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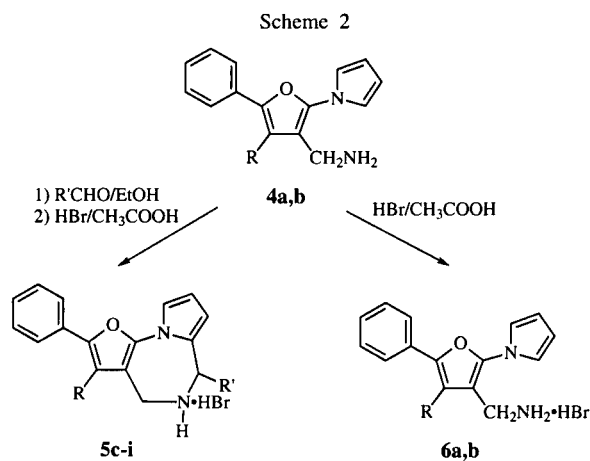
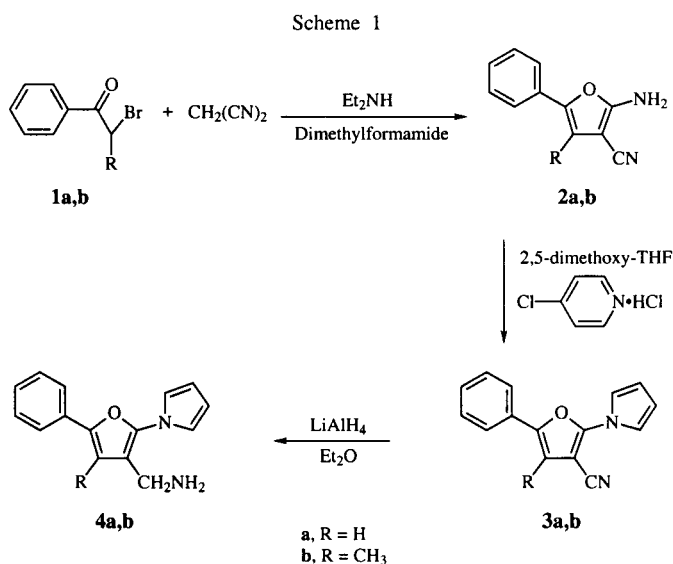
The synthetic pathway leading to 5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepines is described in four steps starting from  $\alpha$ -bromophenones via 2-amino-3-furonitriles.

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Within the framework of our research program concerning the synthesis and the biological evaluation of new tricyclic systems with therapeutic potentiality, we recently described the synthesis of pyrrolothienodiazepines [1-3], pyrrolothienopyrazines [4-6], pyrrolobenzodiazepines [7-10], cyclopentabenzodiazepines [11-12] and tetrahydrodibenzodiazepines [13]. We extended this work to the furan series and we recently published the first synthesis of 4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepines [14]. In the prolongation of this work we present here the synthesis of the first representatives of their homologues 5,6-dihydro derivatives. These new compounds are obtained in four steps starting from  $\alpha$ -bromophenones. Thus,  $\alpha$ -bromoacetophenone **1a** and the 2-bromopropiophenone **1b** provide, by reaction with malonic nitrile according to modified conditions of Gewald [15], the corresponding 2-amino-3-furonitriles **2a,b** with yields of about 60% (Scheme 1). The implementation of the reaction of Clauson Kaas [16] by means of 2,5-dimethoxytetrahydrofuran in dioxan in the presence of 4-chloropyridinium chloride allows the synthesis of the 2-pyrrolyl-3-furonitriles **3a,b** with yields close to 80%. The hydrogenation of

the cyano group with lithium aluminium hydride in refluxing ether leads to the aminomethylfurans **4a,b**.

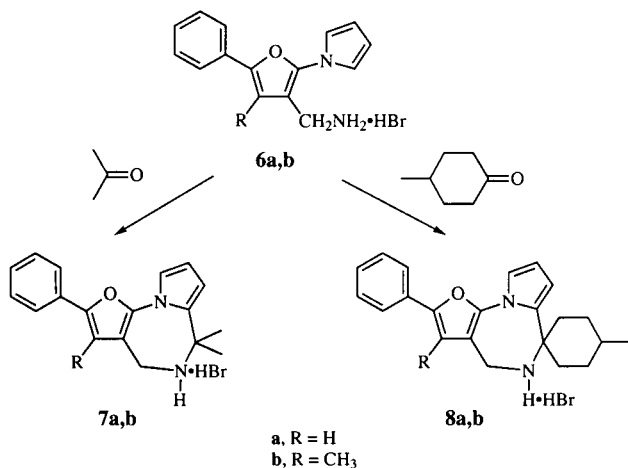
The aminomethylfurans **4a,b** treated by aromatic aldehydes in refluxing ethanol furnish the not isolated Schiff's bases which undergo *in situ* an intramolecular cyclization by means of hydrobromic acid in acetic acid, thus leading to the 6-aryl-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepines **5c-i** in high yields (Scheme 2).



- a**, R = H  
**b**, R = CH<sub>3</sub>  
**c**, R = H, R' = 3-Chlorophenyl  
**d**, R = H, R' = piperonyl  
**e**, R = H, R' = 3,4,5-trimethoxyphenyl  
**f**, R = H, R' = 2-thienyl  
**g**, R = CH<sub>3</sub>, R' = 3-Chlorophenyl  
**h**, R = CH<sub>3</sub>, R' = piperonyl  
**i**, R = CH<sub>3</sub>, R' = 2-thienyl

The reaction cannot be conducted in an identical manner with ketones to carry out the synthesis of disubstituted derivatives in position 6; it is appropriate to prepare beforehand hydrobromides **6a,b** of the aminomethylfurans **4a,b** by means of hydrobromic acid in acetic acid (Scheme 3). When the latter are subjected to a prolonged reflux in acetone or 4-methylcyclohexanone, they lead respectively to the diazepines **7a,b** and **8a,b**. The evaluation of the biological properties of these compounds is currently studied.

Scheme 3



## EXPERIMENTAL

## General Methods.

Melting points were taken on a Köfler bank and are uncorrected. Infrared spectra were recorded on a Philips PU 9716 apparatus and only noteworthy absorptions (reciprocal centimeters) are listed. The nmr spectra were recorded on a Jeol LA 400 using tetramethylsilane as an internal standard. Chemical shifts are reported in ppm downfield ( $\delta$ ) from tetramethylsilane.

2-Amino-5-phenyl-3-furonitrile (**2a**).

To a solution of  $\alpha$ -bromoacetophenone (**1a**) (9.35 g, 0.050 mole) and malononitrile (3.30 g, 0.050 mole) in dimethylformamide (20 ml), was added diethylamine (15 ml, 0.150 mole) at such a rate that the temperature stayed below 40°. The reaction mixture was then stirred at room temperature for 1 hour and poured into water (60 ml). The resulting precipitate was filtered, washed with water and dried. The white solid was recrystallized from ethanol to give 5.40 g (63%) of **2a**, mp 200°; ir (potassium bromide):  $\nu$  3440 (NH<sub>2</sub>), 2210 (CN) cm<sup>-1</sup>; <sup>1</sup>H-nmr (dimethyl-d<sub>6</sub> sulfoxide):  $\delta$  7.42-7.24 (m, 7H, C<sub>6</sub>H<sub>5</sub> and NH<sub>2</sub>), 6.70 (s, 1H, H<sub>4</sub>).

*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O: C, 71.74; H, 4.35; N, 15.22. Found: C, 71.61; H, 4.52; N, 15.38.

2-Amino-4-methyl-5-phenyl-3-furonitrile (**2b**).

2-Bromopropiophenone (**1b**) (4.25 g, 0.020 mole) was converted to **2b** following the procedure described for the preparation of **2a**, using malononitrile (1.30 g, 0.020 mole) and diethylamine (6 ml, 0.060 mole). This gave 2.50 g (64%) of **2b** (white solid), mp 158° (ether); ir (potassium bromide):  $\nu$  3420 (NH), 2210 (CN) cm<sup>-1</sup>; <sup>1</sup>H-nmr (dimethyl-d<sub>6</sub> sulfoxide):  $\delta$  7.53 (s, 2H, NH<sub>2</sub>), 7.43-7.18 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 2.15 (s, 3H, CH<sub>3</sub>).

*Anal.* Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O: C, 72.73; H, 5.05; N, 14.14. Found: C, 72.59; H, 4.88; N, 14.31.

5-Phenyl-2-(1-Pyrrolyl)-3-furonitrile (**3a**).

A solution of 2-amino-5-phenyl-3-furonitrile (**2a**) (8 g, 0.043 mole), 2,5-dimethoxytetrahydrofuran (5.6 ml, 0.043 mole) and 4-chloropyridinium chloride (3.15 g, 0.021 mole) in dioxane

(150 ml) was heated at 70° under argon for 1.5 hours. The dioxane was eliminated under reduced pressure, the residue taken up in ether (150 ml) and extracted with water (3 x 150 ml). The organic layer was dried (magnesium sulfate) and evaporated to yield 8.05 g (79%) of **3a** (yellow oil); ir (potassium bromide):  $\nu$  2230 (C=N) cm<sup>-1</sup>; <sup>1</sup>H-nmr (dimethyl-d<sub>6</sub> sulfoxide):  $\delta$  7.80 (t, 2H, H<sub>2</sub> and H<sub>5</sub>), 7.50-7.14 (m, 6H, C<sub>6</sub>H<sub>5</sub> and H<sub>4</sub>), 6.48 (t, 2H, H<sub>3</sub> and H<sub>4</sub>).

*Anal.* Calcd. for C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O: C, 76.92; H, 4.27; N, 11.96. Found: C, 77.10; H, 4.15; N, 12.19.

4-Methyl-5-phenyl-2-(1-pyrrolyl)-3-furonitrile (**3b**).

2-Amino-4-methyl-5-phenyl-3-furonitrile (**2b**) (10 g, 0.050 mole) was converted to **3b** following the procedure described for the preparation of **3a**, using 2,5-dimethoxytetrahydrofuran (6.5 ml, 0.050 mole) and 4-chloropyridinium chloride (3.75 g, 0.025 mole). This gave 10.50 g (84%) of **3b** (yellow crystals), mp 103° (ether); ir (potassium bromide): 2210 (CN) cm<sup>-1</sup>; <sup>1</sup>H-nmr (dimethyl-d<sub>6</sub> sulfoxide):  $\delta$  7.39-7.10 (m, 7H, H<sub>2</sub>, H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub>), 6.37 (t, 2H, H<sub>3</sub> and H<sub>4</sub>), 2.23 (s, 3H, CH<sub>3</sub>).

*Anal.* Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O: C, 77.42; H, 4.84; N, 11.29. Found: C, 77.60; H, 4.98; N, 11.05.

1-[5-Phenyl-2-(1-pyrrolyl)-3-furyl]methylamine (**4a**).

A solution of 5-phenyl-2-(1-pyrrolyl)-3-furonitrile (**3a**) (7 g, 0.030 mole) in anhydrous diethyl ether (100 ml) was slowly added to a solution of lithium aluminium hydride (2.25 g, 0.060 mole) in anhydrous diethyl ether (150 ml). The resulting mixture was heated at reflux for 3 hours. After cooling in an ice bath, it was carefully poured into water (50 ml). The precipitate was filtered, the organic layer was washed with water (2 x 150 ml), dried (magnesium sulfate) and evaporated under reduced pressure to give 4.40 g (62%) of **4a** as a yellow oil; ir (potassium bromide):  $\nu$  3380 (NH<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H-nmr (dimethyl-d<sub>6</sub> sulfoxide):  $\delta$  7.71 (t, 2H, H<sub>2</sub> and H<sub>5</sub>), 7.40-7.13 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 6.35 (t, 2H, H<sub>3</sub> and H<sub>4</sub>), 3.57 (s, 2H, CH<sub>2</sub>), 1.81 (s, 2H, NH<sub>2</sub>).

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O: C, 75.63; H, 5.88; N, 11.76. Found: C, 75.82; H, 6.02; N, 11.59.

1-[4-Methyl-5-phenyl-2-(1-pyrrolyl)-3-furyl]methylamine (**4b**).

4-Methyl-5-phenyl-2-(1-pyrrolyl)-3-furonitrile (**3b**) (6 g, 0.024 mole) was converted to **4b** following the procedure described for the preparation of **4a**, using lithium aluminium hydride (1.80 g, 0.048 mole). This gave 4.70 g (77%) of **4b** (yellow oil); ir (potassium bromide):  $\nu$  3350 (NH<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H-nmr (dimethyl-d<sub>6</sub> sulfoxide):  $\delta$  7.39-7.09 (m, 7H, C<sub>6</sub>H<sub>5</sub>, H<sub>2</sub> and H<sub>5</sub>), 6.19 (t, 2H, H<sub>3</sub> and H<sub>4</sub>), 3.40 (s, 2H, CH<sub>2</sub>), 2.37 (t, 2H, NH<sub>2</sub>), 2.13 (s, 3H, CH<sub>3</sub>).

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O: C, 76.19; H, 6.35; N, 11.11. Found: C, 76.02; H, 6.12; N, 10.88.

2-Phenyl-5,6-dihydro-4H-furo[3,2-f]pyrrolo[1,2-a][1,4]-diazepine Hydrobromides **5c-f**.

## General Procedure.

A solution of 1-[5-phenyl-2-(1-pyrrolyl)-3-furyl]methylamine (**4a**) (2 g, 0.0084 mole) and the appropriate aldehyde (1 equivalent) in ethanol (20 ml) was heated at reflux for 2 hours. After cooling to room temperature we added slowly hydrobromic acid (4 ml, 0.0164 mole) in acetic acid solution (33%). The reaction mixture was allowed to stir at room temperature for 0.5 hour. The resulting precipitate was collected, dried and recrystallized to give **5c-f**.

6-(3-Chlorophenyl)-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**5c**).

When 3-chlorobenzaldehyde (0.95 ml, 0.0084 mole) was used, white crystals were obtained (39%), mp >260° (ethanol); ir (potassium bromide):  $\nu$  3380 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  10.45 (s, 2H,  $\text{NH}_2^+$ ), 7.79-7.31 (m, 10H,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4$  and  $\text{H}_9$ ), 7.09 (s, 1H,  $\text{H}_3$ ), 6.30 (s, 1H,  $\text{H}_7$ ), 6.12 (s, 1H,  $\text{H}_6$ ), 5.60 (s, 1H,  $\text{H}_8$ ), 4.58-4.24 (m, 2H,  $\text{H}_4$ ).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{OClBr}$ : C, 59.80; H, 4.08; N, 6.34. Found: C, 60.02; H, 4.18; N, 6.51.

6-(3',4'-Methylenedioxyphenyl)-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**5d**).

When piperonal (1.25 g, 0.0084 mole) was used, white crystals were obtained (43%), mp >260° (2-propanol); ir (potassium bromide):  $\nu$  3320 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  10.34 (s, 2H,  $\text{NH}_2^+$ ), 7.78-6.95 (m, 10H,  $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_4$ ,  $\text{H}_9$  and  $\text{H}_3$ ), 6.29 (dd, 1H,  $\text{H}_7$ ), 6.10 (s, 2H,  $\text{OCH}_2\text{O}$ ), 6.04 (s, 1H,  $\text{H}_6$ ), 5.73 (s, 1H,  $\text{H}_8$ ), 4.56-4.17 (m, 2H,  $\text{H}_4$ ).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}_3\text{Br}$ : C, 61.20; H, 4.21; N, 6.21. Found: C, 61.01; H, 4.08; N, 6.50.

2-Phenyl-6-(3',4',5'-trimethoxyphenyl)-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**5e**).

Using 3,4,5-trimethoxybenzaldehyde (1.70 g, 0.0084 mole), we obtained white crystals (46%), mp >260° (ethanol); ir (potassium bromide):  $\nu$  3410 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  10.26 (s, 2H,  $\text{NH}_2^+$ ), 7.79-7.35 (m, 6H,  $\text{C}_6\text{H}_5$  and  $\text{H}_9$ ), 7.07 (s, 1H,  $\text{H}_3$ ), 6.90 (s, 2H,  $\text{C}_6\text{H}_2$ ), 6.31 (dd, 1H,  $\text{H}_7$ ), 5.92 (s, 1H,  $\text{H}_6$ ), 5.77 (dd, 1H,  $\text{H}_8$ ), 3.76 (s, 6H, 2 $\text{CH}_3$ ), 3.70 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_4\text{Br}$ : C, 60.36; H, 5.03; N, 5.63. Found: C, 60.14; H, 5.20; N, 5.40.

2-Phenyl-6-(2-thienyl)-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**5f**).

When thiophene-2-carboxaldehyde (0.80 ml, 0.0084 mole) was used, yellow crystals were obtained (35%), mp >260° (2-propanol); ir (potassium bromide):  $\nu$  3140 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  10.46 (s, 2H,  $\text{NH}_2^+$ ), 7.77-7.13 (m, 9H,  $\text{C}_6\text{H}_5$ ,  $\text{H}_9$ ,  $\text{H}_2$ ,  $\text{H}_3$  and  $\text{H}_4$ ), 7.02 (s, 1H,  $\text{H}_3$ ), 6.62 (s, 1H,  $\text{H}_6$ ), 6.35 (dd, 1H,  $\text{H}_7$ ), 6.17 (m, 1H,  $\text{H}_8$ ), 4.50-4.10 (m, 2H,  $\text{H}_4$ ).

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_2\text{OSBr}$ : C, 58.11; H, 4.12; N, 6.78. Found: C, 57.89; H, 4.01; N, 6.51.

3-Methyl-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromides **5g-i**.

#### General Procedure.

A solution of 1-[4-methyl-5-phenyl-2-(1-pyrrolyl)-3-furyl]methylamine (**4b**) (2.5 g, 0.0100 mole) and the appropriate aldehyde (1 equivalent) in ethanol (20 ml) was heated at reflux for 2 hours. After cooling to room temperature we added slowly a solution of 33% hydrobromic acid in glacial acetic acid (5 ml). The reaction mixture was allowed to stir at room temperature for 0.5 hour. The resulting precipitate was collected, dried and recrystallized to give **5g-i**.

6-(3-Chlorophenyl)-3-methyl-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**5g**).

Using 3-chlorobenzaldehyde (1.15 ml, 0.0100 mole), we obtained white crystals (51%), mp >260° (methanol); ir (potas-

sium bromide):  $\nu$  3270 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  10.51 (s, 2H,  $\text{NH}_2^+$ ), 7.72-7.29 (m, 10H,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4$  and  $\text{H}_9$ ), 6.28 (m, 1H,  $\text{H}_7$ ), 6.07 (s, 1H,  $\text{H}_6$ ), 5.59 (m, 1H,  $\text{H}_8$ ), 4.53-4.25 (m, 2H,  $\text{H}_4$ ), 2.21 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{OClBr}$ : C, 60.59; H, 4.39; N, 6.15. Found: C, 60.72; H, 4.20; N, 6.01.

6-(3',4'-Methylenedioxyphenyl)-3-methyl-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**5h**).

When piperonal (1.50 g, 0.0100 mole) was used, white crystals were obtained (61%), mp >260° (acetonitrile); ir (potassium bromide):  $\nu$  3210 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  10.36 (s, 2H,  $\text{NH}_2^+$ ), 7.71-6.93 (m, 9H,  $\text{C}_6\text{H}_5$ ,  $\text{H}_5$ ,  $\text{H}_6$ ,  $\text{H}_1$  and  $\text{H}_9$ ), 6.32 (m, 1H,  $\text{H}_7$ ), 6.10 (s, 2H,  $\text{OCH}_2\text{O}$ ), 5.96 (s, 1H,  $\text{H}_6$ ), 5.73 (m, 1H,  $\text{H}_8$ ), 4.49-4.16 (m, 2H,  $\text{H}_4$ ), 2.21 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3\text{Br}$ : C, 61.93; H, 4.52; N, 6.02. Found: C, 62.17; H, 4.31; N, 6.20.

3-Methyl-2-phenyl-6-(2-thienyl)-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**5i**).

When thiophene-2-carboxaldehyde (0.90 g, 0.0100 mole) was used, white crystals were obtained (56%), mp >260° (ethanol); ir (potassium bromide):  $\nu$  3160 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  10.53 (s, 2H,  $\text{NH}_2^+$ ), 7.68-7.14 (m, 9H,  $\text{C}_6\text{H}_5$ ,  $\text{H}_2$ ,  $\text{H}_3$ ,  $\text{H}_4$  and  $\text{H}_9$ ), 6.56 (s, 1H,  $\text{H}_6$ ), 6.33 (m, 1H,  $\text{H}_7$ ), 6.17 (m, 1H,  $\text{H}_8$ ), 4.46-4.02 (m, 2H,  $\text{H}_4$ ), 2.17 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{19}\text{N}_2\text{OSBr}$ : C, 59.02; H, 4.45; N, 6.56. Found: C, 58.87; H, 4.28; N, 6.70.

1-[5-Phenyl-2-(1-pyrrolyl)-3-furyl]methylamine Hydrobromide (**6a**).

To a solution of 1-[5-phenyl-2-(1-pyrrolyl)-3-furyl]methylamine (**4a**) (4 g, 0.0168 mole) in ethanol (20 ml), we added at room temperature hydrobromic acid (6 ml, 0.0246 mole) in acetic acid solution (33%). The mixture was stirred at room temperature for 0.5 hour. The resulting white precipitate was collected, dried and recrystallized from 2-propanol to yield 4 g (75%) of **6a**, mp >260°; ir (potassium bromide):  $\nu$  3220 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  8.36 (s, 3H,  $\text{NH}_3^+$ ), 7.67-7.23 (m, 8H,  $\text{C}_6\text{H}_5$ ,  $\text{H}_4$ ,  $\text{H}_2$  and  $\text{H}_5$ ), 6.35 (s, 2H,  $\text{H}_3$  and  $\text{H}_4$ ), 3.89 (s, 2H,  $\text{CH}_2$ ).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OBr}$ : C, 56.43; H, 4.70; N, 8.78. Found: C, 56.77; H, 4.58; N, 8.53.

1-[4-Methyl-5-phenyl-2-(1-pyrrolyl)-3-furyl]methylamine Hydrobromide (**6b**).

The amine **4b** (5 g, 0.0198 mole) was converted to **6b** using the procedure described for the preparation of **6a**. This gave 4.60 g (70%) of **6b** (white solid), mp >260° (ethanol); ir (potassium bromide):  $\nu$  3270 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (dimethyl- $d_6$  sulfoxide):  $\delta$  8.22 (s, 3H,  $\text{NH}_3^+$ ), 7.64-7.28 (m, 7H,  $\text{C}_6\text{H}_5$ ,  $\text{H}_2$  and  $\text{H}_5$ ), 6.35 (s, 2H,  $\text{H}_3$  and  $\text{H}_4$ ), 3.91 (s, 2H,  $\text{CH}_2$ ), 2.33 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{OBr}$ : C, 57.66; H, 5.11; N, 8.41. Found: C, 57.40; H, 5.38; N, 8.55.

6,6-Dimethyl-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**7a**).

1-[5-Phenyl-2-(1-pyrrolyl)-3-furyl]methylamine Hydrobromide (**6a**) (1 g, 0.0031 mole) in acetone (30 ml) was heated at reflux for 10 hours. The resulting precipitate was collected, dried and recrystallized from methanol to give 0.75 g (65%) of **7a** (white solid), mp >260°; ir (potassium bromide):  $\nu$  3220 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$

(dimethyl- $d_6$  sulfoxide):  $\delta$  9.92 (s, 2H,  $\text{NH}_2^+$ ), 7.76-7.06 (m, 7H,  $\text{C}_6\text{H}_5$ ,  $\text{H}_9$  and  $\text{H}_3$ ), 6.39 (m, 1H,  $\text{H}_7$ ), 6.31 (m, 1H,  $\text{H}_8$ ), 4.30 (s, 2H,  $\text{H}_4$ ), 1.71 (s, 6H,  $2\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{OBr}$ : C, 60.17; H, 5.29; N, 7.80. Found: C, 59.93; H, 5.41; N, 7.65.

3,6,6-Trimethyl-2-phenyl-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**7b**).

1-[4-Methyl-5-phenyl-2-(1-pyrrolyl)-3-furyl]methylamine Hydrobromide (**6b**) (1 g, 0.0030 mole) was converted to **7b** using the procedure described for the preparation of **7a**. This gave 0.65 g (60%) of **7b** (white solid), mp  $234^\circ$  (2-propanol); ir (potassium bromide):  $\nu$  3240 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (dimethyl- $d_6$  sulfoxide):  $\delta$  9.89 (s, 2H,  $\text{NH}_2^+$ ), 7.72-7.27 (m, 6H,  $\text{C}_6\text{H}_5$  and  $\text{H}_9$ ), 6.38 (m, 1H,  $\text{H}_7$ ), 6.28 (m, 1H,  $\text{H}_8$ ), 4.33 (s, 2H,  $\text{H}_4$ ), 2.23 (s, 3H,  $\text{CH}_3$ ), 1.69 (s, 6H,  $2\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{OBr}$ : C, 61.13; H, 5.63; N, 7.51. Found: C, 60.91; H, 5.46; N, 7.68.

2-Phenyl-6-[spiro-(4'-methylcyclohexane)]-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**8a**).

1-[5-Phenyl-2-(1-pyrrolyl)-3-furyl]methylamine Hydrobromide (**6a**) (1 g, 0.0031 mole) in 4-methylcyclohexanone (30 ml) was heated at reflux for 4 hours. The resulting precipitate was collected, dried and recrystallized from 2-propanol to give 0.75 g (58%) of **8a** (white solid), mp  $>260^\circ$ ; ir (potassium bromide):  $\nu$  3240 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr (dimethyl- $d_6$  sulfoxide):  $\delta$  9.47 (s, 2H,  $\text{NH}_2^+$ ), 7.77-7.26 (m, 6H,  $\text{C}_6\text{H}_5$  and  $\text{H}_9$ ), 7.06 (s, 1H,  $\text{H}_3$ ), 4.29 (s, 2H,  $\text{H}_4$ ), 2.23-1.50 (m, 9H,  $\text{C}_6\text{H}_9$ ), 0.95 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{25}\text{N}_2\text{OBr}$ : C, 63.92; H, 6.05; N, 6.78. Found: C, 64.09; H, 5.91; N, 6.62.

3-Methyl-2-phenyl-6-[spiro-(4'-methylcyclohexane)]-5,6-dihydro-4*H*-furo[3,2-*f*]pyrrolo[1,2-*a*][1,4]diazepine Hydrobromide (**8b**).

1-[4-Methyl-5-phenyl-2-(1-pyrrolyl)-3-furyl]methylamine Hydrobromide (**6b**) (1 g, 0.0030 mole) was converted to **8b** using the procedure described for the preparation of **8a**. This gave 0.70 g (54%) of **8b** (white solid), mp  $>260^\circ$  (ethanol); ir (potassium bromide):  $\nu$  3210 (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (dimethyl- $d_6$  sulfoxide):  $\delta$  9.48 (s, 2H,  $\text{NH}_2^+$ ), 7.70-7.31 (m, 6H,  $\text{C}_6\text{H}_5$  and  $\text{H}_9$ ), 6.43 (m, 1H,  $\text{H}_7$ ), 6.33 (m, 1H,  $\text{H}_8$ ), 4.24 (s, 2H,  $\text{H}_4$ ), 2.23-1.50 (m, 12H,  $\text{C}_6\text{H}_9$  and  $\text{CH}_3$ ), 1.09 (s, 3H,  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{OBr}$ : C, 64.79; H, 6.10; N, 6.57. Found: C, 64.92; H, 5.96; N, 6.78.

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