

## 2:2 CONDENSATION PRODUCTS FROM THE REACTION OF *N*-SUBSTITUTED 1,2-DIAMINOETHANES AND 1,3-DIAMINOPROPANES WITH SUCCINALDEHYDE AND GLUTARALDEHYDE<sup>1</sup>

Tadashi Okawara,\* Yoshinari Okamoto, Shuji Ehara, Tetsuo Yamasaki, and Mitsuru Furukawa

*Faculty of Pharmaceutical Sciences, Kumamoto University, Oe-hon-machi, Kumamoto 862, Japan*

*Abstract* - The reaction of *N*-substituted 1,2-diaminoethanes and 1,3-diaminopropanes (**1**) with succinaldehyde (**2**) and glutaraldehyde (**9**) in water gave the 2:2 condensation products (**4** and **10**).

### INTRODUCTION

The reaction of succinaldehyde and glutaraldehyde with functionalized compounds, such as amines and 2-aminoethanols, produces various heterocycles, such as pyrrole,<sup>2-7</sup> piperidine,<sup>8</sup> dihydropyridine,<sup>9</sup> tetrahydropyran,<sup>10</sup> pyridodiazocin,<sup>11</sup> and oxazolpiperidine.<sup>12-16</sup> All of these reactions give only 1:1 condensation products. The reaction of glutaraldehyde with hydroxylamine to give dipiperidinoperhydrodioxadiazin is the only reported example of a 2:2 condensation product.<sup>17</sup> Recently, we succeeded in preparing 2:2 condensation products, polyazaperhydroperylenes,<sup>18, 19</sup> by reacting glyoxal and glutaraldehyde with polyfunctionalized compounds.

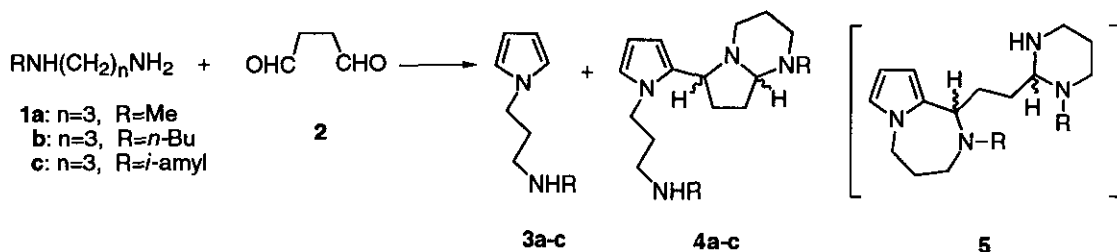
To obtain additional novel polyheterocycles in one-pot reactions, we hoped to prepare of 2:2 condensation products using *N*-substituted diamino groups.

We report here the reaction of *N*-substituted 1,2-diaminoethanes and 1,3-diaminopropanes (**1a-e**) with succinaldehyde (**2**) and glutaraldehyde (**9**) to give the 2:2 condensation products (**4** and **10**).

### RESULTS AND DISCUSSION

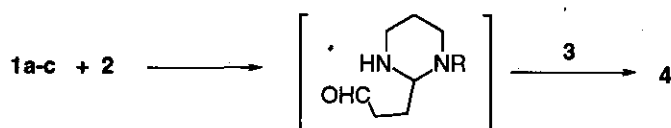
Compounds (**1a-c**) were reacted with **2**, which was derived from 2,5-dimethoxytetrahydrofuran, in aqueous hydrochloric acid at room temperature to give two products (**3** and **4**) in yields of 12-44 and 22-30%, respectively (Scheme 1). These products were purified by distillation under reduced pressure, and structural assignments were made on the basis of spectral data and elemental analyses. The mass spectra for the two products (**3a** and **4a**) from **1a** and **2** showed corresponding molecular ions at *m/z* 138 and 276, which indicated the loss of two and four molecules of water from the combination of one and two equivalents of **1a** and **2**, respectively, and their molecular formulae were equivalent to those of the 1:1 and 2:2 condensation products. In the reaction of **1a** with **2**, the 1:1 condensation product exhibited characteristic pyrrole triplet signals at  $\delta$  6.13 and 6.65 ppm in the <sup>1</sup>H-nmr spectrum. The <sup>13</sup>C-nmr spectrum

showed one methyl carbon at  $\delta$  36.54, three methylene carbons at  $\delta$  31.68, 47.51, and 49.12 ppm, and  $\beta$ - and  $\alpha$ -carbons of pyrrole at  $\delta$  107.95 and 120.49 ppm. Based on these spectral data, the structure for the 1:1 adduct was presumed to be **3a**.

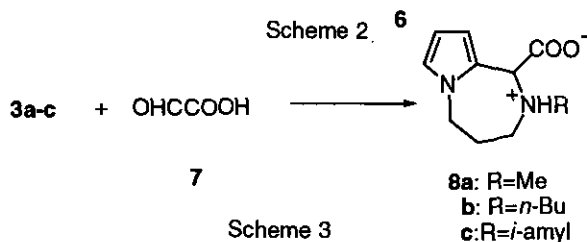


Scheme 1

With regard to the structure of the 2:2 condensation product from **1a**, the ir spectrum showed absorption assignable to the NH group at  $3310\text{ cm}^{-1}$ , while in the  $^1\text{H}$ -nmr spectrum, singlets of two methyl groups appeared at  $\delta$  2.20 and 2.39 ppm, the multiplet and triplet of two methine groups appeared at  $\delta$  2.24 and 3.15 ppm, and each triplet ( $J=2.2\text{ Hz}$ ) of the three hydrogens on the pyrrole was observed at  $\delta$  6.12, 6.54, and 6.58 ppm. The  $^{13}\text{C}$ -nmr spectrum showed 16 carbons; 9 of which were used to calculate the ratios 5:1 of each carbon for the two isomers. The DEPT spectrum indicated 2 methyl carbons at  $\delta$  36.55 and 41.74 ppm, 8 methylene carbons at  $\delta$  21.45-56.16 ppm, 2 methine carbons at  $\delta$  61.38 and 86.55 ppm, and 4 pyrrole carbons at  $\delta$  107.29, 118.69, 120.37, and 125.53 ppm. Based on these spectral data, two possible structures (**4a** and **5**) were deduced. The  $^1\text{H}$ -nmr spectrum of **4a** showed the same chemical shift and  $J$  values as the three methylene hydrogens of the pyrrole 1:1 condensation product. Moreover, the mass spectrum of the 2:2 condensation product indicated a fragment of  $N$ -substituted pyrrole at  $m/z$  137 corresponding to **3a**. These results strongly supported structure (**4a**) rather than **5**. All of the protons and carbons of **4a** were assigned based on  $^1\text{H}$ - $^1\text{H}$ - and  $^1\text{H}$ - $^{13}\text{C}$  COSY. The unequivalent hydrogens on C-7 and C-9 were observed at  $\delta$  1.76 and 2.94 ppm and at  $\delta$  1.93 and 2.94 ppm, respectively, with a shift difference of more than 1 ppm. This result could be attributed to the fact hydrogens which are proximal to the lone pairs on nitrogen are shifted downfield compared to hydrogens in the opposite direction. The following reaction mechanism is proposed based on the spectral data for compounds (**3** and **4**): The intermediates (**6**), which were derived from **1** and **2**, are presumably obtained from **3** via Mannich reactions which proceed through **4** (Scheme 2).



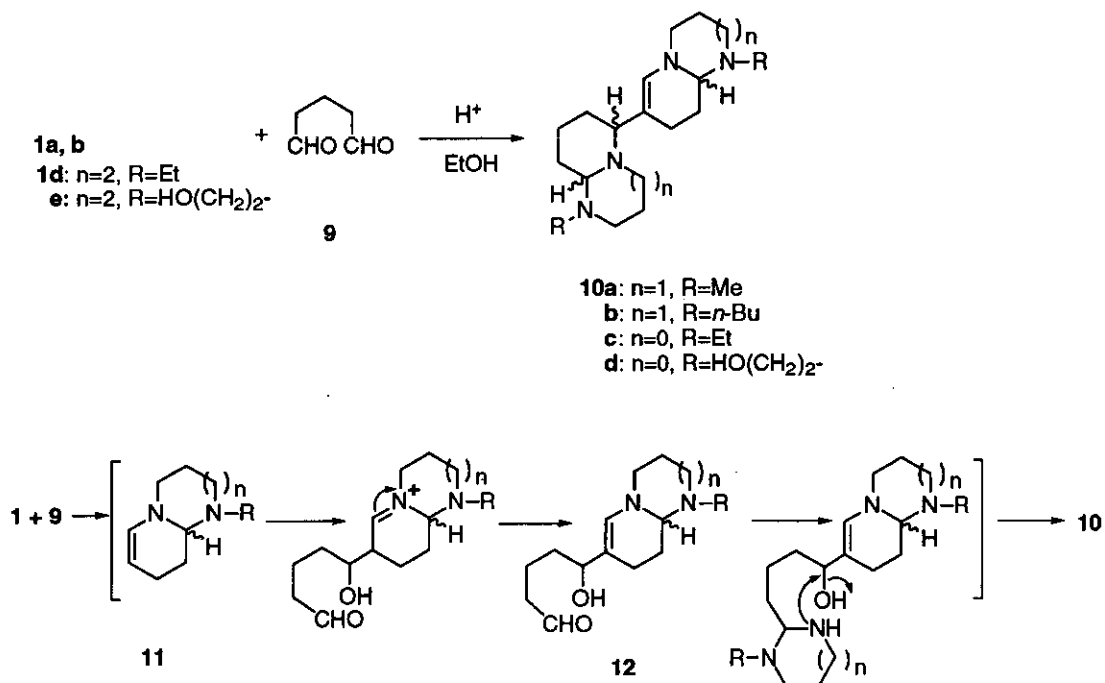
Scheme 2



Scheme 3

To ascertain the structure of **3**, the reaction of **3** with glyoxalic acid (**7**) was carried out in EtOH to give pyrrolodiazepines (**8**) in 74-90 % yields (Scheme 3). Their spectral data were consistent with the proposed structure (**8**). The structure of **3** was confirmed based on these results.

Next, compound (**1**) was reacted with **9** in EtOH to give the 2:2 condensation products (**10**) in 52-64 % yields (Scheme 4), which were then purified by distillation under reduced pressure and recrystallization. The product of the reaction of **1d** with **9** had a molecular ion at  $m/z$  336, which represented the loss of four molecules of water from two equivalents of **1d** and **9**. The ir spectrum showed a characteristic strong absorption for the C=C double bond of the enamine at  $1650\text{ cm}^{-1}$ . The DEPT spectrum exhibited 13 methylene carbons at  $\delta$  19.45-59.60, 4 methine carbons at  $\delta$  66.83-129.34, and a quaternary carbon at 111.64 ppm. Only two of four possible stereoisomers resulted, with the chemical shifts of 8 carbons out of being different for each isomer in the  $^{13}\text{C}$ -nmr spectrum. Relative ratio of these isomers was determined to be 13:8 by the intensities of stereoisomeric carbon pairs. Compound (**10d**) was recrystallized from AcOEt three times, but the ratio of the stereoisomers was unchanged. Based on these results and comparison with the  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr spectral data of related derivatives,<sup>18, 19</sup> the structure for the 2:2 condensation product was deduced to be **10d**. All of the protons and carbons were assigned from  $^1\text{H}$ -  $^1\text{H}$ - and  $^1\text{H}$ - $^{13}\text{C}$  COSY.



Scheme 4

The reaction pathway was deduced to proceed *via* formation of an enamine intermediate (**11**) from **1** and **9**, followed by electrophilic attack of another molecule of **9** to produce intermediate (**12**). This then reacted again with **1** to give **10**.

In conclusion, the reaction of dialdehydes with 1-substituted diamino compounds to give 2:2 condensation products, occurs *via* a 1:1 condensation product intermediate.

## EXPERIMENTAL

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a JASCO IRA-1 grating infrared spectrometer.  $^1\text{H}$ -Nmr spectra were determined with a JEOL JNM GX400 (400 MHz) and EX270 (270 MHz) photospectrometers using tetramethylsilane as an internal standard.  $^{13}\text{C}$ -Nmr spectra were measured with a JEOL JNM GX400 (100 MHz) and EX270 (67.5 MHz) spectrometers. Mass spectra were measured with a JEOL JMX-DX 3030HF mass spectrometer.

### General Procedure for 1-(*N*-Substituted 3-aminopropyl)pyrroles (3) and 1-Substituted 6-[1-(*N*-substituted 3-aminopropyl)pyrrol-2-yl]octahydropyrrole[1,2-*a*]pyrimidines (4)

----- To an aqueous solution of 2,5-dimethoxytetrahydrofuran (3.24 ml, 2.5 mmol) was added concentrated hydrochloric acid (1.1 ml). After the acidic solution was stirred for 20 min at room temperature, a solution of 1 (2.5 mmol) in EtOH (25 ml) was gradually added. The reaction mixture was stirred for 12 h. After evaporation of EtOH and water under reduced pressure, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (25 ml) and washed with sat.  $\text{NaHCO}_3$ . After removal of  $\text{CH}_2\text{Cl}_2$ , the residue was distilled under reduced pressure.

**3a:** yield 0.04 g (12%); bp 43 °C / 0.9 mmHg; ir v (film) 3300 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  1.09 (s, NH), 1.91 (qui,  $\text{CH}_2$ ,  $J=7.0$  Hz), 2.40 (s,  $\text{NCH}_3$ ), 2.55 (t,  $\text{CH}_2$ ,  $J=7.0$  Hz), 3.95 (t,  $\text{CH}_2$ ,  $J=7.0$  Hz), 6.13 (t, 2 x 3-H,  $J=2.2$  Hz), 6.65 (t, 2 x 2-H,  $J=2.2$  Hz);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  36.54 ( $\text{CH}_3$ ), 31.68, 47.51, 49.12 ( $\text{CH}_2$ ), 107.95, 120.49 (pyrrole); HR-ms  $m/z$ : 138.1145 (Calcd for  $\text{C}_8\text{H}_{14}\text{N}_2$ : 138.1157); *Anal.* Calcd for  $\text{C}_8\text{H}_{14}\text{N}_2$ : C, 69.52; H, 10.21; N, 20.27. Found C, 69.77; H, 10.40; N, 19.95.

**3b:** yield 0.15 g (33%); bp 74 °C / 0.6 mmHg; ir v (film) 3300 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  0.84 (t,  $\text{CH}_3$ ,  $J=7.0$  Hz), 1.21-1.58 (m, 2 x  $\text{CH}_2$  and NH), 1.76 (t,  $\text{CH}_2$ ,  $J=7.2$  Hz), 2.31-2.52 (m, 2 x  $\text{CH}_2$ ), 3.89 (d,  $\text{CH}_2$ ,  $J=7.2$  Hz), 5.95 (t, 2 x 3-H,  $J=2.4$  Hz), 6.71 (t, 2 x 2-H,  $J=2.4$  Hz); HR-ms  $m/z$ : 180.1654 (Calcd for  $\text{C}_{11}\text{H}_{20}\text{N}_2$ : 180.1626); *Anal.* Calcd for  $\text{C}_{11}\text{H}_{20}\text{N}_2$ : C, 73.28; H, 11.18; N, 15.54. Found C, 72.97; H, 11.33; N, 15.80.

**3c:** yield 0.21 g (44%); bp 78 °C / 0.5 mmHg; ir v (film) 3300 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  0.92 (d, 2 x  $\text{CH}_3$ ,  $J=7.0$  Hz), 1.13-1.62 (m,  $\text{CH}_2$ , CH, and NH), 1.96 (t,  $\text{CH}_2$ ,  $J=7.2$  Hz), 2.59 (t,  $\text{CH}_2$ ,  $J=6.6$  Hz), 2.63 (t,  $\text{CH}_2$ ,  $J=7.2$  Hz), 4.00 (t,  $\text{CH}_2$ ,  $J=7.2$  Hz), 6.17 (t, 2 x 3-H,  $J=2.4$  Hz), 6.69 (t, 2 x 2-H,  $J=2.4$  Hz); HR-ms  $m/z$ : 194.1780 (Calcd for  $\text{C}_{12}\text{H}_{22}\text{N}_2$ : 194.1783); *Anal.* Calcd for  $\text{C}_{12}\text{H}_{22}\text{N}_2$ : C, 74.17; H, 11.41; N, 14.42. Found C, 74.42; H, 11.60; N, 14.67.

**4a:** yield 0.21 g (30%); bp 68 °C / 0.9 mmHg; ir v (film) 3310 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  1.50-1.53 (m,  $\text{CHH}$ ), 1.74-1.84 (m, 2 x  $\text{CHH}$ ), 1.86-1.97 (m, 5 x  $\text{CHH}$  and  $\text{CH}_2$ ), 2.12 (s, NH), 2.17-2.22 (m,  $\text{CHH}$ ), 2.22 (s,  $\text{CH}_3$ ), 2.39 and 2.40 (s,  $\text{CH}_3$ ), 2.53-2.56 (m,  $\text{NCH}_2$ ), 2.90-2.94 (m, 2 x  $\text{NCHH}$ ), 3.15 (t, CH,  $J=7.0$  Hz), 3.88 (t,  $\text{NCH}_2$ ,  $J=7.0$  Hz), 6.12 (t, 3'-H,  $J=2.2$  Hz), 6.54 (t, 4'-H,  $J=2.2$  Hz), 6.58 (t, 5'-H,  $J=2.2$  Hz);  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  21.45 and 25.29, 28.14 and 28.46, 30.68, 31.56 and 31.77 ( $\text{CH}_2$ ), 36.55, 41.74 and 42.15 ( $\text{CH}_3$ ), 47.59, 49.21 and 49.26, 49.44, 55.77 and 56.16 ( $\text{CH}_2$ ), 61.38, 82.09 and 86.55 (CH), 107.29, 118.69 and 118.96, 120.37 and 120.58, 125.30 and 125.53 (pyrrole); HR-ms  $m/z$ : 276.2258 (Calcd for  $\text{C}_{16}\text{H}_{28}\text{N}_4$ : 276.2314); *Anal.* Calcd for  $\text{C}_{16}\text{H}_{28}\text{N}_4$ : C, 69.52; H, 10.21; N, 20.27. Found C, 69.11; H, 9.90; N, 19.98.

**4b:** yield 0.20 g (22%); bp 120 / 0.6 mmHg; ir v (film) 2950 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  0.91 (t, 2 x  $\text{CH}_3$ ,  $J=6.8$  Hz), 1.26-1.45 (m, 3 x  $\text{CH}_2$ ), 1.51-1.63 (m, 2 x  $\text{CH}_2$ ), 1.77-1.99 (m, 3 x  $\text{CH}_2$ ), 2.08-2.17 (m,  $\text{CH}_2$ ), 2.53-2.60 (m, 2 x  $\text{CH}_2$ ), 2.64-2.68 (m,  $\text{CH}_2$ ), 3.08-3.20 (m, 2 x  $\text{CH}_2$ ), 3.85-3.97 (m,  $\text{NCH}_2$  and  $\text{NCHN}$ ), 6.08 (d, 3'-H,  $J=2.2$  Hz), 6.57 (t, 4'-H,  $J=2.2$  Hz), 6.65 (d, 5'-H,  $J=2.2$  Hz). HR-ms  $m/z$ : 360.3254 (Calcd for  $\text{C}_{22}\text{H}_{40}\text{N}_4$  360.3253); *Anal.* Calcd for  $\text{C}_{22}\text{H}_{40}\text{N}_4$ : C, 73.28; H, 11.18; N, 15.54. Found C, 72.88; H, 10.91; N, 15.15.

**4c:** yield 0.25 g (26%); bp 117  $^\circ\text{C}$  / 0.4 mmHg; ir v (film) 2950 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  ( $\text{CDCl}_3$ )  $\delta$  0.88 (d, 2 x  $\text{CH}_3$ ,  $J=6.6$  Hz), 0.89 (d, 2 x  $\text{CH}_3$ ,  $J=6.6$  Hz), 1.07 (s, NH), 1.32-1.37 (m, 2 x  $\text{CH}_2$ ), 1.56-1.65 (m,  $\text{CH}_2$ ), 1.77-2.08 (m, 3 x  $\text{CH}_2$ ), 2.30-2.56 (m,  $\text{CH}_2$ ), 2.57 (t,  $\text{CH}_2$ ,  $J=6.6$  Hz), 2.58 (t,  $\text{CH}_2$ ,  $J=6.6$  Hz), 2.66-3.30 (m,  $\text{CH}_2$  and CH), 3.88 (t,  $\text{CH}_2$ ,  $J=7.0$  Hz), 3.86-3.90 (m,  $\text{CH}_2$ ), 3.95 (t,  $\text{CH}_2$ ,  $J=7.0$  Hz), 4.22 (t,  $\text{NCHN}$ ,  $J=6.0$  Hz), 6.13 (d, 3'-H,  $J=2.2$  Hz), 6.57 (t, 4'-H,  $J=2.2$  Hz), 6.65 (d, 5'-H,  $J=2.2$  Hz); HR-ms  $m/z$ : 388.3561 (Calcd for  $\text{C}_{24}\text{H}_{44}\text{N}_4$  388.3566); *Anal.* Calcd for  $\text{C}_{24}\text{H}_{44}\text{N}_4$ : C, 74.17; H, 11.41; N, 14.42. Found C, 74.52; H, 11.70; N, 14.03.

**General Procedure for 2-Substituted 1-Carboxy-2,3,4,5-tetrahydro-1H-pyrrolo[1,2-a]-[1,4]diazepines (8)** ----- Glyoxalic acid hydrate (7) (0.46 g, 5 mmol) was added dropwise to a stirred solution of **3** (5 mmol) in EtOH (20 ml) at room temperature. The reaction mixture was stirred for 3 h and evaporated under reduced pressure. The resulting residue was washed with  $\text{Et}_2\text{O}$  and recrystallized from solvent.

**8a:** yield 0.72 g (74%) (recryst. from EtOH- $\text{Et}_2\text{O}$ ); mp 167-168  $^\circ\text{C}$ ; ir v (KBr) 1620 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  ( $\text{DMSO-d}_6$ )  $\delta$  1.56-2.01 (m,  $\text{CH}_2$ ), 2.29 (s,  $\text{CH}_3$ ), 3.11-3.46 (m,  $\text{CH}_2$ ), 3.93-4.21 (m,  $\text{CH}_2$ ), 4.82 (s, CH), 5.02-5.35 (br,  $\text{NH}^+$ ), 5.81-6.14 (m, 2 x CH=), 6.69-6.76 (m CH=); FAB-ms  $m/z$ : 195 (M+1) $^+$ ; *Anal.* Calcd for  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}$ : C, 56.59; H, 7.59; N, 13.20. Found C, 56.37; H, 7.39; N, 13.06.

**8b:** yield 0.92 g (78%) (recryst. from THF-petr. ether); mp 138-139  $^\circ\text{C}$ ; ir v (KBr) 1640 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  ( $\text{DMSO-d}_6$ )  $\delta$  0.86-2.20 (m,  $\text{CH}_3$  and 3 x  $\text{CH}_2$ ), 3.61-3.69 (m, 2 x  $\text{CH}_2$ ), 4.10-4.21 (m,  $\text{CH}_2$ ), 5.16 (s, CH), 6.00 (s, CH=), 6.30 (s, CH=), 6.57 (s, CH=), 8.18 (br,  $\text{NH}^+$ ); FAB-ms ( $m/z$ ) 237 (M+1) $^+$ ; *Anal.* Calcd for  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2$ : C, 66.07; H, 8.53; N, 11.85. Found C, 65.85; H, 8.64; N, 11.81.

**8c:** yield 1.13 g (90%) (recryst. from THF-petr. ether); mp 140-141  $^\circ\text{C}$ ; ir v (KBr) 1640 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  ( $\text{DMSO-d}_6$ )  $\delta$  0.82 (d, 2 x  $\text{CH}_3$ ,  $J=4.2$  Hz), 1.16-3.01 (m, 2 x  $\text{CH}_2$  and CH), 3.17-3.43 (m,  $\text{CH}_2$ ), 3.93-4.23 (m,  $\text{CH}_2$ ), 4.80 (s, CH), 5.80-6.13 (m, 2 x CH=), 6.63-6.94 (m, CH= and  $\text{NH}^+$ ); FAB-ms  $m/z$ : 251 (M+1) $^+$ ; *Anal.* Calcd for  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_2$ : C, 67.17; H, 8.86; N, 11.19. Found C, 67.03; H, 8.62; N, 10.97.

**General Procedure for 1-Substituted 7-(1-Substituted Octahydro-2H-pyrido[1,2-a]-pyrimidin-6-yl)-1,3,4,8,9,9a-hexahydro-2H-pyrido[1,2-a]pyrimidines (10a, b) and 1-Substituted 6-(1-Substituted Octahydroimidazo[1,2-a]pyridin-5-yl)-1,2,3,7,8,8a-hexahydroimidazo[1,2-a]pyridines (10c, d)** ----- Glutaraldehyde (9) (0.6 ml, 3 mmol, 50% w/v in water) was added slowly to a stirred solution of **1** (3 mmol) in EtOH (20 ml) containing a drop of AcOH under cooling with ice and water, over 1 h at room temperature under an atmosphere of argon. The reaction mixture was stirred for 12 h, and then evaporated to dryness under reduced pressure. The residue

was dissolved in water (100 ml), and the aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 20 ml). After removal of  $\text{CH}_2\text{Cl}_2$ , the residue was purified by distillation under reduced pressure or recrystallized from EtOH. All compounds are a mixture of two isomers.

**10a:** yield 0.58 g (64%); bp 90 °C / 0.4 mmHg; ir v (film) 1662 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  1.33-1.47 (m, 2 x  $\text{CH}_2$ ), 1.55-1.79 (m,  $\text{CH}_2$ ), 1.81-1.89 (m, 2 x  $\text{CH}_2$ ), 1.91-1.95 (m, 2 x  $\text{CH}_2$ ), 1.98-2.09 (m, 2 x  $\text{CH}_2$ ), 2.22, 2.26, 2.28, and 2.56 (s, 2 x  $\text{NCH}_3$ ), 2.29-2.86 (m, CH), 2.87-3.12 (m, 2 x  $\text{NCHN}$  and 2 x  $\text{NCH}_2$ ), 5.57 and 5.60 (s,  $\text{CH}=\text{}$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  23.16 and 23.32, 23.89, 24.17 and 24.29, 24.53 and 24.59, 26.11, 26.55 and 26.81, 28.26, 29.90, 31.79 and 31.89 (7 x  $\text{CH}_2$ ), 39.50 and 39.95, 40.36 and 42.18 (2 x  $\text{NCH}_3$ ), 52.22 and 52.26, 52.40, 55.84 and 56.00, 56.25 and 56.30 ( $\text{NCH}_2$ ), 68.00 and 68.12 ( $\text{NCH}$ -), 76.84 and 77.87 ( $\text{NCHN}$ ), 84.15 and 84.23 ( $\text{NCHN}$ ), 113.57 and 113.93 ( $=\text{C}$ -), 132.09 and 132.98 ( $=\text{CH}$ -); EI-ms  $m/z$ : 304 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{18}\text{H}_{32}\text{N}_4$ : C, 71.01; H, 10.59; N, 18.40. Found C, 70.88; H, 10.36; N, 18.14.

**10b:** yield 0.74 g (64%); bp 108 °C / 0.25 mmHg; ir v (film) 1650 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  0.93 and 1.03 (t, 2 x  $\text{CH}_3$ ,  $J=7.3$  Hz), 1.16-1.62 (m, 8 x  $\text{CH}_2$ ), 1.62-1.96 (m, 2 x  $\text{CH}_2$ ), 1.97-2.11 (m, 2 x  $\text{CH}_2$ ), 2.11-2.80 (m, 4 x  $\text{CH}_2$  and CH), 2.80-3.20 (m, 2 x  $\text{NCHN}$  and  $\text{CH}_2$ ), 5.83 and 5.70 (s,  $\text{CH}=\text{}$ ); HR-ms  $m/z$ : 388.3557 (Calcd for  $\text{C}_{24}\text{H}_{44}\text{N}_4$  388.3566); Anal. Calcd for  $\text{C}_{24}\text{H}_{44}\text{N}_4$ : C, 74.17; H, 11.41; N, 14.42. Found C, 74.49; H, 11.63; N, 14.17.

**10c:** yield 0.47 g (52%); bp 156-157 °C / 1.5 mmHg; ir v (film) 1660 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  1.09 (t,  $\text{CH}_3$ ,  $J=7.3$  Hz), 1.15 (t,  $\text{CH}_3$ ,  $J=7.3$  Hz), 1.18-1.44 (m, 2 x  $\text{CH}_2$ ), 1.80-1.85 (m,  $\text{CH}_2$ ), 1.89-2.43 (m, 5 x  $\text{CH}_2$ ), 2.76-2.89 (m,  $\text{CH}_2$  and CH), 3.01-3.14 (m,  $\text{CH}_2$ ), 3.17-3.24 (m,  $\text{CH}_2$ ), 3.28 (q, CH,  $J=6.6$  Hz), 3.47-3.51 (m, CH), 5.97 (s,  $\text{CH}=\text{}$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  13.68, 13.75 ( $\text{CH}_3$ ), 19.51 and 20.33, 22.89 and 23.03, 26.99 and 27.17, 29.19 and 29.30, 30.95 and 31.65, (C- $\text{CH}_2$ -C), 46.58 and 46.62, 47.88, 48.66, 48.85, 49.48, 51.20 and 51.30 ( $\text{NCH}_2$ ), 66.79 and 67.32 (CHN), 77.40 and 77.75, 83.83, and 84.17 ( $\text{NCHN}$ ), 112.11 and 112.46 (-C-), 128.95 and 129.17 ( $\text{CH}=\text{}$ ); EI-ms  $m/z$  304 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{18}\text{H}_{32}\text{N}_4$ : C, 71.00; H, 10.59; N, 18.40. Found C, 71.23; H, 10.75; N, 18.32.

**10d:** yield 0.60 g (60%); mp 122 °C; ir v (KBr) 3500 (OH), 1650 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  1.12-1.36 (m,  $\text{CH}_2$ ), 1.38-1.61 (m,  $\text{CH}_2$ ), 1.84-1.94 (m,  $\text{CH}_2$ ), 1.94-2.04 (m,  $\text{CH}_2$ ), 2.04-2.60 (m, 4 x  $\text{CH}_2$ ), 2.85-3.11 (m, 2 x  $\text{CH}_2$ ), 3.12-3.54 (m, CH and 2 x  $\text{NCH}_2\text{N}$ ), 3.56-3.75 (m, 2 x  $\text{NCH}_2\text{N}$ ), 6.00 and 5.99 (s,  $=\text{CH}$ );  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ )  $\delta$  19.45 and 19.86, 22.74, 26.55 and 26.95, 28.92, 30.65 and 31.11, 48.72, 48.81 and 48.99, 49.64, 51.26, 54.69, 55.17, 59.52, 59.60 ( $\text{CH}_2$ ), 66.83 and 67.34, 76.84 and 77.19, 83.61 and 83.85, 128.99 and 129.34 (CH), 111.64 (-C-); EI-ms  $m/z$ : 336 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{18}\text{H}_{32}\text{N}_4\text{O}_2$ : C, 64.25; H, 9.59; N, 16.65. Found C, 64.32; H, 9.56; N, 16.59.

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