+-CH_3), and the minor methiodide (XIa), mp 250—251.5° (decomp.), NMRτ: 6.60 (N^+-CH_3). Since the N^+-methyl signals of *cis* 9a-substituted quinolizidine methiodides were found to appear at higher field than those of the corresponding *trans* methiodides in their NMR spectra,[10] the former (XIb) could be assigned to be *cis* and the latter (XIa), *trans*. These assignments were further established from their ^{13}C-NMR spectra[10] (see Experimental).

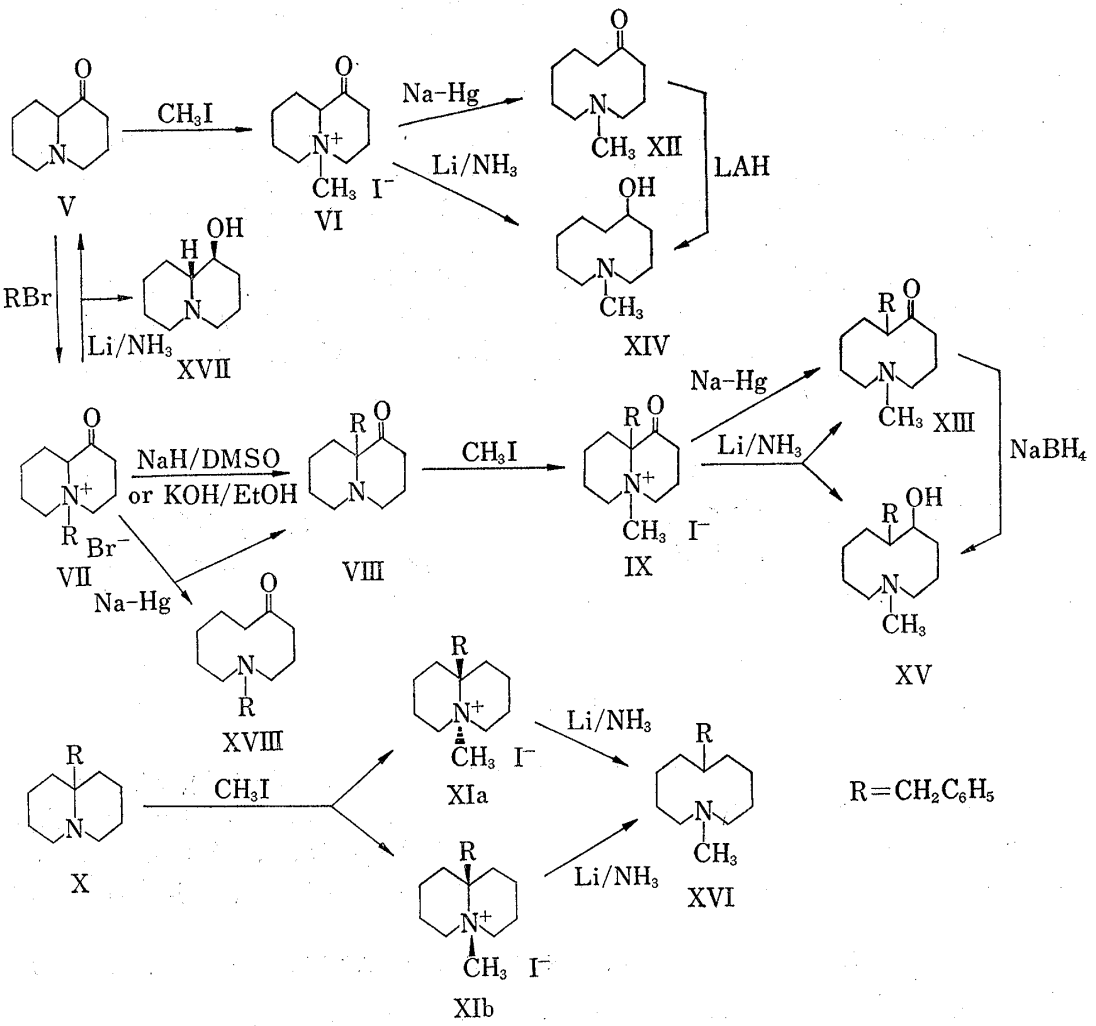


Chart 2

8) S.H. Pine, "Organic Reactions", Vol. 18, John Wiley & Sons, Inc., New York, 1970, p. 403; *Yakugaku Zasshi*, **95**, 830 (1975).
9) The methiodide, mp 261° (decomp.), was already reported but its stereochemistry was not determined.[7b]
10) Y. Arata, T. Aoki, M Hanaoka, and M. Kamei, *Chem. Pharm. Bull.* (Tokyo), **23**, 333 (1975); Y. Arata, M. Hanaoka, and S.K. Kim, *ibid.*, **23**, 1142 (1975).

Reduction of the methiodide (VI) with 3% Na–Hg in 95% ethanol afforded the expected ten-membered aminoketone, 1-methyldecahydroazecin-5-one[11] (XII), in 74% yield. The product showed the bands at 2780 (N–CH_3) and 1700 cm^{-1} (C=O) in its IR spectrum and the signal at 8.00 τ (N–CH_3) in its NMR spectrum. This reductive cleavage reaction provides an alternative route for the synthesis of XII. On similar treatment with Na–Hg, the methiodide (IX) gave 6-benzyl-1-methyldecahydroazecin-5-one (XIII), *m/e* 259 (M^+), IR ν_{max}^{liq} cm^{-1}: 2790 (N–CH_3), 1695 (C=O), NMR τ: 8.00 (N–CH_3), in 99% yield, whereas the methiodides (XIa and XIb) did not afford the expected ten-membered amine (XVI). Reduction of the N-benzyl bromide (VII) with Na–Hg furnished the Stevens rearrangement product (VIII) in 34% yield along with the desired ten-membered amine (XVIII) in 7% yield. Thus, the reductive cleavage of the C_{9a}-benzyl derivative (IX) with Na–Hg leading to the ten-membered amine proceeded more smoothly than that of VI as anticipated, although XIa and XIb did not afford the ten-membered amine.

On the other hand, the Birch reduction of VI with lithium in liquid ammonia (Li/NH_3) afforded in 69% yield 1-methyldecahydroazecin-5-ol[6b] (XIV), IR ν_{max}^{liq} cm^{-1}: 3470 (OH), 2780 (N–CH_3), NMR τ: 7.80 (N–CH_3), which was identified with the product obtained by reduction of XII with lithium aluminum hydride. On similar treatment with Li/NH_3, IX gave the ten-membered amino-ketone (XIII) and alcohol (XV), *m/e* 261 (M^+), IR ν_{max}^{liq} cm^{-1}: 3375 (OH), 2780 (N–CH_3), NMR τ: 7.80 (N–CH_3), in 20% and 52% yield, respectively. The latter was derived from the former by sodium borohydride reduction, however, its stereochemistry remained undetermined. Similarly, treatment of XIa and XIb with Li/NH_3 afforded successfully the ten-membered amine (XVI), *m/e* 245 (M^+), in 63% and 57% yield, respectively. The reduction of VII with Li/NH_3 resulted in debenzylation giving both the ketone (V) and the alcohol[12] (XVII), mp 73—74°, in 39% and 24% yield, respectively. Thus, the C_{9a}-benzyl group produced little effect on the reductive cleavage in the Birch reduction of the C_{9a}-benzyl derivative (IX) in comparison with that of VI, even though XIa and XIb afforded the ten-membered amine (XVI) in considerable yields.

Experimental[13]

5-Methyl-1-oxooctahydroquinolizinium Iodide (VI)——To octahydroquinolizin-5-one[6c] (V) (2.3 g) was added CH_3I (4 ml) dropwise in an ice bath. The mixture was kept standing for 1 hr in an ice bath and overnight at room temperature. The precipitate was collected by filtration and washed with ether to give VI (4.3 g, 98%), which was recrystallized from H_2O to give colorless plates, mp 208—210°. IR ν_{max}^{KBr} cm^{-1}: 1720 (C=O). NMR (D_2O) τ: 6.99 (3/2H, s, N^+-CH_3), 6.86 (3/2H, s, N^+-CH_3). *Anal.* Calcd. for $C_{10}H_{18}ONI$: C, 40.69; H, 6.15; N, 4.75. Found: C, 40.51; H, 6.27; N, 4.84. This mixture of *cis* and *trans*-isomer could not be separated by fractional recrystallization from H_2O, EtOH, and acetic acid.

5-Benzyl-1-oxooctahydroquinolizinium Bromide (VII)——To a solution of V (7.8 g) in acetone (50 ml) was added a solution of benzyl bromide (13.0 g) in acetone (30 ml). The reaction solution was refluxed for 5 hr and evaporated *in vacuo*. The residue was dissolved in H_2O and washed with ether. The aqueous layer was evaporated *in vacuo* to dryness to give the N-benzyl bromide (VII) (16.0 g, 97%) as a syrupy liquid. Perchlorate: colorless needles, mp 166.5—168° (H_2O). IR ν_{max}^{KBr} cm^{-1}: 1725 (C=O). *Anal.* Calcd. for $C_{16}H_{22}O_5NCl$: C, 55.90; H, 6.45; N, 4.07. Found: C, 56.09; H, 6.40; N, 3.92.

11) N.J. Leonard, M. Ōki, and S. Chiavarelli, *J. Am. Chem. Soc.*, 77, 6235 (1955).

12) *a*) G.A. Swan, *J. Chem. Soc.*, **1958**, 2051; *b*) H.S. Aaron, G.E. Wicks Jr., and C.P. Rader, *J. Org. Chem.*, **29**, 2248 (1964).

13) All melting points were measured with a Yanagimoto Micro Melting Point Apparatus. Melting points and boiling points are uncorrected. The extracts were dried over anhydrous Na_2SO_4. Alumina (Brockmann grade II-III, Merck) and silica gel (Wakogel Q-23, Wako) were used for column chromatography. Silica gel (Kieselgel GF_{254} Typ 60, Merck) was used for thin-layer chromatography (TLC) and preparative TLC (p-TLC). IR spectra were measured with a Spectrophotometer IR-G, Japan Spectroscopic Co., NMR spectra with PS-100, Japan Electron Optics Lab. Co., using sodium 2,2,3,3-tetradeutero-3-trimethylsilylpropionate (in D_2O) and tetramethylsilane (TMS) (in $CDCl_3$ and DMSO-d_6) as an internal standard, ^{13}C-NMR spectra with PS-100-PFT-100, Japan Electron Optics Lab. Co., at 25.1 MHz using TMS as an internal standard in CF_3CO_2D, and mass spectra with JMS-01SG, Japan Electron Optics Lab. Co.

9a-Benzyloctahydroquinolizin-1-one (VIII)——1) With NaH in Dimethyl Sulfoxide (DMSO): A solution of NaH (50% in a mineral oil) (3.6 g) in DMSO (80 ml) was stirred for 2 hr at 60°. To this solution was added a solution of VII (6.0 g) in DMSO (20 ml) and the mixture was stirred for 2.5 hr at 60—65°. The reaction mixture was poured on ice (100 g) and extracted with CH_2Cl_2. The CH_2Cl_2 layer was extracted with 10% HCl. The aqueous layer was made alkaline with 30% NaOH and extracted with ether. The extract was washed with H_2O, dried, and evaporated *in vacuo*. The residue was purified with column chromatography (silica gel, ether) to give VIII (1.74 g, 39%), which was recrystallized from iso-Pr_2O to give colorless plates, mp 109.5—111°. IR ν_{max}^{KBr} cm^{-1}: 2750 (Bohlmann band), 1705 (C=O). NMR ($CDCl_3$) τ: 6.90, 6.76 (2H, AB-q, $J=14$ Hz, >C–C<u>H</u>$_2$–Ph). Mass Spectrum *m/e*: 243 (M^+). *Anal.* Calcd. for $C_{16}H_{21}ON$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.02; H, 8.63; N, 5.95.

Methiodide (IX): Colorless plates, mp 244—245° (decomp.) (H_2O). IR ν_{max}^{KBr} cm^{-1}: 1714 (C=O). NMR (D_2O) τ: 6.58 (3H, s, N^+-CH_3). *Anal.* Calcd. for $C_{17}H_{24}ONI$: C, 53.00; H, 6.28; N, 3.64. Found: C, 53.13; H, 6.16; N, 3.78.

2) With KOH in EtOH: A solution of VII (2.00 g) in 2.5% ethanolic KOH solution (40 ml) was warmed at 65—70° for 2 hr. On cooling to room temperature, the precipitate was deposited and filtered off, and the filtrate was evaporated *in vacuo*. The residue was shaken with H_2O and ether. The ether layer was washed with H_2O, dried, and evaporated *in vacuo*. The residue was treated in the same procedure as that described in 1) to give VIII (956 mg, 64%) as colorless plates, mp 109.5—111°, which was identified with VIII obtained in 1) by IR spectra, TLC, and mixed mp.

***trans*- and *cis*-9a-Benzyl-5-methyloctahydroquinolizinium Iodide (XIa and XIb)**——According to the method of Leonard, *et al.*,[7a] X was obtained in 86% yield as a colorless liquid, bp 130—132°/ 5 mmHg, using benzyl bromide instead of benzyl chloride as a benzylation reagent. Picrate: yellow needles, mp 207.5—208° (EtOH) (lit.[7a] 203—204°). *Anal.* Calcd. for $C_{22}H_{26}O_7N_4$: C, 57.63; H, 5.72; N, 12.22. Found: C, 57.47; H, 5.60; N, 12.31. A mixture of X (3.1 g) and CH_3I (10 g) was kept standing at room temeprature for 2 hr. The precipitate was collected by filtration, washed with ether, and fractionally recrystallized from H_2O to give the *cis* methiodide (XIb, 2.8 g, 55%) as colorless needles, mp 286—287° (decomp.). NMR (DMSO-d_6) τ: 6.72 (3H, s, N^+-CH_3). ^{13}C-NMR ppm: 18.50, 19.41 (C_2 or C_8), 21.05, 21.36 (C_3 or C_7), 25.79, 32.22 (C_1 or C_9), 39.25 (-<u>C</u>H_2Ph), 48.48 (N^+-CH_3), 60.49, 63.22 (C_4 or C_6), 73.84 (C_{9a}), 129.53 [Ph (C_4)], 130.26, 132.20 [Ph (C_2,C_6 or C_3,C_5)], 134.93 [Ph (C_1)]. *Anal.* Calcd. for $C_{17}H_{26}NI$: C, 54.99; H, 7.06; N, 3.77. Found: C, 54.90; H, 7.06; N, 3.96.

The mother liquor was evaporated *in vacuo* and the residue was recrystallized from H_2O to give the *trans* methiodide (XIa, 1.3 g, 25%) as colorless scales, mp 250—251.5° (decomp.). NMR (DMSO-d_6) τ: 6.60 (3H, s, N^+- CH_3). ^{13}C-NMR ppm: 18.14 (C_2, C_8), 20.08 (C_3, C_7), 28.27 (C_1, C_9), 32.82 (-<u>C</u>H_2Ph), 44.47 (N^+-CH_3), 60.31 (C_4, C_6), 74.20 (C_{9a}), 129.65 [Ph (C_4)], 130.56, 131.53 [Ph (C_2,C_6 or C_3,C_5)], 135.84 [Ph (C_1)]. *Anal.* Calcd. for $C_{17}H_{26}NI$: C, 54.99; H, 7.06; N, 3.77. Found: C, 54.75; H, 7.03; N, 3.91.

1-Methyldecahydroazecin-5-one (XII)——To a solution of VI (3.0 g) in 95% EtOH (50 ml) was added 3% Na-Hg (106.6 g) in small portions with stirring and the reaction mixture was stirred for 24 hr. The deposited Hg was filtered off and the filtrate was evaporated *in vacuo*. The residue was shaken with H_2O and ether. The ether layer was washed with H_2O, dried, and evaporated *in vacuo*. The residue was distilled to give XII (1.27 g, 74%) as a colorless oil, bp 130—135° (bath temp.)/17 mmHg. IR ν_{max}^{liq} cm^{-1}: 2780 (N-CH_3), 1700 (C=O). NMR ($CDCl_3$) τ: 8.00 (3H, s, N-CH_3). Picrate: yellow needles, mp 194—196° (decomp.) (EtOH) (lit.[11] 194—195° (decomp.)). *Anal.* Calcd for $C_{16}H_{22}O_8N_4$: C, 48.24; H, 5.57, N, 14.07. Found: C, 48.45; H, 5.65; N, 14.26.

6-Benzyl-1-methyloctahydroazecin-5-one (XIII)——To a solution of IX (499 mg) in 90% EtOH (50 ml) was added 3% Na-Hg (20 g) in small portions with stirring and the reaction mixture was treated in the same procedure as that described for XII to give XIII (315 mg, 99%), as a colorless oil, bp 160—165° (bath temp.)/ 3 mmHg. IR ν_{max}^{liq} cm^{-1}: 2790 (N-CH_3), 1695 (C=O). NMR ($CDCl_3$) τ: 8.00 (3H, s, N-CH_3). Mass Spectrum *m/e*: 259 (M^+). Picrolonate: yellow cubes, mp 155—156° (EtOH). *Anal.* Calcd. for $C_{27}H_{33}O_6N_5$: C, 61.93; H, 6.35; N, 13.38. Found: C, 61.69; H, 6.25; N, 13.22.

1-Benzyldecahydroazecin-5-one (XVIII)——To a solution of VII (4.50 g) in 90% EtOH (200 ml) was added 3% Na-Hg (90 g) in small portions with stirring and the reaction mixture was treated in the same procedure as that described for XII. The crude product was chromatographed on silica gel using ether as an eluent.

The first fraction gave XVIII (223 mg, 7%) as a colorless oil. IR ν_{max}^{liq} cm^{-1}: 1695 (C=O). NMR ($CDCl_3$) τ: 6.52 (2H, s, N-C<u>H</u>$_2$-Ph). Perchlorate: colorless needles, mp 194—195° (EtOH). IR ν_{max}^{KBr} cm^{-1}: 1690 (C=O). *Anal.* Calcd. for $C_{16}H_{24}O_5NCl$: C, 55.57; H, 7.00; N, 4.05. Found: C, 55.55; H, 6.91; N, 4.15.

The second fraction gave VIII (1.134 g, 34%) as colorless plates, mp 109.5—111° (iso-Pr_2O), which was identified with VIII obtained from VII by IR spectra, TLC, and mixed mp.

1-Methyldecahydroazecin-5-ol (XIV)——1) From VI: To a solution of VI (4.496 g) in liq. NH_3 (600 ml) was added Li (740 mg) in small portions with stirring. After evaporation of NH_3, the residue was shaken with H_2O and $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried, and evaporated *in vacuo*. The residue was distilled to give XIV (1.795 g, 69%) as a colorless oil, bp 120—125°/20 mmHg. IR ν_{max}^{liq} cm^{-1}: 3470 (OH), 2780 (N-CH_3). NMR ($CDCl_3$)τ: 7.80 (3H, s, N-CH_3). Picrate: yellow needles, mp 256—258° (AcOEt). *Anal.* Calcd. for $C_{16}H_{24}O_8N_4$: C, 47.99; H, 6.04; N, 13.99. Found: C, 48.10; H, 6.03; N, 14.22.

2) From XII: To a suspension of $LiAlH_4$ (75 mg) in anhyd. ether (50 ml) was added dropwise a solution of XII (280 mg) in anhyd. ether (5 ml) with stirring and the reaction mixture was refluxed for 2 hr. The excess hydride was decomposed with H_2O, and the inorganic material was filtered off and washed with ether. The filtrate and washings were combined, dried, and evaporated *in vacuo*. The residue was distilled to give XIV (220 mg, 78%) as a colorless oil, bp 145—150° (bath temp.)/20 mmHg, which was identified with XIV obtained in 1) by IR spectra and mixed mp of their picrates.

6-Benzyl-1-methyldecahydroazecin-5-ol (XV)——1) From IX: To a suspension of IX (515 mg) in liq. NH_3 (250 ml) was added Li (100 mg) in small portions with stirring and the reaction mixture was treated in the same procedure as that described for XIV. The crude product was separated on p-TLC (silica gel, ether).

The fraction with the large R*f*-value (0.65) gave XIII (70 mg, 20%) as a colorless oil, which was identified with XIII obtained from the Emde reduction of IX by IR spectra, TLC, and mixed mp of their picrolonates.

The fraction with the small *Rf*-value (0.22) gave XV (192 mg, 52%) as a colorless viscous oil, bp 150—155° (bath temp.)/0.07 mmHg. IR ν_{max}^{liq} cm^{-1}: 3375 (OH), 2780 (N-CH_3). NMR ($CDCl_3$) τ: 7.80 (3H, s, N-CH_3). Mass Spectrum *m/e*: 261 (M^+). Picrolonate: yellow plates, mp 161.5—163° (EtOH). *Anal.* Calcd. for $C_{27}H_{35}O_6N_5$: C, 61.70; H, 6.71; N, 13.33. Found: C, 61.48; H, 6.74; N, 13.23.

2) From XIII: To a solution of XIII (280 mg) in EtOH (10 ml) was added $NaBH_4$ (100 mg), and the reaction mixture was kept standing at room temperature for 4 days and evaporated *in vacuo*. The residue was shaken with H_2O and $CHCl_3$. The $CHCl_3$ layer was dried and evaporated *in vacuo*. The residue was distilled to give XV (266 mg, 94%) as a colorless viscous oil, bp 150—155° (bath temp.)/0.07 mmHg, which was identified with XV obtained in 1) by IR spectra, TLC, and mixed mp of their picrolonate.

6-Benzyl-1-methyldecahydroazecine (XVI)——1) From XIa: The methiodide (XIa, 574 mg) was treated with Li (150 mg) in liq. NH_3 (300 ml) in the same procedure as that described for XIV to give XVI (239 mg, 63%) as a colorless oil, bp 145—150° (bath temp.)/4 mmHg. IR ν_{max}^{liq} cm^{-1}: 2780 (N-CH_3). NMR ($CDCl_3$) τ: 7.84 (3H, s, N-CH_3). Mass Spectrum *m/e*: 245 (M^+). Picrate: yellow needles, mp 133—134° (EtOH). *Anal.* Calcd. for $C_{23}H_{30}O_7N_4$: C, 58.21; H, 6.37; N, 11.81. Found: C, 58.23; H, 6.35; N, 11.51.

2) From XIb: The methiodide (XIb, 944 mg) was treated with Li (200 mg) in liq. NH_3 (400 ml) in the same procedure as that described for XIV to give XVI (357 mg, 57%) as a colorless oil, bp 145—150° (bath temp.)/4 mmHg, which was identified with XVI obtained in 1) by IR spectra and mixed mp of their picrates.

Reduction of VII with Li/NH_3 (Formation of V and 1-Hydroxy(*e*)-*trans*-octahydroquinolizine (XVII))—— The N-benzyl bromide (VII, 3.00 g) was treated with Li (0.3 g) in liq. NH_3 (600 ml) in the same procedure as that described for XIV. The crude product was chromatographed on alumina using ether as an eluent.

The first fraction gave V (557 mg, 39%) as a pale yellow oil, bp 120—130° (bath temp.)/17 mmHg, which was identified with the authentic sample[6c] by IR spectra and TLC.

The second fraction gave XVII (346 mg, 24%) as a colorless liquid, bp 140—145° (bath temp.)/17 mmHg, which solidified on standing and was recrystallized from iso-Pr_2O to give colorless needles, mp 73—74° (lit. mp 72°,[12a] mp 71—72°[12b]). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640, 3200 (OH), 2800, 2750 (Bohlmann band). NMR ($CDCl_3$) τ: 6.70 (1H, d-d-d, J=11.0, 8.5, 4.9 Hz, $>C\langle^{OH}_{H}$). *Anal.* Calcd. for $C_9H_{17}ON$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.71; H, 10.85; N, 8.97.

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