Pyrrolothieno[1,4]diazepines. Part V. Study of their Chemical Reactivity and First Synthesis of Oxazino[4,3-*c*]pyrrolo[1,2-*a*]thieno[2,3-*f*][1,4]diazepines

Michel Boulouard, Patrick Dallemagne* and Sylvain Rault

Centre d'Etudes et de Recherche sur le Médicament de Normandie,
U.F.R. des Sciences Pharmaceutiques - 1 rue Vaubénard 14032 Caen, France

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The study of the chemical reactivity of methyloxopyrrolothienodiazepinones led to new derivatives such as oximes, methyloximes, hydrazones and alcohols and also, according to an intramolecular cyclization, to new oxazino[4,3-*c*]pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepines.

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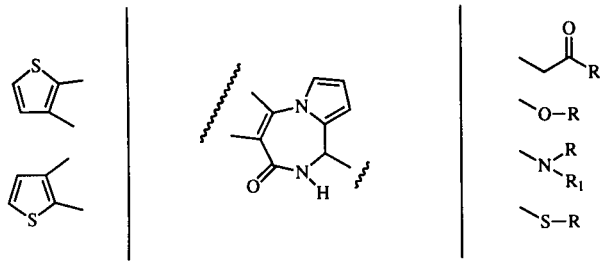
We have described, during the past several years, synthetic routes to numerous pyrrolo[1,2-*a*]thieno[3,2-*f*] and [2,3-*f*][1,4]diazepines, bearing on their C6 position either methyloxo, alkoxy, amino or mercapto groups (Scheme 1) [1,2,3,4]. We wish to complete herein this study describing the chemical reactivity of the methyloxo group of the diazepines **I** (Scheme 2) and particularly its involvement in the synthesis of novel oxazino[4,3*c*]pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepinediones.

Scheme 1



Treatment of the methyloxodiazepines **I**, with hydroxylamine hydrochloride or methoxylamine hydrochloride in refluxing ethanol and in the presence of an aqueous sodium acetate solution, afforded the oximes **II** and the methyloximes **III** respectively (Scheme 2). The ^{1}H-nmr study of the crude products **6**, **7**, **11-15** indicated a mixture of *E* and *Z* forms in various proportions, while **8**, **9** and **10** were obtained as unique isomers (Scheme 3).

On the ^{1}H-nmr spectrum of the mixture **6E** and **6Z** in DMSO-d_6 solution, the methylene protons of the side chain appeared as multiplets at 2.77 ppm for the major form (80%) and 2.86 ppm for the minor one (20%). On the other hand, the methyl group exhibited two singlets at 1.77 ppm for the major form and 1.74 for the minor one. These data were in favor of an *E* structure for the major isomer, whose nitrogen atom of the oxime group contributed to shield the signal of the α methylene group. In the minor *Z* form, the nitrogen atom of the oxime exerted the same shielding effect upon the methyl singlet. In DMSO-d_6 solution, the signals of the other protons were not affected by the *E*/*Z* isomerism.

In deuteriochloroform solution, the ^{1}H-nmr spectrum of **6** exhibited two very different systems for the methylene protons of the side chain. The signal of these protons appeared for the *E* form as a multiplet centered at 2.88 ppm, while, in the *Z* form, the methylene system involved two double doublets at 3.79 and 2.47 ppm (Scheme 4). The more deshielded proton (Ha), which appeared like an apparent triplet, was affected with two equal coupling constants, *gem* (13 Hz) with Hb and *cis* (13 Hz) with H6. The double doublet of Hb shown one *gem* and one *trans* (3 Hz with H6) coupling constants. We explain the aspect of the methylene system in the *Z* form by the hydrogen bond that could be involved, in this solvent, between the endocyclic NH group and the OH group of the oxime, bringing rigidity to the side chain.

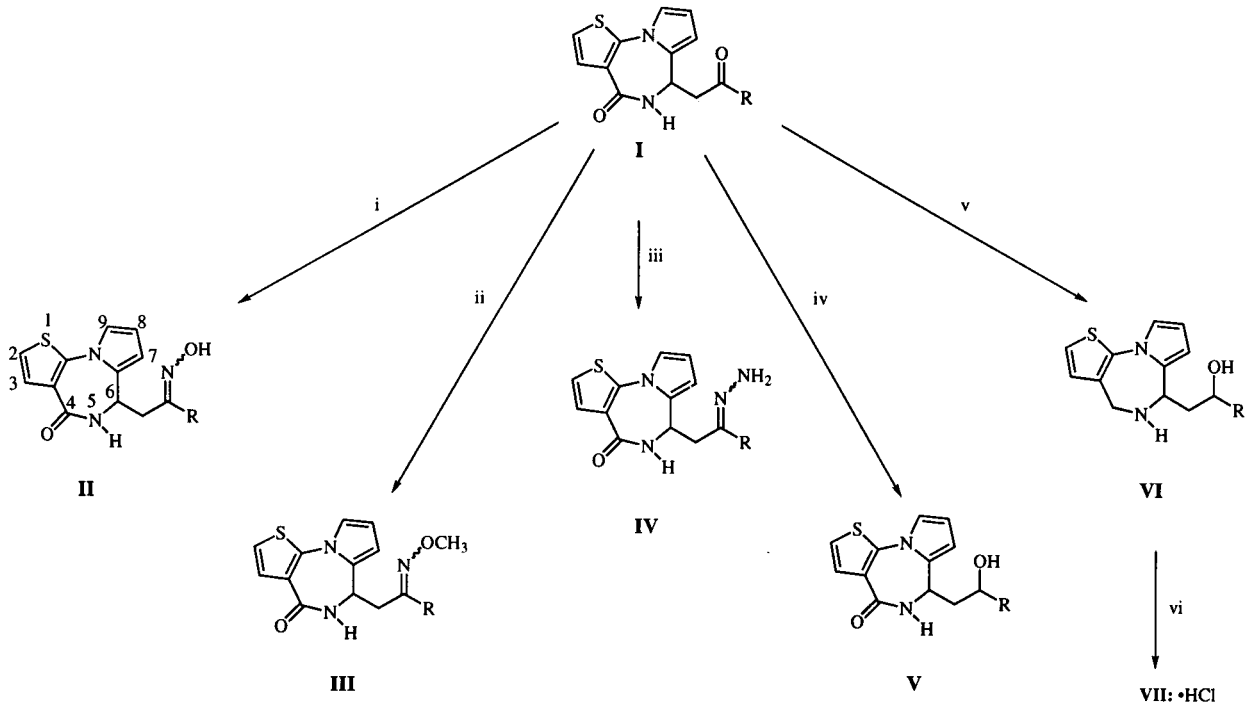
Applied to the ^{1}H-nmr spectra of the oximes **II** and methyloximes **III**, these considerations permitted the establishment of their *E* or *Z* structure.

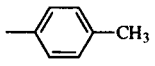
The hydrazones **IV** were obtained starting from **I** by treatment with hydrazine hydrate in refluxing ethanol (Scheme 2). Only one isomer was formed for each product **16-20**, however it has not been possible to establish their **E** or **Z** structure, specially due to their insolubility in deuteriochloroform.

Using sodium borohydride in methanol at room temperature, hydrogenation of **I** led to the alcohols **V**. On the other hand, treatment of **I** with lithium aluminium hydride in refluxing dichloromethane/ether afforded the hydroxydiazepines **VI**. The free bases were quickly unstable (except **30**) and were converted into their ammonium chlorides **VII**.

Reaction of phosgene on a toluene solution of alcohols **V** led to different products depending on the nature of the alkyl or aryl substituents of the side chain (Scheme 5). Thus, the hydroxyl group of **24** and **25** was substituted under these conditions by a chlorine atom yielding **38** and **39**, while the alkylhydroxydiazepines **21-23** underwent a

Scheme 2



R	I	II	III	IV	V	VI	VII
$-CH_3$	1	6	11	16	21	26	31
$-CH_2CH_2CH_3$	2	7	12	17	22	27	32
	3	8	13	18	23	28	33
	4	9	14	19	24	29	34
	5	10	15	20	25	30	–

i: NH_2OH, $HCl/CH_3CO_2Na/CH_3CH_2OH/H_2O$
ii: NH_2OCH_3, $HCl/CH_3CO_2Na/CH_3CH_2OH/H_2O$
iii: $(NH_2)_2$, H_2O/CH_3CH_2OH
iv: $NaBH_4/CH_3OH$
v: $AlLiH_4/CH_2Cl_2/(CH_3CH_2)_2O$
vi: HCl gas/$(CH_3CH_2)_2O$

cyclization reaction into the oxazino[4,3-*c*]pyrrolo-[1,2-*a*]thieno[3,2-*f*][1,4]diazepinediones **35-37**.

The ^{1}H-nmr spectra of these novel compounds exhibited, in a manner similar to that for the *Z* oximes and methyloximes previously described; a methylene system consisted of two separated multiplets.

EXPERIMENTAL

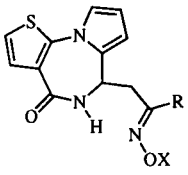
General Methods.

Melting points were determined 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 FX 200 using tetramethylsilane as an internal standard. Chemical shifts are reported in ppm downfield (δ) from tetramethylsilane.

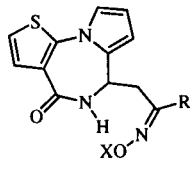
General Procedure for the Synthesis of the Oximes **II**.

A mixture of hydroxylammonium chloride (2.80 g, 0.04 mole) and sodium acetate (3.3 g, 0.04 mole) in water (15 ml) was added to a solution of the appropriate oxomethyldiazepinone **I** (0.01 mole) in ethanol (250 ml). The reaction mixture was refluxed for 1 hour and the solvent was then removed under reduced pressure. The solid residue was taken up in water (100

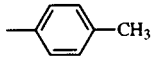
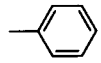
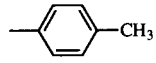
Scheme 3



II and III: *E* form



II and III: *Z* form

	X	R	Crude Product	Recrystallized
6	-H	$-CH_3$	*E*/*Z*: 80/20	*E*
7	-H	$-CH_2CH_2CH_3$	*E*/*Z*: 50/50	*E*/*Z*: 50/50
8	-H		Z	Z
9	-H		Z	Z
10	-H		Z	Z
11	$-CH_3$	$-CH_3$	*E*/*Z*: 60/40	*E*/*Z*: 60/40
12	$-CH_3$	$-CH_2CH_2CH_3$	*E*/*Z*: 50/50	Z
13	$-CH_3$		*E*/*Z*: 40/60	*E*/*Z*: 40/60
14	$-CH_3$		*E*/*Z*: 40/60	Z
15	$-CH_3$		*E*/*Z*: 50/50	Z

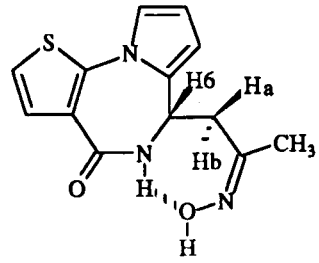
ml) and the insoluble material was filtered, washed with water (20 ml), dried and recrystallized to give **6**-**10**.

5,6-Dihydro-6-(2-hydroxyiminopropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one (*E*) **6**.

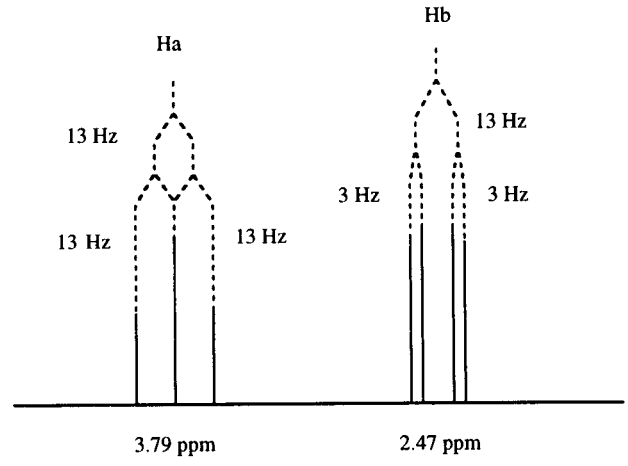
The starting material was 5,6-dihydro-6-(2-oxopropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **1** (2.6 g). The crude product (*E*/*Z* 80/20) was beige crystals (85%); ir (potassium bromide): 3280 (OH), 3200 (NH), 1625 (CO); ^{1}H-nmr (DMSO-d_6): 10.59 (s, OH), 8.14 (d, $J_{NH,H6}$ = 6 Hz, NH), 7.28 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.21 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.14 (m, H9), 6.28 (m, H8), 6.16 (m, H7), 4.62 (m, H6), 2.86 (m, Ha and Hb (*Z*)), 2.77 (m, Ha and Hb (*E*)), 1.74 (s, CH_3 (*Z*)), 1.77 (s, CH_3 (*E*)); ^{1}H-nmr (deuteriochloroform): 10.86 (s, OH), 7.93 (d, $J_{NH,H6}$ = 6 Hz, NH (*E*)), 7.48 (br s, NH (*Z*)), 7.40 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.02 (m, H9), 6.98 (d, $J_{H3,H2}$ = 5.9 Hz, H3 (*E*)), 6.94 (d, $J_{H3,H2}$ = 5.9 Hz, H3 (*Z*)), 6.36 (m, H8 (*E*)), 6.33 (m, H8 (*Z*)), 6.15 (m, H7), 4.60 (m, H6), 3.79 (dd, $J_{Ha,Hb}$ = $J_{Ha,H6}$ = 13 Hz, Ha (*Z*)), 2.88 (m, Ha and Hb (*E*)), 2.47 (dd, $J_{Hb,Ha}$ = 13 Hz, $J_{Hb,H6}$ = 3 Hz, Hb (*Z*)), 1.95 (s, CH_3 (*Z*)), 1.94 (s, CH_3 (*E*)). After recrystallization, colorless crystals (*E* form) had mp 200° (ethanol).

Anal. Calcd. for $C_{13}H_{13}N_3O_2S$: C, 56.71; H, 4.75; N, 15.26. Found: C, 56.62; H, 5.09; N, 15.06.

Scheme 4



6 (*Z* form)



^{1}H-nmr spectrum (deuteriochloroform)

5,6-Dihydro-6-(2-hydroxyiminopentyl)-4*H*-pyrrolo[1,2-*a*]thieno-[3,2-*f*][1,4]diazepin-4-one (*E*/*Z* 50/50) **7**.

The starting material was 5,6-dihydro-6-(2-oxopentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **2** (2.9 g) which provided colorless crystals (82%) with mp 110° (ether); ir (potassium bromide): 3280-3100 (OH, NH), 1640 (CO); ^{1}H-nmr (deuteriochloroform): 9.70 (s, OH), 7.50 (br s, NH), 7.40 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 6.96 (m, H3 and H9), 6.34 (m, H8), 6.17 (m, H7), 4.60 (m, H6), 3.71 (dd, $J_{Ha,Hb}$ = $J_{Ha,H6}$ = 13 Hz, Ha (*Z*)), 2.91 (m, Ha and Hb (*E*)), 2.51 (dd, $J_{Hb,Ha}$ = 13 Hz, $J_{Hb,H6}$ = 3 Hz, Hb (*Z*)), 2.29 (m, CH_2), 1.54 (m, CH_2), 0.94 (t, J = 7 Hz, CH_3).

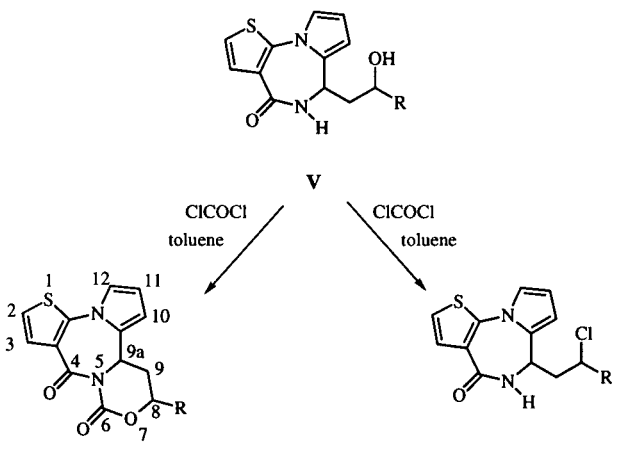
Anal. Calcd. for $C_{15}H_{17}N_3O_2S$: C, 59.39; H, 5.65; N, 13.85 Found: C, 59.28; H, 5.77; N, 13.70.

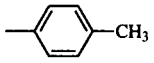
6-(2-Cyclopropyl-2-hydroxyiminoethyl)-5,6-dihydro-4*H*-pyrrolo-[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one (*Z*) **8**.

The starting material was 6-(2-cyclopropyl-2-oxoethyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **3** (2.9 g) which provided colorless crystals (37%) with mp 210° (ether); ir (potassium bromide): 3280-3150 (OH, NH), 1630 (CO); ^{1}H-nmr (deuteriochloroform): 9.68 (s, OH), 7.48 (br s, NH), 7.40 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 6.99 (m, H9), 6.94 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.34 (m, H8), 6.16 (m, H7), 4.60 (m, H6), 3.74 (dd, $J_{Ha,Hb}$ = $J_{Ha,H6}$ = 13 Hz, Ha), 2.44 (dd, $J_{Hb,Ha}$ = 13 Hz, $J_{Hb,H6}$ = 3 Hz, Hb), 1.49 (m, CH), 0.86 (m, CH_2), 0.74 (m, CH_2)

Anal. Calcd. for $C_{15}H_{15}N_3O_2S$: C, 59.78; H, 5.01; N, 13.94. Found: C, 59.91; H, 5.03; N,14.08.

Scheme 5



R	V	VIII	IX
-CH_3	21	35	-
-$CH_2CH_2CH_3$	22	36	-
	23	37	-
	24	-	38
	25	-	39

5,6-Dihydro-6-(2-hydroxyimino-2-phenylethyl)-4*H*-pyrrolo [1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one (*Z*) **9**.

The starting material was 5,6-dihydro-6-phenacyl-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **4** (3.2 g) which provided colorless crystals (82%) with mp 228° (ethanol); ir (potassium bromide): 3300 (OH, NH), 1630 (CO); ^{1}H-nmr (deuteriochloroform): 9.80 (s, OH), 7.86 (br s, NH), 7.60 (m, H2' and H6'), 7.29 (m, H2, H3', H4' and H5'), 6.94 (m, H9), 6.85 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.33 (m, H8), 6.23 (m, H7), 4.57 (m, H6), 4.14 (dd, $J_{Ha,Hb} = J_{Ha,H6}$ = 13 Hz, Ha), 3.14 (dd, $J_{Hb,Ha}$ = 13 Hz, $J_{Hb,H6}$ = 3 Hz, Hb).

Anal. Calcd. for $C_{18}H_{15}N_3O_2S$: C, 64.08; H, 4.48; N, 12.45. Found: C, 63.93; H, 4.60; N, 12.32.

5,6-Dihydro-6-(2-hydroxyimino-2-*p*-tolylethyl)-4*H*-pyrrolo-[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one (*Z*) **10**.

The starting material was 5,6-dihydro-6-(*p*-methylphenacyl)-4*H*-pyrrolo[l,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **5** (3.4 g) which provided colorless crystals (74%) with mp 190° (ether); ir (potassium bromide): 3300-3140 (OH, NH), 1625 (CO); ^{1}H-nmr (deuteriochloroform): 10.77 (s, OH), 7.86 (br s, NH), 7.56 (d, $J_{H2',H3'}$ = 7.8 Hz, H2' and H6'), 7.33 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.14 (d, $J_{H3',H2'}$ = 7.8 Hz, H3' and H5'), 7.00 (m, H9), 6.89 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.38 (m, H8), 6.28 (m, H7), 4.56 (m, H6), 4.12 (dd, $J_{Ha,Hb} = J_{Ha,H6}$ = 13 Hz, Ha), 3.14 (dd, $J_{Hb,Ha}$ = 13 Hz, $J_{Hb,H6}$ = 3 Hz, Hb), 2.33 (s, CH_3).

Anal. Calcd. for $C_{19}H_{17}N_3O_2S$: C, 64.95; H, 4.84; N, 11.96. Found: C, 65.02; H, 5.07; N, 11.88.

General Procedure for the Synthesis of the Methyloximes **III**.

A mixture of methoxylammonium chloride (3.3 g, 0.04 mole) and sodium acetate (3.3 g, 0.04 mole) in water (15 ml) was added to a solution of the appropriate oxomethyldiazepinone **I** (0.01 mole) in ethanol (250 ml). The reaction mixture was refluxed for 1 hour and the solvent was then removed under reduced pressure. The solid residue was taken up in water (100 ml) and the insoluble material was filtered, washed with water (20 ml), dried and recrystallized to give **11**-**15**.

5,6-Dihydro-6-(2-methoxyiminopropyl)-4*H*-pyrrolo[1,2-*a*]thieno-[3,2-*f*][1,4]diazepin-4-one (*E*/*Z* 60/40) **11**.

The starting material was 5,6-dihydro-6-(2-oxopropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **1** (2.6 g) which provided colorless crystals (93%) with mp 138° (ether/petroleum ether); ir (potassium bromide): 3300 (NH), 1630 (CO); ^{1}H-nmr (DMSO-d_6): 8.14 (br s, NH (*Z*)), 8.08 (d, $J_{NH,H6}$ = 6 Hz, NH (*E*)), 7.28 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.21 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.13 (m, H9), 6.28 (m, H8), 6.18 (m, H7 (*E*)), 6.12 (m, H7 (*Z*)), 4.61 (m, H6), 3.71 (s, OCH_3), 2.77 (m, Ha and Hb (*Z*)), 2.69 (m, Ha and Hb (*E*)), 1.76 (s, CH_3 (*E*)), 1.73 (s, CH_3 (*Z*)).

Anal. Calcd. for $C_{14}H_{15}N_3O_2S$: C, 58.11; H, 5.22; N, 14.52. Found: C, 57.99; H, 5.16; N, 14.47.

5,6-Dihydro-6-(2-methoxyiminopentyl)-4*H*-pyrrolo[1,2-*a*]thieno-[3,2-*f*][1,4]diazepin-4-one (*Z*) **12**.

The starting material was 5,6-dihydro-6-(2-oxopentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **2** (2.9 g) which provided colorless crystals (57%) with mp 162° (ether); ir (potassium bromide): 3180 (NH), 1630 (CO); ^{1}H-nmr (DMSO-d_6): 8.26 (br s, NH), 7.27 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.21 d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.13 (m, H9), 6.27 (m, H8), 6.12 (m, H7), 4.65 (m, H6), 3.71 (s, OCH_3), 2.81 (m, Ha and Hb), 2.04 (m, CH_2), 1.35 (m, CH_2), 0.79 (t, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{16}H_{19}N_3O_2S$: C, 60.56; H, 5.99; N, 13.25. Found: C, 60.44; H, 5.86; N, 13.13.

6-(2-Cyclopropyl-2-methoxyiminoethyl)-5,6-dihydro-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one (*E*/*Z* 40/60) **13**.

The starting material was 6-(2-cyclopropyl-2-oxoethyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **3** (2.9 g) which provided beige crystals (82%) with mp 152° (ether); ir (potassium bromide): 3270, 3190 (NH), 1645 (CO); ^{1}H-nmr (deuteriochloroform): 7.34 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 6.91 (m, H3 and H9), 6.67 (br s, NH), 6.26 (m, H8), 6.09 (m, H7 (*Z*)), 6.03 (m, H7 (*E*)), 4.94 (m, H6 (*E*)), 4.63 (m, H6 (*Z*)), 3.90 (s, OCH_3 (*E*)), 3.86 (s, OCH_3 (*Z*)), 3.51 (dd, $J_{Ha,Hb} = J_{Ha,H6}$ = 13 Hz, Ha (*Z*)), 3.23 (d, $J_{CH2,H6}$ = 6.8 Hz, Ha and Hb (*E*)), 2.54 (dd, $J_{Hb,Ha}$ = 13 Hz, $J_{Hb,H6}$ = 3 Hz, Hb (*Z*)), 2.17 (m, CH (*E*)), 1.97 (m, CH (*Z*)), 0.94 (m, $2CH_2$ (*E*)), 0.76 (m, $2CH_2$ (*Z*)).

Anal. Calcd. for $C_{16}H_{17}N_3O_2S$: C, 60.93; H, 5.43; N, 13.32. Found: C, 61.03; H, 5.40; N, 13.50.

5,6-Dihydro-6-(2-methoxyimino-2-phenylethyl)-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepin-4-one (*Z*) **14**.

The starting material was 5,6-dihydro-6-phenacyl-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **4** (3.2 g) which provided colorless crystals (57%) with mp 169° (ether); ir (potassium bromide): 3190 (NH), 1650 (CO); ^{1}H-nmr (DMSO-d_6): 8.10 (br s, NH), 7.43 (m, H2' and H6'), 7.34 (m, H2, H3', H4' and H5'), 7.21 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.04 (m, H9), 6.23 (m,

H8), 6.03 (m, H7), 4.60 (m, H6), 3.84 (s, OCH_3), 3.27 (d, $J_{CH_2,H6}$ = 6.8 Hz, Ha and Hb).

Anal. Calcd. for $C_{19}H_{17}N_3O_2S$: C, 64.94; H, 4.88; N, 11.96. Found: C, 65.15; H, 4.73; N, 12.16.

5,6-Dihydro-6-(2-methoxyimino-2-*p*-tolylethyl)-4*H*-pyrrolo-[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one (*Z*) **15**.

The starting material was 5,6-dihydro-6-(*p*-methylphenacyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **5** (3.4 g) which provided colorless crystals (48%) with mp 175° (ether); ir (potassium bromide): 3210 (NH), 1650 (CO); ^{1}H-nmr (DMSO-d_6): 8.24 (br s, NH), 7.38 (d, $J_{H2',H3'}$ = 7.8 Hz, H2' and H6'), 7.26 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.18 (m, H3, H3' and H5'), 7.09 (m, H9), 6.21 (m, H8), 6.03 (m, H7), 4.51 (m, H6), 3.82 (s, OCH_3), 3.24 (d, $J_{CH_2,H6}$ = 6.8 Hz, Ha and Hb), 2.30 (s, CH_3).

Anal. Calcd. for $C_{20}H_{19}N_3O_2S$: C, 65.73; H, 5.24; N, 11.50. Found: C, 65.94; H, 5.13; N, 11.60.

General Procedure for the Synthesis of the Hydrazones **IV**.

Hydrazine hydrate (2 ml) was added to a solution of the appropriate oxomethyldiazepinone **I** (0.01 mole) in ethanol (250 ml). The reaction mixture was refluxed for 90 minutes and the solvent was then removed under reduced pressure. The solid residue was taken up in water (100 ml) and the insoluble material was filtered, washed with water (20 ml), dried and recrystallized to give **16-20**.

5,6-Dihydro-6-(2-hydrazonopropyl)-4*H*-pyrrolo[1,2-*a*]thieno-[3,2-*f*][1,4]diazepin-4-one **16**.

The starting material was 5,6-dihydro-6-(2-oxopropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **1** (2.6 g) which provided colorless crystals (72%) with mp 158° (ether/petroleum ether); ir (potassium bromide): 3280, 3180 (NH, NH_2), 1640 (CO); ^{1}H-nmr (DMSO-d_6): 7.96 (br s, NH), 7.26 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.21 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.08 (m, H9), 6.26 (m, H8), 6.12 (m, H7), 5.70 (br s, NH_2), 4.63 (m, H6), 2.71 (m, Ha and Hb), 1.64 (s, CH_3).

Anal. Calcd. for $C_{13}H_{14}N_4OS$: C, 56.92; H, 5.14; N, 20.42. Found: C, 57.11; H, 5.31; N, 20.13.

5,6-Dihydro-6-(2-hydrazonopentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*]-[1,4]diazepin-4-one **17**.

The starting material was 5,6-dihydro-6-(2-oxopentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **2** (2.9 g) which provided colorless crystals (76%) with mp 158° (ether); ir (potassium bromide): 3410, 3370, 3190 (NH, NH_2), 1640 (CO); ^{1}H-nmr (DMSO-d_6): 8.91 (br s, NH), 7.28 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.21 d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.11 (m, H9), 6.26 (m, H8), 6.11 (m, H7), 5.76 (br s, NH_2), 4.64 (m, H6), 2.73 (m, Ha and Hb), 2.10 (t, J = 7 Hz, CH_2), 1.44 (m, CH_2), 0.88 (t, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{15}H_{18}N_4OS$: C, 59.52; H, 5.95; N, 18.51. Found: C, 59.75; H, 5.88; N, 18.41.

6-(2-Cyclopropyl-2-hydrazonoethyl)-5,6-dihydro-4*H*-pyrrolo[1,2-*a*]thieno [3,2-*f*][1,4]diazepin-4-one **18**.

The starting material was 6-(2-cyclopropyl-2-oxoethyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **3** (2.9 g) which provided colorless crystals (80%) with mp 184° (ether/ethyl acetate); ir (potassium bromide): 3380, 3260, 3180 (NH, NH_2), 1640 (CO); ^{1}H-nmr (DMSO-d_6): 7.97 (br s, NH), 7.23 (m, H2 and H3), 7.09 (m, H9), 6.26 (m, H8), 6.09 (m, H7), 5.94 (s, NH_2), 4.64 (m, H6), 3.43 (m, Ha and Hb), 1.51 (m, CH), 0.69 (m, $2CH_2$).

Anal. Calcd. for $C_{15}H_{16}N_4OS$: C, 59.98; H, 5.37; N, 18.65. Found: C, 59.89; H, 5.41; N, 18.39.

5,6-Dihydro-6-(2-hydrazono-2-phenylethyl)-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepin-4-one **19**.

The starting material was 5,6-dihydro-6-phenacyl-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **4** (3.2 g) which provided yellow crystals (60%) with mp <60° (ether); ir (potassium bromide): 3380, 3260, 3200 (NH, NH_2), 1640 (CO); ^{1}H-nmr (DMSO-d_6): 8.03 (br s, NH), 7.28 (m, H2, H3, H2', H3', H4', H5' and H6'), 7.12 (m, H9), 6.69 (s, NH_2), 6.23 (m, H8), 6.14 (m, H7), 4.66 (m, H6), 3.26 (m, Ha and Hb).

Anal. Calcd. for $C_{18}H_{16}N_4OS$: C, 64.27; H, 4.79; N, 16.65. Found: C, 63.98; H, 5.07; N, 16.76.

5,6-Dihydro-6-(2-hydrazono-2-*p*-tolylethyl)-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepin-4-one **20**.

The starting material was 5,6-dihydro-6-(*p*-methylphenacyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **5** (3.4 g) which provided orange crystals (65%) with mp <60° (ether); ir (potassium bromide): 3400-3200 (NH, NH_2), 1640 (CO); ^{1}H-nmr (DMSO-d_6): 7.97 (br s, NH), 7.31 (d, $J_{H2',H3'}$ = 7.8 Hz, H2' and H6'), 7.26 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.14 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.10 (m, H9), 7.03 (d, $J_{H3',H2'}$ = 7.8 Hz, H3' and H5'), 6.58 (s, NH_2), 6.23 (m, H8), 6.14 (m, H7), 4.60 (m, H6), 3.20 (m, Ha and Hb), 2.22 (s, CH_3).

Anal. Calcd. for $C_{19}H_{18}N_4OS$: C, 65.12; H, 5.18; N, 15.99. Found: C, 65.10; H, 5.28; N, 16.02.

General Procedure for the Synthesis of the Alcohols **V**.

Sodium borohydride (1.50 g, 0.04 mole) was added portionwise to a solution of the appropriate oxomethyldiazepinone **I** (0.01 mole) in methanol (200 ml). The reaction mixture was stirred at room temperature for 3 hours and the solvent was then removed under reduced pressure. The solid residue was taken up in water (100 ml) and the insoluble material was filtered, washed with water (20 ml), dried and recrystallized to give **21-25**.

5,6-Dihydro-6-(2-hydroxypropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*]-[1,4]diazepin-4-one **21**.

The starting material was 5,6-dihydro-6-(2-oxopropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **1** (2.6 g) which provided colorless crystals (75%) with mp 171° (ether); ir (potassium bromide): 3450 (OH), 3260, 3180 (NH), 1630 (CO); ^{1}H-nmr (DMSO-d_6): 8.14 (d, $J_{NH,H6}$ = 6 Hz, NH), 7.26 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.17 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.07 (m, H9), 6.26 (m, H8), 6.06 (m, H7), 4.66 (d, $J_{OH,CH}$ = 6 Hz, OH), 4.34 (m, CH), 3.86 (m, H6), 1.91 (m, Ha and Hb), 1.11 (d, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{13}H_{14}N_2O_2S$: C, 59.48; H, 5.34; N, 10.67. Found: C, 59.35; H, 5.28; N, 10.75.

5,6-Dihydro-6-(2-hydroxypentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*]-[1,4]diazepin-4-one **22**.

The starting material was 5,6-dihydro-6-(2-oxopentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **2** (2.9 g) which provided yellow crystals (80%) with mp 188° (propan-2-ol); ir (potassium bromide): 3440 (OH), 3250, 3170 (NH), 1630 (CO);

^{1}H-nmr (deuteriochloroform): 7.31 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.00 (d, $J_{NH,H6}$ = 6 Hz, NH), 6.91 (m, H9), 6.87 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.26 (m, H8), 6.03 (m, H7), 4.64 (m, CH), 4.04 (m, H6), 2.40 (d, $J_{OH,CH}$ = 6 Hz, OH), 2.11 (m, Ha and Hb), 1.43 (m, $2CH_2$), 0.96 (t, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.24; N, 9.64. Found: C, 62.10; H, 6.18; N, 9.55.

6-(2-Cyclopropyl-2-hydroxyethyl)-5,6-dihydro-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepin-4-one **23**.

The starting material was 6-(2-cyclopropyl-2-oxoethyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **3** (2.9 g) which provided colorless crystals (80%) with mp 222° (propan-2-ol); ir (potassium bromide): 3450 (OH), 3260, 3180 (NH), 1625 (CO); ^{1}H-nmr (DMSO-d_6): 8.17 (br s, NH), 7.26 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.17 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.11 (m, H9), 6.29 (m, H8), 6.09 (m, H7), 4.71 (d, $J_{OH,CH}$ = 6 Hz, OH), 4.43 (m, CH), 3.11 (m, H6), 2.09 (m, Ha and Hb), 0.86 (m, CH), 0.54 (d, J = 7 Hz, $2CH_2$).

Anal. Calcd. for $C_{15}H_{16}N_2O_2S$: C, 62.47; H, 5.59; N, 9.71. Found: C, 62.18; H, 5.72; N, 9.56.

5,6-Dihydro-6-(2-hydroxy-2-phenylethyl)-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepin-4-one **24**.

The starting material was 5,6-dihydro-6-phenacyl-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **4** (3.2 g) which provided colorless crystals (79%) with mp 190° (ether); ir (potassium bromide): 3450 (OH), 3250, 3180 (NH), 1635 (CO); ^{1}H-nmr (DMSO-d_6): 8.51 (br s, NH), 7.31 (m, H2, H3, H2', H3', H4', H5' and H6'), 7.14 (m, H9), 6.26 (m, H8), 6.08 (m, H7), 5.48 (d, $J_{OH,CH}$ = 6 Hz, OH), 4.85 (m, CH), 4.51 (m, H6), 2.17 (m, Ha and Hb).

Anal. Calcd. for $C_{18}H_{16}N_2O_2S$: C, 66.65; H, 4.97; N, 8.64. Found: C, 66.56; H, 4.89; N, 8.52.

5,6-Dihydro-6-(2-hydroxy-2-*p*-tolylethyl)-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepin-4-one **25**.

The starting material was 5,6-dihydro-6-(*p*-methylphenacyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **5** (3.4 g) which provided colorless crystals (71%) with mp 182° (ether); ir (potassium bromide): 3420 (OH), 3250, 3170 (NH), 1635 (CO); ^{1}H-nmr (DMSO-d_6): 8.47 (br s, NH), 7.20 (m, H2, H3, H9, H2', H3', H5' and H6'), 6.26 (m, H8), 6.06 (m, H7), 5.40 (br s, OH), 4.80 (m, CH), 4.51 (m, H6), 2.29 (s, CH_3), 2.11 (m, Ha and Hb).

Anal. Calcd. for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36; N, 8.27. Found: C, 67.30; H, 5.44; N, 8.16.

General Procedure for the Synthesis of the Amino-Alcohols **VI** and their Ammonium Chlorides **VII**.

A solution of the appropriate oxomethyldiazepinone **I** (0.01 mole) in dichloromethane (200 ml) was added dropwise to a suspension of lithium aluminium hydride (1.50 g, 0.04 mole) in ether (20 ml). The reaction mixture was stirred at room temperature for 30 minutes and then refluxed for 6 hours. The cooled solution was poured into iced water (200 ml) and the precipitate which appeared was filtered and washed with dichloromethane (100 ml). The organic layer was separated from the filtrate, dried over calcium chloride and the solvent was then removed under reduced pressure to give **26-29** as unstable oils and **30** as a colorless solid after recrystallization. The oily residues were dissolved in ether (150 ml) and the solutions were bubbled for 15 seconds with an hydrochloric acid gas flow. The precipitates which appeared were filtered, washed with ether (50 ml), dried and recrystallized to give **31-34**.

5,6-Dihydro-6-(2-hydroxy-2-*p*-tolylethyl)-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepine **30**.

The starting material was 5,6-dihydro-6-(*p*-methylphenacyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **5** (3.4 g) which provided colorless crystals (71%) with mp >260° (ethanol/propan-2-ol); ir (potassium bromide): 3460 (OH, NH); ^{1}H-nmr (DMSO-d_6): 10.24 (br s, NH), 7.44 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.27 (m, H9), 7.22 (d, $J_{H2',H3'}$ = 7.8 Hz, H2' and H6'), 7.13 (m, H3, H3' and H5'), 6.47 (m, H7), 6.34 (m, H8), 5.50 (br s, OH), 4.84 (m, CH), 4.27 (d, $J_{H4a,H4b}$ = 14 Hz, H4a), 4.03 (m, H6), 3.64 (d, $J_{H4b,H4a}$ = 14 Hz, H4b), 2.25 (m, CH_2 and CH_3).

Anal. Calcd. for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63. Found: C, 70.38; H, 6.13; N, 8.59.

5,6-Dihydro-6-(2-hydroxypropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*]-[1,4]diazepinium Chloride **31**.

The starting material was 5,6-dihydro-6-(2-oxopropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **1** (2.6 g) which provided beige crystals (41%) with mp 226° (propan-2-ol); ir (potassium bromide): 3390 (OH), 2960-2580 ($^+NH_2$); ^{1}H-nmr (DMSO-d_6): 9.86 (br s, $^+NH_2$), 7.44 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.27 (m, H9), 7.12 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.49 (m, H7), 6.35 (m, H8), 4.86 (br s, OH), 4.26 (d, $J_{H4a,H4b}$ = 14 Hz, H4a), 4.06 (br s, CH), 3.86 (br s, H6), 3.61 (d, $J_{H4b,H4a}$ = 14 Hz, H4b), 2.21 (m, CH_2), 1.11 (d, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{13}H_{17}N_2OClS$: C, 54.82; H, 6.02; N, 9.84. Found: C, 54.98; H, 6.04; N, 9.89.

5,6-Dihydro-6-(2-hydroxypentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*]-[1,4]diazepinium Chloride **32**.

The starting material was 5,6-dihydro-6-(2-oxopentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **2** (2.9 g) which provided grey crystals (50%) with mp 226° (propan-2-ol); ir (potassium bromide): 3350 (OH), 2960-2550 ($^+NH_2$); ^{1}H-nmr (DMSO-d_6): 9.80 (br s, $^+NH_2$), 7.45 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.26 (m, H9), 7.12 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.44 (m, H7), 6.36 (m, H8), 4.36 (br s, OH), 4.23 (d, $J_{H4a,H4b}$ = 14 Hz, H4a), 3.71 (m, CH), 3.60 (d, $J_{H4b,H4a}$ = 14 Hz, H4b), 3.43 (m, H6), 2.20 (m, CH_2), 1.83 (m, CH_2), 1.37 (m, CH_2), 0.86 (t, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{15}H_{21}N_2OClS$: C, 57.59; H, 6.76; N. 8.95. Found: C, 57.80; H, 6.95; N, 9.01.

6-(2-Cyclopropyl-2-hydroxyethyl)-5,6-dihydro-4*H*-pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepinium Chloride **33**.

The starting material was 6-(2-cyclopropyl-2-oxoethyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **3** (2.9 g) which provided colorless crystals (54%) with mp 236° (propan-2-ol); ir (potassium bromide): 3350 (OH), 2970-2540 ($^+NH_2$); ^{1}H-nmr (DMSO-d_6): 9.86 (br s, $^+NH_2$), 7.46 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.27 (m, H9), 7.12 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.43 (m, H7), 6.36 (m, H8), 4.94 (br s, OH), 4.22 (m, H4a and CH), 3.74 (m, H6), 3.60 (d, $J_{H4b,H4a}$ = 14 Hz, H4b), 2.26 (m, CH_2), 0.83 (m, CH), 0.29 (m, $2CH_2$).

Anal. Calcd. for $C_{15}H_{19}N_2OClS$: C, 57.96; H, 6.16; N, 9.01. Found: C, 57.74; H, 6.07; N, 8.80.

5,6-Dihydro-6-(2-hydroxy-2-phenylethyl)-4*H*-pyrrolo[1,2-*a*]thieno-[3,2-*f*][1,4]diazepinium Chloride **34**.

The starting material was 5,6-dihydro-6-phenacyl-4*H*-pyrrolo-[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **4** (3.2 g) which provided colorless crystals (52%) with mp 186° (propan-2-ol); ir (potassium bromide): 3340 (OH), 2970-2540 ($^+NH_2$); ^{1}H-nmr (DMSO-d_6): 9.86 (br s, $^+NH_2$), 7.48 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.36 (m, H9, H2', H3', H4', H5' and H6'), 7.14 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 6.57 (m, H7), 6.37 (m, H8), 4.83 (m, CH), 4.57 (br s, OH), 4.29 (m, H4a), 4.00 (m, H6), 3.63 (d, $J_{H4b,H4a}$ = 14 Hz, H4b), 2.29 (m, CH_2).

Anal. Calcd. for $C_{18}H_{19}N_2OClS$: C, 62.33; H, 5.52; N, 8.08. Found: C, 62.06; H, 5.77; N, 8.10.

General Procedure for the Synthesis of the Oxazinodiazepines **VIII** and Chloro Derivatives **IX**.

A solution of phosgene in toluene (20%, 10 ml) was added to a solution of the appropriate hydroxyethyldiazepinone **V** (0.01 mole) in toluene (50 ml). The reaction mixture was refluxed for 1 hour and the solvent was then removed under reduced pressure. The solid residue was taken up in water (100 ml) and the insoluble material was filtered, washed with water (20 ml), dried and recrystallized to give **35-39**.

8-Methyl-4,5,6,8,9,9a-hexahydro[1,3]oxazino[4,3-*c*]pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepine-4,6-dione **35**.

The starting material was 5,6-dihydro-6-(2-hydroxypropyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **21** (2.6 g) which provided colorless crystals (52%) with mp 194° (ether); ir (potassium bromide): 1730, 1640 (CO); ^{1}H-nmr (DMSO-d_6): 7.33 (m, H2, H3 and H12), 6.51 (m, H10), 6.40 (m, H11, 5.14 (m, H9a), 5.00 (m, H8), 2.71 (m, H9), 2.31 (m, H9), 1.43 (d, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{14}H_{12}N_2O_3S$: C, 58.32; H, 4.19; N, 9.72. Found: C, 58.10; H, 4.33; N, 9.62.

8-Propyl-4,5,6,8,9,9a-hexahydro[1,3]oxazino[4,3-*c*]pyrrolo[1,2-*a*]-thieno[3,2-*f*][1,4]diazepine-4,6-dione **36**.

The starting material was 5,6-dihydro-6-(2-hydroxypentyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **22** (2.9 g) which provided colorless crystals (89%) with mp 162° (ether); ir (potassium bromide): 1745, 1665 (CO); ^{1}H-nmr (DMSO-d_6): 7.33 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.29 (d, $J_{H3,H2}$ = 5.9 Hz, H3), 7.26 (m, H12), 6.40 (m, H10), 6.34 (m, H11), 5.11 (t, J = 5 Hz, H9a), 4.80 (m, H8), 2.71 (m, H9), 2.34 (m, H9), 1.71 (m, CH_2), 1.49 (m, CH_2), 0.96 (t, J = 7 Hz, CH_3).

Anal. Calcd. for $C_{16}H_{16}N_2O_3S$: C, 60.74; H, 5.10; N, 8.85. Found: C, 60.69; H, 5.12; N, 8.71.

8-Cyclopropyl-4,5,6,8,9,9a-hexahydro[1,3]oxazino[4,3-*c*]pyrrolo-[1,2-*a*]thieno[3,2-*f*][1,4]diazepine-4,6-dione **37**.

The starting material was 6-(2-cyclopropyl-2-hydroxyethyl)-5,6-dihydro-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **23** (2.9 g) which provided colorless crystals (80%) with mp 230° (ether); ir (potassium bromide): 1740, 1650 (CO); ^{1}H-nmr (DMSO-d_6): 7.37 (s, H2 and H3), 7.35 (m, H12), 6.44 (m, H10), 6.40 (m, H11), 5.20 (t, J = 5 Hz, H9a), 4.15 (m, H8), 2.74 (m, H9), 2.54 (m, H9), 1.19 (m, CH), 0.54 (m, $2CH_2$).

Anal. Calcd. for $C_{16}H_{14}N_2O_3S$: C, 61.13; H, 4.49; N, 8.91. Found: C, 61.24; H, 4.39; N, 9.04.

6-(2-Chloro-2-phenylethyl)-5,6-dihydro-4*H*-pyrrolo[1,2-*a*]thieno-[3,2-*f*][1,4]diazepin-4-one **38**.

The starting material was 5,6-dihydro-6-(2-hydroxy-2-phenylethyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **24** (3.2 g) which provided beige crystals (56%) with mp 180° (ether); ir (potassium bromide): 3160 (NH), 1650 (CO); ^{1}H-nmr (DMSO-d_6): 8.62 (d, $J_{NH,H6}$ = 6Hz, NH), 7.54 (d, $J_{H2',H3'}$ = 6.5 Hz, H2' and H6'), 7.34 (m, H2, H3, H3', H4' and H5'), 7.14 (m, H9), 6.29 (m, H8), 6.20 (m, H7), 5.37 (m, H6), 4.51 (m, CH), 2.66 (m, Ha and Hb).

Anal. Calcd. for $C_{19}H_{15}N_2OClS$: C, 63.06; H, 4.41; N, 8.17. Found: C, 63.20; H, 4.59; N, 8.12.

6-(2-Chloro-2-*p*-tolylethyl)-5,6-dihydro-4*H*-pyrrolo-[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **39**.

The starting material was 5,6-dihydro-6-(2-hydroxy-2-*p*-tolylethyl)-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepin-4-one **25** (3.4 g) which provided colorless crystals (49%) with mp 225° (ether); ir (potassium bromide): 3160 (NH), 1630 (CO); ^{1}H-nmr (DMSO-d_6): 8.54 (d, $J_{NH,H6}$ = 6 Hz, NH), 7.40 (d, $J_{H2,H3}$ = 5.9 Hz, H2), 7.26 (m, H3, H2', H3', H5' and H6'), 7.11 (m, H9), 6.29 (m, H8), 6.17 (m, H7), 5.34 (m, H6), 4.49 (m, CH), 2.66 (m, Ha and Hb), 2.31 (s, CH_3).

Anal. Calcd. for $C_{19}H_{17}N_2OClS$: C, 63.95; H, 4.80; N, 7.85. Found: C, 64.16; H, 5.11; N, 7.75.

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