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Rearrangement in Dihydroresorcinol Derivatives. VII.[1] Curtius Rearrangement of 3-Azido-2-cyclohexen-1-ones and a Ring Contraction of 2-Alkoxy-4,5,6,7-tetrahydro-1H-azepin-4-ones[2]

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Curtius-type rearrangement of 3-azido-2-cyclohexen-1-ones (IIa,b) to 2-alkoxy-4,5,6,7-tetrahydro-1H-azepin-4-ones (IVa,b and VIIa,b) and a novel ring contraction of IVa,b and VIIa,b to alkyl pyrrolidylideneactates (IXa,b and X) were described. The imine-enamine tautomerism of IVa,b and VIIa,b were also mentioned.

In the previous communication,[2] we reported, without experimental details, the preparation of 4,5,6,7-tetrahydro-2-methoxy-1H-azepin-4-one (IVa,b) by the Curtius rearrangement of 3-azido-2-cyclohexen-1-one (IIa,b), the imine-enamine tautomerism of IVa,b in solution and the ring contraction of IVa,b to methyl pyrrolidylideneacetate (IXa,b). The present paper describes a full account of these experiments.

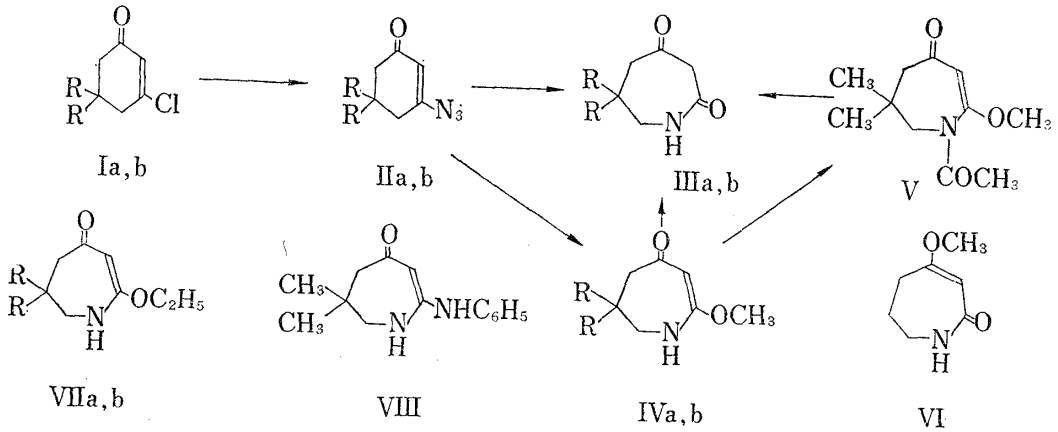
Recently, it has been reported[4] that photo-irradiation of 3-azido-5,5-dimethyl-2-cyclohexen-1-one (IIa) in aqueous tetrahydrofuran produced hexahydro-6,6-dimethyl-azepine-2,-4-dione (IIIa) but in low yield. We found that thermal treatment of a benzene solution of IIa in the presence of water increased the yield of IIIa and that in the same reaction employment of alcohols instead of water gave 4,5,6,7-tetrahydro-2-methoxy-6,6-dimethyl-1H-azepin-4-one (IVa) and 2-ethoxy-4,5,6,7-tetrahydro-6,6-dimethyl-1H-azepin-4-one (VIIa).

3-Chloro-5,5-dimethyl-2-cyclohexen-1-one (Ia) was reacted with sodium azide in methanolic solution (containing small amount of water) followed by chromatographical purification over alumina to give oily 3-azido-5,5-dimethyl-2-cyclohexen-1-one (IIa), which was subjected to Curtius rearrangement without further purification. Heating of a benzene solution of IIa in the presence of water under nitrogen streams at 80—90° for 1 hour caused Curtius rearrangement to give hexahydro-6,6-dimethylazepine-2,4-dione (IIIa) in 25% yield from Ia. This rearrangement was also found to be effected with polyphosphoric acid. The structure of IIIa was confirmed unequivocally by direct comparison with authentic specimen of IIIa.[4,5]

Refluxing a methanolic solution of IIa under nitrogen streams for 4 hours gave a 36% yield of 4,5,6,7-tetrahydro-2-methoxy-6,6-dimethyl-1H-azepin-4-one (IVa). The structure of IVa was proved by the following evidences. Hydrolysis of IVa with 10% perchloric acid or 10% potassium hydroxide gave IIIa in 67%or 63% yield. Treatment of IVa with acetic anhydride in pyridine gave the N-acetyl derivatives (V) in 83% yield, which was hydrolyzed with 10% hydrochloric acid to give IIIa in 98% yield. The nuclear magnetic resonance (NMR) spectrum of IVa in deutero dimethyl sulfoxide exhibits a singlet at τ 9.08 (6H, di-CH_3), a singlet at τ 7.83 (2H, CH_2CO), a doublet at τ 7.13 (2H, CH_2N, J=5 cps), a singlet at τ 6.40

1) Part VI: Y. Tamura and Y. Kita, *Chem. Pharm. Bull.* (Tokyo), **19**, 1735 (1971).
2) A brief communication of this work has appeared: Y. Tamura, Y. Yoshimura and Y. Kita, *Chem. Pharm. Bull.* (Tokyo), **19**, 1069 (1971).
3) Location: *6-1-1, Toyeyama, Toyonaka, Osaka.*
4) S. Sato, *Bull. Chem. Soc. Japan*, **41**, 2524 (1968).
5) Y. Tamura, Y. Kita, Y. Matsutaka and M. Terashima, *Chem. Ind.* (London), **1970**, 1350; Y. Tamura, Y. Kita and M. Terashima, *Chem. Pharm. Bull.* (Tokyo), **19**, 529 (1971).

(3H, OCH_3), a doublet at τ 5.65 (1H, CH=, J=3 cps) and a broad singlet at τ 2.1—2.7 (1H, NH). However, these data could not decide whether the structure is IVa or 2,5,6,7-tetrahydro-4-methoxy-6,6-dimethyl-1H-azepin-2-one (VI). The latter structure is excluded from comparison of the ultraviolet (UV) spectrum of IVa [λ_{max}^{EtOH}: 290 mμ (log ε 4.42)] with that of VI [λ_{max}^{EtOH}: 227 mμ (log ε 4.06)], prepared by the Beckmann rearrangement of 3-methoxy-2-cyclohexen-1-one oxime tosylate.[5] As reported in the previous paper,[2] the NMR and infrared (IR) spectra of IVa in chloroform show that IVa exists in imine-enamine tautomeric equilibrium, and the UV, NMR and IR spectra of IVa in carbon tetrachloride show that IVa exists solely as the imine tautomer, as described in experimental parts.



a : R=CH_3, b : R=H

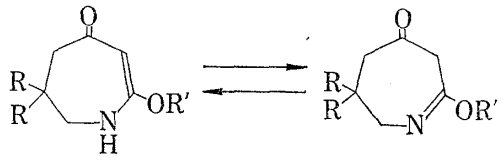
Chart 1

When the rearrangement of IIa was carried out in the presence of ethanol or aniline instead of methanol, 2-ethoxy-4,5,6,7-tetrahydro-6,6-dimethyl-1H-azepin-4-one (VIIa) and 2-anilino-4,5,6,7-tetrahydro-6,6-dimethyl-1H-azepin-4-one (VIII) were obtained. The structures of VIIa and VIII are also supported by the spectral data (see experimental part).

A series of reactions employed for IIa were applied to IIb. The reaction proceeded similarly to give hexahydroazepine-2,4-dione (IIIb), 4,5,6,7-tetrahydro-2-methoxy (IVb) and 2-ethoxy-4,5,6,7-tetrahydro-1H-azepin-4-one (VIIb). Similar to the previous results[2] IVb and VIIa,b exist in imine-enamine tautomeric equilibrium as shown in Table I.

Concerning the pathway of the rearrangement from IIa into IIIa, two types of mechanisms, Curtius type[2,4] and Schmidt type,[6] could be considered as shown in Chart 2. The

TABLE I.



Compound No.	R	R′	Ratio of A: B (in $CDCl_3$)
IVa	CH_3	CH_3	3: 2[2]
IVb	H	CH_3	2: 1
VIIa	CH_3	C_2H_5	3: 2
VIIb	H	C_2H_5	2: 1

Measured in $CDCl_3$ at room temperature.

6) A. Hassner, E.S. Ferdinandi and R.J. Isbister, *J. Am. Chem. Soc.*, **92**, 1672 (1970).

rearrangements under the photochemical and thermal conditions are thought to be the former type, while the rearrangement with polyphosphoric acid to be the latter type.

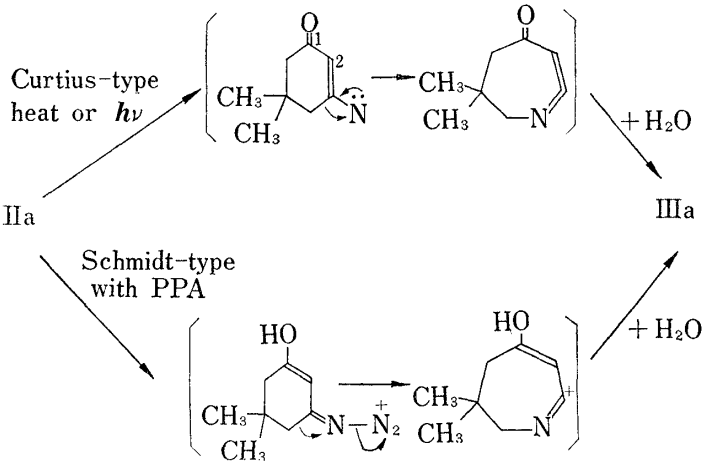
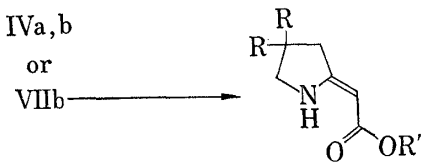


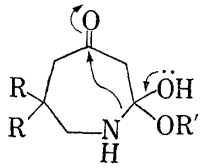
Chart 2



IXa : R=CH_3, R'=CH_3
IXb : R=H, R'=CH_3
X : R=H, R'=C_2H_5

Chart 3

A variety of azepines are known to undergo ring contractions with base or acid, giving pyrrole,[7a] pyridine[7b] and γ-lactone derivatives.[7c] For example, 3,4,6-tricyano-4,5-dihydro-2,7-dimethyl-1H-azepine gave 3,4-dicyano-2,5-dimethylpyrrole[7a] with ethanolic sodium hydroxide, and N-ethyl-4,5-dihydro-1H-azepine gave cyclopentene-1-carboxaldehyde N-ethylimine[7d] with hydrogen chloride. The present ring contraction of IVa,b provides a novel type of example and also a facile synthetic route to methyl pyrrolidylideneacetate (IXa,b) and analogous. When IVb was heated with 10% acetic acid a ring contraction occured to give methyl 2-pyrrolidylideneacetate (IXb) in 54% yield. Similar treatment of IVa and VIIb afforded IXa and ethyl 2-pyrrolidylideneacetate (X) in 71% and 21% yields, respectively. The structure of X was identified with authentic specimen prepared by the alternative route.[8]



i

As for the reaction mechanism of the ring contraction, it is speculated to proceed through the intermediate (i) as reported in the previous communication.[2]

Experimental[9]

3-Azido-5,5-dimethyl-2-cyclohexen-1-one (IIa)——Freshly distilled 3-chloro-2-cyclohexen-1-one (Ia; 2.81 g) was added dropwise to a stirred solution of NaN_3 (1.27 g) in MeOH (40 ml) and water (8 ml) under ice-cooling, and after addition stirring was continued at room temperature for 4 hr. The reaction mixture was poured into water and extracted with ether. The extract was dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow-brown oil. Chromatography of the oil on alumina with C_6H_6 gave 2.56 g of IIa as a yellow oil, which was used for the next Curtius rearrangement without further purification. Ia; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1650 and 1610.

3-Azido-2-cyclohexen-1-one (IIb)——Prepared from 3-chloro-2-cyclohexen-1-one (4.69 g) and NaN_3 (2.08 g) in EtOH (40 ml) and water (8 ml) by the same method as described for the preparation of IIa. IIb (3.15 g) was obtained as a yellow oil, which was used for the next Curtius rearrangement without further purification. IIb; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1650 and 1605.

7) *a*) P.J. Brignell, E. Bullock, U. Eisner, B. Gregory, A.W. Johnson and H. Williams, *J. Chem. Soc.*, **1963**, 4819; M. Anderson and A.W. Johnson, *J. Chem. Soc. (C)*, **1966**, 1075; R.F. Childs and A.W. Johnson, *ibid.*, **1966**, 1050; *b*) M. Anderson and A.W. Johnson, *J. Chem. Soc.*, **1965**, 2411; *c*) Leo A. Paquette, *J. Am. Chem. Soc.*, **85**, 3288 (1963); *d*) E.L. Stogryn and S.J. Brois, *J. Am. Chem. Soc.*, **30**, 88 (1965).

8) Z. Horii, K. Morikawa and I. Ninomiya, *Chem. Pharm. Bull.* (Tokyo), **17**, 2230 (1969).

9) Boiling and melting points were uncorrected. The NMR spectra were measured on a Hitachi Perkin-Elmer H-60 type (60 Mc) spectrometer with tetramethylsilane as internal reference and IR spectra on a Hitachi-EPI G2 spectrophotometer and UV spectra on a Hitachi EPS-3T spectrophotometer.

Hexahydro-6,6-dimethylazepine-2,4-dione (IIIa)——i) A mixture of IIa (2.93 g) [prepared from Ia (4.40 g)] and water (2 ml) in C_6H_6 (15 ml) was heated under N_2 in a water bath at 80° for 1.5 hr. The reaction mixture was concentrated *in vacuo* to give brown crystals. Recrystallization from C_6H_6–ether gave 0.690 g (16%; from Ia) of IIIa as colorless needles, mp 145—146.5° (lit.[4,5] 145.5—146.5°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 1715 and 1670. This material was identified with authentic sample of IIIa prepared by the Beckmann rearrangement[5] of 3-alkoxy-5,5-dimethyl-2-cyclohexen-1-one oxime, in all respects.

ii) A solution of IIa [prepared from Ia (4.40 g)] in PPA (30 g) was heated under N_2 in a water bath at 80° for 1.5 hr. The reaction mixture was concentrated *in vacuo* to give brown crystals. Recrystallization from C_6H_6 gave 0.650 g (15%; from Ia) of IIIa as colorless needles, mp 145—146.5° (lit.[4,5] 145.5—146.5°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425 and 1715.

Hexahydroazepine-2,4-dione (IIIb)——A mixture of IIb (0.661 g) [prepared from Ib (1.72 g)] and water (2 ml) in C_6H_6 (15 ml) was heated under N_2 in a water–bath at 80° for 1.5 hr. The reaction mixture was concentrated *in vacuo* to give a brown paste which was chromatographed by use of column of alumina. The column was eluted successively with pet. ether (50 ml), C_6H_6 (100 ml) and C_6H_6: EtOAc=2:1 (200 ml). Elution with C_6H_6: EtOAc=2:1 gave crude IIIb. Sublimation at 110—140° (0.03 mmHg, bath temp.) gave 0.125 g (7%; from Ib) of IIIb as colorless crystals, mp 91.5—92.5° (lit.[5] 94.5°), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 1720 and 1670. This material was identified with authentic sample of IIIb prepared by the Beckmann rearrangement[5] of 3-alkoxy-2-cyclohexen-1-one oxime, in all respects.

Curtius Rearrangement of IIa in MeOH——A solution of IIa [prepared from Ia (3.92 g)] in abs. MeOH (50 ml) was refluxed under N_2 in a water bath for 4 hr. The reaction mixture was concentrated *in vacuo*. The resulted yellow-brown crystals were washed with pet. ether, and recrystallized from acetone–pet. ether to give 1.41 g (36%; from Ia) of IVa as colorless needles, mp 146—146.5°. UV λ_{max}^{EtOH} $m\mu$ (log ε): 290 (4.42). Mass Spectrum *m/e*: 169 (M^+), 154, 126, 112, 85, 57 and 55. The spectra in CCl_4 show that IVa exists solely as the imine tautomer, 3,4,5,6-tetrahydro-7-methoxy-3,3-dimethyl-2H-azepin-5-one (B); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 and 1665. NMR (in CCl_4) τ; 8.98 (6H, s, di-CH_3), 7.78 (2H, s, $COCH_2$), 6.86 (4H, s, CH_2N and $COCH_2C$=N) and 6.34 (3H, s, OCH_3). The spectra in $CHCl_3$ show that IVa exists as a 3:2 mixture of 4,5,6,7-tetrahydro-2-methoxy-6,6-dimethyl-1H-azepin-4-one (A) and B: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3425, 1710, 1660 and 1570. NMR (in $CDCl_3$) τ: Signals due to A; 8.92 (3/5×6H, s, di-CH_3), 7.58 (3/5×2H, s, CH_2CO), 6.98 (3/5×2H, d, CH_2N, J=5 cps), 6.33 (3/5×3H, s, OCH_3), 5.36 (3/5×1H, d, CH=, J=3 cps) and 4.5—4.9 (3/5×1H, b-s, NH). Signals due to B; 8.96 (2/5×6H, s, di-CH_3), 7.67 (2/5×2H, s, CH_2CO), 6.77 (2/5×2H, s, CH_2N), 6.71 (2/5×2H, s, $COCH_2C$=N) and 6.28 (2/5×3H, s, OCH_3). *Anal.* Calcd. for $C_9H_{15}O_2N$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.93; H, 8.95; N, 8.37.

Curtius Rearrangement of IIb in MeOH——A solution of IIb [prepared from Ib (2.50 g)] in abs. MeOH (40 ml) was refluxed under N_2 in a water bath for 4 hr. The reaction mixture was concentrated *in vacuo*. Sublimation of the remained paste at 110—120° (8 mmHg, bath temp.) gave 0.700 g (28% from Ib) of IVb as colorless crystals, mp 90—91°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1715, 1660 and 1570. UV λ_{max}^{EtOH} $m\mu$ (log ε): 293 (4.27). NMR (in $CDCl_3$) τ; The NMR spectrum shows that IVb exists as a 2:1 mixture of 4,5,6,7-tetrahydro-2-methoxy-1H-azepine-4-one (A) and its tautomer, 3,4,5,6-tetrahydro-7-methoxy-2H-azepin-5-one (B). Signals due to A; 7.83—8.15 (2/3×2H, m, C-CH_2-C), 7.35 (2/3×2H, t, CH_2CO, J=6 cps), 6.45—6.72 (2/3×2H, m, CH_2N), 6.28 (2/3×2H, s, OCH_3), 5.30 (2/3×1H, b-s, CH=) and 2.8—3.7 (2/3×1H, b-s, NH). Signals due to B; 7.83—8.22 (1/3×2H, m, C-CH_2-C), 7.35 (1/3×2H, t, CH_2CO, J=6 cps), 6.45—6.72 (1/3×4H, m, CH_2N and $COCH_2C$=N) and 6.30 (1/3×3H, s, OCH_3). *Anal.* Calcd. for $C_7H_{11}O_2N$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.69; H, 7.61; N, 10.26.

Hydrolysis of IVa to IIIa——i) with 10% $HClO_4$: Compound IVa (95.0 mg) in 10% $HClO_4$ (9 ml) was stirred at 40° for 2 hr and then at 90° for 5 min. The reaction mixture was neutralized with 10% aq. Na_2CO_3 and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated *in vacuo*. Recrystallization of the residue from C_6H_6 gave 58.9 mg (67%) of IIa as colorless crystals, mp 144—146° (lit.[5] 145.5—146.5°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 1715 and 1670.

ii) with 10% KOH: Compound IVa (130 mg) in 10% KOH (20 ml) was stirred at 40° for 2 hr, and then at 90° for 5 min. The reaction mixture was neutralized with 10% HCl and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated *in vacuo*. Recrystallization of the resulted crystals from C_6H_6 gave 70 mg (59%) of IIIa as colorless crystals, mp 145—147° (lit.[5] 145.5—146.5°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 1715 and 1670. This material was identified with authentic sample of IIIa prepared in i).

N-Acetyl-4,5,6,7-tetrahydro-2-methoxy-6,6-dimethylazepin-4-one (V)——A mixture of IVa (94 mg), Ac_2O (2 ml) and abs. pyridine (2 ml) was allowed to stand at room temperature for 2 days. Concentration of the solution *in vacuo* gave a residue. A solution of the residue in C_6H_6 was washed with sat. aq. $NaHCO_3$ and sat. NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. Recrystallization of the residue from pet. ether gave 106 mg (86%) of V as colorless crystals, mp 82.5—83.0°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1630 and 1600. UV λ_{max}^{EtOH} $m\mu$ (log ε): 276 (4.34). NMR (in $CDCl_3$) τ: 8.95 (6H, s, di-CH_3), 7.88 (3H, s, $COCH_3$), 7.57 (2H, s, CH_2CO), 6.30 (2H, s, CH_2N), 6.22 (3H, s, OCH_3) and 4.89 (1H, s, CH=). *Anal.* Calcd. for $C_{11}H_{17}O_3N$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.13; H, 8.06; N, 6.84.

Hydrolysis of V to IIIa——Compound V (97.6 mg) in 10% HCl (7 ml) was stirred at 40° for 1 hr, and then at 90° for 5 min. The reaction mixture was neutralized with 10% aq. Na_2CO_3 and extracted with

CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated *in vacuo*. Recrystallization of the residue from C_6H_6 gave 71.0 mg (98%) of IIIa as colorless crystals, mp 145—146° (lit.[5] 145.5—146.5°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 1710 and 1670. This material was identified with authentic sample of IIIa.

Curtius Rearrangement of IIa in EtOH——A solution of IIa [prepared from Ia (2.83 g)] in abs. EtOH (40 ml) was refluxed under N_2 in water bath for 1.5 hr. The reaction mixture was concentrated *in vacuo* to give yellow-brown crystals. Recrystallization from pet. ether gave 1.17 g (36%; from Ia) of VIIa as colorless crystals, mp 127.5—128.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 1710, 1660 and 1575. UV λ_{max}^{EtOH} $m\mu$ (log ε): 292 (4.19). NMR (in $CDCl_3$) τ; The NMR spectrum shows that VIIb exists as a 3:2 mixture of 2-ethoxy-4,5,6,7-tetrahydro-6,6-dimethyl-1H-azepin-4-one (A) and 7-ethoxy-3,4,5,6-tetrahydro-3,3-dimethyl-2H-azepin-5-one (B). Signals due to A: 8.95 ($3/5\times6$H, s, di-CH_3), 8.68 ($3/5\times3$H, t, J=7 cps, CH_2CH_3), 7.56 ($3/5\times2$H, s, CH_2CO), 6.96 ($3/5\times2$H, d, J=6 cps, CH_2N), 6.00 ($3/5\times2$H, q, OCH_2, J=7 cps), 5.35 ($3/5\times1$H, d, CH=, J=3 cps) and 4.0—4.8 ($3/5\times1$H, b-s, NH). Signals due to B; 8.95 ($2/5\times6$H, s, di-CH_3), 8.68 ($2/5\times3$H, t, J=7 cps, CH_2CH_3), 7.63 ($2/5\times2$H, s, CH_2CO), 6.75 ($3/5\times2$H, s, $COCH_2C$=N), 6.70 ($2/5\times2$H, s, CH_2N) and 5.95 ($2/5\times2$H, q, J=7 cps, OCH_2). *Anal.* Calcd. for $C_{10}H_{17}O_2N$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.93; H, 9.15; N, 8.31.

Curtius Rearrangement of IIb in EtOH——A solution of IIb, [prepared from Ib (3.68 g)] in abs. EtOH (40 ml) was refluxed under N_2 in water bath for 1.5 hr. The reaction mixture was concentrated *in vacuo* to give yellow-brown crystals. Sublimation of the crystals at 100—110° (15 mmHg, bath temp.) gave 0.777 g (18%; from Ib) of VIIb as colorless crystals, mp 78—78.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1710, 1665 and 1570. UV λ_{max}^{EtOH} $m\mu$ (log ε): 294 (4.30). NMR (in $CDCl_3$) τ; The NMR spectrum shows that VIIb exists as a 2:1 mixture of 2-ethoxy-4,5,6,7-tetrahydro-1H-azepin-4-one (A) and its tautomer, 7-ethoxy-3,4,5,6-tetrahydro-2H-azepin-5-one (B). Signals due to A; 8.72 ($2/3\times3$H, t, CH_2CH_3, J=7 cps), 7.73—8.28 ($2/3\times2$H, m, C-CH_2-C), 7.38 ($2/3\times2$H, t, CH_2CO, J=7 cps), 6.44—6.74 ($2/3\times2$H, m, CH_2N), 6.02 ($2/3\times2$H, q, OCH_2, J=7 cps), 5.33 ($2/3\times1$H, b-s, CH=) and 2.6—3.7 ($2/3\times1$H, b-s, NH). Signals due to B; 8.75 ($1/3\times3$H, t, CH_2CH_3, J=7 cps), 7.73—8.28 ($1/3\times2$H, m, C-CH_2-C), 7.38 ($1/3\times2$H, t, CH_2CO, J=7 cps), 6.44—6.74 ($1/3\times4$H, m, CH_2N and $COCH_2C$=N) and 6.02 ($1/3\times2$H, q, OCH_2, J=7 cps). *Anal.* Calcd. for $C_8H_{13}O_2N$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.66; H, 8.44; N, 8.89.

Curtius Rearrangement of IIa in the Presence of Aniline (VIII)——A solution of IIa (0.770 g), [prepared from Ia (2.56 g)] in freshly distilled abs. $C_6H_5NH_2$ (10 ml) was heated under N_2 in a water bath at 80° for 1.5 hr. The reaction mixture was concentrated *in vacuo* to give yellow-brown crystals. Recrystallization of the crystals from acetone gave 92.5 mg (9%; from IIa) of VIII as colorless crystals, mp 214—214.5°. UV λ_{max}^{EtOH} $m\mu$ (log ε): 316 (4.36). IR ν_{max}^{KBr} cm^{-1}: 3200, 1640, 1595, 1575 and 1500; $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 1635 and 1590. NMR (in pyridine) τ: 8.97 (6H, s, di-CH_3), 7.31 (2H, s, CH_2CO), 6.83 (2H, d, CH_2-N, J=6 cps), and 4.71 (1H, d, CH=, J=3 cps). *Anal.* Calcd. for $C_{14}H_{18}ON_2$: C, 73.01; H, 7.88; N, 12.17. Found: C, 72.43; H, 7.83; N, 12.25.

Methyl 4,4-Dimethyl-2-pyrrolidylideneactate (IXa)——i) A solution of IVa (0.550 g) in 10% aq. HCl (10 ml) was stirred at 40° for 1.5 hr, and at 90° for 5 min. The solution was neutralized with 10% aq. Na_2CO_3 and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated *in vacuo*. Recrystallization of the residual crystals from water gave 0.348 g (63%) of IXa as colorless crystals, mp 85°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 1660 and 1600. UV λ_{max}^{EtOH} $m\mu$ (log ε): 282 (4.24). NMR (in $CDCl_3$) τ: 8.88 (6H, s, di-CH_3), 7.66 (2H, s, CH_2), 6.76 (2H, s, CH_2N), 6.38 (3H, s, OCH_3), 5.50 (1H, s, vinyl proton) and 2.30—2.10 (1H, b-s, NH). Mass Spectrum *m/e*: 169 (M^+), 138, 122, 110. *Anal.* Calcd. for $C_9H_{15}O_2N$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.89; H, 8.75; N, 7.95.

ii) A solution of IVa (96.0 mg) in 10% aq. AcOH (10 ml) was stirred at 40° for 1 hr and 80° for 10 min. The solution was treated in a similar manner to that described in i) to give 65.5 mg (71%) of IXa, mp 84—85°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 1660 and 1600.

Methyl 2-Pyrrolidylideneactate (IXb)——i) with 10% Acetic Acid: A solution of IVb (85.9 mg) in 10% aq. AcOH (5 ml) was stirred at 40° for 1.5 hr and 90° for 5 min. The solution was neutralized with 10% Na_2CO_3 and extracted with CH_2Cl_2. The extract was dired (Na_2SO_4) and concentrated under atomspheric pressure. Sublimation of the residue at 80° (10—15 mmHg; bath temp.) gave 46.8 mg (54%) of IXb as colorless crystals, mp 100—101°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350, 1640 and 1580. UV λ_{max}^{EtOH} $m\mu$ (log ε): 282 (4.12). NMR (in $CDCl_3$) τ: 8.05 (2H, m, CH_2), 7.42 (2H, t, CH_2C=C, J=7 cps), 6.50 (2H, t, CH_2N, J=6 cps), 6.40 (3H, s, OCH_3), 5.50 (1H, s, CH=) and 1.9—2.5 (1H, b-s, NH). *Anal.* Calcd. for $C_7H_{11}O_2N$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.48; H, 8.11; N, 9.78.

Ethyl 2-Pyrrolidylideneacetate (X)——A solution of VIIb (0.137 g) in 10% aq. HCl (10 ml) was stirred at 40° for 1.5 hr and at 90° for 5 min. The solution was neutralized with 10% aq. K_2CO_3 and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and concentrated under atmospheric pressure. Sublimation of the residue at 75—80° (20—25 mmHg; bath temp.) gave 28.5 mg (21% of X as colorless crystals, mp 63°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3340, 1665, 1595. UV λ_{max}^{EtOH} $m\mu$ (log ε): 280 (4.34). NMR (in $CDCl_3$) τ: 8.75 (3H, t, CH_2CH_3, J=7 cps), 7.80—8.30 (2H, m, CH_2), 7.40 (2H, t, =C-CH_2), J=7 cps), 6.47 (2H, t, CH_2N, J=6 cps), 5.90 (2H, q, OCH_2-CH_3, J=7 cps) and 5.46 (1H, s, CH=). This material was identified with authentic sample prepared by Z. Horii, *et al.*[8] in all respects.