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5,7-Dihydropyrrolo[3,4-*d*][1,2]diazepin-1(2*H*)-ones. Synthesis and Transformations

O. I. Kharaneko[a]* and S. L. Bogza[b]

[a] *Litvinenko Institute of Physical Organic and Coal Chemistry, ul. R. Lyuksemburg 70, Donetsk, 83114 Ukraine*
**e-mail: o_kharaneko@mail.ru*

[b] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 5, Kiev, 02660 Ukraine*

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Abstract—A preparative procedure has been developed for the synthesis of substituted 5,7-dihydropyrrolo-[3,4-*d*][1,2]diazepines by recyclization of 6-phenylpyrano[3,4-*c*]pyrrol-4(2*H*)-one with hydrazine hydrate. The stability of the seven-membered ring in the products under acidic conditions, alkylation, and heteroring fusion to the diazepine ring have been studied.

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Heterocyclic compounds containing a 1,2-diazepine fragment exhibit a broad spectrum of biological activity [1]. In particular, 2,3-benzodiazepines were reported to possess tranquilizing [2], anxiolytic, and anticonvulsant activity [3]. Drugs for the treatment of Parkinson's and Alzheimer's diseases [4] and amyotrophic lateral sclerosis [5] have been designed on the basis of 2,3-benzodiazepines. Unlike 1,4-benzodiazepine drugs, 2,3-benzodiazepine derivatives are characterized by not only selective action but also the lack of side effects. Therefore, synthesis of new 2,3-benzodiazepine compounds is an important problem.

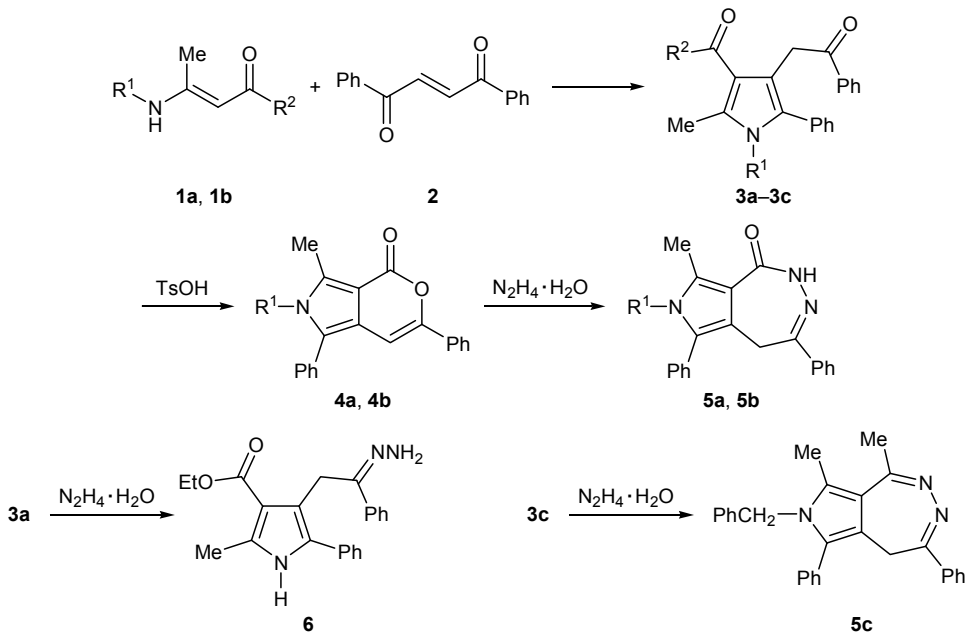
1,2-Diazepines fused to a pyrrole ring are equally interesting since the pyrrole ring is a structural unit of many biologically active compounds which play an important role in physiological processes. Currently known pyrrolo[1,2-*a*][1,4]benzodiazepines affect central nervous system [6–11] due to their sedative, anticonvulsant, myorelaxant, and other properties. Pyrrolo-[2,3]diazepines still remain poorly studied. To the best of our knowledge, only one procedure has been reported for the synthesis of pyrrolo[2,3]diazepines by cycloaddition of 4-methylbenzenesulfonyl thiocyanate to 1,2-diazepines [12]. Depending on the substituent in the diazepine ring, the yield of the target products varied from 20 to 59%.

Analysis of published data revealed the possibility of an alternative synthetic approach to fused diazepines [13], which implies diazepine ring closure on already existing benzene ring or heterocycle. Mutual arrangement of the C=O groups in 1,5-dicarbonyl compounds favors their cyclization to carbo- and heterocyclic structures [14–16]. This ability of 1,5-dicarbonyl compounds with a benzophenone fragment [17] was successfully utilized previously in the synthesis of 2,3-benzodiazepines by reactions with hydrazine hydrate and its derivatives.

We have developed a synthetic approach to 5,7-dihydropyrrolo[3,4-*d*][1,2]diazepines starting from 1,5-dicarbonyl compounds **3a**–**3c** containing a pyrrole fragment (Scheme 1). Initial compounds **3a**–**3c** were prepared by addition of enamines **1** derived from ethyl acetoacetate and acetylacetone to dibenzoylethene **2**, which was accompanied by cyclization [18]. This procedure ensured very good yields of pyrrole derivatives **3a**–**3c**, and it can be readily extended to other related compounds.

By heating compound **3c** with hydrazine hydrate in methanol we obtained 7-benzyl-1,8-dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine (**5c**) which characteristically showed in the ^{1}H NMR spectrum doublet signals at δ 2.91 and 3.79 ppm (J = 14 Hz) from nonequivalent methylene protons on C^5, indicating nonplanar structure of the diazepine ring. Under analogous conditions, compound **3a** afforded exclusively the corresponding hydrazone **6** instead of expected diazepinone **5a**. Thus, the direction of the reaction of pyrroles **3** with hydrazine hydrate is determined by the substituent on the nitrogen atom.

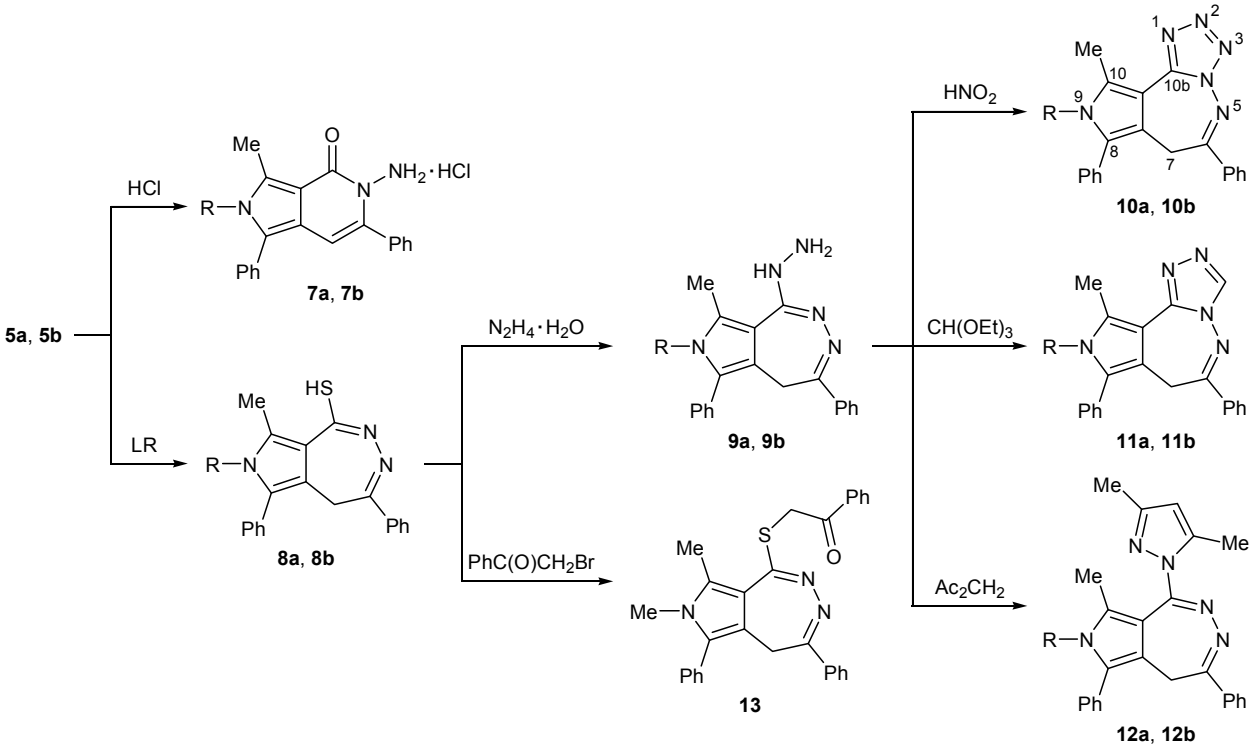
Scheme 1.



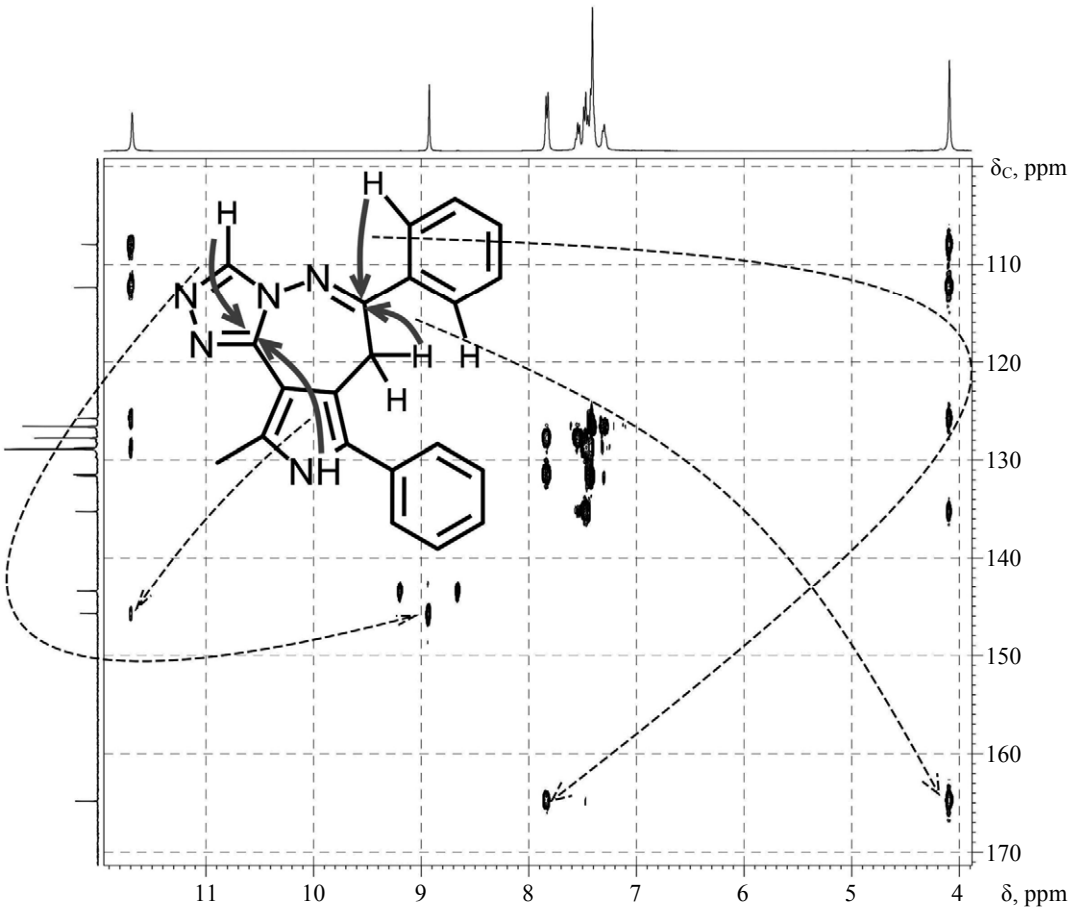
1, **3**, R^1 = H, R^2 = EtO (**a**); R^1 = Me, R^2 = EtO (**b**); R^1 = $PhCH_2$, R^2 = Me (**c**); **4**, **5**, R = H (**a**), Me (**b**), $PhCH_2$ (**c**).

In order to obtain pyrrolodiazepine derivatives from compounds **3a** and **3b**, the latter were preliminarily converted to pyranopyrroles **4a** and **4b** by fusion with a catalytic amount of *p*-toluenesulfonic acid. The procedures for the synthesis of 6-phenylpyrano[3,4-*c*]-pyrrol-4(2*H*)-ones **4a** and **4b** and 4-phenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepin-1(2*H*)-ones **5a** and **5b** were described previously [19].

Scheme 2.



R = H (**a**), Me (**b**); LR stands for Lawesson's reagent.



Two-dimensional ^{1}H–^{13}C HMBC spectrum of 10-methyl-6,8-diphenyl-7,9-dihydropyrrolo[3,4-*d*][1,2,4]triazolo[4,3-*b*]diazepine (**11a**).

Scheme 2 illustrates main transformations of diazepinones **5a** and **5b**.

Heating of **5a** and **5b** with excess aqueous HCl quantitatively afforded 5-amino-3-methyl-1,6-diphenyl-2,5-dihydro-4*H*-pyrrolo[3,4-*c*]pyridin-4-one (**7a**) and 5-amino-2,3-dimethyl-1,6-diphenyl-2,5-dihydro-4*H*-pyrrolo[3,4-*c*]pyridin-4-one (**7b**), respectively. Protons on C^{7} resonated in the ^{1}H NMR spectra at δ 6.48 (**7a**) and 6.10 ppm (**7b**), and the C^{7} signals were observed in the ^{13}C NMR spectra at δ_C 101.4 (**7a**) and 99.2 ppm (**7b**).

Treatment of **5a** and **5b** with Lawesson's reagent resulted in quantitative replacement of the carbonyl oxygen atom by sulfur with formation of 8-methyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine-1-thiol (**8a**) and 7,8-dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine-1-thiol (**8b**). In the ^{13}C NMR spectra of **8a** and **8b**, the C^{1} signal appeared in a weaker field (δ_C 187.2 and 187.0 ppm, respectively) relative to the C=O signal of **5** [12]. Compounds **8a** and **8b** reacted with excess hydrazine hydrate to give the corresponding 1-hydrazinyl derivatives **9a** and **9b** in 75% yield. Unlike diazepinones **5a** and **5b**, thiols **8a** and **8b** and hydrazines **9a** and **9b** are stable under acidic conditions, and no contraction of the diazepine ring therein was observed on heating in boiling aqueous HCl.

Like 2,3-benzodiazepin-1-ylhydrazines reported previously [20], compounds **9a** and **9b** may be precursors to tricyclic structures with an additional nitrogen heterocycle fused to the diazepine ring. The reaction of pyrrolodiazepines **9a** and **9b** with nitrous acid ($NaNO_2$/AcOH) led to tetrazole ring fusion with formation of 10-methyl-6,8-diphenyl-7,9-dihydropyrrolo[3,4-*d*]tetrazolo[1,5-*b*][1,2]diazepine (**10a**) and 9,10-dimethyl-6,8-diphenyl-7,9-dihydropyrrolo[3,4-*d*]-tetrazolo[1,5-*b*][1,2]diazepine (**10b**). 10-Methyl-6,8-diphenyl-7,9-dihydropyrrolo[3,4-*d*][1,2,4]triazolo-[4,3-*b*]diazepine (**11a**) and 9,10-dimethyl-6,8-diphenyl-7,9-dihydropyrrolo[3,4-*d*][1,2,4]triazolo[4,3-*b*]diazepine (**11b**) were obtained by heating compounds **9a** and **9b** in triethyl orthoformate. The structure of **11a** was confirmed by ^{1}H and ^{13}C NMR spectra, as well as by two-dimensional ^{1}H–^{13}C HMBC data (see figure).

The C^{10b} signal was located in the ^{13}C NMR spectra of **10a** and **10b** at δ_C 146.1 and 145.7 ppm, respectively, which is typical of tetrazole ring. Compounds **11a** and **11b** characteristically showed in the ^1H NMR spectra a signal at δ 8.60 and 8.60 ppm, respectively, due to 3-H (triazole ring), and the C^{10b} and C^3 atoms resonated in the ^{13}C NMR spectra at δ_C 145.6 (**11a**) or 145.4 ppm (**11b**) and 142.6 ppm (**11a**, **11b**) [21].

Like benzodiazepinethiol described in [13], compound **8b** was readily alkylated at the sulfur atom with 2-bromo-1-phenylethan-1-one to give 2-[(7,8-dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepin-1-yl)sulfanyl]-1-phenylethan-1-one (**13**). 1-Hydrazinylpyrrolodiazepines **9a** and **9b** reacted with acetylacetone, yielding 1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-substituted derivatives **12a** and **12b**.

The ^1H NMR spectra of **12a**, **12b**, and **13** displayed doublet signals at δ 3.17 and 4.72 (J = 12.8 Hz) (**12a**), 3.04 and 4.02 (J = 13.6 Hz) (**12b**), and 2.94 and 3.79 ppm (J = 13.6 Hz) (**13**) from nonequivalent methylene protons on C^5. The SCH_2 protons in **13** were also nonequivalent because of restricted rotation, and they gave rise to two doublets at δ 4.71 and 4.82 ppm with a coupling constant ^2J of 12.8 Hz.

Thus, we have developed a preparative method for the synthesis of 5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine derivatives from ethyl 4-(2-oxo-2-phenylethyl)-1*H*-pyrrole-3-carboxylates, studied some their transformations, and obtained new heterocyclic systems, 6-phenyl-7,9-dihydropyrrolo[3,4-*d*]tetrazolo[1,5-*b*]-[1,2]diazepines and 6-phenyl-7,9-dihydropyrrolo-[3,4-*d*][1,2,4]triazolo[4,3-*b*][1,2]diazepines.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II spectrometer at 400 and 100 MHz, respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The IR spectra were measured in KBr on a Specord IR-75 spectrometer. The melting points were determined on a Boetius hot stage and are uncorrected. The elemental analyses were obtained on a Vario EL Cube Elementar analyzer.

2-(4-Acetyl-1-benzyl-5-methyl-2-phenyl-1*H*-pyrrol-3-yl)-1-phenylethan-1-one (3c). A mixture of 0.85 g (8.5 mmol) of acetylacetone and 0.9 g (8.5 mmol) of benzylamine was stirred for 5 min at 100°C, 8.5 mmol of 1,4-diphenylbut-2-ene-1,4-dione was added, and the mixture was heated to 160°C, kept for 5 min at that temperature, and cooled to room temperature. The resulting brown material was dissolved in 8 mL of methanol, and a crystalline solid separated from the solution after a time. After 2–3 h, the precipitate was filtered off and washed with a small amount of methanol. Yield 1.46 g (41%), colorless crystals, mp 137–138°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1600 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 2.34 s (3H, CH_3CO), 2.46 s (3H, CH_3), 4.16 s (2H, CH_2COPh), 5.10 s (2H, C**H**$_2$Ph), 6.93 d (2H, Ph, J = 7.2 Hz), 7.15–7.36 m (8H, Ph), 7.47 t (2H, Ph, J = 7.6 Hz), 7.56 t (1H, Ph, J = 7.6 Hz), 7.95 d (2H, Ph, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.8 (CH_3), 30.4 (CH_3CO), 36.2 (**C**H_2COPh), 47.1 (**C**H_2Ph), 115.1, 121.2, 125.2, 126.7, 127.6, 127.8, 128.0, 128.0, 128.3, 130.1, 130.7, 132.0, 133.2, 134.0, 137.2, 137.5, 192.7 (CO), 197.1 (CO). Found, %: C 83.51; H 6.19; N 3.45. $C_{28}H_{25}NO_2$. Calculated, %: C 83.53; H 6.18; N 3.44.

7-Benzyl-1,8-dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine (5c). A mixture of 1 g (2.5 mmol) of compound **3c** and 0.25 g (5.0 mmol) of hydrazine hydrate in 5 mL of methanol was refluxed for 4 h. The initial compound gradually dissolved, and a solid separated. After cooling to room temperature, the precipitate was filtered off and washed with a small amount of methanol. Yield 0.8 g (81%), fine light yellow crystals, mp 172–173°C. IR spectrum, ν, cm^{-1}: 1600, 1580 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3), 2.47 s (3H, CH_3), 2.91 d and 3.79 d (1H each, CH_2, J = 14 Hz), 5.08 d.d (2H, C**H**$_2$Ph, J = 16, 9.2 Hz), 6.80 d (2H, Ph, J = 7.2 Hz), 7.10–7.30 m (8H, Ph), 7.35–7.41 m (3H, Ph), 7.45 d (2H, Ph, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.4 (CH_3), 24.7 (CH_3), 25.8 (CH_2), 47.1 (**C**H_2Ph), 116.0, 120.7, 125.1, 126.5, 126.6, 126.7, 126.7, 127.4, 127.7, 128.2, 128.3, 128.7, 129.9, 130.5, 136.1, 137.6, 149.9, 153.6. Found, %: C 83.30; H 6.31; N 10.39. $C_{28}H_{25}N_3$. Calculated, %: C 83.34; H 6.24; N 10.41.

Ethyl 4-[(2*Z*)-2-hydrazinylidene-2-phenylethyl]-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (6). A mixture of 1 g (2.8 mmol) of compound **3a** and 0.14 g (2.8 mmol) of hydrazine hydrate in 5 mL of 2-ethoxyethanol was refluxed for 2 h. The solvent was removed under reduced pressure, 5 mL of metanol was added to the residue, and the viscous oily material was crystallized on grinding and heating. After cooling, the precipitate was filtered off and washed with methanol. Yield 0.95 g (91%), colorless crystals, mp 141–142°C. IR spectrum, ν, cm^{-1}: 3360 (NH_2), 3110 (NH), 1680 (OC=O), 1640 ($C=C_{arom}$), 1600 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 1.28 t (3H, CH_3, J = 7.2 Hz), 2.42 s (3H, CH_3), 4.08 s (2H, CH_2), 4.13 q (2H, OCH_2, J =

6.8 Hz), 5.99 s (2H, NH_2), 7.13 t (2H, Ph, J = 3.6 Hz), 7.21 t (1H, Ph, J = 7.2 Hz), 7.26–7.34 m (4H, Ph), 10.66 s (1H, NH). Found, %: C 72.84; H 6,52; N 11.5. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.11; H 6.41; N 11.63.

5-Amino-3-methyl-1,6-diphenyl-2,5-dihydro-4*H*-pyrrolo[3,4-*c*]pyridin-4-one hydrochloride (7a). A mixture of 1 g (3.18 mmol) of compound **5a** and 10 mL of 1,4-dioxane was heated to the boiling point, 0.4 mL of 30% aqueous HCl was added, and the mixture was refluxed for 5 min. A finely crystalline solid began to separate from the solution in a few seconds after addition of HCl. The mixture was cooled to room temperature, and the precipitate was filtered off and washed with a small amount of dioxane. If no solid separated, the mixture was diluted with a small amount of water. The oily material was ground with a glass rod. Yield 1 g (90%), fine colorless crystals, mp 204–205°C. IR spectrum, ν, cm^{-1}: 3220 (NH_2), 2810 (NH), 1660 (C=O), 1600 (C=C_{arom}), 1570 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 2.75 s (3H, CH_3), 4.55 br.s (3H, NH_3^+), 6.48 s (1H, 7-H), 7.14 t (1H, Ph, J = 7.6 Hz), 7.32–7.43 m (5H, Ph), 7.59 t (4H, Ph, J = 6.4 Hz), 12.19 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.84 (CH_3), 101.4 (CH), 109.9, 118.6, 121.0, 125.0, 127.4, 127.5, 128.3, 129.2, 130.6, 132.3, 135.1, 138.4, 158.9, 162.5 (C=O). Found, %: C 68.31; H 5.19; Cl 10.07; N 12.01. $C_{20}H_{18}ClN_3O$. Calculated, %: C 68.28; H 5.16; Cl 10.08; N 11.94.

5-Amino-2,3-dimethyl-1,6-diphenyl-2,5-dihydro-4*H*-pyrrolo[3,4-*c*]pyridin-4-one hydrochloride (7b) was synthesized in a similar way from 1 g (3.04 mmol) of **5b**. Yield 0.7 g (63%), fine colorless crystals, mp 172–173°C. ^{1}H NMR spectrum, δ, ppm: 2.82 s (3H, CH_3), 3.70 s (3H, CH_3), 4.55 br.s (3H, NH_3^+), 6.10 s (1H, 7-H), 7.25–7.35 m (4H, Ph), 7.35–7.48 m (6H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 10.8 (CH_3), 31.7 (CH_3), 99.2 (C^7), 119.7, 123.4, 126.4, 126.8, 126,9, 128.2, 129.0, 129.1, 129.4, 131.1, 136.6, 139.9, 159.3, 165.1 (C=O). Found, %: C 68.96; H 5.54; Cl 9.68; N 11.52. $C_{21}H_{20}ClN_3O$. Calculated, %: C 68.94; H 5.51; Cl 9.69; N 11.49.

8-Methyl-4,6-diphenyl-5,7-dihydropyrrolo-[3,4-*d*][1,2]diazepine-1-thiol (8a). A solution of 0.91 g (2.25 mmol) of Lawesson's reagent in 20 mL of ethyl benzene (chlorobenzene or xylene can also be used as solvent) was added to 1 g (3.18 mmol) of compound **5a**, and the mixture was refluxed for 1 h. The mixture was cooled to room temperature, and the yellow finely crystalline solid was filtered off and washed with a small amount of anhydrous benzene. Yield 1 g (95%), fine greenish–yellow crystals, mp 216–217°C. IR spectrum, ν, cm^{-1}: 3040 (NH), 1600 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 2.62 s (3H, CH_3), 3.94 s (2H, CH_2), 7.20–7.45 m (8H, Ph), 7.64 d (2H, Ph, J = 7.6 Hz), 11.5 s (1H, NH), 11.6 s (1H, SH). ^{13}C NMR spectrum, δ_C, ppm: 13.5 (CH_3), 26.9 (CH_2), 113.4, 120.2, 123.2, 126.2, 126.7, 126.8, 128.1, 128.3, 129.9, 131.4, 135.1, 136.4, 162.7, 187.2 (CS). Found, %: C 72.51; H 5.18; N 12.67; S 9.63. $C_{20}H_{17}N_3S$. Calculated, %: C 72.48; H 5.17; N 12.68; S 9.67.

7,8-Dimethyl-4,6-diphenyl-5,7-dihydropyrrolo-[3,4-*d*][1,2]diazepine-1-thiol (8b) was synthesized in a similar way from 1 g (3.04 mmol) of **5b**. Yield 1 g (95%), fine greenish–yellow crystals, mp 218–219°C. ^{1}H NMR spectrum, δ, ppm: 2.69 s (3H, CH_3), 3.44 s (3H, CH_3), 3.67 s (2H, CH_2), 7.21 d (2H, Ph, J = 7.2 Hz), 7.28 t (2H, Ph, J = 7.2 Hz), 7.38 t (1H, Ph, J = 6.8 Hz), 7.40–7.50 m (3H, Ph), 7.52 d (2H, Ph, J = 8.0 Hz), 11.80 s (1H, SH). ^{13}C NMR spectrum, δ_C, ppm: 11.8 (CH_3), 26.5 (CH_2), 31.6 (CH_3), 114.6, 119.2, 126.3, 126.7, 127.4, 127.9, 128.1, 129.7, 130.0, 130.1, 134.6, 136.1, 162.7, 187.0 (CS). Found, %: C 73.02; H 5.57; N 12.15; S 9.26. $C_{21}H_{19}N_3S$. Calculated, %: C 73.01; H 5.54; N 12.16; S 9.28.

1-Hydrazinyl-8-dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine (9a). A mixture of 1 g (2.9 mmol) of compound **8a** and 10 g of hydrazine hydrate was slowly heated to the boiling point with stirring and was then refluxed for 1 h with stirring. The mixture was cooled and diluted with 20 mL of water, and the precipitate was filtered off, washed with water, and recrystallized from methanol. Yield 0.75 g (75%), fine colorless crystals, mp 134–136°C. IR spectrum, ν, cm^{-1}: 3370 (NH_2), 3210 (NH), 1600 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 2.37 s (3H, CH_3), 3.19 s (1H, NH), 3.94 s (2H, CH_2), 4.58 br.s (2H, NH_2), 7.37–7.40 m (4H, Ph), 7.38 m (4H, Ph), 7.51 d (2H, Ph, J = 7.2 Hz), 10.96 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.3 (CH_3), 26.6 (CH_2), 113.4, 115.4, 124.3, 126.6, 126.8, 127.1, 128.6, 129.0, 129.3, 129.7, 132.9, 137.5, 146.8, 160.9. Found, %: C 72.95; H 5.85; N 21.20. $C_{20}H_{19}N_5$. Calculated, %: C 72.93; H 5.81; N 21.26.

1-Hydrazinyl-7,8-dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine (9b) was synthesized in a similar way from 1 g (2.9 mmol) of **8b**. Yield 0.75 g (75%), fine colorless crystals, mp 182–183°C. ^{1}H NMR spectrum, δ, ppm: 2.47 s (3H, CH_3), 3.41 s (3H, CH_3), 3.69 s (2H, CH_2), 7.30–7.15 m (5H, Ph), 7.48–7.35 m (5H, Ph). ^{13}C NMR spectrum, δ_C,

ppm: 11.9 (CH_3), 26.4 (CH_2), 31.9 (CH_3), 112.3, 115.7, 126.5, 127.5, 127.9, 128.8, 129.0, 129.1, 129.7, 130.5, 131.5, 137.2, 146.3, 160.9. Found, %: C 73.43; H 6.18; N 20.39. $C_{21}H_{21}N_5$. Calculated, %; C 73.44; H 6.16; N 20.39.

10-Methyl-6,8-diphenyl-7,9-dihydropyrrolo-[3,4-*d*]tetrazolo[1,5-*b*][1,2]diazepine (10a). Sodium nitrite, 0.21 g (3 mmol), was added with stirring to a solution of 0.5 g (1.52 mmol) of compound **9a** in 3 mL of acetic acid, and the mixture was stirred for 2 h. The finely crystalline solid was filtered off and washed with a small amount of acetic acid and with water. Yield 0.267 g (53%), fine colorless crystals, mp 187–188°C. IR spectrum, ν, cm^{-1}: 3160 (NH), 1610 (C=C_{arom}), 1580 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 2.58 s (3H, CH_3), 4.21 s (2H, CH_2), 7.35 t (1H, Ph, J = 6.8 Hz), 7.50–7.40 m (4H, Ph), 7.53 t (2H, Ph, J = 7.2 Hz), 7.62 t (1H, Ph, J = 7.6 Hz), 7.93 d (2H, Ph, J = 8.0 Hz), 12.02 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.9 (CH_3), 27.5 (CH_2), 104.9, 112.7, 126.6, 126,8, 127.1, 128.3, 129.0, 129.1, 130.5, 131.1, 132.2, 134.5, 146.1, 165.6 (C^6). Found, %: C 70.59; H 4.75; N 24.66. $C_{20}H_{16}N_6$. Calculated, %: C 70.57; H 4.74; N 24.69.

9,10-Dimethyl-6,8-diphenyl-7,9-dihydropyrrolo-[3,4-*d*]tetrazolo[1,5-*b*][1,2]diazepine (10b) was synthesized in a similar way from 0.5 g (1.46 mmol) of **9b**. Yield 0.258 g (50%), fine colorless crystals, mp 184–185°C. ^1H NMR spectrum, δ, ppm: 7.75 d (2H, Ph, J = 8.0 Hz), 2.64 s (3H, CH_3), 3.53 s (3H, CH_3), 3.86 s (2H, CH_2), 7.25 d (2H, Ph, J = 7.2 Hz), 7.56–7.38 m (6H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 10.9 (CH_3), 26.9 (CH_2), 31.8 (CH_3), 103.7, 113.0, 127.8, 129.6, 129.9, 130.4, 131.5, 134.1, 145.7, 164.1 (C^6). Found, %: C 71.20; H 5.15; N 23.65. $C_{21}H_{18}N_6$. Calculated, %: C 71.17; H 5.12; N 23.71.

10-Methyl-6,8-diphenyl-7,9-dihydropyrrolo-[3,4-*d*][1,2,4]triazolo[4,3-*b*]diazepine (11a). A solution of 0.5 g (1.52 mmol) of compound **9a** in 3 mL of triethyl orthoformate was refluxed for 4 h. After cooling, the precipitate was filtered off and washed with a small amount of methanol. Yield 0.252 g (49%), fine yellow crystals, mp 241–242°C. IR spectrum, ν, cm^{-1}: 3380 (NH), 1600 (C=C_{arom}), 1550 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 2.57 s (3H, CH_3), 4.05 s (2H, CH_2), 7.27 t (1H, Ph, J = 6.0 Hz), 7.40–7.35 m (4H, Ph), 7.43 t (2H, Ph, J = 7.2 Hz), 7.50 t (1H, Ph, J = 7.2 Hz), 7.81 d (2H, Ph, J = 7.6 Hz), 8.60 s (1H, 3-H), 11.49 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.7 (CH_3), 27.0 (CH_2), 107.8, 111.8, 125.6, 126.1, 126.6, 127.5, 128.3, 128.4, 128.6, 130.7, 131.7, 135.2, 142.6 (C^3), 145.6, 163.8 (C^6). Found, %: C 74.35; H 5.08; N 20.57. $C_{21}H_{17}N_5$. Calculated, %: C 74.32; H 5.05; N 20.63.

9,10-Dimethyl-6,8-diphenyl-7,9-dihydropyrrolo-[3,4-*d*][1,2,4]triazolo[4,3-*b*]diazepine (11b) was synthesized in a similar way from 0.5 g (1.46 mmol) of **9b**. Yield 0.105 g (20%), fine yellow crystals, mp 198–199°C. ^1H NMR spectrum, δ, ppm: 2.62 s (3H, CH_3), 3.50 s (3H, CH_3), 3.78 s (2H, CH_2), 7.22 d (2H, Ph, J = 7.6 Hz), 7.51–7.31 m (6H, Ph), 7.63 d (2H, Ph, J = 7.6 Hz), 8.58 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 10.8 (CH_3), 26.7 (CH_2), 31.5 (CH_3), 106.7, 112.6, 127.3, 127.5, 128.2, 128.3, 128.5, 128.9, 129.9, 130.2, 130.8, 134.9, 142.6 (C^3), 145.4, 163.6 (C^6). Found, %: C 74.75; H 5.45; N 19.80. $C_{22}H_{19}N_5$. Calculated, %: C 74.77; H 5.42; N 19.82.

1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-8-methyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine (12a). A solution of 0.5 g (1.52 mmol) of compound **9a** and 0.16 g (1.6 mmol) of acetylacetone in 3 mL of 2-ethoxyethanol was refluxed for 4 h. The mixture was cooled, 5 mL of water was added, and the precipitate was filtered off, washed with a small amount of water, and recrystallized from methanol. Yield 0.23 g (38%), fine light yellow crystals, mp 214–215°C. IR spectrum, ν, cm^{-1}: 3380 (NH), 1600 (C=C_{arom}), 1550 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.80 s (3H, CH_3), 2.20 s (3H, CH_3), 2.62 s (3H, CH_3), 3.17 d and 4.42 d (1H each, 5-H, J = 12.8 Hz), 5.99 s (1H, 4′-H), 7.22–7.35 m (3H, Ph), 7.36–7.46 m (3H, Ph), 7.50 d (2H, Ph, J = 7.2 Hz), 7.61 d (2H, Ph, J = 7.2 Hz), 11.55 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 11.9 (CH_3), 13.4 (CH_3), 13.9 (CH_3), 27.7 (CH_2), 107.6, 112.6, 120.1, 124.0, 126.5, 126.8, 127.5, 128.6, 129.1, 129.7, 130.1, 132.6, 136.9, 141.5, 144.8, 149.0, 156.5 (C^6). Found, %: C 76.30; H 5.92; N 17.78. $C_{25}H_{23}N_5$. Calculated, %: C 76.31; H 5.89; N 17.80.

1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-7,8-dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepine (12b) was synthesized in a similar way from 0.5 g (1.46 mmol) of **9b**. Yield 210 mg (35%), fine light yellow crystals, mp 200–201°C. ^1H NMR spectrum, δ, ppm: 1.77 s (3H, CH_3), 2.21 s (3H, CH_3), 2.63 s (3H, CH_3), 3.04 d (1H, 5-H, J = 13.6 Hz), 3.48 s (3H, CH_3), 4.02 d (1H, 5-H, J = 13.6 Hz), 6.03 s (1H, 4′-H), 7.23 t (2H, Ph, J = 7.2 Hz), 7.35–7.28 m (3H, Ph), 7.60–7.40 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 9.4 (CH_3), 11.6 (CH_3), 12.0 (CH_3), 25.3 (CH_2), 30.4 (CH_3), 105.9, 109.4, 118.5, 125.3, 125.5, 126.1, 126.6, 127.1,

127.9, 128.1, 128.6, 129.2, 134.6, 139.6, 142.5, 147.3, 154.3 (C^6). Found, %: C 76.60; H 6.21; N 17.19. $C_{26}H_{25}N_5$. Calculated, %: C 76.63; H 6.18; N 17.19.

2-[(7,8-Dimethyl-4,6-diphenyl-5,7-dihydropyrrolo[3,4-*d*][1,2]diazepin-1-yl)sulfanyl]-1-phenylethan-1-one (13). A mixture of 0.5 g (1.45 mmol) of compound **8b**, 0.3 g (1.5 mmol) of 2-bromo-1-phenylethan-1-one, and 0.12 g (3.0 mmol) of finely powdered sodium hydroxide in 10 mL of acetone was stirred for 4 h at room temperature. The mixture was diluted with 15 mL of water, and the precipitate was filtered off and recrystallized from methanol. Yield 0.55 g (82%), fine light yellow crystals, mp 138–139°C. IR spectrum, ν, cm^{-1}: 1690 (C=O), 1580 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 2.56 s (3H, CH_3), 2.94 d (1H, 5-H, J = 13.6 Hz), 3.47 s (3H, CH_3), 3.79 d (1H, 5-H, J = 13.6 Hz), 4.71 d and 4.82 d (1H each, CH_2S, J = 12.8 Hz), 7.17 t (2H, Ph, J = 7.6 Hz), 7.55–7.22 m (11H, Ph), 7.61 t (1H, Ph, J = 7.2 Hz), 8.09 d (2H, Ph, J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.4 (CH_3), 25.9 (CH_3), 31.5 (CH_2), 36.9 (CH_2S), 113.0, 119.6, 126.5, 126.8, 127.3, 127.6, 128.0, 128.1, 128.2, 128.7, 129.8, 130.3, 132.6, 135.9, 143.6, 148.0, 155.3, 180.4, 193.0 (C=O). Found, %: C 75.10; H 6.48; N 9.10. $C_{29}H_{25}N_3OS$. Calculated, %: C 75.13; H 5.44; N 9.06.

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