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Studies on Fused Hydrazines. II.[1] The Stevens-Type Rearrangement of 2,3,5,10-Tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one Methiodide and Related Compounds

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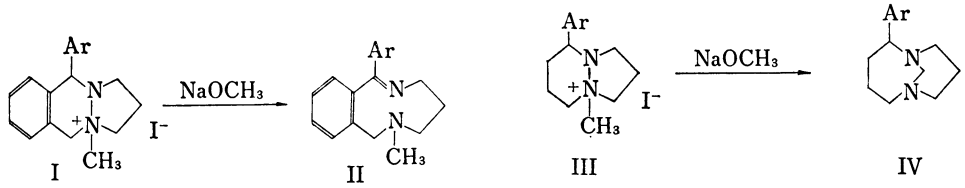
The alkaline decomposition of 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one methiodide (VIIa), its methyl derivatives (VIIb—d), and 1,2,3,4,6,11-hexahydropyridazo-[1,2-*b*]phthalazin-6-one methiodide (XIV) was examined. Compounds VIIa—d afforded 1-methyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-ones (VIIIa—d), and XIV afforded 1-methyl-1,2,3,4,5,11b-hexahydro-7H-1,3-diazepino[2,1-*a*]isoindol-7-one (XV). In all cases the Stevens-type rearrangement involving lactam nitrogen migration from nitrogen to carbon occurred. Their configuration and conformation were discussed.

Recently, fused hydrazines, which possess two bridgehead nitrogen atoms in fused ring systems, have received much attention from the view points of stereochemistry[1,3] and chemical behavior.[4] Aeberli and Houlihan[4] first reported that the alkaline decomposition of a fused hydrazine methiodide, 5-aryl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine methiodide (I), with sodium methoxide gave a Hofmann-type elimination product, 1-aryl-6-methyl-4,5,6,7-tetrahydro-3H-2,6-benzodiazonine (II), while 2-aryl-1,6-diazabicyclo[4.3.0]nonane methiodide (III) gave an N-CH_2-N bridged product, 2-aryl-1,6-diazabicyclo[4.3.1]decane (IV), through the Stevens-type rearrangement.



This paper describes the alkaline decomposition of fused hydrazine methiodides,[5] 2,3,-5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one methiodide (VIIa) and related compounds (VIIb, VIIc, VIId, XIV).

As shown in Chart 1 and 2, these methiodides were prepared by sodium borohydride reduction of the corresponding 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine-5,10-diones (Va,b,c)[6] and 1,2,3,4,6,11-hexahydropyridazo[1,2-*b*]phthalazine-6,11-dione (XII),[7] followed by quaternization with methyl iodide in acetone, in good yields.

1) The first report of this series: A. Nakamura, *Chem. Pharm. Bull.* (Tokyo), **18**, 1426 (1970).
2) Location: *Kamiyoga 1-18-1, Setagaya, Tokyo.*
3) J.P. Kintzinger, J.M. Lehn, and J. Wagner, *Chem. Commun.*, **1967**, 206; B. Junge and H.A. Staab, *Tetrahedron Letters*, **1967**, 709.
4) P. Aeberli and W.J. Houlihan, *J. Org. Chem.*, **34**, 2715, 2720 (1969).
5) Although this type of compounds belongs to a cyclic hydrazide in a strict sense, we, in this paper, call them fused hydrazines in a broad meaning for the continuation of our research on "Fused Hydrazines".
6) A. Nakamura and S. Kamiya, *Chem. Pharm. Bull.* (Tokyo), **18**, 1526 (1970).
7) M. Rink and K. Grabowski, *Naturwissenschaften*, **43**, 326 (1956). This compound was easily prepared in high yield by a catalytic hydrogenation of 1,4,6,11-tetrahydropyridazo[1,2-*b*]phthalazine-6,11-dione (R.A. Clement, *J. Org. Chem.*, **27**, 1115 (1962)).

On the sodium borohydride reduction of these diones, 1-methyl derivative Vc afforded a pale yellow syrup which was a mixture of 3-methyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]-phthalazin-5-one (VIc) and 1-methyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one (VId) in a ratio of 3:1. Namely, the nuclear magnetic resonance (NMR) spectrum of the syrupy product showed two doublets due to the C-CH_3 at 8.65 τ and 8.80 τ (the relative intensity ratio=3:1), while, after quaternization with methyl iodide, these signals shifted to downfield at 8.48 τ and 8.43 τ (the relative intensity ratio=3:1), respectively. Since the chemical shift difference (0.37 ppm) of C-CH_3 signal of free base from that of quaternary salt ($\Delta\delta_{F-Q}$)[8] in the case of the minor product, was 0.20 ppm larger than that (0.17 ppm) in the case of the major one, it was concluded that the minor product was compound VIId and the major was compound VIIc.

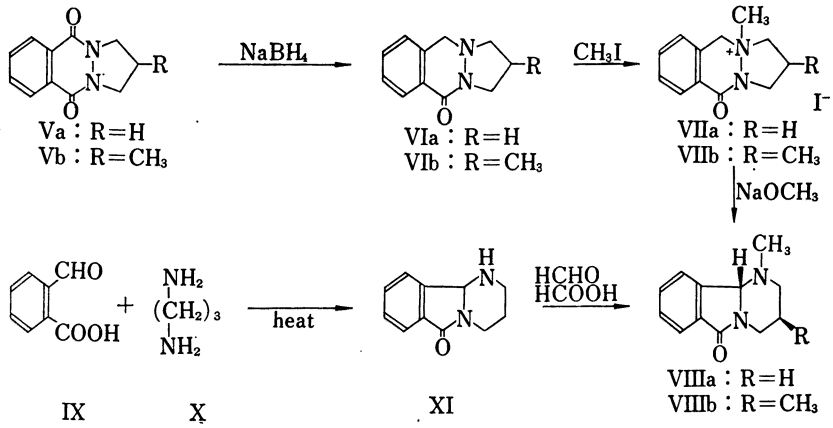


Chart 1

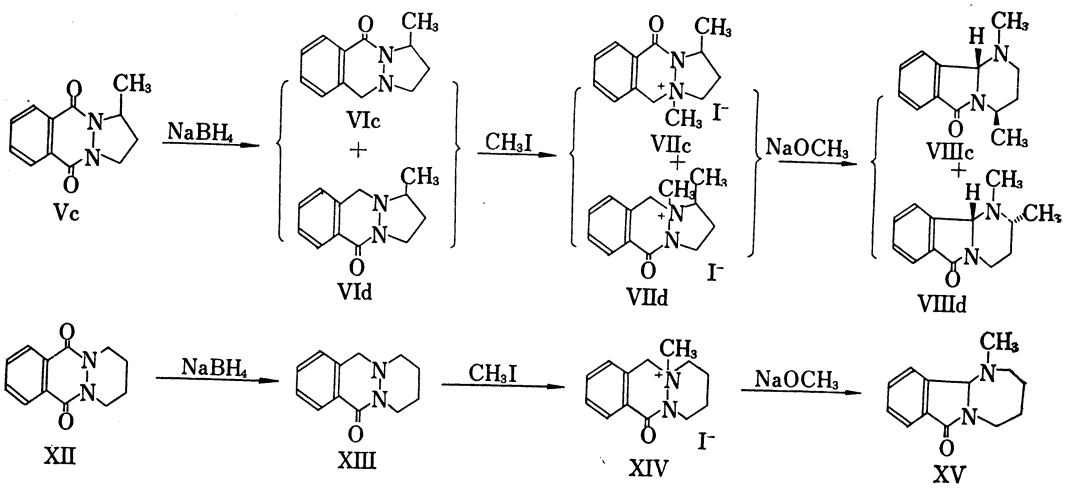


Chart 2

8) Moynehan, *et al.*, determined the NMR spectra of methylquinolizidines, methylquinolizidinium salts and N-methyl-methylquinolizidinium salts, and indicated that the influence of the positive pole of the β-position for the signal was remarkable, *i.e.*, $\Delta\delta_{F-Q}$ of *cis*-4-methylquinolizidine was 0.28 ppm, but that of *trans*-3-methylquinolizidine was only 0.08 ppm (T.M. Moynehan, K. Schofield, R.A.Y. Jones, and A.R. Katritzky, *J. Chem. Soc.*, **1962**, 2637).

When VIIa was heated with sodium methoxide in methanol at the boiling temperature, a product, mp 77—79°, was obtained, and its analytical data coincided with a formula, $C_{12}H_{14}O_2$ (Chart 1). The infrared (IR) spectrum in nujol showed the presence of a five membered lactam-CO[9] at 1693 cm^{-1} and, on irradiation of ultraviolet (UV) light, its alcoholic solution produced a yellow fluorescence.[10] These facts suggested the existence of an isoindolone moiety. As shown in Fig. 1-a, its NMR spectrum in deuterochloroform indicates a 1H singlet due to the angular CH at 5.00 τ, a 3H singlet due to the N-CH_3 at 7.76 τ, and a 1H doublet-doublet due to the equatorial proton of the CO-N-CH_2- at 5.48 τ, that was unusually shifted to down-field by anisotropy of the carbonyl group.[11] Thus, the structure of this product should be 1-methyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIIa).

The structure of this ring transformed product was further confirmed by an independent synthesis as shown in Chart 1. The condensation of *o*-phthalaldehydic acid (IX) with 1, 3-diaminopropane (X) gave 1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one[11] (XI) in 43% yield. Then, XI was methylated with a mixture of formalin and formic acid to give compound VIIIa, in 79% yield, which was entirely identical with the compound obtained from the methiodide VIIa. In the same manner, VIIb gave 1,3-dimethyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIIb) in 56% yield. Its NMR spectrum at 60 MHz was shown in Fig. 1-b, and, in the last part of this paper, its conformation will be discussed in detail.

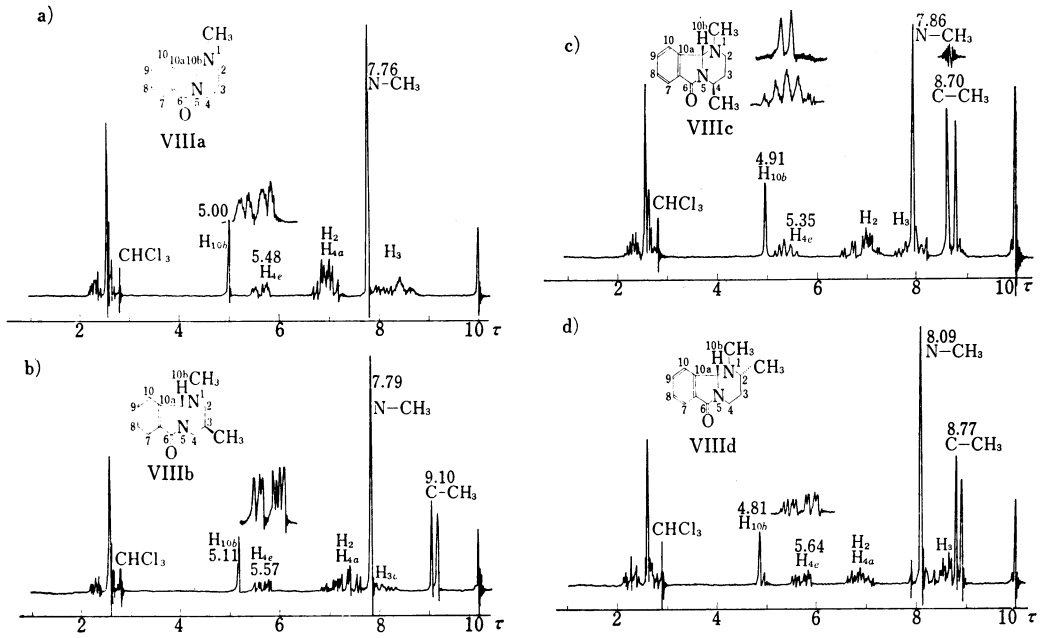


Fig. 1. The NMR Spectra of 1-Methyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-ones

Treatment of the mixture of VIIc and VIId with sodium methoxide in boiling methanol gave a pale yellow syrup, the thin-layer chromatogram of which showed the presence of two kinds of products, A and B. The NMR spectrum of the syrup showed two doublets due

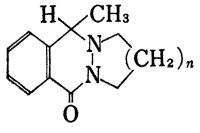
9) W. Theilacker and W. Schmidt, *Ann.*, **567**, 95 (1956); A.E. Kellie, D.G. O'Sullivan, and P.W. Sadler, *J. Chem. Soc.*, **1956**, 3809.
10) T. Amano and T. Sakano, *Yakugaku Zasshi*, **90**, 1 (1970).
11) P. Aeberli and W.J. Houlihan, *J. Org. Chem.*, **34**, 165 (1969).

to the C-CH_3 at 8.77 τ (J=6.75 Hz) and 8.70 τ (J=6.75 Hz), two singlets due to the N-CH_3 at 8.09 τ and 7.86 τ, and two singlets due to the angular CH at 4.81 τ and 4.91 τ. The relative intensity ratios of each pairs of these signals were about 1: 3.5. These facts indicated that the syrup was a mixture cons isting of two rearranged products in a ratio of 1: 3.5. Finally, this mixture could be separated by preparative thin-layer chromatography to give compound A and B. Compound A afforded its picrate, mp 185—187°, and methiodide, mp 186—190°. And compound B also gave its picrate, mp 226—227° (decomp.), and methiodide, mp 209—210° (decomp.). The analytical data of these picrates and methiodides coincided with the calculated values. In the NMR spectrum of compound B (Fig. 1-c), the signal centered at 5.35 τ splits into quintet (J=6.75 Hz), and, when the CH_3 signal at 8.70 τ was irradiated, it changed to a broad doublet (J=6.3 Hz). From these facts, compound B was 1,4-dimethyl-1,3,4,-10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIIc). Accordingly, compound A was 1,2-dimethyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIId).

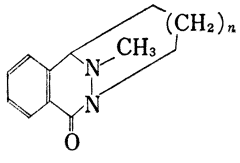
The quaternary fused hydrazines containing a 6/6 ring system as XIV would be expected to resemble VII in their reaction with sodium methoxide. Actually, treatment of XIV with sodium methoxide in boiling methanol gave a $C_{13}H_{16}ON_2$ compound, mp 122—124°, in 64% yield, and the IR and NMR data of this product well agreed with the structure of 1-methyl-1,2,3,4,5,11b-hexahydro-7H-1,3-diazepino[2,1-*a*]isoindol-7-one (XV). These spectral data were summerized in this experimental part.

Discussion

These molecular rearrangement which involve both ring expansion and ring contraction, are an example of the Stevens rearrangement involving migration of lactam nitrogen from nitrogen to carbon. It should be pointed out that, if the methyl or methylene carbon migrates from nitrogen to carbon, as observed in usual Stevens rearrangements, the product will be compound XVI or XVII. But, such compounds were not obtained in our experiment.



XVI: n=1, 2



XVII: n=1, 2

As shown in Fig. 1, each of these compounds, VIIIa—d and XV, gave a low-field proton at 5.35—5.64 τ. This fact could be readily explained according to the following assumption: Molecular models of this system suggest that the five-membered isoindolone ring having an sp_2 hybridized nitrogen atom is planar and that their conformation can be represented by those described in Chart 3, in which an equatorial proton at the 4-position (H_{4e}) lies in the same plane as the lactam oxygen atom.[11,12] Accordingly, the CH_3 group in VIIIc was unequivocally determined to be in axial. The NMR spectrum of VIIIb at 100 MHz, as shown in Fig. 2, shows two sets of quartet (1H) due to the H_{4e} centered at 5.57 τ, two sets of quartet (1H) centered at 6.98 τ, and two overlapped quartets (2H) centered at 7.35 τ and 7.38 τ. When the signal of H_{4e} at 5.57 τ was irradiated, the signal at 6.98 τ changed to a quartet and the signal at 7.35 τ to a doublet, but the quartet at 7.38 τ remained unchanged. From these results, the signals at 6.98 τ, 7.35 τ, and 7.38 τ were assigned to the H_{2e}, H_{4a}, and H_{2a}, respectively, in which assignment coupling constants were determined as follows; $J_{H2a,H2e}$=13.0 Hz, $J_{H4a,H4e}$=13.0 Hz, $J_{H3a,H4a}$=11.4 Hz, $J_{H2a,H3a}$=11.2 Hz, $J_{H2e,H3a}$=3.9 Hz,

12) The analogous deshielding effect of the lactam oxygen atom was described on quinolizidones, where the equatorial proton attached to C_4 resonated at 5.37τ (F. Bohlmann and D. Schumann, *Tetrahedron Letters*, **1965**, 2435).

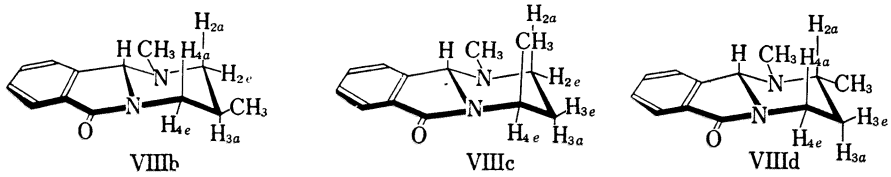


Chart 3

$J_{H3a,H4e}$=5.0 Hz, and $J_{H2a,H4e}$=1.8 Hz.[13] Thus, the CH_3 group of compound VIIIb was decided to be in equatorial. The NMR spectrum of VIIId, as shown in Fig. 1-d, could not be completely interpreted because of its complexity. Though we have, in this stage, no conclusive evidence for the conformation of VIIId, we propose it as VIIId of Chart 3 on the following bases: The signal of H_{4e} in VIIId also appears as two sets of quartet splitted with coupling constants, *i.e.*, J=13.2 Hz, 5.7 Hz, and 2.2 Hz. If the C-CH_3 group was in axial, the H_{4e} signal should split further to appear more broad as in the case of VIIIa (Fig. 1-a) by long-range coupling, but, in fact, this is not what is found. The proposed conformational structures for VIIIb—d are more thermodynamically stable ones between the two possible ones.

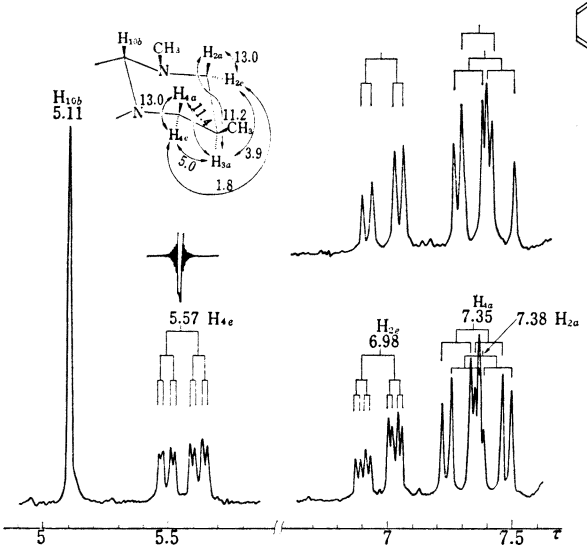


Fig. 2. The NMR Spectrum of 1,3-Dimethyl-1,3,4,-10b-tetrahydro-2H-pyrimido [2, 1-*a*] isoindol-6-one (VIIIb) at 100 MHz

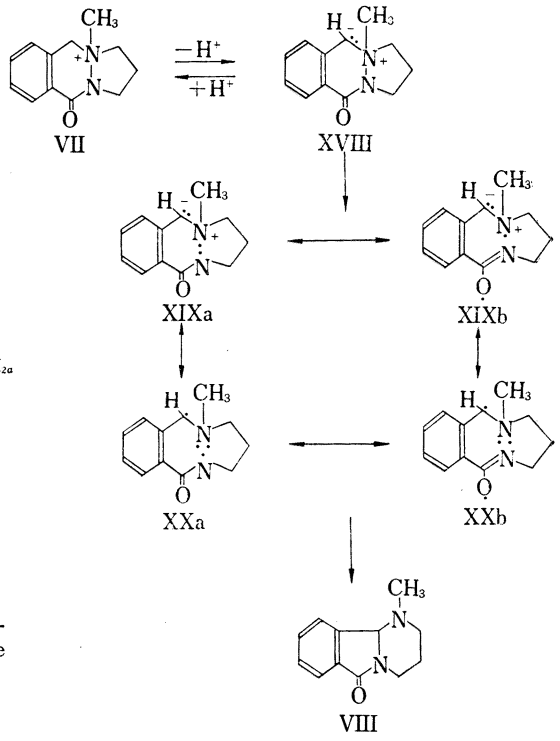


Chart 4

It has recently been shown that, in ylide isomerization, *i.e.*, in the Stevens rearrangement, the sulfoniumylide-sulfide rearrangement, and also in the Meisenheimer rearrange-

13) H_{2e} and H_{4e} appear in better arrangement for W-plan coupling (A. Rasset, C.W. Jefford, J.M. Lehn, and B. Waegell, *Tetrahedron Letters*, **1964**, 233).

ment, migration probably proceeds *via* a radical pair.[14] The benzyl migration from nitrogen to nitrogen in the Stevens rearrangement of N,N-dimethyl-*p*-nitrobenzylamide acetamide was also proved to proceed *via* a radical pair according to an observation of chemically induced dynamic nuclear polarization (CIDNP) effect.[15] Bearing these facts in mind, we propose the mechanism in Chart 4, where biradical intermediates, XIX and XX, are stabilized because of delocalization of unpaired electron with the lactam carbonyl group, and recombination step of the biradical intermediates is slow enough to give the products having thermodynamically stable conformations.

Experimental[16]

1-Methyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one (VId), 3-Methyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one (VIc), and Their Methiodides (VIIc,d)——A mixture of 5.25 g (0.024 mole) of 1-methyl-2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine-5,10-dione (Vc), 2.77 g (0.073 mole) of sodium borohydride, and 30 ml of ethanol was stirred for 22 hr at room temperature. The reaction mixture was evaporated under reduced pressure and 20 ml of acetone was carefully added to the residue. The solution was evaporated on a steam bath and 50 ml of water was added to the residue. The solution was then extracted with chloroform several times. The chloroform extract was washed with water, dried over anhyd. sodium sulfate, and the solvent was evaporated to dryness. The residue was distilled under reduced pressure to give a yellow syrup, bp 156—164° (6 mmHg). Yield, 2.85 g (55%). IR (CCl_4) cm^{-1}: 1655, 1650 (CO). NMR ($CDCl_3$) τ: 8.65 (d, J=6.2 Hz, C-CH_3 of VIc), 8.80 (d, J=6.2 Hz, C-CH_3 of VId). The syrup was dissolved in acetone and a large excess of methyl iodide was added and the mixture was allowed to stand at room temperature for 12 hr. The crystals separated were filtered, washed with acetone and dried. Yield, 4.05 g (83%). Recrystallization from ethanol gave colorless leaflets, mp 166—185°. IR (Nujol) cm^{-1}: 1675 (CO). NMR (D_2O) τ: 8.48 (d, J=6.6 Hz, C-CH_3 of VIIc), 8.43 (d, J=6.6 Hz, C-CH_3 of VIId), 6.59 (s, N-CH_3 of VIIc), 6.54 (s, N-CH_3 of VIId). *Anal.* Calcd. for $C_{13}H_{17}ON_2I$: C, 45.36; H, 4.98; N, 8.14. Found: C, 45.24; H, 5.22; N, 7.75.

1,2,3,4,6,11-Hexahydropyridazo[1,2-*b*]phthalazin-6-one (XIII) and Its Methiodide (XIV)——1,2,3,4,6,11-Hexahydropyridazo[1,2-*b*]phthalazine-6,11-dione (XII) was reduced with sodium borohydride to give a colorless syrup, XIII, bp 145° (4 mmHg), as described for VIc and VId. Yield, 71%. IR (CCl_4) cm^{-1}: 1655 (CO). NMR ($CDCl_3$) τ: 2.01 (m, 1H, aromatic H), 2.75 (m, 3H, aromatic H), 5.81 (s, 2H, Ar-CH_2-N), 6.18 (t, 2H, J=5.3 Hz, -CO-N-CH_2-), 7.27 (t, 2H, J=5.6 Hz, -N-CH_2-), 8.30 (m, 4H, C-CH_2-CH_2-C). The methiodide (XIV) was similarly prepared in almost quantitative yield. Colorless needles (from ethanol), mp 169—171° (decomp.). IR (Nujol) cm^{-1}: 1685 (CO). *Anal.* Calcd. for $C_{13}H_{17}ON_2I$: C, 45.36; H, 4.98; N, 8.14. Found: C, 45.35; H, 5.04; N, 8.12.

Compound XII was prepared by catalytic hydrogenation of 1,4,6,11-tetrahydropyridazo[1,2-*b*]phthalazine-6,11-dione with platinum oxide in ethanol containing a small amount of acetic acid. Colorless needles, mp 156—159° (lit.[7] mp 158—160°). Yield, 93%.

Alkaline Decomposition of These Quaternary Fused Hydrazines (VIIa—d, XIV)——A general procedure for this alkaline decomposition is described with 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazin-5-one methiodide (VIIa).

1-Methyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIIa): a) Alkaline Decomposition of VIIa: To a freshly prepared solution of 1.20 g (0.05 gram atom) of metallic sodium in 70 ml of abs. methanol was added 3.30 g (0.01 mole) of VIIa. The mixture was refluxed for 29 hr and the solvent was removed under reduced pressure. To the residue was added 50 ml of water and the mixture was extracted with chloroform. The extract was washed with water, dried over anhyd. sodium sulfate, and the solvent was removed under reduced pressure. The residue was treated with pet. ether, the crystals separated were filtered, and washed with pet. ether. Recrystallization from pet. ether gave colorless granules, mp 77—79°. Yield, 1.28 g (63%). IR (Nujol) cm^{-1}: 1693 (CO). *Anal.* Calcd. for $C_{12}H_{14}ON_2$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.63; H, 7.10; N, 13.94. Picrate of VIIIa: Yellow needles (from methanol), mp 217—218° (decomp.). IR (Nujol) cm^{-1}: 1723 (CO). *Anal.* Calcd. for $C_{12}H_{14}ON_2 \cdot C_6H_3O_7N_3$: C, 50.12; H, 3.97; N, 16.24. Found: C, 50.00; H, 3.94; N, 16.30. Methiodide of VIIIa: Colorless needles (from ethanol), mp 209—210°. IR (Nujol) cm^{-1}: 1735 (CO). *Anal.* Calcd. for $C_{13}H_{17}ON_2I$: C, 45.36; H, 4.98; N, 8.14. Found: C, 45.62; H, 5.08; N, 8.15.

14) U. Schoellkopf, *Angew. Chem. Intern. Ed.*, **9**, 763 (1970).
15) R.W. Jemison and D.G. Morris, *Chem. Commun.*, **1969**, **1226**.
16) All melting points are uncorrected. IR spectra were measured on a JASCO Model IR-S spectrophotometer. NMR spectra were measured on a JEOL JNM-C-60HL (at 60 MHz) and a Varian HR-100 (at 100 MHz) spectrometers, and tetramethylsilane for $CDCl_3$ or sodium 3-(trimethylsilyl)propanesulfonate for D_2O was used as an internal standard.

b) From 1,3,4,10b-Tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one[11] (XI): To a solution of 0.56 g (0.003 mole) of XI in 0.78 g (0.015 mole) of formic acid was added 0.5 ml of 37% formalin. The solution was heated at 95—105° for 8 hr, allowed to stand at room temperature, and mixed with 20 ml of diluted hydrochloric acid. The solution was concentrated under reduced pressure, made alkaline with a 5% sodium hydroxide solution to litmus paper, and the solution was extracted with dichloromethane. The extract was washed with water, dried over anhyd. sodium sulfate, and the solvent was removed under reduced pressure. The residue was treated with pet. ether and the colorless granules separated, mp 75—78°, were filtered. Yield, 0.48 g (79%). The product was recrystallized twice from pet. ether to give colorless granules, mp 78—79°. This product was entirely identical with the compound VIIIa obtained from VIIa by mixed melting point determination and IR spectrum.

1,3-Dimethyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIIb): Colorless plates (from pet. benzin), mp 123—124°. IR (Nujol) cm^{-1}: 1695 (CO). Yield, 56% from VIIb. *Anal.* Calcd. for $C_{13}H_{16}ON_2$: C, 72.19; H, 7.46; N, 12.95. Found: C, 71.99; H, 7.57; N, 12.86. Picrate of VIIIb: Yellow plates (from ethanol), mp 202—205° (decomp.). IR (Nujol) cm^{-1}: 1726, 1710 (CO). *Anal.* Calcd. for $C_{13}H_{16}ON_2 \cdot C_6H_3O_7N_3$: C, 51.23; H, 4.30; N, 15.73. Found: C, 51.33; H, 4.30; N, 15.65. Methiodide of VIIIb: Colorless needles (from ethanol), mp 220—223° (decomp.). IR (Nujol) cm^{-1}: 1732 (CO). *Anal.* Calcd. for $C_{14}H_{19}ON_2I$: C, 46.94; H, 5.35; N, 7.82. Found: C, 46.75; H, 5.63; N, 7.45.

1,2-Dimethyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIId) and 1,4-Dimethyl-1,3,4,10b-tetrahydro-2H-pyrimido[2,1-*a*]isoindol-6-one (VIIIc): In the same manner as described for VIIIa, 1.72 g (0.005 mole) of the mixture consisting of VIIc and VIId in a ratio of 3:1 reacted with sodium methoxide to give a pale yellow syrup which was a mixture of VIIIc and VIIId in a ratio of 3.5:1. Yield, 1.00 g (93%). The syrup showed two spots on TLC,[17] one having a higher *Rf* value (A) corresponded to VIIId, and another having a lower *Rf* value (B) to VIIIc. A part of the syrup could be separated by preparative TLC[17] to give 0.06 g of the syrup A (VIIId) and 0.17 g of the syrup B (VIIIc). IR (Liquid film) of VIIId cm^{-1}: 1695 (CO). Picrate of VIIId: Yellow needles (from ethanol), mp 185—187°. IR (Nujol) cm^{-1}: 1725 (CO). *Anal.* Calcd. for $C_{13}H_{16}ON_2 \cdot C_6H_3O_7N_3$: C, 51.23; H, 4.30; N, 15.73. Found: C, 51.01; H, 4.37; N, 15.49. Methiodide of VIIId: Colorless prisms (from ethanol), mp 186—190°. IR (Nujol) cm^{-1}: 3520, 3460 (OH), 1725 (CO). *Anal.* Calcd. for $C_{14}H_{19}ON_2I \cdot H_2O$: C, 44.69; H, 5.63; N, 7.44. Found: C, 45.00; H, 5.57; N, 6.96. IR (Liquid film) of VIIIc cm^{-1}: 1695 (CO). Picrate of VIIIc: Yellow needles (from ethanol), mp 226—227° (decomp.). IR (Nujol) cm^{-1}: 1725 (CO). *Anal.* Calcd. for $C_{13}H_{16}ON_2 \cdot C_6H_3O_7N_3$: C, 51.23; H 4.30; N, 15.73. Found: C, 51.18; H, 4.37; N, 15.67. Methiodide of VIIIc: Colorless plates (from ethanol), mp 209—210° (decomp.). IR (Nujol) cm^{-1}: 3510, 3450 (OH), 1729 (CO). *Anal.* Calcd. for $C_{14}H_{19}ON_2I \cdot H_2O$: C, 44.69; H, 5.63; N, 7.44. Found: C, 44.59; H, 5.70; N, 6.85.

1-Methyl-1,2,3,4,5,11b-hexahydro-7H-1,3-diazepino[2,1-*a*]isoindol-7-one (XV): Colorless needles (from ether), mp 122—124°. Yield, 64% from XIV. IR (Nujol) cm^{-1}: 1678 (CO). NMR ($CDCl_3$) τ: 2.2—2.5 (m, 1H, aromatic H), 2.5—2.8 (m, 3H, aromatic H), 4.50 (s, 1H, angular CH), 6.04 (broad-d, 1H, CO-$\dot{N}$-CH_e-), 6.4—7.1 (m, 3H, CO-$\dot{N}$-CH_a-, -$\dot{N}$-CH_2-), 7.6—8.4 (m, 4H, C-CH_2CH_2-C), 8.09 (s, 3H, >N-CH_3). *Anal.* Calcd. for $C_{13}H_{16}ON_2$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.53; H, 7.56; N, 13.04. Picrate of XV: Yellow needles (from ethanol), mp 194—196° (decomp.). IR (Nujol) cm^{-1}: 1720 (CO). *Anal.* Calcd. for $C_{13}H_{16}ON_2 \cdot C_6H_3O_7N_3$: C, 51.23; H, 4.30; N, 15.73. Found: C, 51.22; H, 4.22; N, 15.84.

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17) Analytical TLC: Adsorbent, Wakogel B5-UA; Developing solvent, benzene–acetone (5:3), twice repeated development; Visualized under UV-irradiation. Preparative TLC: Adsorbent, Wakogel B5-UA 0.75 mm thickness; Developing solvent, benzene–acetone (16:5), twice repeated development; Adsorbent gathered was eluted with methanol.