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Rearrangement in Dihydroresorcinol Derivatives. VIII.[1] Beckmann Rearrangement *versus* Semmler-Wolff Aromatization of 3-Acylamino-2-cyclohexen-1-one Oximes

YASUMITSU TAMURA, YASUYUKI KITA and JUNKO URAOKA

Faculty of Pharmaceutical Sciences, Osaka University[2]

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Beckmann rearrangement of 1,2,3,4,5,6,7,8-octahydro-2,5-dioxoquinoline oxime (Ia,b) and 1,2,3,4,5,6,7,10-octahydro-2,7-dioxoquinoline oximes (VIa,b) with PPA gives 1,2,3,-4,5,6,7,8,9-nonahydro-2,5-dioxopyrido[3,2-*c*]azepine (IIa,b) and 1,2,3,4,5,6,7,8,10-nonahydro-2,8-dioxopyrido[2,3-*d*]azepine (VIIa,b), respectively. Under the same reaction conditions, 3-acetylamino-2-methyl-2-cyclohexen-1-one oxime (X) and 1-acetyl-1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline oxime (XIII) undergo a Semmler–Wolff aromatization to give 2-methyl-1,3-phenylenediamine (XI) and 5-amino-1,2,3,4-tetrahydroquinoline (XIV), respectively.

Recently, it has been shown[3] that in the Beckmann rearrangement of 3-alkoxy, hydroxy and chloro-2-cyclohexen-1-one oximes with polyphosphoric acid (PPA), the migration of alkyl site (C-6) is preferential to that of double bond site (C-2), and thus gives the hexahydroazepine-2,4-dione derivatives in good yields (Chart 1). Concurrent with this study, reactions of 3-acylamino-2-cyclohexen-1-one oximes with PPA were investigated. When 1,2,3,4,5,6,-7,8octahydro-2,5-dioxoquinoline oximes (Ia,b) and 1,2,3,4,5,6,7,10-octahydro-2,7-dioxoquinoline oximes (VIa,b) were treated with PPA, Beckmann rearrangement occured as in the case of the 3-alkoxy, hydroxy and chloro-2-cyclohexen-1-one oximes,[3] and gave the lactams, 1,2,3,4,5,6,7,8,9-nonahydro-2,5-dioxopyrido[3,2-*c*]azepines (IIa,b) and 1,2,-3,4,5,6,7,8,10-nonahydro-2,8-dioxopyrido-[2,3-*d*]azepines (VIIa,b), respectively. On the other hand, treatments of 3-acetylamino-2-methyl-2-cyclohexen-1-one oxime (X) and 1-acetyl-1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline oxime (XIII) with PPA caused Semmler–Wolff aromatization[4] and afforded the aromatic diamino compounds, 2-methyl-1,3-phenylenediamine (XI) and 5-amino-1,2,3,4-tetrahydroquinoline (XIV). The different behaviors in both cases would be attributed to easy hydrolysis of the N-acetyl groups of X and XIII in the reaction medium.

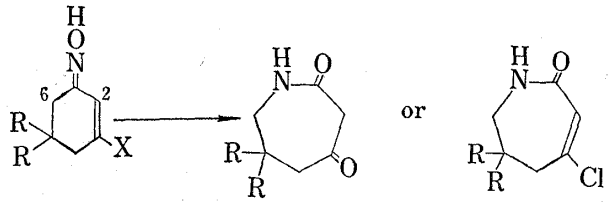

Chart 1

Beckmann Rearrangement of 1,2,3,4,5,6,7,8-Octahydro-2,5-dioxoquinoline Oximes (Ia,b) and 1,2,3,4,5,6,7,10-Octahydro-2,7-dioxoquinoline Oximes (VIa, b)

Treatments of 1,2,3,4,5,6,7,8-octahydro-2,5-dioxoquinoline oxime (Ia) and its N-methyl derivative (Ib) with PPA at 120° for 2 hours afforded 1,2,3,4,5,6,7,8,9-nonahydro-2,5-dioxo-

1) Part VII: Y. Tamura, Y. Yoshimura and Y. Kita, *Chem. Pharm. Bull.* (Tokyo), **20**, 871 (1972).
2) Location: *6-5, Toneyama, Toyonaka, Osaka.*
3) Y. Tamura, Y. Kita and M. Terashima, *Chem. Pharm. Bull.* (Tokyo), **19**, 529 (1971).
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pyrido[3,2-*c*]azepine (IIa) and its N-methyl derivative (IIb) in 61% and 46% yields, respectively. Two possible structures, II and III, are considerable for the product. The following spectral and chemical data support strongly the structure II. The infrared (IR) spectra of IIa and IIb show the presence of two amide carbonyl groups (IIa; ν_{max}^{KCl} cm^{-1}: 1680 and 1650, IIb; $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 and 1640, ν_{max}^{KCl} cm^{-1}: 1650). The ultraviolet (UV) spectra exhibit two absorptions at 279 and 225 mμ (IIa) and at 283 and 223 mμ (IIb). If III is the reaction product, the UV maximum is expected to be at 250 mμ.[5] The nuclear magnetic resonance (NMR) spectrum of IIb in $CDCl_3$ has a multiplet of two protons at τ 6.78 and a broad peak of one proton at τ 2.80—3.0. After deuterium exchange, the former is reduced to a triplet and the latter disappears; there are no noticeable changes in other regions of the spectrum. Therefore, the signal at τ 6.78 is assigned to the methylene protons adjacent to the nitrogen and the broad signal at τ 2.80—3.0 to NH proton. The spectrum of IIa in D_2O displays a triplet of two protons centered at τ 6.75, which is assigned to NCH_2. Treatment of IIa with CH_3I–KOH in acetone gave 3-carbomethoxyethyl hexahydroazepine-

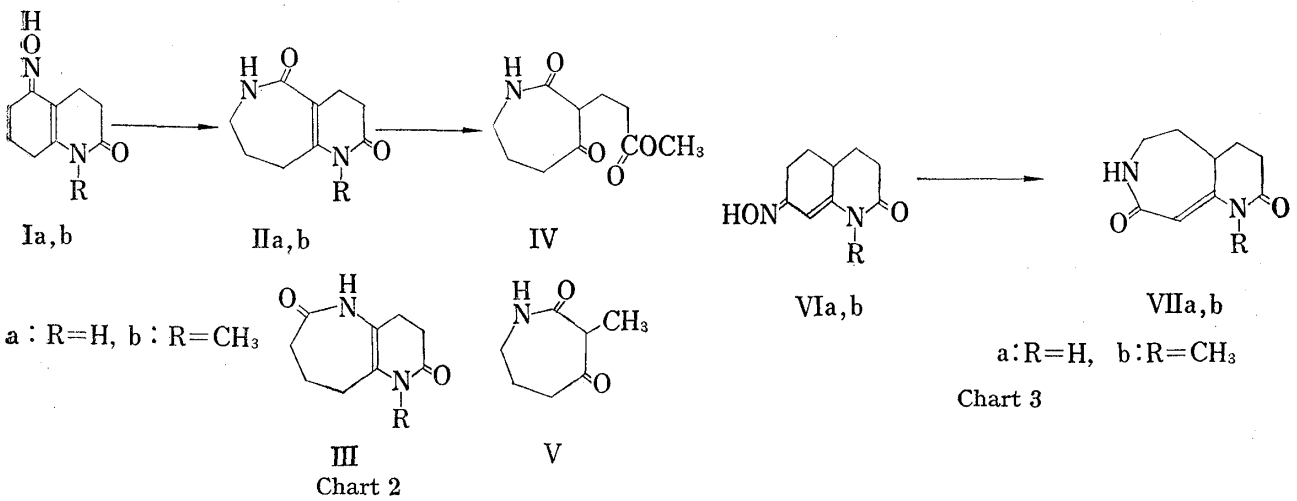

Chart 2 Chart 3

Table I. Spectral Data of Lactams

Compound No.	IR ν_{max}^{KCl} cm^{-1}	UV λ_{max}^{EtOH} mμ (log ε)	NMR τ-Value	NMR Multiplicity	NMR No. of Remarks	NMR Protons
IIa	3180, 1680 3100, 1650	279 (3.79) 225 (3.64)	6.75	t (J=6 cps)[a]	2	$NDCH_2$
IIb	3170, 1650	283 (4.65)	6.78	m[b]	2	$NHCH_2$
	(3400, 1660 1640)[c]	223 (3.83)	2.80—3.00[d]	br. p	1	NHCO
VIIa	3250, 1685 1630	266 (3.48)		—[e]		
VIIb	3230, 1680 1650	265 (4.02)	6.69 2.72—2.90[d]	m[b] br. p	2 1	$NHCH_2$ NHCO
	(3430, 1680 1640 1600)[c]					

t: triplet, m: multiplet, br. p: broad peak
a) Was measured in D_2O. *b*) Changed to a triplet on addition of D_2O.
c) $\nu_{max}^{CHCl_3}$ cm^{-1} *d*) Disappeared on addition of D_2O. *e*) insoluble in $CDCl_3$ and D_2O

5) H. Singh and S. Padmanbhan, *Chem. Ind.* (London), **1967**, 118.

2,4-dione (IV), whose structure was assigned from elemental analysis and comparison of its IR, NMR, and mass spectra with those of hexahydro-3-methylazepine-2,4-dione (V) prepared from reaction of hexahydroazepine-2,4-dione[3] and CH_3I (see experimental part).

Treatments of 1,2,3,4,5,6,7,10-octahydro-2,7-dioxoquinoline oxime (VIa) and its N-methyl compound (VIb) with PPA gave the lactams, 1,2,3,4,5,6,7,8,10-nonahydro-2,8-dioxopyrido[2,3-*d*]azepine (VIIa) and its N-methyl derivative (VIIb) in 39% and 46% yields, respectively. The structures of these compounds (VIIa,b) were confirmed from their IR, UV, and NMR spectral data, which resembled to those of IIa,b (Table I).

This work provides the further examples of the Beckmann rearrangements[3] of the α,β-unsaturated ketooximes that the migration of alkyl site is preferential to that of double bond site.

Semmler–Wolff Aromatization of 3-Acetylamino-2-methyl-2-cyclohexen-1-one Oxime (X) and 1-Acetyl-1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline Oxime (XIII)

Amination of 2-methyl-cyclohexane-1,3-dione followed by acetylation of the resulted 3-amino-2-methyl-2-cyclohexen-1-one (VIII) with acetic anhydride gave 3-acetylamino-2-cyclohexen-1-one (IX). Oximation of IX gave 3-acetylamino-2-methyl-2-cyclohexen-1-one oxime (X). Treatment of X with PPA at 80° for 2 hr gave the azepinedione (V) and 2-methyl-1,3-phenylenediamine (XI) in 3% and 57% yields, respectively. The former compound (V) was identified with the authentic specimen prepared by methylation of hexahydroazepine-2,4-dione. The structure of compound (XI) was assigned from its elemental and spectral analyses. The IR spectrum of XI shows the presence of primary amine (3450 and 3400 cm^{-1}) and 1,2,3-trisubstituted benzene ring (1620, 1470, and 1150 cm^{-1}). The NMR spectrum of XI shows a methyl proton at τ 8.05 as a singlet, two amino protons at τ 6.56 as a broad singlet, two aromatic protons at τ 3.82 as a doublet (J=7.8 cps, C-4 and C-6 protons) and an aromatic proton at τ 3.18 as a triplet (J=7.8 cps, C-5 proton). When the reaction temperature was raised from 80°, yield of the aromatization product (XI) increased and that of the rearrangement product (V) decreased. Operation of this reaction below 50° gave no V and XI but the hydrolysed products, (VIII) and (IX), of the starting material (X). The

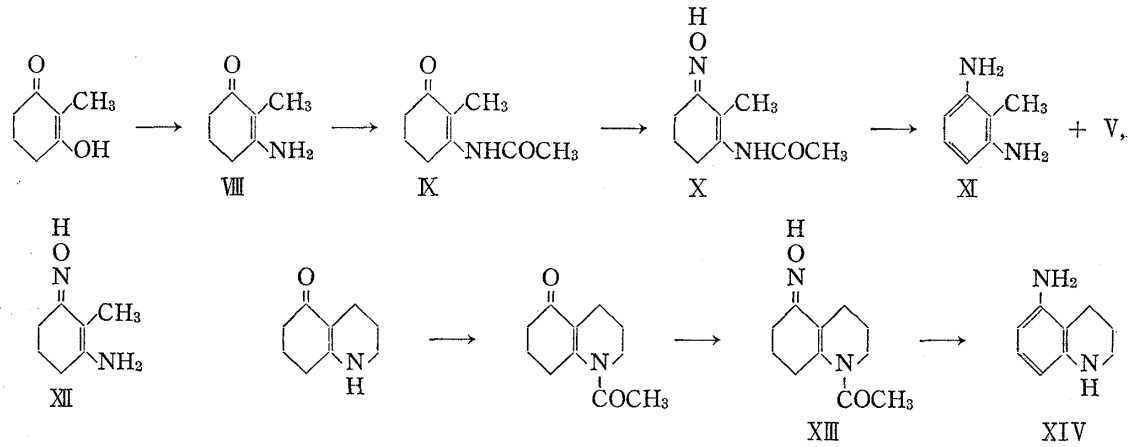

Chart 4

results, associated with the fact that in the Beckmann rearrangements of I and VI to II and VII there were no hydrolysed products detected, would suggest that initial hydrolysis of X to XII enables this Semmler–Wolff aromatization to XI.

Treatment of 1-acetyl-1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline oxime (XIII), which was prepared from 1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline by acetylation followed by oximation with PPA, was found similarly to give 5-amino-1,2,3,4-tetrahydroquinoline (XIV) as a main

product. The structure was confirmed by its IR, UV, and NMR spectral data referering to the data of XI.

Experimental

1,2,3,4,5,6,7,8-Octahydro-2,5-dioxoquinoline Oxime (Ia)——A solution of $NH_2OH \cdot HCl$ (3.19 g) and AcONa (3.78 g) in H_2O (25 ml) was added to a solution of 1,2,3,4,5,6,7,8-octahydro-2,5-dioxoquinoline[6] (5.00 g) in EtOH (25 ml). The mixture was refluxed for 1 hr and precipitate was collected by filtration and washed with water. Recrystallization from MeOH yielded 4.98 g (92%) of Ia as colorless crystals, mp 258.5°. IR ν_{max}^{KCl} cm^{-1}: 3200, 3100, 1680, 1650, 950 and 930. *Anal.* Calcd. for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.94; H, 7.06; N, 15.31.

p-Toluenesulfonyl chloride (0.706 g) was added to a stirred solution of I (0.650 g) in dry pyridine (4 ml) under ice-cooling. The reaction mixture was kept at 5° for 2 days. It was then poured into ice-water (10 ml). The resulted solid was collected by filtration and washed with water. Recrystallization from $CHCl_3$–AcOEt gave 1.04 g (93%) of I·tosylate, mp 148.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1695, 1645, 1370, 1180 and 830; ν_{max}^{KCl} cm^{-1}: 3200, 3100 1690, 1645, 1370, 1195 and 830. *Anal.* Calcd. for $C_{16}H_{18}O_4N_2S$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.48; H, 5.34; N, 8.57.

1,2,3,4,5,6,7,8-Octahydro-1-methyl-2,5-dioxoquinoline Oxime (Ib)——Prepared from 1,2,3,4,5,6,7,8-octahydro-1-methyl-2,5-dioxoquinoline[6] (0.363 g), $NH_2OH \cdot HCl$ (0.211 g) and AcONa (0.251 g) in EtOH–H_2O (4 ml) by the same method as described for I. Yield of Ib was 0.392 g (99%). Ib, colorless crystals, mp 200—206.5°. IR ν_{max}^{KCl} cm^{-1}: 3220, 3050, 1635, 990 and 930. *Anal.* Calcd. for $C_{10}H_{14}O_2N_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 62.14; H, 7.15; N, 14.13.

1,2,3,4,5,6,7,8,9-Nonahydro-2,5-dioxopyrido[3,2-*c*]azepine (IIa)——A mixture of Ia (1.250 g) and PPA (38 g) was heated at 120° for 1 hr. It was then cooled and poured into a mixture of crushed ice and water. The aqueous solution was neutralized with dil. K_2CO_3 and extracted with CH_2Cl_2. The extract was dried (K_2CO_3) and concentrated *in vacuo* to give 0.763 g of a solid. Recrystallization from water gave pure IIa as colorless crystals, mp 283—288° (decomp.). *Anal.* Calcd. for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.05; H, 6.70; N, 15.26.

1,2,3,4,5,6,7,8,9-Nonahydro-1-methyl-2,5-dioxopyrido[3,2-*c*]azepine (IIb)——Treatment of Ib (0.348 g) with PPA (10 g) at 120° for 1.5 hr gave 0.193 g of crude IIb, mp 157—169°. Recrystallization from AcOEt gave yellow needles, mp 187.5—188°, sublimation point 115—155° (0.1 mmHg). Yield, 46%. *Anal.* Calcd. for $C_{10}H_{14}O_2N_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.80; H, 7.15; N, 14.37.

3-Carbomethoxyethyl Hexahydroazepine-2,4-dione (IV)——To a suspension of IIa (0.310 g) in a mixture of KOH powder (0.145 g) and acetone (20 ml) was added a solution of CH_3I (4 ml) in acetone (4 ml) in portions. After refluxing for 3 hr, a further 2 ml of CH_3I was added and allowed to stand at room temperature for 1 day. The mixture was concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ and the insoluble stuff (KI) was removed by filtration. The $CHCl_3$ solution was evaporated *in vacuo* to give 0.528 g of a pale yellow liquid, which was distilled at 150—200° (0.1 mmHg) (bath temp.) to yield 0.231 g of a pale yellow syrup. The syurup crystallized on standing at room temperature. IV; colorless crystals, mp 121—124°. Recrystallization from C_6H_6–AcOEt gave IV as colorless needles, mp 124—124.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1730—1710 and 1670. NMR (in $CDCl_3$) τ: 3.05—3.20 (b-s, 1H, NH), 5.95 (m, 1H, CH), 6.62 (m, 2H, $NHCH_2$), 7.31 (t, 2H, $COCH_2$, J=6 cps), 7.65 (m, 6H, $CH_2 \times 3$) and 6.36 (s, 3H, OCH_3); (in $CDCl_3+D_2O$) τ: 6.62 (t, 2H, CH_2ND) and 5.95 (t, 1H, CH). Mass Spectrum *m/e*: 213 (M^+), 182 ($M-OCH_3$), 154 ($M-COOCH_3$) and 86 (base peak). *Anal.* Calcd. for $C_{10}H_{15}O_4N$: C, 56.32; H, 7.09; N, 6.57. Found: C, 56.32; H, 6.99; N, 6.50.

3-Methyl Hexahydroazepine-2,4-dione (V)——To a mixture of hexahydroazepine-2,4-dione (508 mg),[3] Na (92 mg) and MeOH (13 ml), was added CH_3I (1.13 g) in portions with stirring at room temperature. The reaction mixture was heated at 80° for 8 hr, and concentrated *in vacuo*. Chloroform was added to the residue and the precipitated NaI was removed by filtration. The $CHCl_3$ solution was evaporated *in vacuo* to give quantitative yield of crude V. Recrystallization from benzene yielded V as colorless needles, mp 150—153°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 1720 and 1675. NMR (in $CDCl_3$) τ: 2.85—3.05 (b-s, 1H, NH), 6.45 (m, 1H, CH_2), 6.20 (m, 2H, $NHCH_2$), 7.26 (t, 2H, $COCH_2$, J=8 cps), 7.87 (m, 2H, CH_2) and 8.70 (d, 3H, CH_3, J=7.5 cps); (in $CDCl_3+D_2O$) τ: 6.20 (t, 2H, CH_2ND). Mass Spectum *m/e*: 141 (M^+) and 86 (base peak). *Anal.* Calcd. for $C_7H_{11}O_2N$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.43; H, 7.59; N, 9.79.

1,2,3,4,5,6,7,10-Octahydro-2,7-dioxoquinoline Oxime (VIa)——Prepared from 1,2,3,4,5,6,7,10-octahydro-2,7-dioxoquinoline[7] (0.793 g), $NH_2OH \cdot HCl$ (0.500 g) and AcONa (0.596 g) in EtOH–H_2O (8 ml) by the same method as described for I. Yield of VIa was 0.854 g (99%). VIa, colorless crystals, mp 235—243°. Recrystallization from EtOH gave VIa as colorless crystals, mp 249—251°. IR ν_{max}^{KCl} cm^{-1}: 3170, 1680, 1620, 960 and 910. *Anal.* Calcd. for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.79; H, 6.73; N, 15.46.

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1,2,3,4,5,6,7,10-Octahydro-1-methyl-2,7-dioxoquinoline Oxime (VIb)——Prepared from 1,2,3,4,5,6,7,10-octahydro-1-methyl-2,7-dioxoquinoline[8] (0.537 g), $NH_2OH \cdot HCl$ (0.315 g) and AcONa (0.371 g) in EtOH–H_2O (4 ml) by the method described for I. Yield of VIb was 0.497 g (85%). VIb, colorless crystals, mp 241—245°. Recrystallization from EtOH gave VIb as colorless crystals, mp 245—246.5°. IR ν_{max}^{KCl} cm^{-1}: 3250, 1640, 1600 and 1140. *Anal.* Calcd. for $C_{10}H_{14}O_2N_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.75; H, 7.28; N, 14.23.

1,2,3,4,5,6,7,8,10-Nonahydro-2,8-dioxopyrido[2,3-*d*]azepine (VIIa)——Treatment of VIa (0.623 g) with PPA (18 g) according to the method described for II gave 0.245 g (39%) of crude VIIa as yellow crystals, mp 265—277°. Recrytasllization from EtOH yielded VIIa, mp 275—279°. *Anal.* Calcd. for $C_9H_{12}O_2N_2$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.12; H, 6.59; N, 15.33.

1,2,3,4,5,6,7,8,10-Nonahydro-1-methyl-2,8-dioxopyrido[2,3-*d*]azepine (VIIb)——Treatment of VIb (0.284 g) with PPA (9 g) according to the method described for II gave 0.130 g (46%) of crude VIIb as yellow needles, mp 165°. Recrystallization from C_6H_6 yielded IX, mp 169—171.5°. *Anal.* Calcd. for $C_{10}H_{14}O_2N_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 62.15; H, 7.45; N, 14.25.

3-Amino-2-methyl-2-cyclohexen-1-one (VIII)——2-Methylcyclohexane-1,3-dione (1.28 g) was suspended in EtOH (50 ml) saturated with NH_3. The reaction mixture was heated in a sealed tube at 90—100° for 10 hr and then concentrated *in vacuo* to give a solid. Recrystallization of the solid from acetone gave 1.32 g (quantitative yield) of VIII, mp 163—164°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1605 and 1585; ν_{max}^{KCl} cm^{-1}: 3350, 3180 and 1670. UV λ_{max}^{EtOH} $m\mu$ (log ε): 292 (4.27). *Anal.* Calcd. for $C_7H_{11}ON$: C, 67.17; H, 8.86; N, 11.19. Found C, 67.00; H, 8.92; N, 11.19.

3-Acetylamino-2-methyl-2-cyclohexen-1-one (IX)——A solution of VIII (1.83 g) in pyridine (7 ml) and acetic anhydride (7 ml) was allowed to stand at 30° for 22 hr and concentrated *in vacuo*. The residue was extracted with $CHCl_3$ (30 ml). The extract was washed with $NaHCO_3$ (5 ml) and water (5 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give an oil. The oil was distilled *in vacuo* to afford 1.38 g (56%) of IX, bp 144—146° (0.2 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1710, 1680, 1650 and 1620. UV λ_{max}^{EtOH} $m\mu$: 277. This stuff was used for the next reaction without further purification.

3-Acetylamino-2-methyl-2-cyclohexen-1-one Oxime (X)——Prepared from IX (0.987 g), $NH_2OH \cdot HCl$ (0.615 g) and AcONa (0.728 g) in EtOH–H_2O (10 ml) by the same method as described for I. Yield of X was 0.574 g (53.3%). X; colorless crystals, mp 211—214°. Recrystallization from EtOH–H_2O gave X as colorless needles, mp 203—204°. IR ν_{max}^{KCl} cm^{-1}: 3260, 1660 and 970. UV λ_{max}^{EtOH} $m\mu$ (log ε): 253 (4.45). *Anal.* Calcd. for $C_9H_{14}O_2N_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.54; H, 7.76; N, 15.30.

Treatment of X with PPA——A stirred mixture of X (0.650 g) and PPA (20 g) was heated at 80—90° for 2 hr. It was then cooled and poured into a mixture of crushed ice and water. The aqueous solution was extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated *in vacuo* to give 0.017 g (3%) of V. Recrystallization from C_6H_6 gave an analytical sample, colorless needles, mp 149°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 1720 and 1680; ν_{max}^{KCl} cm^{-1}: 3300, 3200, 3100, 1700 and 1680. No obvious absorptions appeared in UV spectrum. *Anal.* Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.43; H, 7.59; N, 9.79.

The above aqueous solution was neutralized with 10% K_2CO_3 and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated *in vacuo* to give 0.250 g (57%) of XI. Recrystallization from ligroin gave an analytical sample of yellow crystals, mp 103—104°. *Anal.* Calcd. for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 68.96; H, 8.20; N, 22.90.

1-Acetyl-1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline Oxime (XIII)——A solution of 1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline[9] (486 mg) in pyridine (2 ml) and acetic anhydride (2 ml) was allowed to stand at 30° for 40 hr and concentrated *in vacuo*. The residue was extracted *in vacuo*. The residue was extracted with $CHCl_3$, dried ($MgSO_4$) and concentrated *in vacuo* to give 650 mg of an oil. The oil was distilled *in vacuo* to afford 430 mg (70%) of 1-acetyl-1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline, bp 138—140° (0.2 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 and 1600. This stuff was used for the oximation without further purification. XIII was prepared from 1-acetyl-1,2,3,4,5,6,7,8-octahydro-5-oxoquinoline (2.78 g), $NH_2OH \cdot HCl$ (1.36 g) and AcONa (1.73 g) in EtOH–H_2O (20 ml) by the method described for I. Recrystallization from EtOH–H_2O gave 2.03 g (70%) of XIII as colorless plates, mp IR 176—177°. $\nu_{max}^{CHCl_3}$ cm^{-1}: 3200, 1630—1610, 1600, 1000 and 970. UV λ_{max}^{EtOH} $m\mu$ (log ε): 274 (4.33). *Anal.* Calcd. for $C_{11}H_{16}O_2N_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.43; H, 7.84; N, 13.27.

5-Amino-1,2,3,4-tetrahydroquinoline (XIV)——A mixture of XIII (0.500 g) and PPA (15 g) was heated at 100° for 1 hr. It was then cooled and poured into a mixture of crushed ice and water. The aqueous solution was neutralized with dil. K_2CO_3 and extracted with CH_2Cl_2. The extract was dried (K_2CO_3) and concentrated *in vacuo* to give a solid. Recrystallization from pet. benzine gave 150 mg (42%) of XIV as colorless needles, mp 97—98°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 3390, 1620, 1595 and 1140. NMR (in $CDCl_3$) τ: 7.95 (2H, quintet, C-3, J=6 cps), 7.52 (2H, t, C-4, J=6 cps), 6.78 (2H, t, C-2, J=6 cps), 6.50 (3H, s, NH_2 and NH), 3.95 (1H, d, C-6 or C-8, J=8 cps), 4.05 (1H, d, C-6 or C-8, J=8 cps) and 3.20 (1H, t, C-7, J=8 cps). *Anal.* Calcd. for $C_9H_{12}N_2$: C, 72.94; H, 8.16; N, 18.90. Found: C, 73.17; H, 8.33; N, 19.19.

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