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Studies on Fused Hydrazines. III.[1] The Alkaline Decomposition of 2,3,5,10-Tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine Methiodide and Related Compounds

Akitada Nakamura and Shozo Kamiya

National Institute of Hygienic Sciences[2]

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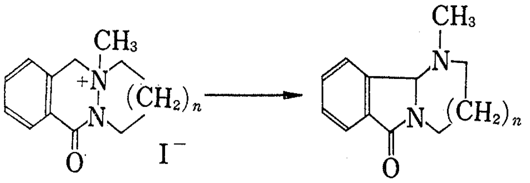
The alkaline decomposition of quaternary fused hydrazines containing 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine methiodide (III) and 1,2,3,4,6,11-hexahydropyridazo[1,2-*b*]phthalazine methiodide (VI) was examined. While compound VI having 6/6 ring system gave a Hofmann-type elimination product, 2-methyl-1,2,3,4,5,6-hexahydrobenzo[c][1,6]diazacyclodecine (XII), compound III having 6/5 ring system gave a rearranged quaternary salt, 5-methyl-1,2,3,4,6,10b-hexahydropyrimido[2,1-*a*]isoindolium iodide (X) together with an elimination product, 6-methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VII).

In the preceding paper,[1] we have reported that the alkaline decomposition of 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one methiodide (1a) and 1,2,3,4,6,11-hexahydropyridazo[1,2-*b*]phthalazin-6-one methiodide (1b) gives the ring contracted products, 2a and 2b, through the Stevens-type rearrangement involving migration of the lactam nitrogen from nitrogen to carbon.



1a : $n=1$
1b : $n=2$

2a : $n=1$
2b : $n=2$

This paper deals with the Hofmann-type elimination reaction of 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine methiodides (IIIa, b, c) and of the corresponding 6/6 fused hydrazine, 1,2,3,4,6,11-hexahydropyridazo[1,2-*b*]phthalazine methiodide (VI).

Methiodides IIIa, b, c were prepared by quaternization of compounds IIa, b, c, which were obtained by lithium aluminum hydride reduction of the corresponding 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine-5,10-diones (Ia, b, c)[3] (Chart 1).

Among these methiodides, since the nuclear magnetic resonance (NMR) spectrum of the 2-methyl derivative IIIb shows two C-CH_3 doublets at 8.82 τ and 8.73 τ, and two N-CH_3 singlets at 6.84 τ and 6.81 τ, IIIb must be a mixture of *cis*- and *trans*-2,4-dimethyl derivatives. On the other hand, the NMR spectrum of the 1-methyl derivative IIIc shows only one C-CH_3 doublet at 8.61 τ and one N-CH_3 singlet at 6.94 τ. Thus, IIIc was one of the four possible *cis*- and *trans*-isomers of 1,4- and 1,11-dimethyl derivatives. Finally, as described later, the structure of this methiodide was 1,4-dimethyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazinium iodide (IIIc) from its alkaline decomposition. The configuration of IIIc is, however, not yet known in this stage.

Methiodide VI was prepared by lithium aluminum hydride reduction of 1,2,3,4,6,11-hexahydropyridazo[1,2-*b*]phthalazine-6,11-dione (IV)[1,4] followed by quaternization with methyl iodide (Chart 1).

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[1] A. Nakamura and S. Kamiya, *Chem. Pharm. Bull.* (Tokyo), **20**, 69 (1972).
[2] Location: *Kamiyoga 1-18-1, Setagaya, Tokyo.*
[3] A. Nakamura and S. Kamiya, *Chem. Pharm. Bull.* (Tokyo), **18**, 1526 (1970).
[4] M. Rink and K. Grabowski, *Naturwissenschaften*, **43**, 326 (1956).

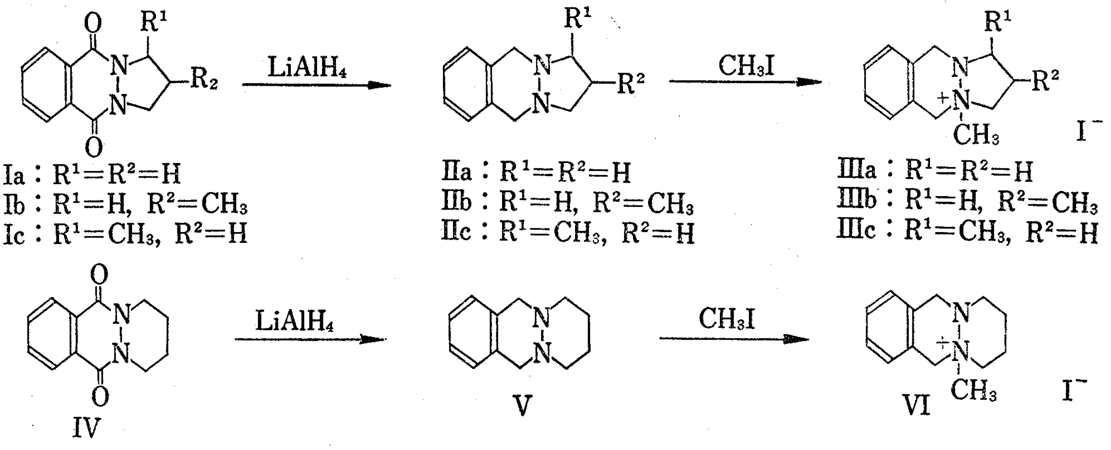

Chart 1

When IIIa was heated with sodium methoxide at the boiling temperature for 8 hr, two kinds of product, A (mp 184—186°, 72%) and B (mp 115—117°, 12%), were obtained. Product A gave a positive Beilstein test and formed yellow precipitates on silver nitrate test. The empirical formula was just the same as that of the starting material. The infrared (IR) spectrum of this compound shows an NH stretching band (ν_{NH}) at 3250 cm^{-1}, and the NMR spectrum (Fig. 1-a) in hexadeuterodimethylsulfoxide (DMSO-d_6) shows a singlet (3H) due to the $>\overset{+}{N}\text{-C}\underline{H}_3$ at 6.73 τ, a singlet (2H) due to the $\text{Ar-C}\underline{H}_2\text{-}\overset{+}{N}<$ at 5.38 τ, a doublet (1H) at 4.04 τ (J=6.6 Hz), and a broad signal (1H) at 5.55 τ. Since, on deuteration with deuter-

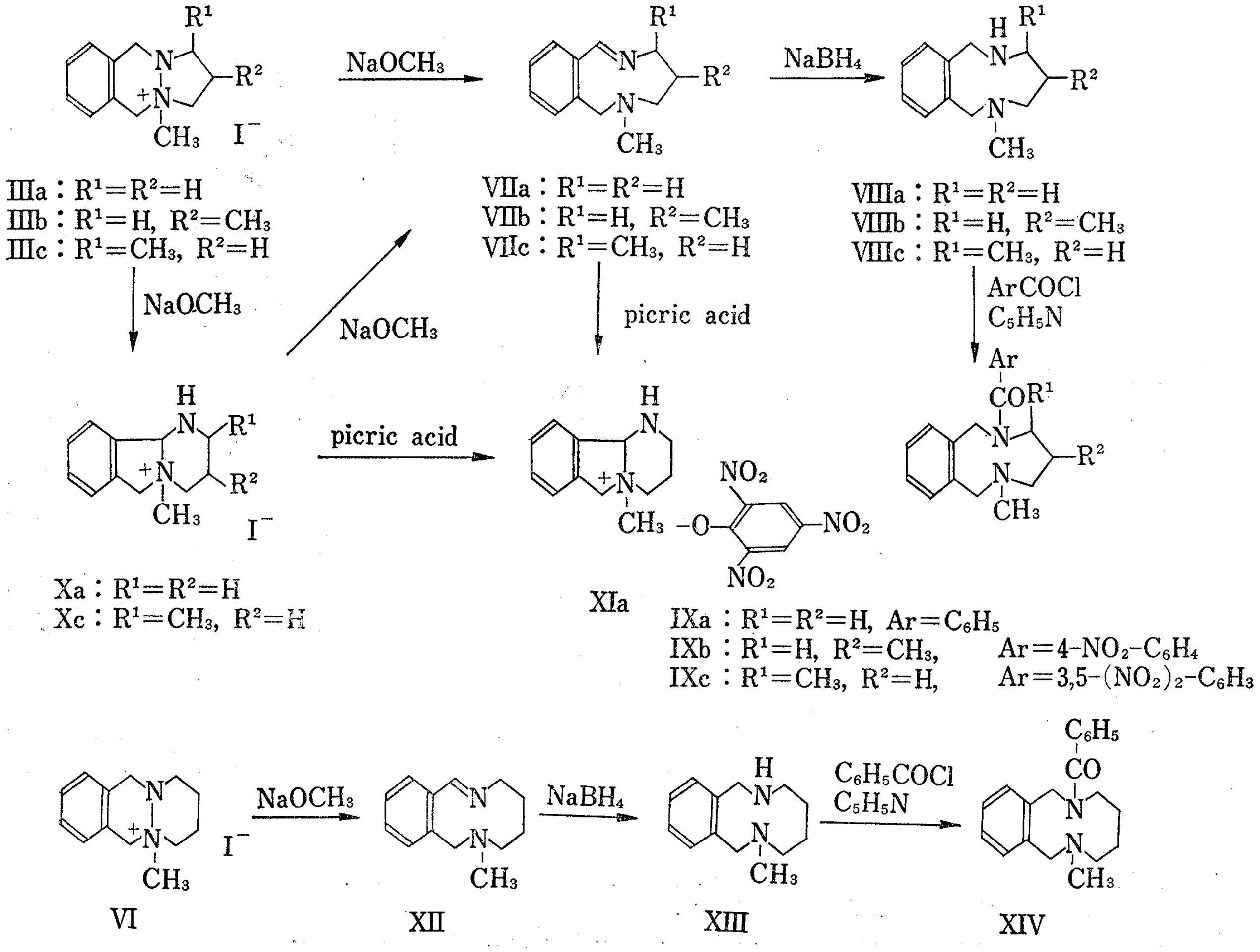

Chart 2

ium oxide (D_2O), the broad signal at $5.55\,\tau$ vanished and the doublet at $4.04\,\tau$ changed to a singlet, the former was assigned to an NH and the latter to an angular CH adjacent to the NH. These data for A were in agreement with the structure of 5-methyl-1,2,3,4,6,10b-hexahydropyrimido[2,1-*a*]isoindolium iodide (Xa).

The structure of B was, then, elucidated to be a Hofmann-type elimination product, 6-methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIa). Namely, its analytical data gave a formula $C_{12}H_{16}N_2$. The IR spectrum shows a $\nu_{C=N}$ band at 1640 cm^{-1}, and the NMR spectrum in deuterochloroform ($CDCl_3$), as shown in Fig. 1-b, shows a singlet (3H) due to the $\rangle N\text{-}C\underline{H}_3$ at $8.01\,\tau$, a singlet (2H) due to $\text{-}C\underline{H}_2{}^b\text{-}$ at $6.44\,\tau$, and a triplet (1H, $J=1.4$ Hz) due to H^a of the $Ar\text{-}CH^a{=}N\text{-}CH^c_2\text{-}$ at $1.01\,\tau$. In the same spectrum the triplet (2H, $J=6.0$ Hz) centered at $6.22\,\tau$ which further splits into a small doublet ($J=1.4$ Hz) is reasonable to assign as H^c_2 of the $\text{-}CH^a{=}N\text{-}CH^c_2\text{-}$. The structure of B was, therefore, 6-methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIa). Further evidence for this structure was obtained by its sodium borohydride reduction to give a nine-membered cyclic amine, 6-methyl-2,3,4,5,6,7-hexahydro-1H-2,6-benzodiazonine (VIIIa) which afforded 2-benzoyl-6-methyl-2,3,4,5,6,7-hexahydro-1H-2,6-benzodiazonine (IXa) by treatment with benzoyl chloride and pyridine. When IIIa was heated with sodium methoxide for 25 hr, the product was only VIIa in 75% yield. This Hofmann-type elimination product VIIa would be also derived from the rearranged quaternary salt Xa. As a matter of fact, Xa could be converted to VIIa in 72% yield by heating with sodium methoxide for 25 hr. It is noteworthy that VIIa gave a picrate, mp 154—155°, which was entirely identical with the picrate prepared from the methiodide (Xa). Its IR spectrum indicates a ν_{NH} band at 3340 cm^{-1} that is different from the ν^{+}_{NH} band of picrates of tertiary amines. This picrate was, therefore, 5-methyl-1,2,3,4,6,10b-hexahydropyrimido[2,1-*a*]isoindolium picrate (XIa) which was formed through a transannular addition reaction between the imino group and the tertiary amino nitrogen promoted with picric acid.

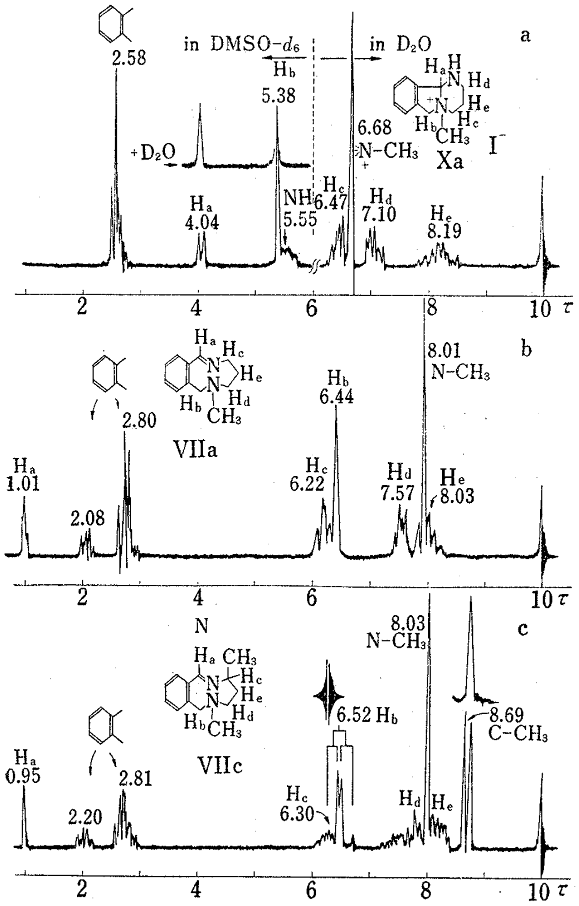

Fig. 1. The Nuclear Magnetic Resonance Spectra of Xa, VIIa, and VIIc

In the same manner as with IIIa, IIIb was treated with sodium methoxide to give 4,6-dimethyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIb) as an orange red syrup in 50% yield, but, in this case, a rearranged quaternary salt like Xa could not be obtained. The structure of VIIb was determined by its sodium borohydride reduction to give the corresponding syrupy amine (VIIIb) which gave 2-(4-nitrophenyl)-4,6-dimethyl-2,3,4,5,6,7-hexahydro-1H-2,6-benzodiazonine (IXb) as a pale yellow leaflets, mp 123—125°.

In the analogous alkaline decomposition, the methiodide IIIc also gave both a Hofmann-type elimination product, 3,6-dimethyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIc) and a rearranged quaternary salt, 2,5-dimethyl-1,2,3,4,6,10b-hexahydropyrimido[2,1-*a*]isoindolium iodide (Xc), but, in contrast to Xa, Xc reacted very slowly. Namely, when Xc was heated with sodium methoxide for 25 hr, VIIc was obtained in 10% yield together with 67% recovery of the starting material. As shown in Fig. 1-c, the NMR spectrum of VIIc shows a 1H multiplet centered at 6.30 τ,[5] and, on irradiation of this signal, a 3H doublet due to the C-C$\underline{H}_3$ at 8.69 τ changed to a singlet. On the other hand, a methine proton of the corresponding hexahydro compound VIIIc resonates at 6.97 τ. These facts indicate that the CH_3 group attaches to not 5-position but 3-position, and accordingly the structure of IIIc was elucidated to be quaternized at 4-position.

The same reaction of the corresponding 6/6 fused hydrazine methiodide (VI), resulted in the formation of only a Hofmann-type elimination product, 2-methyl-1,2,3,4,5,6-hexahydrobenzo[*c*][1,6]diazacyclodecine (XII). The sodium borohydride reduction of this product gave a diamine XIII, from which the N-benzoyl derivative (XIV) was prepared. The NMR parameters for XII and XIII were consistent with the proposed structures.

Though the Hofmann elimination reaction is one of the most familiar reactions in the field of nitrogen heterocyclic chemistry, there is only one report concerned with that of fused hydrazines. Namely, Aeberli and Houlihan synthesized 1-aryl-6-methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine from a fused hydrazine, 5-aryl-2,3,5,10-tetrahydro-1H-pyrazolo-[1,2-*b*]phthalazine methiodide.[6] However, our reactions from III to VII and X described above can not be considered as a usual Hofmann elimination because of formation of the rearranged quaternary salts (Xa, c). A possible mechanistic scheme accounting for these products is under investigation, and it will be reported in a separate paper.

Experimental[7]

1-Methyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine (IIc) and Its Methiodide (IIIc)——To a mixture of 4 g (0.12 mole) of lithium aluminum hydride in 150 ml of dehyd. tetrahydrofuran was added 6.5 g (0.03 mole) of 1-methyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine-5,10-dione[3] with stirring, and the mixture was stirred for 40 hr at room temperature. Then, the reaction mixture was carefully poured into ice-water, and the precipitates separated were filtered. The precipitates on the filter paper were washed with tetrahydrofuran and then with chloroform. The filtrate and the washings were combined, and the mixture was extracted with chloroform. The chloroform extract was dried over anhyd. sodium sulfate, the chloroform was evaporated to dryness, and the residue was distilled under reduced pressure. Pale yellow liquid, bp 114—118° (5 mmHg), was obtained. Yield, 3.0 g (53%). IR (CCl_4) cm^{-1} (ε): 2823 (134), 2790 (135), 2705 (46), 2665 (13). NMR (CS_2) τ: 3.13 (4H, m, aromatic H), 6.35 (2H, AB-quartet, $J_{AB}=13.5$ Hz, Ar-C$\underline{H}_2$-N), 6.39 (2H, AB-quartet, $J_{AB}=13.5$ Hz, Ar-C$\underline{H}_2$-N), 6.89 (1H, m, N-$\dot{C}\underline{H}$-Me), 7.3—8.8 (4H, m, N-C$\underline{H}_2$-C and C-C$\underline{H}_2$-C), 8.90 (3H, d, $J=6.0$ Hz, C-C$\underline{H}_3$). Methiodide of IIc (IIIc): Colorless granules (from ethanol), mp 198—200°. NMR (D_2O) τ: 6.94 (3H, s, $>\overset{+}{N}$-C$\underline{H}_3$), 8.61 (3H, d, $J=6.0$ Hz, C-C$\underline{H}_3$). *Anal.* Calcd. for $C_{13}H_{19}N_2I$: C, 47.29; H, 5.80; N, 8.48. Found: C, 47.55; H, 6.07; N, 8.38.

1,2,3,4,6,11-Hexahydropyridazo[1,2-*b*]phthalazine (V) and Its Methiodide (VI)——In the same manner as described for IIIc, 1,2,3,4,6,11-hexahydropyridazo[1,2-*b*]phthalazine-6,11-dione (IV)[4] was reduced with lithium aluminum hydride to produce compound V as a pale yellow solid, mp 84—88°, bp 118—126° (4mmHg), in 43% yield. Recrystallization from petroleum ether gave colorless leaflets, mp 86—89°. IR (CCl_4) cm^{-1} (ε): 2800 (92), 2750 (70), 2670 (24). NMR ($CDCl_3$) τ; 3.05 (4H, m, aromatic H), 6.23 (4H, s, Ar-C$\underline{H}_2$-N), 7.23 (4H, broad s, N-C$\underline{H}_2$-C), 8.32 (4H, broad m, C-C$\underline{H}_2$-C$\underline{H}_2$-C). Picrate of V: Yellow granules (from ethanol), mp 137—139° (decomp.). *Anal.* Calcd. for $C_{12}H_{16}N_2\cdot C_6H_3O_7N_3$: C, 51.80; H, 4.59; N, 16.78. Found: C, 51.96; H, 4.52; N, 16.91. Methiodide of V (VI): Colorless needles (from ethanol), mp 217—218° (decomp.). NMR (D_2O) τ: 6.86 (3H, s, $>\overset{+}{N}$-C$\underline{H}_3$). *Anal.* Calcd. for $C_{13}H_{19}N_2I$: C, 47.29; H, 5.80; N, 8.48. Found: C, 47.31; H, 5.73; N, 8.27.

Alkaline Decomposition of the Quaternary Fused Hydrazines (IIIa, b, c and VI) and Reduction of Their Reaction Products (VIIa, b, c and XII)——Each general procedure for the alkaline decomposition of these

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[5] The methine proton of N-benzylidenebutylamine-2 resonates at 6.87 τ, while that of 2-butylamine does at 7.22 τ.

[6] P. Aeberli and W.J. Houlihan, *J. Org. Chem.*, 34, 2715 (1969).

[7] All melting points and boiling points are uncorrected. IR spectra were measured on a JASCO Model IR-S spectrophotometer. NMR spectra were measured on a JEOL JNM-C-60HL spectrometer. Tetramethylsilane for $CDCl_3$, CS_2 and DMSO-d_6, and sodium 3-(trimethylsilyl)propanesulfonate for D_2O were used as an internal standard.

quartenary salts and for the reduction of the products is described with 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine methiodide (IIIa) and 6-methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIa).

6-Methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIa) and 5-methyl-1,2,3,4,6,10b-hexahydropyrimido[2,1-*a*]isoindolium Iodide (Xa)——To a freshly prepared solution of 1.20 g (0.05 gram atom) of metallic sodium in 50 ml of abs. methanol was added 3.16 g (0.01 mole) of 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine methiodide (IIIa). The mixture was refluxed for 8 hr, concentrated to a half volume, and allowed to stand at room temperature overnight. 5-Methyl-1,2,3,4,6,10b-hexahydropyrimido[2,1-*a*]isoindolium iodide (Xa) separated was filtered, washed with methanol, and dried. Yield, 2.29 g (72%). mp 185—186° (decomp.). Recrystallization from methanol gave colorless needles, mp 184—186° (decomp.). IR (Nujol) cm^{-1}: 3250 (NH). *Anal.* Calcd. for $C_{12}H_{17}N_2I$: C, 45.59; H, 5.42; N, 8.86. Found: C, 45.45; H, 5.27; N, 8.85. Picrate of Xa (XIa): Yellow prisms (from ethanol), mp 154—155°. IR (Nujol) cm^{-1}: 3340 (NH). *Anal.* Calcd. for $C_{12}H_{17}N_2 \cdot C_6H_2O_7N_3$: C, 51.80; H, 4.59; N, 16.78. Found: C, 52.09; H, 4.63; N, 16.63. The filtrate and washings mentioned above were combined, and the solvent was removed under reduced pressure. Water was added to the residue and the mixture was extracted with chloroform. The extract was washed with water, dried over anhyd. sodium sulfate and the chloroform was evaporated to dryness. The residue was treated with a small amount of ethanol to separate 6-methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIa) as colorless granules. The crystals were filtered, washed with ethanol, and dried. Yield, 0.22 g (12%). Recrystallization from methanol gave colorless prisms, mp 115—117°. IR (Nujol) cm^{-1}: 1640 (C=N). *Anal.* Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.65; H, 8.53; N, 14.87. Picrate of VIIa (XIa): Yellow prisms (from ethanol), mp 154—155°. This picrate was entirely identical with the picrate obtained from Xa by mixed melting point determination and IR spectrum. In the same manner, Xa reacted with sodium methoxide for 25 hr to give VIIa in 72% yield.

6-Methyl-2,3,4,5,6,7-hexahydro-1H-2,6-benzodiazonine (VIIIa)——A mixture of 0.4 g (0.0021 mole) of VIIa, 0.20 g (*ca.* 0.0041 mole) of sodium borohydride, and 10 ml of ethanol was refluxed for 2 hr, then the solvent was removed under reduced pressure. The residue was mixed with 10 ml of acetone and the mixture was evaporated to dryness on a water-bath. The residue was dissolved in 15 ml of water, the solution was extracted with chloroform, and the chloroform extract was washed with two 20 ml portions of diluted hydrochloric acid. The aqueous layer was separated, made alkaline with anhyd. sodium carbonate, and extracted with chloroform. The extract was washed with water, dried over anhyd. sodium sulfate, and the solvent was removed under reduced pressure. Orange red syrup. Yield, 0.30 g (74%). IR (liquid film) cm^{-1}: 3250 (NH), no $\nu_{C=N}$. NMR ($CDCl_3$) τ: 2.85 (4H, m, aromatic H), 6.21 (2H, s, Ar-C$\underline{H}_2$-NH-), 6.23 (1H, s, NH), 6.55 (2H, s, Ar-C$\underline{H}_2$-N-Me), 7.50 (4H, sextet, -N-C$\underline{H}_2$-C), 7.93 (3H, s, N-C$\underline{H}_3$), 8.23 (2H, sextet, C-C$\underline{H}_2$-C). Benzoate of VIIIa (IXa): Colorless, hexagonal plates (from ethanol), mp 121—123°. IR (Nujol) cm^{-1}: 1628 (CO). *Anal.* Calcd. for $C_{19}H_{22}ON_2$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.17; H, 7.67; N, 9.32.

4,6-Dimethyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIb)——In the same manner as with VIIa, IIIb reacted with sodium methoxide for 8 hr. No crystalline precipitate separated from the reaction mixture, and finally an orange red syrup was obtained in 50% yield. IR (liquid film) cm^{-1}: 1643 (C=N). The syrupy product must be a mixture of three isomers[8] on the basis of the NMR spectrum, which shows three singlets due to the Ar-C$\underline{H}$=N- at 1.15 τ, 1.24 τ, and 1.39 τ, three singlets due to the N-C$\underline{H}_3$ at 7.88 τ, 7.93 τ, and 8.03 τ, and three doublets due to the C-C$\underline{H}_3$ at 8.90 τ, 9.00 τ, and 9.14 τ respectively.

4,6-Dimethyl-2,3,4,5,6,7-hexahydro-1H-2,6-benzodiazonine (VIIIb)——The syrupy mixture consisting of three isomers of VIIb was reduced with sodium borohydride to give orange red syrup in 45% yield. IR (liquid film) cm^{-1}: 3250 (NH), no $\nu_{C=N}$. NMR ($CDCl_3$) τ: 2.85 (4H, m, aromatic H), 6.23 (2H, s, Ar-C$\underline{H}_2$-NH), 6.56 (2H, s, Ar-C$\underline{H}_2$-N-Me), 7—8.5 (5H, broad m, N-C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-N), 7.29 (1H, broad s, NH), 7.92 (3H, s, N-C$\underline{H}_3$), 9.08 (3H, d, C-C$\underline{H}_3$). 4-Nitrobenzoate of VIIIb (IXb): Colorless needles (from ethanol), mp 123—125°. IR (Nujol) cm^{-1}: 1632 (CO), 1525, 1350 (NO_2). *Anal.* Calcd. for $C_{20}H_{23}O_3N_3$: C, 67.97; H, 6.56; N, 11.89. Found: C, 68.36; H, 6.57; N, 12.01.

3,6-Dimethyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (VIIc) and 2,5-Dimethyl-1,2,3,4,6,10b-hexahydropyrimido[2,1-*a*]isoindolium Iodide (Xc)——The quaternary fused hydrazine IIIc reacted with sodium methoxide for 25 hr to give VIIc in 25% yield and Xc in 42% yield, respectively. VIIc: Colorless prisms (from ethanol), mp 157—160°. IR (Nujol) cm^{-1}: 1637 (C=N). *Anal.* Calcd. for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.03; H, 9.04; N, 13.79. Xc: Colorless granules (from ethanol), mp 202—203° (decomp.). IR (Nujol) cm^{-1}: 3250 (NH). NMR (DMSO-d_6) τ: 2.60 (4H, m, aromatic H), 4.03 (1H, d, J=6.0 Hz, Ar-C$\underline{H}$-NH), 5.45 (2H, s, Ar-C$\underline{H}_2$-$\overset{+}{N}$-Me), 5.81 (1H, broad m, NH), 6.68 (3H, s, $>\overset{+}{N}$-C$\underline{H}_3$), 6.5—8.0 (3H, m, Me-$\overset{+}{N}$-C$\underline{H}_2$-C and -NH-C$\underline{H}$-Me), 8.53 (2H, m, C-C$\underline{H}_2$-C), 8.92 (3H, d, J=6.1 Hz, C-C$\underline{H}_3$). *Anal.* Calcd. for $C_{13}H_{19}$-

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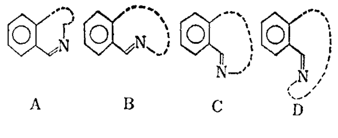
[8] Such a medium-sized ring compound containing an imino group as VII may exist as the following three streoisomeric forms (A, B, C) because of slow inversion of the imino nitrogen and restricted rotation of the C-aryl bond. The ring-size is, however, not large enough for VII to exist as form D.



N_2I: C, 47.29; H, 5.80; N, 8.48. Found: C, 47.00; H, 5.85; N, 8.17. Analogously, IIc reacted for 8 hr to produce VIIc in 8% yield and Xc in 64% yield, respectively.

3,6-Dimethyl-2,3,4,5,6,7-hexahydro-1H-2,6-benzodiazonine (VIIIc)——Yellow syrup. Yield, almost quantitative. IR (liquid film) cm^{-1}: 3230 (NH), no $\nu_{C=N}$. NMR ($CDCl_3$) τ: 2.90 (4H, m, aromatic H), 6.13 (2H, s, Ar-C$\underline{H}_2$-NH), 6.48 (3H, s. Ar-C$\underline{H}_2$-$\overset{|}{N}$-Me and NH), 6.97 (1H, m, NH-$\dot{C}$$\underline{H}$-Me), 7.32 (2H, m, N-C$\underline{H}_2$-C), 7.73 (3H, s, N-C$\underline{H}_3$), 8.18 (2H, m, C-C$\underline{H}_2$-C), 8.85 (3H, d, $J=7.0$ Hz, C-C$\underline{H}_3$). 3,5-Dinitrobenzoate of VIIIc (IXc): Pale yellow leaflets, mp 157—159°. IR (Nujol) cm^{-1}: 1630 (CO), 1545, 1345 (NO_2). *Anal.* Calcd. for $C_{20}H_{22}O_5N_4$: C, 60.29; H, 5.57; N, 14.06. Found: C, 59.99; H, 5.70; N, 14.15.

2-Methyl-1,2,3,4,5,6-hexahydrobenzo[*c*][1,6]diazacyclodecine (XII)——Compound VI reacted with sodium methoxide for 7 hr to give XII as an orange red oil in 84% yield. IR (liquid film) cm^{-1}: 1644 (C=N). NMR ($CDCl_3$) τ: 1.50 (1H, t, $J=1.8$ Hz, Ar-C$\underline{H}$=N-), 2.20 (1H, m, aromatic H), 2.87 (3H, m, aromatic H), 6.46 (2H, t, $J=5.3$ Hz, =N-C$\underline{H}_2$-C), 6.50 (2H, s, Ar-C$\underline{H}_2$-$\overset{|}{N}$-Me), 7.75 (2H, t, $J=6.8$ Hz, Me-$\overset{|}{N}$-C$\underline{H}_2$-C), 7.93 (3H, s, N-C$\underline{H}_3$), 8.49 (4H, m, C-C$\underline{H}_2$-C$\underline{H}_2$-C).

2-Methyl-1,2,3,4,5,6,7,8-octahydrobenzo[c][1,6]diazacyclodecine (XIII)——Colorless needles (from ether), mp 133—135°. Yield, 48%. IR (Nujol) cm^{-1}: 3230 (NH), no $\nu_{C=N}$. NMR ($CDCl_3$) τ: 2.83 (4H, m, aromatic H), 6.30 (2H, s, Ar-C$\underline{H}_2$-NH), 6.57 (2H, s, Ar-C$\underline{H}_2$-$\overset{|}{N}$-Me), 6.91 (1H, s, NH), 7.44 (2H, broad t, NH-C$\underline{H}_2$-C), 7.70 (2H, broad t, Me-$\overset{|}{N}$-C$\underline{H}_2$-C), 7.90 (3H, s, N-C$\underline{H}_3$), 8.57 (4H, broad quintet, C-C$\underline{H}_2$-C$\underline{H}_2$-C). *Anal.* Calcd. for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.20; H, 10.06; N, 13.58. Benzoate of XIII (XIV): Colorless granules (from ethanol), mp 204—207°. IR (Nujol) cm^{-1}: 1635 (CO). *Anal.* Calcd. for $C_{20}H_{24}ON_2$: C, 77.88; H, 7.84; N, 9.08. Found: C, 77.69; H, 8.08; N, 8.90.