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Studies on 1-Azabicyclo Compounds. XI.[1] Syntheses of Ten-membered Ring Amine Derivatives from Di(10-octahydroquinolizinyl)-hydroxylamine[2]

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Reaction of di(10-octahydroquinolizinyl)hydroxylamine (I) with methyl iodide in methanol gave 6-hydroxyimino-1-methyldecahydroazecine methiodide (II), 5-methyl-10-methoxyoctahydroquinolizinium iodide (III) and 3,4,6,7,8,9-hexahydro-2H-qunolizine (IV). Reduction of II with lithium in liquid ammonia afforded 6-hydroxyimino-1-methyldecahydroazecine (X), 6-amino-1-methyloctahydroazecine (XI) and IV. In addition, the similar reduction of III led to the formation of IV, VIII and *cis*-1-methyl-1,2,3,4,7,8,9,10-octahydroazecine (XIV).

In a previous paper,[4] we reported that condensation reaction of $\Delta^{1,10}$-hexahydroquinolizine (IV) with RNH_2 derivatives such as semicarbazide, hydroxylamine and hydrazine gave 10-substituted octahydroquinolizines, each of which, on neutralization with mineral acid, gave the iminium salt of IV. This paper deals with syntheses of some derivatives of decahydroazecine from di(10-octahydroquinolizinyl)hydroxylamine[4] (I) prepared by the reaction of IV with hydroxylamine. I was treated with an excess of methyl iodide in methanol to deposit a crystalline methiodide, $C_{11}H_{23}ON_2I$, mp 252—253° (decomp.), in 30% yield. The infrared spectrum of the methiodide showed bands at 3380, 1640 and 935 cm^{-1} attributable to an oxime and the magnetic resonance spectrum exhibited an N,N-dimethyl signal at τ 7.04 (6H, singlet) and a hydroxyl signal at τ 0.40 (1H, singlet, disappeared by treating with D_2O). Based on the above evidences, the methiodide was characterized as 6-hydroxyimino-1-methyldecahydroazecine methiodide (II). In addition, from the reaction mother liquor, a small amount of a quarternary ammonium salt, $C_{11}H_{22}ONI$, mp 260—261° (decomp.), was isolated besides a preponderance of IV. The by-product indicated a band at 1090 cm^{-1} owing to an ether in the infrared spectrum, and an O-methyl signal at τ 6.68 (3H, singlet) and an N-methyl signal at τ 6.83 (3H, singlet) in the nuclear magnetic resonance spectrum. The presence of the two methyl groups was also supported by the analytical measurement according to micro Zeisel method. From these data, the structure of the product was confirmed as 5-methyl-10-methoxyoctahydroquinolizinium iodide (III). A mechanism for the reaction of I with methyl iodide producing II, III and IV might be postulated as follows: the decomposition of I was partially effected to give XII and IV in the first step and the further reaction of the former with methyl iodide afforded the methiodide (II) along with hydriodic acid, while the other was condensed with methanol yielding XIII which was further converted into III. Hydriodic acid which was produced during the course of the reaction presumably accelerated the decompostion of I into XII and IV (Chart 2).

Acid hydrolysis of II led to the formation of two products; *i.e.*, a methiodide, mp 245.5—246°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1690 (carbonyl), as a major product and a tertiary amine, IR $\nu_{\max}^{\mathrm{liq.}}$ cm^{-1}: 2800 (N-methyl), 1690 (carbonyl), as a minor product. The latter was identified with the

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[1] Part X: Y. Arata and T. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **20**, (325) (1972).
[2] Reported at the Annual Meeting of Pharmaceutical Society of Japan, April, 1971, Fukuoka.
[3] Location: *13-1 Takaramachi, Kanazawa, 920, Japan.*
[4] Y. Arata, S. Yoshifuji, and T. Shioda, *Yakugaku Zasshi*, **92**, 69 (1972).

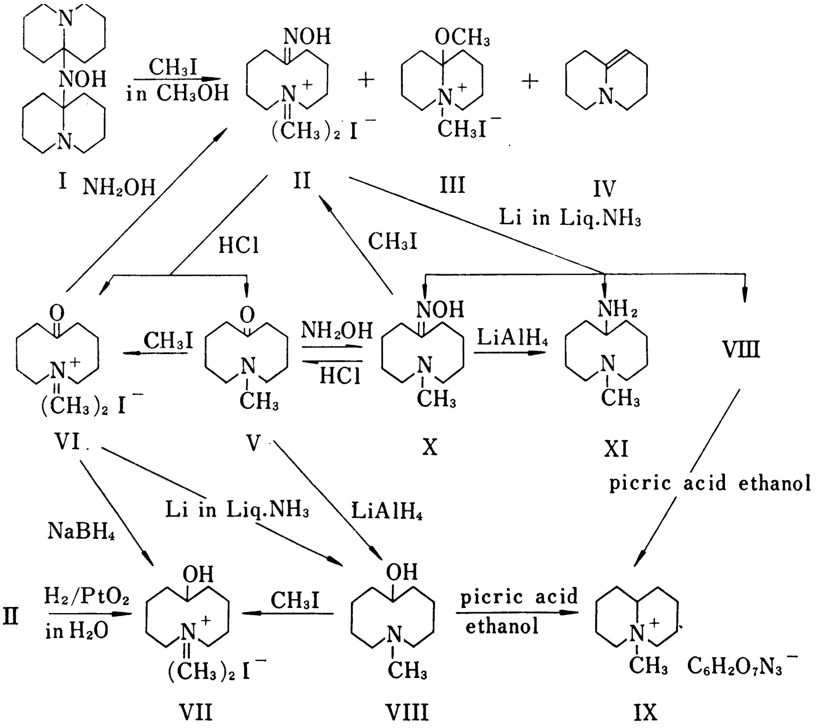

Chart 1

sample of 1-methyl-6-decahydroazecinone[5,6] (V) by the infrared spectral comparison and the former was proved to be identical with the methiodide (VI), mp 245—246°, derived from V by the direct comparison. On the other hand, hydrogenation of II over paltinum oxide in water yielded an alcohol, mp 243—244°, IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3360 (hydroxyl) in an excellent yield. The alcohol thus obtained did not show any melting point depression when mixed with VII, mp 246—247°, obtained by sodium borohydride reduction of VI and the infrared spectra of both alcohols did not show any difference. The reduction of II to VII may have taken place by the preceding formation of 6-iminodecahydroazecine which was hydrolized followed by the further reduction. Reaction of VI with lithium in liquid ammonia gave an alcohol (VIII), IR $\nu_{\max}^{\mathrm{liq.}}$ cm^{-1}: 3360 (hydroxyl), 2795 (N-methyl), which was identified with the product prepared by lithium aluminum hydride reduction of V by the infrared spectral comparison. No depression of melting point was observed by the admixture of methiodide, mp 245—246°, of VIII with VII mentioned above. Recrystallization of picrate of VIII from ethanol caused transannular cyclization to give *trans*-5-methyloctahydroquinolizinium picrate[7,8] (IX), mp 243—245°, as reported by Sisti, *et al.*[7]

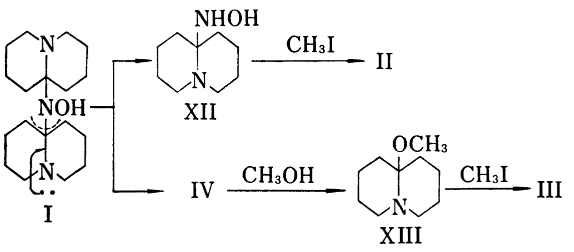

Chart 2

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[5] N.J. Leonard and M. Oki, *J. Am. Chem. Soc.*, **76**, 3463 (1954).

[6] Y. Arata, S. Yoshifuji, and Y. Yasuda, *Chem. Pharm. Bull.* (Tokyo), **17**, 1363 (1969).

[7] A.J. Sisti and D.L. Lohner, *J. Org. Chem.*, **32**, 2026 (1967).

[8] T.M. Meynehan, K. Schofield, R.A.Y. Johnes, and A.R. Katritzky, *J. Chem. Soc.*, **1962**, 2637.

Furthermore, reduction of II with lithium in liquid ammonia gave a colorless liquid which was subjected to fractional distillation to yield two fractions distilled at 110—140° (bath temperature)/18 mmHg and 160—180° (bath temperature)/18 mmHg in the approximate ratio 2:1. The latter fraction was composed mainly of an oxime, mp 101—102°, whose infrared spectrum exhibited bands at 3200, 1660 and 935cm^{-1} owing to an oxime and 2780cm^{-1} ascribable to an N-methyl group. The oxime did not show any melting point depression by the admixture with the oxime (X), mp 101—102°, derived from V and the infrared spectrum of methiodide of X was coincident with that of II as well as with that of oxime of VI. Acid-hydrolysis of X gave V. The former fraction was once converted into its picrate. It was then fractionally recrystallized from ethanol giving two picrates, mp 198.5—200°, sparingly soluble in ethanol, and mp 243—243.5°, comparatively soluble in ethanol. The amine, IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 3360, 3320, 1610 (NH_2), 2800 ($N\text{-}CH_3$), recovered from the former picrate was found to be identical with 6-amino-1-methyldecahydroazecine[6] (XI, picrate: mp 199—200°) by the infrared spectrum comparison and mixed melting point determination of the picrates. The latter picrate, on the other hand, did not show any melting point depression by the admixture with IX. Thus, it has been clarified that the reduction of II afforded X, XI and VIII, in 40%, 40%, and 10% yields, respectively. Lithium aluminum hydride reduction of X also gave XI. The compound III was also subjected to the reduction with lithium in liquid ammonia. Separation of the reaction products was performed according to similar procedure in the case of the reduction of II. Thus, three kinds of amino compounds were obtained: they gave picrates of mp 108—109°, mp 241—242° and 180—181°, $C_{10}H_{19}N \cdot C_6H_3O_7N_3$, respectively. The first two picrates were identified with those of IV and IX by mixed melting point determination, respectively. The infrared spectrum of the oily base purified through the last picrate showed bands at 2800 cm^{-1} based on an N-methyl group and at 2990, 1650, 895 and 700 cm^{-1} owing to *cis*-olefin, being different from that of *trans*-1-methyl-$\Delta^{5,6}$-octahydroazecine.[9] Thus, the structure of the base was deduced as *cis*-1-methyl-1,2,3,4,7,8,9,10-octahydroazecine (XIV). Catalytic reduction of XIV on palladium-charcoal afforded, as expected, 1-methyldecahydroazecine (XV) which gave a picrate, mp 188—189°. No depression of melting point was observed by the admixture of the picrate with that of 1-methyl decahydroazecine.[6]

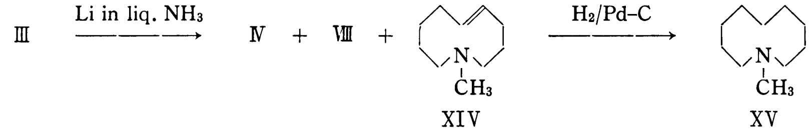

Chart 3

Experimental[10]

Reaction of Di(10-octahydroquinolizinyl)hydroxylamine (I) with Methyl Iodide (Formation of II, III and IV)——To a solution of 10 g of di(10-octahydroquinolizinyl)hydroxylamine[4] (I) in methanol was added 10 g of methyl iodide and the solution was kept standing for 24 hr to deposit a crystalline methiodide. The reaction solution was filtered to obtain the methiodide (A) and the mother liquor (B).

6-Hydroxyimino-1-methyldecahydroazecine Methiodide (II): The methiodide (A) was recrystallized from ethanol to give colorless plates, mp 252—253° (decomp.). Yield: 3.2 g, IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3300, 1640, 935 (oxime). NMR (10% solution in DMSO) τ: 7.04 [6H, singlet, $(CH_3)_2{=}N$], -0.40 (1H, singlet, $\rangle$N-OH). *Anal.* Calcd. for $C_{11}H_{23}ON_2I$: C, 40.50; H, 7.11; N, 8.57; I, 38.90. Found: C, 40.69; H, 7.13; N, 8.56; I, 39.00.

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9) K. Schofield and R.J. Wells, *Chem. Ind.* (London), **1963**, 572; *idem*, *Aust. J. Chem.*, **18**, 1423 (1965).

10) All melting points were measured with a Yanagimoto Micro Melting point Apparatus and uncorrected. IR spectra were measured with a Spectrophotometer S, Japan Spectroscopic Co., Ltd., and NMR with a H-60-C of Japan Electron Lab. Co., Ltd., using tetramethylsilane as an internal standard.

Methoperchlorate: To a solution of 0.1 g of III in water was added 50 mg of sodium perchlorate. The mixture was warmed to dissolve the salt and then cooled to deposit the precipitates, which were treated with heating alcohol followed by the filtration. The alcohol solution was evaporated *in vacuo* and the residue was recrystallized from ethanol to give colorless prisms, mp 199—200°. Yield: 70 mg. *Anal.* Calcd. for $C_{11}H_{23}ON_2ClO_4$: C, 44.22, H, 7.76; N, 9.38. Found: C, 44.15; H, 7.60; N, 9.39.

5-Methyl-10-methoxyoctahydroquinolizinium Iodide (III) and 3,4,6,7,8,9-Hexahydro-2*H*-quinolizine (IV): The reaction mother liquor (B) was evaporated *in vacuo*, and the residue was made alkaline with aqueous sodium hydroxide. The precipitates deposited were extracted with ether and the ether solution was washed with water, desiccated and then evaporated. The residue was distilled at 98—100°/18 mmHg to give a colorless liquid. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 3060, 1640 (enamine). The infrared spectrum of the base was coincident with that of $\Delta^{1,10}$-hexahydroquinolizine (IV). Picrate: recrystallizied from ethanol to give yellow needles, mp 108—109°. No depression of melting point by the admixture of the picrate with that of IV. The alkaline solution was extracted with chloroform. The chloroform layer was desiccated followed by the evaporation of the solvent. The residue was recrystallized from methanol to yield colorless cubic crystals (III), mp 260—261° (decomp.). Yield: 0.8 g. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1090 (ether). NMR (5% solution in D_2O) τ: 6.68 (3H, singlet, $-OCH_3$), 6.83 (3H, singlet, $-NCH_3$). *Anal.* Calcd. for $C_{11}H_{22}ONI$: C, 42.45; H, 7.13; N, 4.50; I, 40.78. Found: C, 42.47; H, 7.04; N, 4.64; I, 40.26. Perchlorate: recrystallized from ethanol to afford colorless prisms, mp >300°. *Anal.* Calcd. for $C_{11}H_{22}ONClO_4$: C, 46.56; H, 7.81; N, 4.94. Found: C, 46.67; H, 7.81; N, 5.20. Picrate: To a solution of 50 mg of III in water was added a solution of picric acid in water. The precipitates deposited were recrystallized from ethanol to yield yellow needles, mp 262—263°. Yield: 40 mg. *Anal.* Calcd. for $C_{11}H_{22}ON \cdot C_6H_2O_7N_3$: C, 49.51; H, 5.86; N, 13.59. N- and $O-CH_3$, 9.66. Found: C, 49.82; H, 6.00; N, 13.98; N- and $O-CH_3$, 8.83.

Acid Hydrolysis of 6-Hydroxyimino-1-methyldecahydroazecine Methiodide (II) (Formation of V and VI) The oxime (II) was refluxed with 15% hydrochloric acid for 2 hr. The reaction solution was made alkaline with sodium hydroxide and shaken with ether. The aqueous layer which was added with potassium iodide (0.1 g) was then extracted with chloroform.

1-Methyl-6-decahydroazecinone (V): The ether layer was evaporated. The residue was distilled at 120—125° (bath temperature)/18 mmHg to give a colorless liquid. Yield: 30 mg. IR $\nu_{\max}^{\text{liq}}$ cm^{-1}: 2800 (NCH_3), 1690 (C=O). The infrared spectrum of the amine was coincident with that of 1-methyl-6-decahydroazecinone.[6] Picrate: recrystallized from ethanol affording yellow needles, mp 244—246° (decomp.). *Anal.* Calcd. for $C_{10}H_{19}ON \cdot C_6H_3O_7N_3$: C, 48.24; H, 5.57; N, 14.07. Found: C, 48.38; H, 5.61; N, 13.83. Methiodide (VI): recrystallized from ethanol to give colorless prisms, mp 245—246°. No depression of melting point was observed by the admixture of the methiodide with 1-methyl-6-decahydroazecinone methiodide.[1] Oxime (X): recrystallized from ethanol to yield colorless needles, mp 102°. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3200, 1660, 935 (oxime), 2780 ($N-CH_3$). *Anal.* Calcd. for $C_{10}H_{20}ON_2$: C, 65.17; H, 10.94; N, 15.20. Found: C, 65.30; H, 10.91; N, 15.17.

1-Methyl-6-decahydroazecanone Methiodide (VI): The chloroform layer mentioned above was evaporated and the residue was recrystallized from ethanol to yield colorless prisms, mp 245.5—246°. Yield: 0.4 g. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1690 (C=O). The methiodide did not show any melting point depression by the admixture with VI mentioned above.

Methoperchlorate: recrystallized from ethanol giving coloress sandy crystals, mp 188—189°. *Anal.* Calcd. for $C_{11}H_{22}ON \cdot ClO_4$: C, 46.56; H, 7.81; N, 4.94. Found: C, 46.25; H, 7.71; N, 5.20. Oxime (II): recrystallized from ethanol to afford colorless prisms, mp 257—258° (decomp.). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3300, 1640, 935 (oxime). *Anal.* Calcd. for $C_{11}H_{23}ON_2I$: C, 40.50; H, 7.11; N, 8.59. Found: C, 40.67; H, 7.10; N, 8.54. The infrared spectrum of the methiodide was in accordance with that of II.

6-Hydroxy-1-methyldecahydroazecine Methiodide (VII)——1) Sodium borohydride Reduction of VI: To a solution of 0.4 g of VI in methanol was added sodium borohydride (0.2 g) and the mixture was warmed with stirring for 50 hr, followed by the evaporation of the solvent. The residue was treated with ethanol and filtered. The mother liquor was evaporated *in vacuo* and the residue was recrystallized from ethanol giving colorless needles, mp 246—247°. Yield: 0.26 g. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3360 (OH). *Anal.* Calcd. for $C_{11}H_{24}ONI$: C, 42.18; H, 7.72; N, 4.47. Found: C, 42.24; H, 7.86; N, 4.62.

2) Hydrogenation of II: Hydrogenation of 0.6 g of II over platinum oxide (0.1 g) in water was carried out. After the reaction, the catalyst was filtered off. Evaporation of the filtrate gave the residue which was recrystallized from ethanol to afford colorless prisms, mp 243—244°. Yield: 0.48 g, IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3360 (OH). *Anal.* Calcd. for $C_{11}H_{24}ONI$: C, 42.18; H, 7.72; N, 4.47. Found: C, 42.34; H, 7.76; N, 4.60. This alcohol did not show any melting point depression with the admixture of VII mentioned above, and the infrared spectra of both alcohols were coincident.

6-Hydroxy-1-methyldecahydroazecine (VIII)——1) Lithium aluminum hydride reduction of V. To a solution of 110 mg of V in ether was added lithium aluminum hydride (50 mg) and the mixture was stirred for 24 hr at room temperature. To this was added water and the mixture was shaken with ether. The ether layer was washed with water and desiccated, followed by the evaporation of the solvent. The residue was distilled at 145—150° (bath temperature)/18 mmHg. The distillate soon solidified. mp 47—47.5°. Yield: 80 mg. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3330 (OH), 2790 ($N-CH_3$). Methiodide (VII): recrystallized from ethanol affording colorless prisms, mp 245—246°. No depression of melting point was observed by the admixture of this methiodide with VII derived from II.

2) Reduction of VI with Lithium in Liquid Ammonia: To a solution of 0.5 g of the methiodide (VI) in liquid ammonia (250 ml) was added 0.1 g of lithium with stirring. The solution changed its color into deep blue. After 15 min, to this was added a small amount of water. The solution was evaporated and to the residue were added water and ether with stirring. The ether layer was washed with water and desiccated followed by the evaporation of the solvent. A colorless liquid thus obtained was distilled at 145—155° (bath temperature)/18 mmHg. IR $\nu_{max}^{liq.}$ cm^{-1}: 3360 (OH), 2795 ($N\text{-}CH_3$). *Anal.* Calcd. for $C_{10}H_{21}ON$: C, 70.12; H, 12.36; N, 8.18. Found: C, 69.65; H, 12.49; N, 8.18. NMR (10% solution in $CDCl_3$) τ: 7.43 (1H, singlet, $O\underline{H}$), 6.10 (1H, multiplet, $\rangle C\underline{H}\text{-}OH$), 7.90 (3H, singlet, $N\text{-}C\underline{H}_3$). The infrared spectra of this compound and VIII derived from V in carbon tetrachloride were coincident. Methiodide (VII): recrystallized from ethanol to give colorless prisms, mp 244—245°. *Anal.* Calcd. for $C_{11}H_{24}ONI$: C, 42.18; H, 7.72; N, 4.47. Found: C, 42.30; H, 7.75; N, 4.58. No depression of melting point was observed by the admixture of this methiodide with VII derived from V.

***trans*-5-Methyl-octahydroquinolizinium Picrate (IX)**——Picrate of VIII was recrystallized from ethanol to yield yellow needles, mp 243—245°. *Anal.* Calcd. for $C_{10}H_{20}N\cdot C_6H_2O_7N_3$: C, 50.25; H, 5.80; N, 14.65. Found: C, 50.26; H, 5.82; N, 14.35. The picrate did not show any melting point depression with the admixture of the corresponding picrate,⁷⁾ mp 243—244° (IX) derived from *trans*-5-methyloctahydroquinolizinium iodide.

Reduction of 6-Hydroxyimino-1-methyldecahydroazecine Methiodide (II) with Lithium in Liquid Ammonia (Formation of VIII, X and XI)——To a solution of 3 g of II dissolved in liquid ammonia (500 ml) was added 0.2 g of lithium with stirring. After 15 min, to the blue solution was added a small amount of water. After the evaporation of ammonia, to the residue were added ether and water with stirring. The ether layer was desiccated followed by the evaporation of the solvent. The residue was distilled to afford two fractions boiling at 110—140° (bath temperature) and at 160—180° (bath temperature)/18 mmHg. The former fraction was once converted into its picrate, which, on recrystallization from ethanol, separated into a sparingly soluble picrate (0.7 g) and a comparatively soluble picrate (80 mg).

6-Amino-1-methyldecahydroazecine (XI): A colorless liquid made free from the sparing soluble picrate was distilled at 120—130° (bath temperature)/18 mmHg. IR $\nu_{max}^{liq.}$ cm^{-1}: 3360, 3320, 1610 (NH_2), 2800 ($N\text{-}CH_3$). The infrared spectrum of this base was completely coincident with that of 6-amino-1-methyldecahydroazecine⁶⁾ (XI). Picrate: recrystallized from ethanol to give yellow scales, mp 198.5—200°. No depression of melting point was observed by the admixture of this picrate with that of 6-amino-1-methyldecahydroazecine.⁶⁾

5-Methylocatahydroquinolizinium Picrate (IX): The comparatively soluble picrate mentioned above was recrystallized from ethanol to afford yellow needles, mp 243—243.5°. No depression of melting point was observed by the admixture of this picrate with IX derived from VIII. This fact indicated that the reduction of II gave VIII, whose picrate underwent transannular cyclization reaction⁷⁾ to afford IX.

6-Hydroxyimino-1-methyldecahydroazecine (X): The latter fraction soon solidified and was recrystallized from ethanol to give colorless needles, mp 101—101.5°. Yield: 0.23 g. IR ν_{max}^{KBr} cm^{-1}: 2780 ($N\text{-}CH_3$), 3200, 1660, 935 (oxime). *Anal.* Calcd. for $C_{10}H_{20}O\ N_2$: C, 65.17; H, 10.94; N, 15.20. Found: C, 65.30; H, 10.91; N, 15.17. The oxime did not show any melting point depression by the admixture with X derived from V. Methiodide (II): recrystallized from ethanol to afford colorless prisms, mp 253—255° (decomp.). IR ν_{max}^{KBr} cm^{-1}: 3300, 1640, 935 (oxime). The infrared spectra of this methiodide and II were coincident.

Acid Hydrolysis of 6-Hydroxyimino-1-methyldecahydroazecine (X) (Formation of V)——The oxime (X) (100 mg) was refluxed with 15% hydrochloric acid for 10 hr. The reaction solution was made alkaline with sodium hydroxide and shaken with ether. The ether layer was desiccated followed by the evaporation of the solvent. The residue was distilled at 120—130° (bath temperature)/18 mmHg. A colorless liquid. Yield: 65 mg. IR $\nu_{max}^{liq.}$ cm^{-1}: 1690 (C=O), 2800 ($N\text{-}CH_3$). The infrared spectra of this amine and V were in accordance.

Lithium Aluminum Hydride Reduction of 6-Hydroxyimino-1-methyldecahydroazecine (X) (Formation of XI)——To a solution of 120 mg of X in ether was added 100 mg of lithium aluminum hydride and the mixture was stirred for 20 hr. To this were added water and ether with stirring. The ether layer was washed with water and desiccated followed by the evaporation of the solvent. The residue was distilled at 120—130° (bath temperature)/18 mmHg. Yield: 80 mg. IR $\nu_{max}^{liq.}$ cm^{-1}: 3360, 3320, 1610 (NH_2), 2800 ($N\text{-}CH_3$). The infrared spectra of this amine and XI derived from II were in accordance. Picrate: recrystallized from ethanol to afford yellow prisms, mp 199—200°. *Anal.* Calcd. for $C_{10}H_{22}N_2\cdot 2C_6H_3O_7N_3$: C, 42.04; H, 4.49; N, 17.83. Found: C, 42.05; H, 4.37; N, 17.98. No depression of melting point was observed by the admixture of this picrate with that of XI.

Reduction of 1-Methyl-10-methoxyoctahydroquinolizinium Iodide (III) with Lithium in Liquid Ammonia (Formation of VIII, IV and XIV)——This reaction was carried out in the same condition as the case of II, using 3 g of III and 0.25 g of lithium. After working up in the same manner as for II, two fractions boiling at 110—120° (bath temperature) and at 140—150° (bath temperature)/18 mmHg were obtained. The former fraction was once converted into its picrate, which was recrystallized from ethanol giving both a sparingly soluble picrate (0.8 g) and a comparatively soluble picrate (0.5 g).

cis-1-Methyl-1,2,3,4,7,8,9,10-octahydroazecine (XIV): A colorless liquid distilled at 110° (bath temperature)/18 mmHg was obtained from the former picrate. IR $\nu_{\text{max}}^{\text{liq.}}$ cm^{-1}: 2990, 1650, 895, 700 (*cis* olefine), 2800 (N-CH_3). Picrate: recrystallized from ethanol to yield yellow needles, mp 180—181°. *Anal.* Calcd. for $C_{10}H_{19}N \cdot C_6H_3O_7N_3$: C, 50.26; H, 5.80; N, 14.65. Found: C, 50.44; H, 5.88; N, 14.65.

3,4,6,7,8,9-Hexahydro-2*H*-quinolizine (IV): A colorless liquid was obtained from the latter picrate. The infrared spectra of the amine and IV were coincident. Picrate: recrystallized from ethanol to give yellow needles, mp 108—109°. No melting point depression was observed by the admixture of this picrate with that of IV.

6-Hydroxy-1-methyldecahydroazecine (VIII): The latter fraction was converted into its picrate which was recrystallized from ethanol giving yellow needles, mp 241—242°. Yield: 60 mg. The picrate did not show any melting point depression with the admixture of IX. This fact[7] indicated that the reduction of III gave VIII.

1-Methyldecahydroazecine (XV): Catalytic reduction of 0.1 g of XIV on palladium-charcoal in ethanol was carried out. After the reaction, the catalyst was filtered off and the filtrate was evaporated *in vacuo*. The residue was distilled at 95—100° (bath temperature)/18 mmHg. A colorless liquid. Yield: 80 mg. IR $\nu_{\text{max}}^{\text{liq.}}$ cm^{-1}: 2800 (N-CH_3). The infrared spectra of this amine and 1-methyldecahydroazecine[6] (XV) were coincident. Picrate: recrystallized from ethanol giving yellow needles, mp 188—189°. No depression of melting point was observed by the admixture of the picrate with that of 1-methyldecahydroazecine.

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