Chem. Pharm. Bull.
17(7)1363—1368(1969)

UDC 547.834.04 : 547.897.2.07

Studies on 1-Azabicyclo Compounds. VII.[1] Syntheses of Ten-membered Ring Amines from Octahydroquinolizine[2]

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(Received November 18, 1968)

10-Cyano-5-methyloctahydroquinolizinium iodide (V) was treated with silver oxide to give carbamoyl methohydroxide (VI), which was further converted to carbamoyl methobromide (VII). Reaction of V and VII with lithium in liquid ammonia afforded 1-methylazecane (IX) and 10-cyano-1-methylazecane (VIII), and 1-methylazecane-6-carboxamide (XI) and a demethylated compound (IX), respectively. 10-Amino-5-methyloctahydroquinolizinium bromide (XIV) which was derived from VII was heated in an alkaline solution affording 1-methyl-6-azecanone (XV), whose ring appears in the majority of the medium sized ring alkaloids.

The medium-sized, nitrogen containing ring alkaloids have recently attracted considerable attention because of their structural relation to the corresponding 1-azabicycloalkane alkaloids and because of their steadily increasing number. In connection with studies in these areas, we have developed the syntheses of a series of ten-membered ring amines from octahydroquinolizine, as reported previously in a preliminary note.[2] The details of the syntheses are described here. The application of the new synthesic methods might allow the production of a wide variety of complex medium-sized ring amines from readily available starting materials: 1-azabicyclic compounds.

According to the method by Leonard, *et al.*,[4] the perchlorate (III) of dehydro compound (II) obtained by mercuric acetate oxidation of octahydroquinolizine (I) was treated with potassium cyanide to yield 10-cyanooctahydroquinolizine (IV). The cyano compound (IV) was neutralized with perchloric acid or picric acid followed by the recrystallization only to give the iminium salt (III). IV was heated with methyl iodide affording a stable methiodide (V), mp 242—243° (decomp.), which showed a cyano band at 2210 cm^{-1} in the infrared spectrum and gave a single spot on the thin-layer chromatography. The methiodide (V), when treated with silver oxide, gave a carbamoyl methohydroxide (VI), which was neutralized with hydrobromic acid to give a methobromide (VII), mp 286—289° (decomp.) in excellent yields in both. VII indicated bands attributable to a primary amide at 3350, 3200, 1670, and 1605 cm^{-1}.

Now, attempts to produce the respective medium-sized ring amines from the compounds V, VI, and VII were successfully carried out, as shown in Chart 1.

Reaction of the methiodide (V) with lithium in liquid ammonia gave both 6-cyano-1-methylazecane (VIII) which formed a picrate, mp 181—182°, and 1-methylazecane (IX) which formed a picrate, mp 189—190°, in 7% and 70% yields, respectively. The infrared spectrum of the former compound showed the absorption bands based on an N-methyl (2800 cm^{-1}) and a cyano (2210 cm^{-1}) groups, while that of the latter showed a band ascribable to an N-methyl group (2800 cm^{-1}).

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[1] Part VI: Y. Arata, T. Shioda, J. Yamada, and Y. Hayashi, *Yakugaku Zasshi*, **89**, 389 (1969).

[2] A preliminary communication has been published: Y. Arata, S. Yoshifuji, and Y. Yasuda, *Chem. Pharm. Bull.* (Tokyo), **16**, 569 (1968).

[3] Location: *Takara-machi 13, Kanazawa.*

[4] N.J. Leonard and A.S. Hay, *J. Am. Chem. Soc.*, **78**, 1984 (1956).

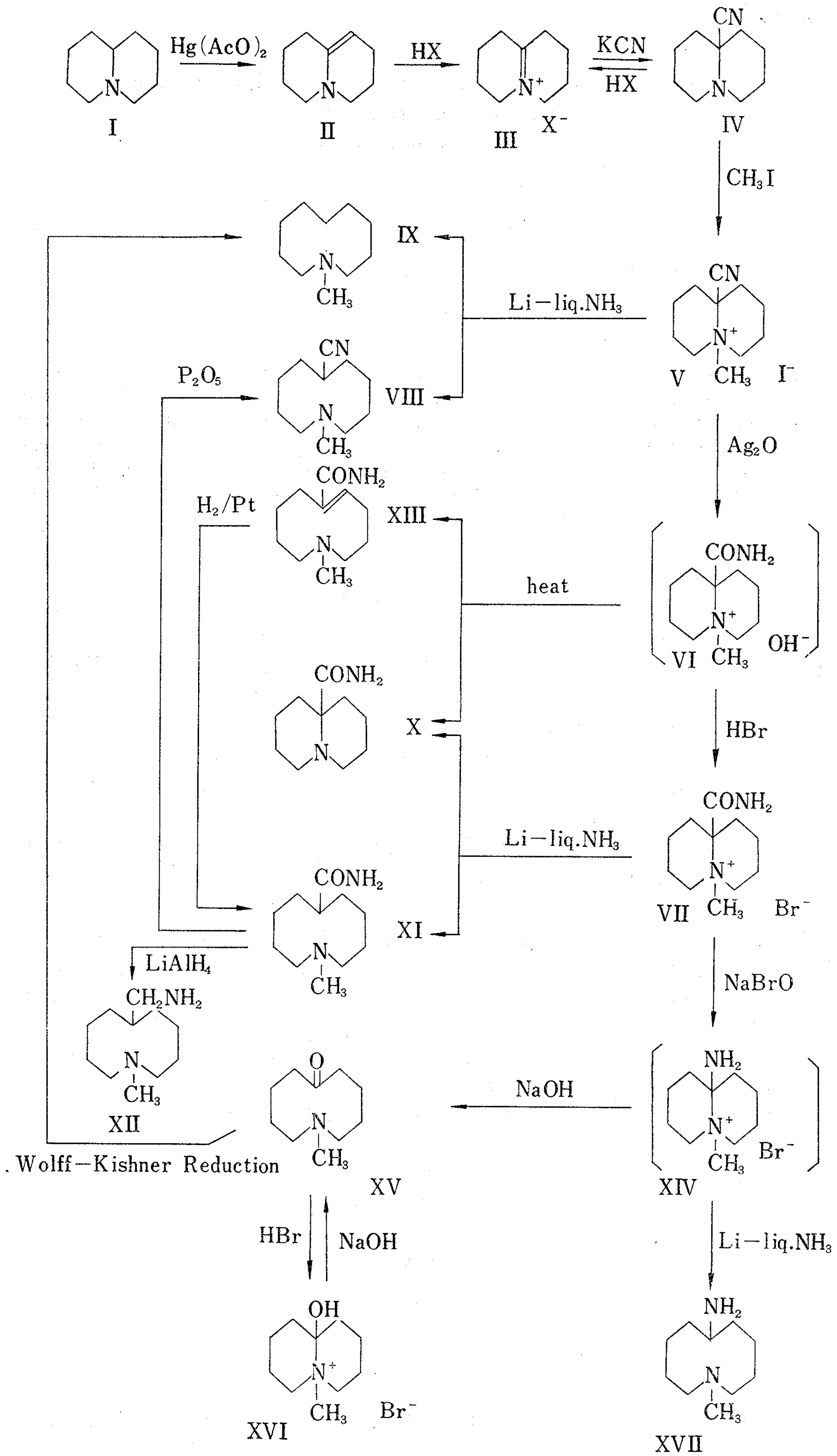

Hg(AcO)$_2$
HX
KCN
HX
CN
I
II
III
X$^-$
IV
CH$_3$I
IX
CH$_3$
Li−liq.NH$_3$
CN
V
CH$_3$
I$^-$
P$_2$O$_5$
VIII
Ag$_2$O
CONH$_2$
H$_2$/Pt
XIII
heat
VI
OH$^-$
X
HBr
Li−liq.NH$_3$
VII
Br$^-$
XI
LiAlH$_4$
CH$_2$NH$_2$
NaBrO
XII
NaOH
NH$_2$
XIV
Wolff−Kishner Reduction
XV
HBr
NaOH
Li−liq.NH$_3$
OH
XVI
Br$^-$
XVII

Chart 1

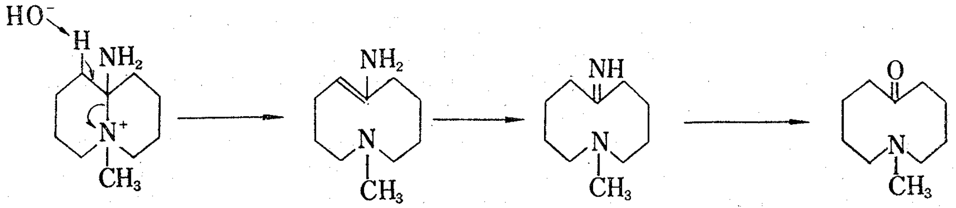
Reaction of the methobromide (VII) with lithium in liquid ammonia gave a demethylated amine (X), mp 115—116°, in 18% yield and 1-methylazecane-6-carboxamide (XI), mp 177—178°, in 65% yield. The infrared spectrum of X indicated bands at 3400, 3170, 1680 and 1600 (weak) cm^{-1} owing to a primary amide, and that of XI showed bands at 3400, 3180 and 1650 cm^{-1} based on a primary amide, and at 2800 cm^{-1} due to an N-methyl group. The nuclear magnetic resonance spectrum of XI showed the presence of the N-methyl group (7.91 τ, 3H, singlet), but not C-methyl protons.

The action of phosphorous pentoxide on XI gave a nitrile which formed a picrate, mp 181—182°. The spectrum of the nitrile was completely in accordance with that of VIII derived from V. No depression of melting point was observed by the admixture of both picrates. On the other hand, reduction of XI with lithium aluminium hydride afforded in 86% yield 6-aminomethyl-1-methylazecane (XII) which gave a picrate, mp 178—179°. The infrared spectrum of XII showed primary amino bands at 3370 and 3320 cm^{-1}, and an N-methyl band at 2800 cm^{-1}.

Hofmann degradation of the carbamoyl methohydroxide (VI) by heating gave a demethylated amine, mp 115—116°, and 1-methyloctahydroazecine-6-carboxamide (XIII), mp 154—155°, in 25% and 10% yields, respectively. The former compound was found to be identical with the compound X derived from VII by mixed melting point determination and infrared spectral comparison. The infrared spectrum of the latter (XIII) indicated carbamoyl bands at 3400, 3180, 1650, and 1600 cm^{-1}, and an N-methyl band at 2800 cm^{-1}, and its nuclear magnetic resonance spectrum showed the presence of the N-methyl group (7.88 τ, 3H, singlet) and $\rangle C{=}\underset{|}{C}H$ grouping (3.77 τ, 1H, triplet). Catalytic hydrogenation of XIII using platinic oxide afforded the dihydro amine, mp 176—178°, which did not show any melting point depression by the admixture with the compound XI derived from VII, and the infrared spectra of both compounds were completely in accordance.

Furthermore, the action of sodium hypobromite on the carbamoyl methobromide (VII) afforded a methobromide (XIV) in 40% yield and its analytical results were a little different from the calculated values of the molecular formula, $C_{10}H_{21}N_2Br$, which was assumed by the following experiments. Reaction of XIV with lithium in liquid ammonia gave 6-amino-1-methylazecane (XVII) which formed a picrate, mp 199—200°. The infrared spectrum of XVII showed bands at 3340 and 3280 cm^{-1} owing to a primary amine and 2800 cm^{-1} attributable to an N-methyl group. Heating of XIV in an alkaline solution gave in 77% yield the expected 1-methyl-6-azecanone (XV) which gave a picrate, mp 255—256° (decomp.).

By the way, its ring system is known to appear in the majority of the medium-sized ring alkaloids. The infrared spectrum of XV indicated a band at 1680 cm^{-1} owing to a carbonyl band which was under *trans*-annular interaction[5,6] between N and $C_{C=O}$, while that of its hydrobromide (XVI) indicated a band at 3120 cm^{-1} attributable to a hydroxyl group in trans-annular quaternary form, $R{-}\overset{|}{\underset{|}{N^{+}}}{-}\overset{|}{\underset{|}{C}}{-}OH$, but not a carbonyl band. These data were in accordance with those of XV and its salt, which had been already synthesized[6] by



XIV XV

Chart 2

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5) N.J. Leonard, R. C. Fox, M. Oki, and S. Chiavarelli, *J. Am. Chem. Soc.*, **76**, 630 (1954).
6) N.J. Leonard and M. Oki, *J. Am. Chem. Soc.*, **76**, 3463 (1954).

ring closure of an acylic precursor. As shown in Chart 2, the degradation of XIV to XV was presumably caused by the cleavage of the C–N bond to give a methine base, which, through the shift of the double bond, afforded an imino compound, followed by hydrolysis.

In addition, Wolff–Kishner reduction of XV afforded an amine, which gave a picrate, mp 188—189°. The infrared spectra of the amine and IX derived from V were completely in accordance and no depression of melting point was observed by the admixture of both picrates.

Experimental[7]

3,4,6,7,8,9-Hexahydro-2H-quinolizine (II)——According to the method by Leonard, *et al.*,[4] II was afforded by mercuric acetate oxidation of octahydroquinolizine (I).

Perchlorate (III): Recrystallized from ethanol to give colorless scales, mp 233—234° (decomp.). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 1680 (iminium).

Picrate: Recrystallized from ethanol to give yellow scales, mp 105—106°.

Hydroiodide: Recrystallized from ethyl acetate to give colorless needles, mp 141—142°. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 1680 (iminium).

10-Cyanooctahydroquinolizine (IV)——To a solution of 20 g of the perchlorate (III) in water (500 ml), 500 ml of 5% potassium cyanide solution was added dropwise with stirring and the stirring was continued for 3 hr. The solution was shaken with ether, the ether layer was washed with water and then desiccated, followed by the evaporation of the solvent. The residue was distilled to give 13.2 g of colorless liquid, bp 123° (18 mmHg). IR $\nu_{\text{max}}^{\text{liq.}}$ cm^{-1}: 2210 (nitrile).

An ether solution of picric acid was added to IV depositing yellow picrate, mp 116—118°, which was recrystallized from ethanol to give picrate of II, yellow scales, mp 105—106°. No melting point depression was observed by the admixture of the picrate with that of II. IV was neutralized with perchloric acid to give perchlorate (III), colorless scales of mp 232—233° (decomp.). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 1680 (iminium). The IR spectra of the perchlorate obtained here and III were completely coincident.

5-Methyl-10-cyanooctahydroquinolizinium Iodide (V)——A mixture of 13 g of the cyano compound (IV) and an excess of methyl iodide was heated for 45 hr to yield a crystalline methiodide (V), which was recrystallized from water to give colorless scales, mp 242—243° (decomp.). Yield: 23 g. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 2210 (nitrile). *Anal.* Calcd. for $C_{11}H_{19}N_2I$ (V): C, 43.14; H, 6.26; N, 9.15. Found: C, 43.16; H, 6.26; N, 9.33. V was developed over the thin–layer chromatography of alumina–gipsum (85:15) with dioxane–water (1:1) and water indicating one spot of *Rf* 0.58 and that of *Rf* 0.88, respectively.

10-Carbamoyl-5-methyloctahydroquinolizinium Hydroxide (VI)——To a solution of 3 g of the methiodide (V) in water (200 ml) 8 g of silver oxide was added. The mixture was stirred for 8 hr and then filtered. A part of the filtrate was evaporated to dryness *in vacuo*, leaving a viscous liquid (VI).

10-Carbamoyl-5-methyloctahydroquinolizinium Bromide (VII)——The filtrate containing VI was neutralized with dilute hydrobromic acid and evaporated to dryness *in vacuo*. The residue (VII) was recrystallized from ethanol to give colorless needles, mp 286—289° (decomp.). IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1}: 3350, 3200, 1670, and 1605 (primary amide). *Anal.* Calcd. for $C_{11}H_{21}ON_2Br$ (VII): C, 47.66; H, 7.63; N, 10.11; Found: C, 47.34; H, 7.43; N, 10.33.

Reaction of 10-Cyano-5-methyloctahydroquinolizinium Iodide (V) with Lithium in Liquid Ammonia (Formation of 6-Cyano-1-methylazecane (VIII) and 1-Methylazecane (IX))——To a solution of the methiodide (V) (0.5 g) in liquid ammonia (300 ml) 0.15 g of lithium was added with stirring. The solution changed its color into deep blue. After the evaporation of ammonia, to the residue water (5 ml) and ether (300 ml) were added with stirring. From the ether soluble extract, colorless liquid (IX) of bp 93—95° (18 mmHg, bath temperature) and that (VIII) of bp 170—175° (18 mmHg, bath temperature) were afforded in yields of 0.35 g and 0.03 g, respectively.

6-Cyano-1-methylazecane (VIII): IR $\nu_{\text{max}}^{\text{liq.}}$ cm^{-1}: 2800 (N-methyl), 2210 (nitrile).

Picrate: Recrystallized from ethanol to give yellow needles, mp 181—182°. *Anal.* Calcd. for $C_{17}H_{23}O_7N_5$ (picrate of VIII): C, 49.87; H, 5.66; N, 17.11. Found: C, 50.00; H, 5.52; N, 17.38.

1-Methylazecane (IX): IR $\nu_{\text{max}}^{\text{liq.}}$ cm^{-1}: 2800 (N-methyl).

Picrate: Recrystallized from ethanol to give yellow needles, mp 189—190°. *Anal.* Calcd. for $C_{16}H_{24}O_7N_2$ (picrate of IX): C, 49.99; H, 6.29; N, 14.58. Found: C, 49.91; H, 6.29; N, 14.36.

Reaction of 10-Carbamoyl-5-methyloctahydroquinolizinium Bromide (VII) with Lithium in Liquid Ammonia (Formation of Octahydroquinolizine-10-carboxamide (X) and 1-Methylazecane-6-carboxamide (XI))——

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[7] IR spectra were measured with a Spectrophotometer S and DS-402G, Japan Spectroscopic Co., Ltd., and NMR with a H-60-C of Japan Electron Optics Lab. Co., Ltd. Melting points were measured with a Yanagimoto Micro Melting Point Apparatus.

To a solution of 0.5 g of the methobromide (VII) dissolved in liquid ammonia (150 ml) 0.1 g of lithium was added with stirring. After being kept for ten min, to the solution a small amount of water was added. After the evaporation of ammonia, to the residue water (5 ml) and ether (30 ml) were added with stirring. The ether layer was washed with water, and desiccated, followed by the evaporation of the solvent. The residue soon solidified and was recrystallized from isopropyl ether giving colorless needles (XI), mp 177—178°. Yield: 0.2 g. The recrystallization mother liquor of XI was evaporated to dryness. The residue was recrystallized from isopropyl ether to give colorless plate (X), mp 115—116°. Yield: 0.07 g.

Octahydroquinolizine-10-carboxamide (X): IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 3170, 1680, and 1600 (weak)(primary amide). *Anal.* Calcd. for $C_{10}H_{18}ON_2$ (X); C, 65.87; H, 9.96; N, 15.37. Found: C, 65.20; H, 9.91; N, 15.14.

Perchlorate: Recrystallized from ethanol to give colorless sandy crystals, mp 255—257° (decomp.). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3480, 3370, 1680, and 1605 (primary amide). *Anal.* Calcd. for $C_{10}H_{19}O_5N_2Cl$ (perchlorate of X): C, 42.49; H, 6.77; N, 9.91. Found: C, 42.54; H, 6.51; N, 9.96.

1-Methylazecane-6-carboxamide (XI): IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 3180, 1650 (primary amide), 2800 (N-methyl). NMR ($CDCl_3$) τ: 7.91 (3H, singlet, N-CH_3). *Anal.* Calcd. for $C_{11}H_{22}ON_2$ (XI): C, 66.62; H, 11.18; N, 14.13. Found: C, 67.05; H, 11.30; N, 13.79.

Reaction of 1-Methylazecane-6-carboxamide (XI) with Phosphorous Pentoxide (Formation of 6-Cyano-1-methylazecane (VIII))——A mixture of 105 mg of XI and 0.2 g of phosphorous pentoxide was heated for 30 min at 180—190°. To the mixture water (2 ml) was added in drops, the mixture was made alkaline with sodium carbonate and shaken with ether. The ether layer was washed with water, desiccated and evaporated. From the residue, colorless viscous liquid (VIII), bp 170—180° ((18 mmHg) bath temperature) was afforded. Yield: 81 mg. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 2210 (nitrile), 2800 (N-methyl).

Picrate: Recrystallized from ethanol to give yellow needles, mp 181—182°. No depression of melting point was observed by the admixture of this picrate with that of VIII derived from V.

6-Aminomethyl-1-methylazecane (XII)——To a solution of 100 mg of the carbamoyl compound (XI) in ether (15 ml) 100 mg of lithium aluminium hydride was added and the mixture was stirred for 12 hr at room temperature. To this water (4 ml) was added and the mixture was extracted with ether. The ether layer was washed with water and desiccated, followed by the evaporation of the solvent. The residue was distilled to give colorless viscous liquid (XII), bp 110—120° (3 mmHg, bath temperature). Yield: 79 mg. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 3370, 3320 (primary amine), 2800 (N-methyl).

Picrate: Recrystallized from a 1:1 mixture of ethanol and water to give yellow prisms, mp 178—179°. *Anal.* Calcd. for $C_{17}H_{27}O_5N_5$ (monopicrate of XII): C, 49.38; H, 6.58; H, 17.45. Found: C, 49.42; H, 6.58; N, 17.56.

Hofmann Degradation of 10-Carbamoyl-5-methyloctahydroquinolizinium Hydroxide (VI) (Formation of Octahydroquinolizine-10-carboxamide (X) and 1-Methyl-1,2,3,4,7,8,9,10-octahydroazecine-6-carboxamide (XIII))——To a solution of 3.1 g of the methiodide (V) in 200 ml of 20% methanol silver oxide (6.5 g) was added. After the stirring for 10 hr followed by the filtration, the filtrate was evaporated to dryness *in vacuo*. The residue was heated under the reduced pressure to give 1.35 g of very viscous liquid, which was distilled at 135—137° under 4 mmHg pressure.

1-Methyl-1,2,3,4,7,8,9,10-octahydroazecine-6-carboxamide (XIII): Treatment of the distillate effected solidification and recrystallization of this solid from petroleum ether gave colorless needles (XIII), mp 154—155°. Yield: 0.15 g. *Anal.* Calcd. for $C_{11}H_{20}ON_2$ (XIII): C, 67.38; H, 10.27; N, 14.27. Found: C, 67.38; H, 10.18; N, 14.38. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 3180, 1650, 1620, 1600 (primary amide and double bond), 2800 (N-methyl). NMR ($CDCl_3$) τ: 7.88 (3H, singlet, N-methyl), 3.77 (1H, triplet, C=CH–).

Octahydroquinolizine-10-carboxamide (X): The recrystallization mother liquor of XIII was evaporated to dryness leaving the compound (X). Recrystallized from isopropyl ether to give colorless plates, mp 116—117°. Yield: 0.45 g. No depression of melting point was observed by the admixture of this compound with X derived from VII. The IR spectra of both compounds were completely in accordance.

Catalytic Reduction of 1-Methyl-1,2,3,4,7,8,9,10-octahydroazecine-6-carboxamide (XIII) (Formation of 1-Methylazecane-6-carboxamide (XI))——Catalytic reduction of 80 mg of XIII in methanol (6 ml) was carried out with platinic oxide (50 mg). Reaction was stopped when 11.2 ml of hydrogen (1.1 mole equivalent) was absorbed and then the catalyst was filtered. Evaporation of the filtrate gave the residue which was recrystallized from isopropyl ether to give 52 mg of colorless needles, mp 176—178°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 3180, 1650 (primary amide), 2800 (N-methyl). No melting point depression was observed by the admixture of this compound with XI derived from VII. IR spectra of both compounds were in accordance.

10-Amino-5-methyloctahydroquinolizinium Bromide (XIV)——2.8 g of the methobromide (VII) was dissolved in sodium hypobromite solution (prepared from 2.4 g of bromine and 30 ml of 10% sodium hydroxide solution). It was kept for 30 min at 0° and for 1 hr at room temperature. The solution was warmed slowly and then kept for 30 min at 65°. The reaction solution was shaken with ether and the aqueous layer was extracted with chloroform. The chloroform layer was desiccated, followed by the evaporation of the solvent. The residue (0.9 g) was recrystallized from chloroform to give colorless needles, mp 222—224° (decomp.). *Anal.* Calcd. for $C_{10}H_{21}N_2Br$ (XIV): C, 48.20; H, 8.49; N, 11.20. Found: C, 47.19; H, 8.47; N, 10.83. The analytical results were a little different from the calculated values for the molecular formula, $C_{10}N_{21}N_2Br$, which was assumed by the following experiments.

The ether layer obtained as above was washed with water and desiccated, followed by the evaporation of the solvent. The residue was distilled to give 0.3 g of colorless liquid, bp 120—122° (18 mmHg, bath temperature). Its IR spectrum was coincident with that of XV derived from XIV. It formed yellow picrate, mp 255—256° (decomp.).

1-Methyl-6-azecanone (XV)——A mixture of 0.5 g of XIV and 20% sodium hydroxide solution (4 ml) was heated for 5 hr at 90—95°, deposing an oil. The reaction solution was shaken with ether. The ether layer was washed with water and desiccated followed by the evaporation of the solvent. The residue was distilled to collect 0.26 g of colorless liquid (XV), bp 123—125° (20 mmHg, bath temperature). IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1680 (carbonyl), 2820 (N-methyl).

Picrate: Recrystallized from ethanol to give yellow prisms, mp 255—256° (decomp.). *Anal.* Calcd. for $C_{16}H_{22}O_8N_4$ (picrate of XV): C, 48.24; H, 5.57; N, 14.07. Found: C, 48.38; H, 5.61; N, 13.83.

Hydrobromide (XVI): Recrystallized from a 1:1 mixture of ethanol and isopropyl ether to give colorless needles, mp 241—242° (decomp.). *Anal.* Cacld. for $C_{10}H_{20}ONBr$ (hydrobromide of XV): C, 48.00; H, 8.04; N, 5.60. Found: C, 48.04; H, 7.90; N, 6.06. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3120 (hydroxyl).

6-Amino-1-methylazecane (XVII)——To a solution of 200 mg of XIV dissolved in liquid ammonia (80 ml) 0.15 g of lithium was added with stirring. After 15 min, to the blue solution a small amount of water was added. After the evaporation of ammonia, to the residue water (5 ml) and ether (30 ml) were added. The ether layer was desiccated, followed by the evaporation of the solvent. The residue was distilled to give colorless liquid (XVII), bp 125—130° (17 mmHg, bath temperature). Yield: 98 mg. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 3340, 3280 (primary amine), 2800 (N-methyl).

Picrate: Recrystallized from ethanol to give yellow sandy crystals, mp 199—200°. *Anal.* Calcd. for $C_{22}H_{28}O_{14}N_8$ (dipicrate of XVII): C, 42.04; H, 4.49; N, 17.83. Found: C, 42.07; H, 4.59; N, 17.92.

Wolff-Kischner Reduction of 1-Methyl-6-azecanone (XV) (Formation of 1-Methylazecane (IX))——A mixture of 100 mg of XV and 1 ml of 90% hydrazine hydrate was heated for 8 hr at 60° and then extracted with ether. The ether layer was desiccated followed by the evaporation of the solvent. The residue (90 mg) was dissolved in the ethanol containing sodium ethoxide (prepared from ethanol (3 ml) and sodium (0.8 g)) and this solution was heated for 16 hr at 160° in a sealed tube. After the reaction, the solvent was evaporated *in vacuo*. To the residue water (3 ml) was added, the mixture was shaken with ether. The ether layer was washed with water, desiccated and then evaporated. The residue (0.3 g) afforded colorless liquid, bp 100° (18 mmHg, bath temperature). IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 2800 (N-methyl).

Picrate: Recrystallized from ethanol to give yellow needles, mp 188—189°. No depression of melting point was observed by the admixture of the picrate with that of IX derived from V.

Acknowledgement The authers are very grateful to Prof. Eiji Ochiai for his encouragement. They are indebted to Mr. Yoshitaka Itatani for the elementary analyses and NMR measurements.