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Synthesis of New Di-, Tetra-, and Hexahydropyrazolo[3,4-*e*][1,4]diazepine Derivatives

A. V. Bol'but, S. V. Kemskii, and M. V. Vovk

Institute of Organic Chemistry, National Academy of Sciences of Ukraine,
ul. Murmanskaya 5, Kiev, 02660 Ukraine
e-mail: mvovk@i.com.ua

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Abstract—Alkaline hydrolysis of 5-(2,2-diethoxyethyl-, aroylmethyl-, or ethoxycarbonylmethyl)-1*H*-pyrazolo[3,4-*e*]pyrimidin-4(5*H*)-ones gave 5-amino-*N*-(2,2-diethoxyethyl-, aroylmethyl-, or carboxymethyl)-1*H*-pyrazole-4-carboxamides which underwent cyclization to the corresponding 7-hydroxy-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-ones, 5,6-dihydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-ones, and 1,5,6,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepine-4,7-diones. Reduction of the cyclization products with $NaBH_4$ and $LiAlH_4$ afforded 5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-ones and 1,4,5,6,7,8-hexahydropyrazolo[3,4-*e*][1,4]diazepines.

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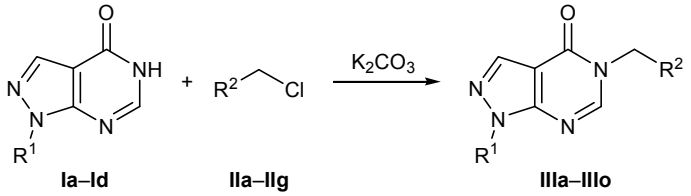
Pyrazolo[1,4]diazepines constitute a pharmacologically important class of fused heterocyclic systems. Pyrazolo[1,4]diazepine derivatives include such medical agents as anticonvulsant and anxiolytic Zolazepam [1], anxiolytic Ripazepam [2, 3], and antidepressant Zometapine [4]. In addition, selective phosphodiesterase inhibitors [5] and oxytocin receptor agonists [6] were found among compounds of this series.

Pyrazolo[1,4]diazepine compounds are generally synthesized by annulation of a diazepine ring to pyrazole ring, which leads to pyrazolo[3,4-*e*]- or pyrazolo[4,3-*e*][1,4]diazepines. The known procedures [3, 7–10] generally include a number of steps and are not always selective; furthermore, they require the use of difficultly accessible and relatively expensive reagents and often involve preparative difficulties. For example, in the synthesis of 1,3-diphenylpyrazolo[3,4-*e*][1,4]diazepine-4,7-dione [8] the most difficult is the preparation of intermediate 5-amino-*N*-(methoxycarbonylmethyl)pyrazole-4-carboxamides, which considerably restricts the scope of application of this method. Up to now, a few *N*-substituted 5-aminopyrazole-4-carboxamides have been reported, and their preparation required preliminary protection of the amino group [8] or activation of the carboxy group [11] with subsequent condensation with amines in the presence of carbodiimides.

In view of the above stated, it seemed important to develop an efficient procedure for the synthesis of N-substituted 5-aminopyrazole-4-carboxamides capable of undergoing intramolecular diazepine ring closure via condensation involving the amino group.

Hydrolytic opening of the 1,3-diazine ring in fused pyrimidines with formation of compounds having

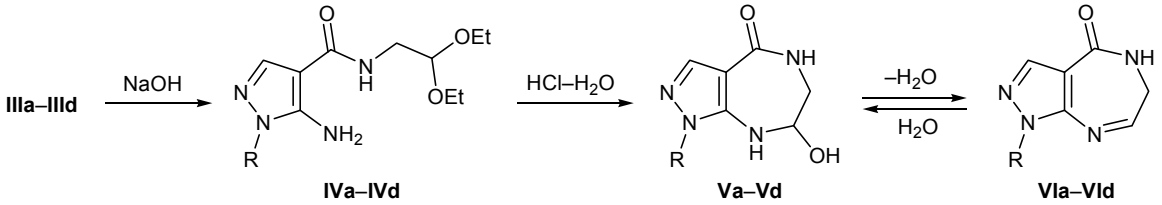
Scheme 1.



Ia–Id **IIa–IIg** **IIIa–IIIo**

I, R^1 = Me (**a**), $PhCH_2$ (**b**), Ph (**c**), 4-FC_6H_4 (**d**); **II**, R^2 = $(EtO)_2CH$ (**a**), PhC(O) (**b**), 4-$FC_6H_4C(O)$ (**c**), 3-$ClC_6H_4C(O)$ (**d**), 4-$ClC_6H_4C(O)$ (**e**), 4-$MeOC_6H_4C(O)$ (**f**), EtOC(O) (**g**); **III**, R^2 = $(EtO)_2CH$, R^1 = Me (**a**), $PhCH_2$ (**b**), Ph (**c**), 4-FC_6H_4 (**d**); R^1 = Me, R^2 = PhC(O) (**e**), 4-$ClC_6H_4C(O)$ (**f**), 4-$MeOC_6H_4C(O)$ (**g**); R^1 = $PhCH_2$, R^2 = PhC(O) (**h**); R^1 = Ph, R^2 = PhC(O) (**i**), 4-$FC_6H_4C(O)$ (**j**); R^1 = 4-FC_6H_4, R^2 = 3-$ClC_6H_4C(O)$ (**k**); R^2 = EtOC(O), R^1 = Me (**l**), $PhCH_2$ (**m**), Ph (**n**), 4-FC_6H_4 (**o**).

Scheme 2.



R^1 = Me (**a**), $PhCH_2$ (**b**), Ph (**c**), 4-FC_6H_4 (**d**).

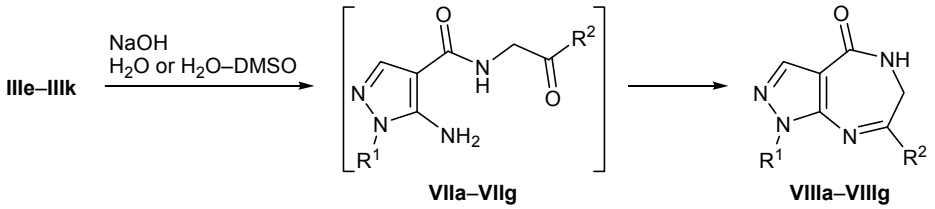
vicinal amino and carbamoyl groups was studied using 3-benzylpteridinone [12] and 1-substituted hypoxanthines [13–18] as examples. In the latter case, the ring-opening products turned out to be convenient reagents for the synthesis of imidazo[4,5-*e*][1,4]diazepine derivatives. Taking into account that alkaline cleavage of pyrimidine ring is inherent only to N^3-substituted structures [16], we made an attempt to perform analogous transformation of a number of 5-substituted pyrazolo[3,4-*d*]pyrimidin-4(5H)-ones. We have developed a procedure for the synthesis of these compounds by alkylation of readily accessible [19] 1*H*-pyrazolo-[3,4-*d*]pyrimidin-4(5*H*)-ones **Ia**–**Id** with chloroacetaldehyde diethyl acetal (**IIa**), chloroacetophenones **IIb**–**IIf**, and ethyl chloroacetate (**IIg**). The reaction of **Ia**–**Id** with **IIa**–**IIg** in boiling acetonitrile in the presence of anhydrous K_2CO_3 gave the corresponding 5-substituted 1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones **IIIa**–**IIIo** in high yields (Scheme 1).

By heating compounds **IIIa**–**IIId** with an equimolar amount of sodium hydroxide in ethanol we obtained 5-amino-*N*-(2,2-diethoxyethyl)-1*H*-pyrazole-4-carboxamides **IVa**–**IVd** as a result of opening of the pyrimidine ring. Subsequent heating of **IVa**–**IVd** in boiling water (5 min) in the presence of a catalytic amount of hydrochloric acid smoothly afforded 7-hydroxy-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-ones **Va**–**Vd** (Scheme 2). It is most probable that the primary cyclization products are diazepines **VIa**–**VId** in which the azomethine group is activated by electron-withdrawing pyrazole ring, so that compounds **VIa**–**VId** relatively readily take up water molecule.

The IR spectra of crystalline compounds **Va**–**Vd** contained carbonyl absorption band at 1660–1680 cm^{-1}, OH stretching vibrations gave rise to absorption at 3640–3650 cm^{-1}, and stretching vibrations of the NH groups were characterized by two bands, a broad band at 3340–3350 cm^{-1} (associated, NH···O=C) and a narrow band at 3430–3450 cm^{-1} (unassociated). Freshly prepared solutions of **Va**–**Vc** in DMSO-d_6 displayed in the ^{1}H NMR spectra multiplet signals at δ 3.00–3.36 ppm due to methylene protons, a signal at δ 4.89–5.00 ppm from methine proton, and a doublet at δ 5.56–5.69 ppm due to 8-H. After 24 h, the intensity of the above signals decreased, and a doublet of doublets appeared at δ 3.67–3.76 ppm (CH_2), indicating spontaneous elimination of water and equilibration between structures **Va**–**Vc** and **VIa**–**VIc**. In the ^{13}C NMR spectra of the same compounds in DMSO-d_6 (freshly prepared solutions) we observed a signal at δ_C 74.0–74.1 ppm (C^7), which is typical of an O–CH–N fragment; after 24 h, the C^7 signal appeared at δ_C 164.6–164.9 ppm, which is typical of a CH=N fragment. The ^{1}H and ^{13}C NMR spectra of a freshly prepared solution of **Vd** in DMSO-d_6 already contained signals assignable to structure **VId** in addition to those typical of **Vd**. According to the analytical and GC–MS data, a solid sample of **Vd** contained no impurity of **VId**.

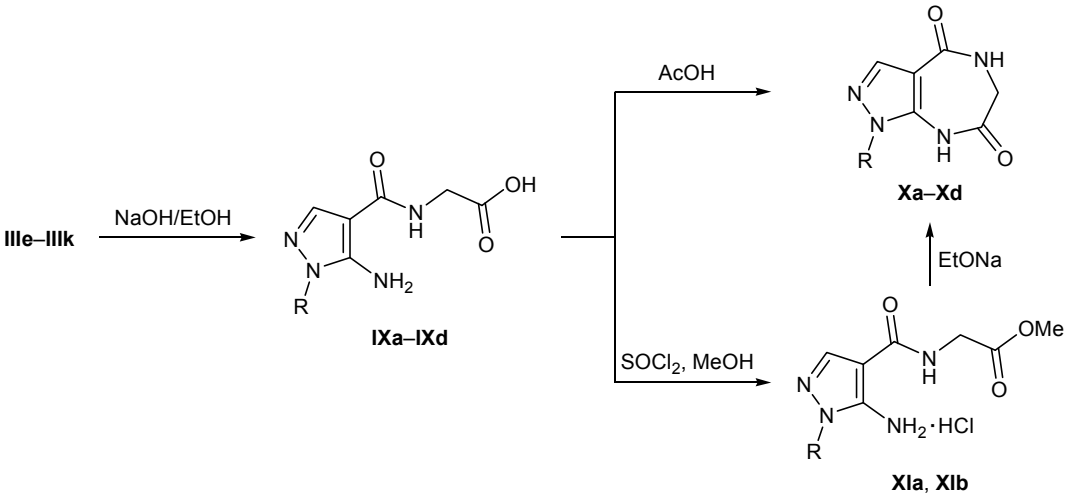
5-Aroylmethylpyrazolopyrimidin-4(5H)-ones **IIIe**–**IIIk** were subjected to alkaline hydrolysis by heating in boiling water or aqueous dimethyl sulfoxide. Under

Scheme 3.



R^1 = Me, R^2 = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**); R^1 = $PhCH_2$, R^2 = Ph (**d**); R^1 = Ph, R^2 = Ph (**e**), 4-FC_6H_4 (**f**); R^1 = 4-FC_6H_4, R^2 = 3-ClC_6H_4 (**g**).

Scheme 4.



R = Me (**a**), $PhCH_2$ (**b**), Ph (**c**), 4-FC_6H_4 (**d**).

these conditions we failed to isolate the corresponding ring opening products, 5-amino-*N*-(aroylmethyl)-1*H*-pyrazole-4-carboxamides **VIIa**–**VIIg**, for they underwent fast intramolecular cyclization to 1,7-disubstituted 5,6-dihydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-ones **VIIIa**–**VIIIc** and **VIIIe**–**VIIIg** (yield 72–95%; Scheme 3). However, in the reaction with compound **IIIh** having a benzyl substituent in the pyrazole ring, the cyclization of **VIId** occurred only by half, and its complete transformation into **VIIId** required additional heating of a solid mixture of products in isobutyric acid.

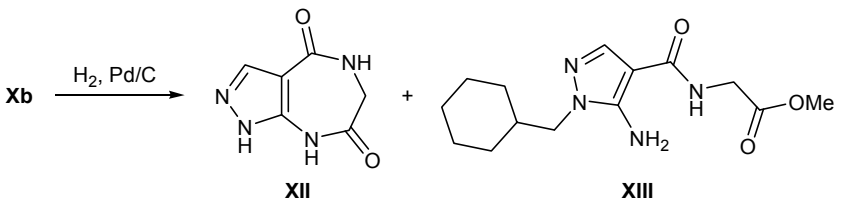
The assumed structure of compounds **VIIIa**–**VIIIg** was consistent with their IR spectra which contained absorption bands due to carbonyl (1695–1705 cm^{-1}) and N–H stretching vibrations (3190–3240 cm^{-1}) and ^{1}H NMR spectra (δ 4.10–4.27 ppm, d, J = 5.1–5.3 Hz, methylene protons).

The hydrolysis of pyrazolopyrimidinones **IIIl**–**IIIo** in a boiling solution of sodium hydroxide in ethanol produced 2-(5-amino-1*H*-pyrazol-4-ylcarbonylamino)-acetic acids **IXa**–**IXd** as a result of opening of the pyrimidine ring and hydrolysis of the ester group (Scheme 4). Their cyclization in boiling acetic acid (reaction time 40–45 h, cf. [13]) was effective only for 1-aryl-substituted derivatives **IXc** and **IXd** which were thus converted into 1-aryl-1,5,6,8-tetrahydropyrazolo-[3,4-*e*][1,4]diazepine-4,7-diones **Xc** and **Xd** in 80–84% yield. The cyclization of 1-alkyl-substituted compounds **IXa** and **IXb** was accompanied by considerable tarring, and the yield of **Xa** and **Xb** was as poor as 15–21%. We synthesized compounds **Xa** and **Xb** in 69–77% yield by cyclization of esters **XIa** and **XIb** (prepared preliminary from acids **IXa** and **IXb**) in the presence of sodium ethoxide.

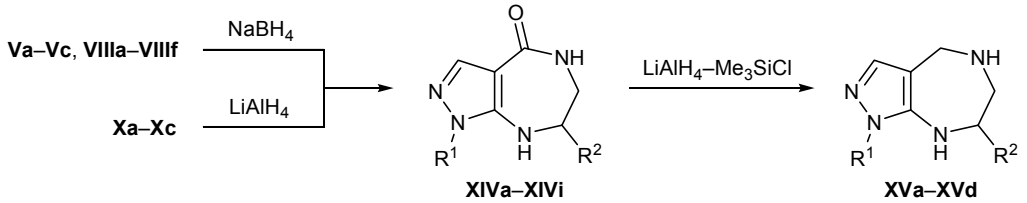
In the IR spectra of **Xa**–**Xd** we observed carbonyl absorption bands at 1660–1670 and 1705–1710 cm^{-1}, and their ^{1}H NMR spectra contained a doublet at δ 3.66–3.80 ppm from methylene protons in the diazepine ring and a triplet at δ 7.89–8.03 ppm (J = 5.0 Hz) due to 5-H.

With a view to obtain pyrazolo[3,4-*e*][1,4]diazepinones having no substituent on N^1, *N*-benzyl derivative **Xb** was reduced with hydrogen over 20% Pd/C in methanol. The reaction was not selective: apart from target product **XII**, 33% of amide **XIII** was formed as a result of opening of the diazepine ring and simultaneous hydrogenation of the benzyl group (Scheme 5).

Scheme 5.



Scheme 6.



XIV, R^2 = H, R^1 = Me (**a**), $PhCH_2$ (**b**), Ph (**c**); R^1 = Me, R^2 = Ph (**d**), 4-ClC_6H_4 (**e**), 4-$MeOC_6H_4$ (**f**); R^1 = $PhCH_2$, R^2 = Ph (**g**); R^1 =Ph, R^2 = Ph (**h**), 4-FC_6H_4 (**i**); **XV**, R^1 = Me, R^2 = H (**a**), R^1 = $PhCH_2$, R^2 = H (**b**), Ph (**c**); R^1 = Ph, R^2 = H (**d**).

From the viewpoint of using pyrazolodiazepine systems as templates for the design of focused libraries for biological screening, of particular interest were their representatives with partly or completely hydrogenated diazepine ring. Diazepine fragments in compounds **V**, **VIII**, and **X** possess nitrogen-containing moieties characterized by different reactivities toward common reducing agents. Treatment of **Va**–**Vc** and **VIIIa**–**VIIIf** with $NaBH_4$ in propan-2-ol at room temperature led to reduction of the corresponding hydroxymethylamino and azomethine groups with formation of tetrahydropyrazolo[3,4-*e*][1,4]diazepinones **XIVa**–**XIVi**. The reduction of **Xa**–**Xc** with 2 equiv of $LiAlH_4$ in boiling tetrahydrofuran in 4 h afforded tetrahydropyrazolodiazepines **XIVa**–**XIVc** (Scheme 6).

Compounds **XIVa**–**XIVc** displayed in the ^{1}H NMR spectra multiplet signals at δ 3.11–3.35 ppm from methylene protons in the diazepine ring. In the spectra of **XIVd**–**XIVi**, the 6-H methylene protons resonated as a multiplet at δ 3.25–3.58 ppm, and the 7-H proton gave rise to a multiplet at δ 4.59–4.79 ppm. In the ^{13}C NMR spectra of **XIVa**–**XIVc**, the C^6 and C^7 signals were located at δ_C 42 and 45 ppm, respectively, whereas the corresponding signals of **XIVd**–**XIVi** were displaced downfield to δ_C 45–46 and 57 ppm, respectively.

Compounds **Xa**–**Xc**, **XIVa**–**XIVc** and **XIVg** were reduced to hexahydro derivatives **XVa**–**XVd** by the action of 5 equiv of $LiAlH_4$–Me_3SiCl in boiling tetrahydrofuran over a period of 40–45 h. Hexahydropyrazolodiazepines **XV** were isolated as free bases (**XVa**, **XVd**) or dihydrochlorides (**XVb**, **XVc**), and their structure was confirmed by spectral data.

EXPERIMENTAL

The IR spectra were recorded in KBr (or in CH_2Cl_2 solution for **XVa**) on a UR-20 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance DRX-500 spectrometer at 500.13 and 125.75 MHz, respectively, using TMS as internal reference. The mass spectra were obtained using an Agilent 1100\DAD\HSD\VLG 119562 instrument.

1*H*-Pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones IIIa–IIIo (*general procedure*). Alkylating agent **IIa**–**IIf**, 40 mmol, was added to a mixture of 40 mmol of pyrazolopyrimidine **Ia**–**Id** and 5.52 g (40 mmol) of anhydrous potassium carbonate in 70 ml of acetonitrile–DMF (3:1), and the mixture was heated for 7 h under reflux while stirring. The mixture was cooled and poured into 200 ml of water, and the precipitate was filtered off, washed with 50 ml of water, and dried.

5-(2,2-Diethoxyethyl)-1-methyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIIa). Yield 81%, mp 95–97°C. IR spectrum: ν 1700 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 1.05 t (6H, CH_3, J = 7.1 Hz), 3.41–3.48 m (2H, CH_2), 3.62–3.69 m (2H, CH_2), 3.91 s (3H, CH_3), 4.06 d (2H, CH_2, J = 7.1 Hz), 4.70 t (1H, CH, J = 5.3 Hz), 8.09 s (1H, 3-H), 8.28 s (1H, 6-H). Found, %: C 53.81; H 6.96; N 20.91. $C_{12}H_{18}N_4O_3$. Calculated, %: C 54.12; H 6.81; N 21.04.

1-Benzyl-5-(2,2-diethoxyethyl)-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIIb). Yield 94%, mp 83–85°C. IR spectrum, ν 1695 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 1.04 t (6H, CH_3, J = 7.1 Hz), 3.41–3.48 m (2H, CH_2), 3.63–3.69 m (2H, CH_2), 4.06 d (2H, CH_2, J = 7.1 Hz), 4.71 t (1H, CH, J = 5.2 Hz), 5.51 s (2H, CH_2), 7.21–7.34 m (5H, H_{arom}), 8.14 s (1H, 3-H), 8.31 s (1H, 6-H). Found, %: C 62.93; H 6.63; N 16.57. $C_{18}H_{22}N_4O_3$. Calculated, %: C 63.14; H 6.48; N 16.36.

5-(2,2-Diethoxyethyl)-1-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIIc). Yield 87%, mp 117–118°C. IR spectrum: ν 1705 cm^{-1} (C=O). ^{1}H NMR spectrum, δ, ppm: 1.07 t (6H, CH_3, J = 7.0 Hz), 3.40–3.72 m (4H, CH_2), 4.11 d (2H, CH_2, J = 7.0 Hz), 4.74 t (1H, CH, J = 5.1 Hz), 7.43–7.75 m (5H, H_{arom}), 8.03 s (1H, 3-H), 8.40 s (1H, 6-H). Found, %: C 61.83; H 6.29; N 16.72. $C_{17}H_{20}N_4O_3$. Calculated, %: C 62.18; H 6.14; N 17.06.

5-(2,2-Diethoxyethyl)-1-(4-fluorophenyl)-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIId). Yield 89%, mp 119–120°C. IR spectrum: ν 1700 cm^{-1} (C=O). ^1H NMR spectrum, δ, ppm: 1.07 t (6H, CH_3, J = 6.9 Hz), 3.41–3.53 m (2H, CH_2), 3.62–3.73 m (2H, CH_2), 4.11 d (2H, CH_2, J = 6.9 Hz), 4.74 t (1H, CH, J = 5.4 Hz), 7.44–7.63 m (4H, H_{arom}), 8.07 s (1H, 3-H), 8.40 d (1H, 6-H). Found, %: C 58.61; H 5.75; N 15.90. $C_{17}H_{19}FN_4O_3$. Calculated, %: C 58.95; H 5.53; N 16.18.

1-Methyl-5-(2-oxo-2-phenylethyl)-1*H*-pyrazolo-[3,4-*d*]pyrimidin-4(5*H*)-one (IIIe). Yield 88%, mp 214–216°C. IR spectrum, ν, cm^{-1}: 1715, 1695 (C=O). ^1H NMR spectrum, δ, ppm: 3.96 s (3H, CH_3), 5.63 s (2H, CH_2), 7.62 t (2H, H_{arom}, J = 7.1 Hz), 7.75 t (1H, H_{arom}, J = 7.1 Hz), 8.07–8.12 m (2H, H_{arom}, 3-H), 8.38 s (1H, 6-H). Found, %: C 63.03; H 4.34; N 20.96. $C_{14}H_{12}N_4O_2$. Calculated, %: C 62.68; H 4.51; N 20.88.

5-[2-(4-Chlorophenyl)-2-oxoethyl]-1-methyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIIf). Yield 85%, mp 229–231°C. IR spectrum, ν, cm^{-1}: 1720, 1700 (C=O). ^1H NMR spectrum, δ, ppm: 3.96 s (3H, CH_3), 5.63 s (2H, CH_2), 7.69 d (2H, H_{arom}, J = 8.6 Hz), 8.09–8.14 m (3H, H_{arom}, 3-H), 8.37 s (1H, 6-H). Found, %: C 55.45; H 3.75; N 18.33. $C_{14}H_{11}ClN_4O_2$. Calculated, %: C 55.55; H 3.66; N 18.51.

5-[2-(4-Methoxyphenyl)-2-oxoethyl]-1-methyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIIg). Yield 92%, mp 199–201°C. IR spectrum, ν, cm^{-1}: 1720, 1705 (C=O). ^1H NMR spectrum, δ, ppm: 3.89 s (3H, OCH_3), 3.95 s (3H, CH_3), 5.57 s (2H, CH_2), 7.13 d (2H, H_{arom}, J = 8.8 Hz), 8.04–8.12 m (3H, H_{arom}, 3-H), 8.36 s (1H, 6-H). Found, %: C 60.67; H 4.82; N 18.55. $C_{15}H_{14}N_4O_3$. Calculated, %: C 60.40; H 4.73; N 18.78.

1-Benzyl-5-(2-oxo-2-phenylethyl)-1*H*-pyrazolo-[3,4-*d*]pyrimidin-4(5*H*)-one (IIIh). Yield 91%, mp 173–175°C. IR spectrum, ν, cm^{-1}: 1715, 1700 (C=O). ^1H NMR spectrum, δ, ppm: 5.52 s (2H, CH_2), 5.60 s (2H, CH_2), 7.24–7.37 m (5H, H_{arom}), 7.59–7.70 m (3H, H_{arom}), 7.94–8.03 m (2H, H_{arom}), 8.07 s (1H, 3-H), 8.34 s (1H, 6-H). Found, %: C 69.47; H 4.54; N 16.54. $C_{20}H_{16}N_4O_2$. Calculated, %: C 69.76; H 4.68; N 16.27.

5-(2-Oxo-2-phenylethyl)-1-phenyl-1*H*-pyrazolo-[3,4-*d*]pyrimidin-4(5*H*)-one (IIIi). Yield 95%, mp 198–200°C. IR spectrum, ν, cm^{-1}: 1720, 1700 (C=O). ^1H NMR spectrum, δ, ppm: 5.71 s (2H, CH_2), 7.44 t (1H, H_{arom}, J = 6.8 Hz), 7.56–7.69 m (4H, H_{arom}), 7.76 t (1H, H_{arom}, J = 6.5 Hz), 8.03–8.12 m (4H, H_{arom}), 8.34 s (1H, 3-H), 8.50 s (1H, 6-H). Found, %: C 68.95; H 4.18; N 16.88. $C_{19}H_{14}N_4O_2$. Calculated, %: C 69.08; H 4.27; N 16.96.

5-[2-(4-Fluorophenyl)-2-oxoethyl]-1-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIIj). Yield 87%, mp 189–191°C. IR spectrum, ν, cm^{-1}: 1720, 1695 (C=O). ^1H NMR spectrum, δ, ppm: 5.69 s (2H, CH_2), 7.40–7.51 m (3H, H_{arom}), 7.60 t (2H, H_{arom}, J = 7.9 Hz), 8.07 d (2H, H_{arom}, J = 7.6 Hz), 8.18–8.26 m (2H, H_{arom}), 8.42 s (1H, 3-H), 8.48 s (1H, 6-H). Found, %: C 65.31; H 3.85; N 15.95. $C_{19}H_{13}FN_4O_2$. Calculated, %: C 65.51; H 3.76; N 16.08.

5-[2-(3-Chlorophenyl)-2-oxoethyl]-1-(4-fluorophenyl)-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IIIk). Yield 86%, mp 239–241°C. IR spectrum, ν, cm^{-1}: 1710, 1695 (C=O). ^1H NMR spectrum, δ, ppm: 5.71 s (2H, CH_2), 7.45 t (2H, H_{arom}, J = 8.1 Hz), 7.67 t (1H, H_{arom}, J = 7.2 Hz), 7.83 d (1H, H_{arom}, J = 6.8 Hz), 8.03–8.12 m (3H, H_{arom}), 8.13 s (1H, H_{arom}), 8.41 s (1H, 3-H), 8.46 s (1H, 6-H). Found, %: C 59.34; H 3.31; N 14.72. $C_{19}H_{12}ClFN_4O_2$. Calculated, %: C 59.62; H 3.16; N 14.64.

Ethyl 2-(1-methyl-4-oxo-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]pyrimidin-5-yl)acetate (IIIl). Yield 95%, mp 130–131°C. IR spectrum, ν, cm^{-1}: 1735, 1695 (C=O). ^1H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3, J = 6.8 Hz), 3.93 s (3H, CH_3), 4.16 q (2H, OCH_2, J = 6.8 Hz), 4.81 s (2H, CH_2), 8.11 s (1H, 3-H), 8.41 s (1H, 6-H). Found, %: C 50.56; H 5.28; N 23.55. $C_{10}H_{12}N_4O_3$. Calculated, %: C 50.84; H 5.12; N 23.72.

Ethyl (1-benzyl-4-oxo-4,5-dihydro-1*H*-pyrazolo-[3,4-*d*]pyrimidin-5-yl)acetate (IIIm). Yield 96%, mp 114–115°C. IR spectrum, ν, cm^{-1}: 1730, 1685 (C=O). ^1H NMR spectrum, δ, ppm: 1.22 t (3H, CH_3, J = 7.0 Hz), 4.16 q (2H, OCH_2, J = 7.1 Hz), 4.82 s (2H, CH_2), 5.53 s (2H, CH_2), 7.23–7.36 m (5H, H_{arom}), 8.17 s (1H, 3-H), 8.45 s (1H, 6-H). Found, %: C 61.45; H 5.10; N 18.08. $C_{16}H_{16}N_4O_3$. Calculated, %: C 61.53; H 5.16; N 17.94.

Ethyl 2-(1-phenyl-4-oxo-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]pyrimidin-5-yl)acetate (IIIn). Yield 97%, mp 157–158°C. IR spectrum, ν, cm^{-1}: 1725, 1680 (C=O). ^1H NMR spectrum, δ, ppm: 1.23 t (3H, CH_3, J = 7.0 Hz), 4.19 q (2H, OCH_2, J = 7.0 Hz), 4.88 s (2H, CH_2), 7.44–7.60 m (3H, H_{arom}), 8.04 d (2H, H_{arom}, J = 7.6 Hz), 8.42 s (1H, 3-H), 8.53 s (1H, 6-H). Found, %: C 60.12; H 4.82; N 19.02. $C_{15}H_{14}N_4O_3$. Calculated, %: C 60.40; H 4.73; N 18.78.

Ethyl [1-(4-fluorophenyl)-4-oxo-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]pyrimidin-5-yl]acetate (IIIo). Yield

92%, mp 155–157°C. IR spectrum, ν, cm^{-1}: 1735, 1690 (C=O). ^1H NMR spectrum, δ, ppm: 1.23 t (3H, CH_3, J = 6.9 Hz), 4.19 q (2H, OCH_2, J = 6.9 Hz), 4.88 s (2H, CH_2), 7.44–7.87 m (4H, H_{arom}), 8.41 s (1H, 3-H), 8.52 s (1H, 6-H). Found, %: C 57.22; H 4.32; N 17.46. $C_{15}H_{13}FN_4O_3$. Calculated, %: C 56.96; H 4.14; N 17.71.

5-Amino-*N*-(2,2-diethoxyethyl)-1*H*-pyrazole-4-carboxamides IVa–IVd (*general procedure*). A solution of 1.2 g (30 mmol) of sodium hydroxide in 20 ml of ethanol was added to a suspension of 30 mmol of pyrazolopyrimidine **IIIa**–**IIId** in 80 ml of ethanol, and the mixture was heated for 5 h under reflux. The mixture was then evaporated, the solid residue was treated with 70 ml of benzene, the mixture was filtered, the filtrate was evaporated, and the residue was crystallized from hexane–propan-2-ol (10:1).

5-Amino-*N*-(2,2-diethoxyethyl)-1-methyl-1*H*-pyrazole-4-carboxamide (IVa). Yield 97%, mp 144–145°C. IR spectrum, ν, cm^{-1}: 3340 (NH), 1625 (C=O). ^1H NMR spectrum, δ, ppm: 1.07–1.17 m (6H, CH_3), 3.17–3.26 m (2H, CH_2), 3.42–3.56 m (5H, OCH_2, NCH_3), 3.58–3.68 m (2H, OCH_2), 4.53 t (1H, CH, J = 5.4 Hz), 6.12 s (2H, NH_2), 7.66 s (1H, 3-H), 7.75 t (1H, NH, J = 5.4 Hz). Found, %: C 51.32; H 7.78; N 21.63. $C_{11}H_{20}N_4O_3$. Calculated, %: C 51.55; H 7.87; N 21.86.

5-Amino-1-benzyl-*N*-(2,2-diethoxyethyl)-1*H*-pyrazole-4-carboxamide (IVb). Yield 90%, mp 153–154°C. IR spectrum, ν, cm^{-1}: 3350 (NH), 1630 (C=O). ^1H NMR spectrum, δ, ppm: 1.07–1.18 m (6H, CH_3), 3.18–3.28 m (2H, CH_2), 3.42–3.53 m and 3.57–3.69 m (2H each, OCH_2), 4.54 t (1H, CH, J = 5.5 Hz), 5.13 s (2H, CH_2), 6.32 s (2H, NH_2), 7.11–7.19 m (2H, H_{arom}), 7.22–7.28 m (1H, H_{arom}), 7.28–7.36 m (2H, H_{arom}), 7.74 s (1H, 3-H), 7.80 t (1H, NH, J = 5.7 Hz). Found, %: C 61.12; H 7.42; N 16.78. $C_{17}H_{24}N_4O_3$. Calculated, %: C 61.43; H 7.28; N 16.85.

5-Amino-*N*-(2,2-diethoxyethyl)-1-phenyl-1*H*-pyrazole-4-carboxamide (IVc). Yield 63%, mp 86–87°C. IR spectrum, ν, cm^{-1}: 3335 (NH), 1620 (C=O). ^1H NMR spectrum, δ, ppm: 1.13 t (6H, CH_3, J = 6.9 Hz), 3.22–3.28 m (2H, CH_2), 3.40–3.72 m (4H, CH_2), 4.57 t (1H, CH, J = 5.5 Hz), 6.37 s (2H, NH_2), 7.32–7.64 m (5H, H_{arom}), 7.95–8.07 m (2H, 3-H, NH). Found, %: C 60.15; H 6.87; N 17.65. $C_{16}H_{22}N_4O_3$. Calculated, %: C 60.36; H 6.97; N 17.60.

5-Amino-*N*-(2,2-diethoxyethyl)-1-(4-fluorophenyl)-1*H*-pyrazole-4-carboxamide (IVd). Yield 95%, mp 96–97°C. IR spectrum, ν, cm^{-1}: 3345 (NH), 1625 (C=O). ^1H NMR spectrum, δ, ppm: 1.13 t (6H, CH_3, J = 6.9 Hz), 3.21–3.30 m and 3.44–3.54 m (2H each, OCH_2), 3.58–3.69 m (2H, CH_2), 4.57 t (1H, CH, J = 5.0 Hz), 6.35 s (2H, NH_2), 7.29–7.42 m (2H, H_{arom}), 7.51–7.63 m (2H, H_{arom}), 7.97 s (1H, 3-H), 8.01 t (1H, NH, J = 5.5 Hz). Found, %: C 56.96; H 6.16; N 16.83. $C_{16}H_{21}FN_4O_3$. Calculated, %: C 57.13; H 6.29; N 16.66.

1-Substituted 7-hydroxy-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-ones Va–Vd (*general procedure*). A suspension of 20 mmol of pyrazolecarboxamide **IVa**–**IVd** in 20 ml of water containing 5 drops of hydrochloric acid was heated for 5–7 min at the boiling point until it became homogeneous. The solution was cooled, and the precipitate was filtered off and recrystallized from water.

7-Hydroxy-1-methyl-5,6,7,8-tetrahydropyrazolo-[3,4-*e*][1,4]diazepin-4(1*H*)-one (Va). Yield 82%, mp 195–197°C. IR spectrum, ν, cm^{-1}: 3650 (O–H); 3445, 3345 (N–H); 1665 (C=O). ^1H NMR spectrum, δ, ppm: 3.00–3.13 m (1H, CH), 3.15–3.28 m (1H, CH), 3.50 s (3H, CH_3), 4.89–5.00 m (1H, 7-H), 5.69 d (1H, NH, J = 5.8 Hz), 7.02–7.14 m (1H, OH), 7.38–7.46 m (2H, 3-H, NH). ^{13}C NMR spectrum, δ_C, ppm: 34.69 (NCH_3), 45.44 (C^6), 74.33 (C^7), 99.46 (C^{3a}), 139.51 (C^3), 143.92 (C^{8a}), 165.62 (C^4). Found, %: C 46.35; H 5.41; N 30.85. m/z 183 $[M + 1]^+$. $C_7H_{10}N_4O_2$. Calculated, %: C 46.15; H 5.53; N 30.75. M 182.18.

1-Benzyl-7-hydroxy-5,6,7,8-tetrahydropyrazolo-[3,4-*e*][1,4]diazepin-4(1*H*)-one (Vb). Yield 79%, mp 193–195°C. IR spectrum, ν, cm^{-1}: 3635 (O–H); 3435, 3350 (N–H); 1660 (C=O). ^1H NMR spectrum, δ, ppm: 3.02–3.13 m and 3.15–3.30 m (1H each, CH_2), 4.92–4.99 m (1H, 7-H), 5.14 s (2H, CH_2), 5.61 d (1H, NH, J = 5.6 Hz), 7.05–7.37 m (6H, H_{arom}, OH), 7.51 s (1H, 3-H), 7.65 m (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 45.49 (C^6), 50.04 (CH_2), 74.09 (C^7), 99.22 (C^{3a}); 127.00, 127.10, 128.39 (C_{arom}); 137.22 ($C^{1'}$), 140.56 (C^3), 143.98 (C^{8a}), 165.84 (C^4). Found, %: C 60.53; H 5.39; N 21.94. m/z 259 $[M + 1]^+$. $C_{13}H_{14}N_4O_2$. Calculated, %: C 60.46; H 5.46; N 21.69. M 258.28.

7-Hydroxy-1-phenyl-5,6,7,8-tetrahydropyrazolo-[3,4-*e*][1,4]diazepin-4(1*H*)-one (Vc). Yield 84%, mp 257–260°C. IR spectrum, ν, cm^{-1}: 3645 (O–H); 3450, 3345 (N–H); 1660 (C=O). ^1H NMR spectrum, δ, ppm: in 1 h after dissolution: 3.11–3.22 m and 3.23–3.36 m (1H each, CH_2), 4.90–4.98 m (1H, 7-H), 5.56 d (1H, NH, J = 5.2 Hz), 7.09–7.22 m (2H, NH, OH), 7.40–7.50 m (5H, H_{arom}), 7.63 s (1H, 3-H); after 24 h (additional signals belonging to **VIc**): 3.67–3.76 m

(CH_2), 7.38–7.58 m (H_{arom}), 7.83–7.92 m (7-H), 8.04–8.13 m (3-H, NH). ^{13}C NMR spectrum, δ_C, ppm: in 1 h after dissolution: 45.18 (C^6), 74.08 (C^7), 100.27 (C^{3a}), 124.53 ($C^{2'}$), 127.61 ($C^{4'}$), 129.46 ($C^{3'}$), 138.13 ($C^{1'}$), 141.98 (C^3), 143.62 (C^{8a}), 165.54 (C=O); after 24 h (signals of **VIc**): 40.12 (C^6), 110.38 (C^{3a}), 124.04 ($C^{2'}$), 127.77 ($C^{4'}$), 128.91 ($C^{3'}$), 138.11 ($C^{1'}$), 140.19 (C^3), 144.98 (C^{8a}), 163.90 (C=O), 164.60 (C^7). Found, %: C 59.27; H 5.03; N 22.70. *m*/*z* 245 $[M + 1]^+$. $C_{12}H_{12}N_4O_2$. Calculated, %: C 59.01; H 4.95; N 22.94. *M* 244.26.

1-(4-Fluorophenyl)-7-hydroxy-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (Vd). Yield 85%, mp 222–224°C. IR spectrum, ν, cm^{-1}: 3640 (O–H); 3445, 3340 (N–H); 1680 (C=O). ^1H NMR spectrum (mixture **Vd**/**VId**), δ, ppm: 3.09–3.20 m and 3.22–3.35 m (1H each, CH), 3.71 t (2H, CH_2, *J* = 4.6 Hz), 4.89–4.98 m (1H, 7-H), 5.67 d (1H, NH, *J* = 5.4 Hz), 7.22–7.73 m (10H, OH, 3-H, H_{arom}), 7.88 t (1H, NH, *J* = 4.3 Hz), 8.03–8.12 m (2H, 3-H, NH). ^{13}C NMR spectrum (mixture **Vd**/**VId**), δ_C, ppm: 40.03 and 45.21 (C^6), 74.14 (C^7), 100.16 and 110.35 (C^{3a}), 115.73 d and 116.23 d ($C^{3'}$, J_{CF} = 23.0 Hz), 126.09 d and 127.12 d ($C^{2'}$, J_{CF} = 8.8 Hz), 134.48 d ($C^{1'}$, J_{CF} = 2.8 Hz), 140.18 d and 141.92 d (C^3, J_{CF} = 1.8 Hz), 143.90 and 144.99 (C^{8a}), 161.11 d and 161.15 d ($C^{4'}$, J_{CF} = 244.6 Hz), 163.87 and 165.55 (C=O), 164.86 (C^7). Found, %: C 55.24; H 4.08; N 22.01. *m*/*z* 263 $[M + 1]^+$. $C_{12}H_{11}FN_4O_2$. Calculated, %: C 54.96; H 4.23; N 21.36. *M* 262.25.

1,7-Disubstituted 5,6-dihydropyrazolo[3,4-*e*]-[1,4]diazepin-4(1*H*)-ones VIIIa–VIIIg (*general procedure*). A mixture of 15 mmol of pyrazolopyrimidine **IIIe**–**IIIg** and 150 ml of a 0.1 M aqueous solution of sodium hydroxide or a mixture of 15 mmol of **IIIh**–**IIIk** and 165 ml of a 0.1 M solution of sodium hydroxide in H_2O–DMSO (3 : 1) was heated at the boiling point over a period of 5 (**IIIe**–**IIIg**) or 10 h (**IIIh**–**IIIk**). The mixture was cooled, and the precipitate was filtered off, washed with water (2×50 ml), dried, and recrystallized from acetonitrile. The product isolated in the reaction with **IIIh** was heated in 50 ml of boiling isobutyric acid, the solvent was removed under reduced pressure (water-jet pump), and the solid residue was recrystallized from acetonitrile.

1-Methyl-7-phenyl-5,6-dihydropyrazolo[3,4-*e*]-[1,4]diazepin-4(1*H*)-one (VIIIa) was synthesized from compound **IIIe**. Yield 92%, mp 241–243°C. IR spectrum, ν, cm^{-1}: 3200 (N–H), 1695 (C=O). ^1H NMR spectrum, δ, ppm: 3.91 s (3H, CH_3), 4.14 d (2H, CH_2, *J* = 5.3 Hz), 7.53–7.66 m (3H, H_{arom}), 7.80 t (1H, NH, *J* = 5.3 Hz), 7.88 s (1H, 3-H), 8.14 d (2H, H_{arom}, *J* = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 34.88 (NCH_3), 40.25 (CH_2), 108.56 (C^{3a}), 128.30 ($C^{2'}$), 128.93 ($C^{3'}$), 132.00 ($C^{4'}$), 136.05 ($C^{1'}$), 138.41 (C^3), 145.66 (C^{8a}), 164.32 (C^7), 167.07 (C=O). Found, %: C 64.83; H 5.22; N 23.15. *m*/*z* 241 $[M + 1]^+$. $C_{13}H_{12}N_4O$. Calculated, %: C 64.99; H 5.03; N 23.32. *M* 240.27.

7-(4-Chlorophenyl)-1-methyl-5,6-dihydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (VIIIb) was synthesized from compound **IIIf**. Yield 93%, mp 210–212°C. IR spectrum, ν, cm^{-1}: 3240 (N–H), 1700 (C=O). ^1H NMR spectrum, δ, ppm: 3.90 s (3H, CH_3), 4.12 d (2H, CH_2, *J* = 5.3 Hz), 7.60 d (2H, H_{arom}, *J* = 8.6 Hz), 7.77 t (1H, NH, *J* = 5.3 Hz), 7.88 s (1H, 3-H), 8.15 d (2H, H_{arom}, *J* = 8.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 34.92 (NCH_3), 40.11 (CH_2), 108.68 (C^{3a}), 129.02 and 130.06 ($C^{2'}$, $C^{3'}$), 134.83 ($C^{4'}$), 136.93 ($C^{1'}$), 138.47 (C^3), 145.45 (C^{8a}), 164.21 (C^7), 165.90 (C=O). Found, %: C 56.98; H 4.02; N 20.64. *m*/*z* 275 $[M + 1]^+$. $C_{13}H_{11}ClN_4O$. Calculated, %: C 56.84; H 4.04; N 20.39. *M* 274.71.

7-(4-Methoxyphenyl)-1-methyl-5,6-dihydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (VIIIc) was synthesized from compound **IIIg**. Yield 95%, mp 244–246°C. IR spectrum, ν, cm^{-1}: 3230 (N–H), 1695 (C=O). ^1H NMR spectrum, δ, ppm: 3.87 s (3H, CH_3O), 4.10 d (2H, CH_2, *J* = 5.3 Hz), 7.12 d (2H_{arom}, *J* = 8.4 Hz), 7.71 t (1H, NH, *J* = 5.3 Hz), 7.83 s (1H, 3-H), 8.12 d (2H, H_{arom}, *J* = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 34.78 (NCH_3), 39.95 (CH_2), 55.55 (OCH_3), 108.19 (C^{3a}), 114.38 ($C^{3'}$), 128.33 ($C^{1'}$), 130.38 ($C^{2'}$), 138.31 (C^3), 146.01 (C^{8a}), 162.50 ($C^{4'}$), 164.51 (C^7), 166.23 (C=O). Found, %: C 62.47; H 5.31; N 20.78. *m*/*z* 271 $[M + 1]^+$. $C_{14}H_{14}N_4O_2$. Calculated, %: C 62.21; H 5.22; N 20.73. *M* 270.29.

1-Benzyl-7-phenyl-5,6-dihydropyrazolo[3,4-*e*]-[1,4]diazepin-4(1*H*)-one (VIIId) was synthesized from compound **IIIh**. Yield 35%, mp 172–173°C. IR spectrum, ν, cm^{-1}: 3240 (N–H), 1700 (C=O). ^1H NMR spectrum, δ, ppm: 4.10 d (2H, CH_2, *J* = 5.3 Hz), 5.52 s (2H, CH_2), 7.23–7.37 m (5H, H_{arom}), 7.54–7.65 (3H, H_{arom}), 7.82 t (1H, NH, *J* = 5.3 Hz), 7.93 s (1H, 3-H), 8.08–8.20 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 40.30 (CH_2), 51.00 (CH_2), 108.69 (C^{3a}); 127.50, 127.52, 128.34, 128.51, 128.95, 132.06 (C_{arom}); 135.98 and 137.09 ($C^{1'}$, $C^{1''}$), 139.02 (C^3), 145.54 (C^{8a}), 164.26 (C^7), 167.52 (C=O). Found, %: C 72.40; H 5.27; N 17.85. *m*/*z* 317 $[M + 1]^+$. $C_{19}H_{16}N_4O$. Calculated, %: C 72.14; H 5.10; N 17.71. *M* 316.37.

1,7-Diphenyl-5,6-dihydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (VIIIe) was synthesized from compound **IIIi**. Yield 74%, mp 230–232°C. IR spectrum, ν, cm^{-1}: 3200 (N–H), 1705 (C=O). ^1H NMR spectrum, δ, ppm: 4.27 d (2H, CH_2, J = 5.1 Hz), 7.45 t (1H, NH, J = 5.1 Hz), 7.51–7.67 m (5H, H_{arom}), 7.75 d (2H, H_{arom}, J = 7.8 Hz), 7.96–8.01 m (3H, H_{arom}) 8.15 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 40.21 (CH_2), 109.99 (C^{3a}); 123.80, 127.52, 128.42, 128.90, 129.03, 132.12 (C_{arom}); 135.94 and 138.27 ($C^{1'}$, $C^{1''}$), 140.13 (C^3), 145.70 (C^{8a}), 164.02 (C^7), 167.61 (C=O). Found, %: C 71.82; H 4.47; N 8.74. *m*/*z* 303 $[M + 1]^+$. $C_{18}H_{14}N_4O$. Calculated, %: C 71.51; H 4.63; N 18.53. *M* 302.34.

7-(4-Fluorophenyl)-1-phenyl-5,6-dihydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (VIIIf) was synthesized from compound **IIIj**. Yield 72%, mp 256–258°C. IR spectrum, ν, cm^{-1}: 3190 (N–H), 1705 (C=O). ^1H NMR spectrum, δ, ppm: 4.27 d (2H, CH_2, J = 5.1 Hz), 7.36–7.50 m (3H, H_{arom}), 7.57 t (2H, H_{arom}, J = 7.8 Hz), 7.74 d (2H, H_{arom}, J = 7.8 Hz), 7.97 t (1H, NH, J = 5.1 Hz), 8.05–8.14 m (3H, H_{arom}, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 39.85 (CH_2), 109.91 (C^{3a}), 116.10 d ($C^{3''}$, J_{CF} = 21.9 Hz), 123.76 ($C^{2'}$), 127.48 ($C^{4'}$), 128.86 ($C^{3'}$), 131.04 d ($C^{2''}$, J_{CF} = 9.0 Hz), 132.47 d ($C^{1''}$, J_{CF} = 2.5 Hz), 138.22 ($C^{1'}$) 140.07 (C^3), 145.57 (C^{8a}), 163.92 (C^7), 164.41 d ($C^{4''}$, J_{CF} = 251.3 Hz), 166.44 (C=O). Found, %: C 67.75; H 4.12; N 17.25. *m*/*z* 321 $[M + 1]^+$. $C_{18}H_{13}FN_4O$. Calculated, %: C 67.49; H 4.09; N 17.49. *M* 320.33.

7-(3-Chlorophenyl)-1-(4-fluorophenyl)-5,6-dihydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (VIIIg) was synthesized from compound **IIIk**. Yield 84%, mp 264–266°C. IR spectrum, ν, cm^{-1}: 3210 (N–H), 1695 (C=O). ^1H NMR spectrum, δ, ppm: 4.26 d (2H, CH_2, J = 5.1 Hz), 7.25–8.25 m (10H, H_{arom}, 3-H, NH). ^{13}C NMR spectrum, δ_C, ppm: 40.25 (CH_2), 110.12 (C^{3a}), 115.75 d ($C^{3'}$, J_{CF} = 22.9 Hz), 125.97 d ($C^{2'}$, J_{CF} = 9.0 Hz); 126.97, 128.01 130.90, 131.72, 133.83 (C_{arom}); 134.54 ($C^{1'}$), 138.00 (C_{arom}), 140.15 (C^3), 145.26 (C^{8a}), 161.03 d ($C^{4'}$, J_{CF} = 245.3 Hz), 163.70 (C^7), 166.64 (C=O). Found, %: C 61.09; H 3.35; N 15.62. *m*/*z* 355 $[M + 1]^+$. $C_{18}H_{12}ClFN_4O$. Calculated, %: C 60.94; H 3.41; N 15.79. *M* 354.8.

2-(5-Amino-1*H*-pyrazol-4-ylcarbonylamino)-acetic acids IXa–IXd (*general procedure*). A solution of 2.4 g (60 mmol) of sodium hydroxide in 40 ml of ethanol was added to a suspension of 30 mmol of pyrazolopyrimidine **IIIa–IIId** in 80 ml of ethanol, and the mixture was heated under reflux for 5 h. The solvent was removed, the residue was treated with 40 ml of water, the mixture was heated for 15 min at 70°C and filtered, the filtrate was neutralized with 10% aqueous HCl, and the precipitate was filtered off, washed with 20 ml of water, and dried.

2-(5-Amino-1-methyl-1*H*-pyrazol-4-ylcarbonylamino)acetic acid (IXa). Yield 78%, mp 230–232°C. IR spectrum, ν, cm^{-1}: 3410–2480 (OH, NH), 1650 (C=O). ^1H NMR spectrum, δ, ppm: 3.51 s (3H, CH_3), 3.80 d (2H, CH_2, J = 5.8 Hz), 6.15 s (2H, NH_2), 7.65 s (1H, 3-H), 8.01 t (1H, NH, J = 5.8 Hz), 12.25 br.s (1H, COOH). Found, %: C 42.26; H 5.03; N 28.36. $C_7H_{10}N_4O_3$. Calculated, %: C 42.42; H 5.09; N 28.27.

2-(5-Amino-1-benzyl-1*H*-pyrazol-4-ylcarbonylamino)acetic acid (IXb). Yield 94%, mp 178–180°C. IR spectrum, ν, cm^{-1}: 3390–2430 (OH, NH), 1660 (C=O). ^1H NMR spectrum, δ, ppm: 3.81 d (2H, CH_2, J = 5.8 Hz), 5.14 s (2H, CH_2), 6.33 s (2H, NH_2), 7.09–7.17 m (2H, H_{arom}), 7.20–7.36 m (3H, H_{arom}), 7.73 s (1H, 3-H), 8.09 t (1H, NH, J = 5.8 Hz), 12.48 br.s (1H, COOH). Found, %: C 56.90; H 5.25; N 20.69. $C_{13}H_{14}N_4O_3$. Calculated, %: C 56.73; H 5.14; N 20.43.

2-(5-Amino-1-phenyl-1*H*-pyrazol-4-ylcarbonylamino)acetic acid (IXc). Yield 89%, mp 212–214°C. IR spectrum, ν, cm^{-1}: 3400–2490 (OH, NH), 1650 (C=O). ^1H NMR spectrum, δ, ppm: 3.84 d (2H, CH_2, J = 5.6 Hz), 6.28 s (2H, NH_2), 7.30–7.40 m (1H, H_{arom}), 7.44–7.62 m (4H, H_{arom}), 7.91 s (1H, 3-H), 8.19 t (1H, NH, J = 5.6 Hz), 12.37 br.s (1H, COOH). Found, %: C 55.57; H 4.74; N 21.46. $C_{12}H_{12}N_4O_3$. Calculated, %: C 55.38; H 4.65; N 21.53.

2-[5-Amino-1-(4-fluorophenyl)-1*H*-pyrazol-4-ylcarbonylamino]acetic acid (IXd). Yield 91%, mp 220–222°C. IR spectrum, ν, cm^{-1}: 3360–2460 (NH, OH), 1655 (C=O). ^1H NMR spectrum, δ, ppm: 3.86 d (2H, CH_2, J = 6.0 Hz), 6.35 s (2H, NH_2), 7.32–7.40 m (2H, H_{arom}), 7.54–7.62 m (2H, H_{arom}), 7.94 s (1H, 3-H), 8.27 t (1H, NH, J = 6.0 Hz), 12.50 br.s (1H, COOH). Found, %: C 51.59; H 3.82; N 20.43. $C_{12}H_{11}FN_4O_3$. Calculated, %: C 51.80; H 3.98; N 20.14.

Compounds XIa and XIb (*general procedure*). Thionyl chloride, 3.1 ml (42 mmol), was added under stirring to a suspension of 20 mmol of acid **IXa** or **IXb** in 100 ml of methanol, and the mixture was heated for 8 h under reflux. The solvent was removed, and the residue was washed with diethyl ether and dried.

Methyl 2-(5-amino-1-methyl-1*H*-pyrazol-4-ylcarbonylamino)acetate hydrochloride (XIa). Yield 96%, mp 161–162°C. IR spectrum, ν, cm^{-1}: 3340–3295 (NH); 1725, 1655 (C=O). ^1H NMR spectrum, δ,

ppm: 3.60 s (3H, CH_3N), 3.64 s (3H, CH_3O), 3.91 s (2H, CH_2), 6.05 br.s (2H, NH_2), 8.01 s (1H, 3-H), 8.55 s (1H, NH). Found, %: C 38.83; H 5.43; N 22.33. $C_8H_{13}ClN_4O_3$. Calculated, %: C 38.64; H 5.27; N 22.53.

Methyl 2-(5-amino-1-benzyl-1*H*-pyrazol-4-ylcarbonylamino)acetate hydrochloride (XIb). Yield 98%, mp 164–165°C. IR spectrum, ν, cm^{-1}: 3350–3300 (NH); 1725, 1660 (C=O). ^1H NMR spectrum, δ, ppm: 3.62 s (3H, OCH_3), 3.91 s (2H, CH_2), 5.23 s (2H, CH_2), 6.50 s (2H, NH_2), 7.14–7.22 m (2H, H_{arom}), 7.23–7.37 m (3H, H_{arom}), 7.96 s (1H, 3-H), 8.43 br.s (1H, NH). Found, %: C 52.04; H 5.09; N 17.13. $C_{14}H_{17}ClN_4O_3$. Calculated, %: C 51.78; H 5.28; N 17.25.

1-Substituted 1,5,6,8-tetrahydropyrazolo[3,4-*e*]-[1,4]diazepine-4,7-diones Xa–Xd (*general procedures***).** *a*. A solution of 20 mmol of acid **IXa**–**IXd** in 40 ml of glacial acetic acid was heated for 40–45 h under reflux. The mixture was evaporated, the residue was treated with 40 ml of water, and the precipitate was filtered off, washed with 20 ml of water, and dried in air.

b. Hydrochloride **XIa** or **XIb**, 20 mmol, was added in portions under stirring to a solution of sodium methoxide prepared by dissolution of 1.84 g (80 mmol) of metallic sodium in 150 ml of anhydrous ethanol, and the mixture was heated for 16 h under reflux. The solvent was removed, the residue was treated with 50 ml of water, and the undissolved material was filtered off. The filtrate was acidified to pH 5 with 10% aqueous HCl, and the precipitate was filtered off and dried.

1-Methyl-1,5,6,8-tetrahydropyrazolo[3,4-*e*][1,4]-diazepine-4,7-dione (Xa). Yield 15% (*a*), 72% (*b*); mp >300°C. IR spectrum, ν, cm^{-1}: 3450, 3230 (N–H); 1705, 1660 (C=O). ^1H NMR spectrum, δ, ppm: 3.66 d (2H, CH_2, J = 5.0 Hz), 3.74 s (3H, CH_3), 7.66 s (1H, 3-H), 7.91 t (1H, NH, J = 5.0 Hz), 11.10 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 35.65 (NCH_3), 45.94 (CH_2), 106.24 (C^{3a}), 138.45 (C^3), 138.60 (C^{8a}), 164.58 (C^4), 168.75 (C^7). Found, %: C 46.92; H 4.32; N 30.91. *m*/*z* 181 $[M + 1]^+$. $C_7H_8N_4O_2$. Calculated, %: C 46.67; H 4.48; N 31.10. *M* 180.17.

1-Benzyl-1,5,6,8-tetrahydropyrazolo[3,4-*e*][1,4]-diazepine-4,7-dione (Xb). Yield 21% (*a*), 79% (*b*); mp 179–180°C. IR spectrum, ν, cm^{-1}: 3460, 3200 (N–H); 1710, 1660 (C=O). ^1H NMR spectrum, δ, ppm: 3.66 d (2H, CH_2, J = 5.0 Hz), 5.36 s (2H, Ph**CH**$_2$), 7.14–7.33 m (5H, H_{arom}), 7.74 s (1H, 3-H), 7.89 t (1H, NH, J = 5.0 Hz), 11.20 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 45.91 (C^6), 51.09 (CH_2), 106.33 (C^{3a}); 127.16, 127.52, 128.51 (C_{arom}); 136.43 ($C^{1'}$), 138.37 (C^3), 139.40 (C^{8a}), 164.49 (C^4), 168.69 (C^7). Found, %: C 61.24; H 4.88; N 22.05. *m*/*z* 257 $[M + 1]^+$. $C_{13}H_{12}N_4O_2$. Calculated, %: C 60.93; H 4.72; N 21.86. *M* 256.27.

1-Phenyl-1,5,6,8-tetrahydropyrazolo[3,4-*e*][1,4]-diazepine-4,7-dione (Xc). Yield 76%, mp >300°C. IR spectrum, ν, cm^{-1}: 3290, 3220 (N–H); 1710, 1670 (C=O). ^1H NMR spectrum, δ, ppm: 3.80 d (2H, CH_2, J = 5.0 Hz), 7.42–7.64 m (5H, H_{arom}), 7.93 s (1H, 3-H), 8.02 t (1H, NH, J = 5.0 Hz), 11.01 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 45.89 (CH_2), 107.99 (C^{3a}); 124.45, 128.17, 129.25 (C_{arom}); 137.62 ($C^{1'}$), 138.15 (C^3), 140.21 (C^{8a}), 164.15 (C^4), 168.50 (C^7). Found, %: C 59.23; H 4.01; N 23.36. *m*/*z* 243 $[M + 1]^+$. $C_{12}H_{10}N_4O_2$. Calculated, %: C 59.50; H 4.16; N 23.13. *M* 242.24.

1-(4-Fluorophenyl)-1,5,6,8-tetrahydropyrazolo-[3,4-*e*][1,4]diazepine-4,7-dione (Xd). Yield 80%, mp >300°C. IR spectrum, ν, cm^{-1}: 3430, 3240 (N–H); 1705, 1660 (C=O). ^1H NMR spectrum, δ, ppm: 3.80 d (2H, CH_2, J = 5.0 Hz), 7.40 m (2H, H_{arom}), 7.66 m (2H, H_{arom}), 7.93 s (1H, 3-H), 8.03 t (1H, NH, J = 5.0 Hz), 10.81 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 45.88 (CH_2), 107.77 (C^{3a}), 116.06 d ($C^{3'}$, J_{CF} = 23.4 Hz), 126.99 d ($C^{2'}$, J_{CF} = 9.0 Hz), 133.94 ($C^{1'}$), 138.37 (C^{8a}), 140.19 (C^3), 161.49 d ($C^{4'}$, J_{CF} = 245.8 Hz), 164.10 (C^4), 168.54 (C^7). Found, %: C 55.63; H 3.40; N 21.78. *m*/*z* 261 $[M + 1]^+$. $C_{12}H_9FN_4O_2$. Calculated, %: C 55.39; H 3.49; N 21.53. *M* 260.23.

1,5,6,8-Tetrahydropyrazolo[3,4-*e*][1,4]diazepine-4,7-dione (XII) and methyl *N*-[5-amino-1-(cyclohexylmethyl)-1*H*-pyrazol-4-ylcarbonylamino]acetate (XIII). A 250-ml high-pressure reactor was charged with a solution of 1 g (3.91 mmol) of compound **Xb** in 50 ml of methanol, 0.5 g of 20% Pd/C was added, gaseous hydrogen was supplied, and the mixture was heated for 12 h at 80°C at a hydrogen pressure of 40 atm. The reactor was cooled, the catalyst was filtered off, the filtrate was evaporated, 10 ml of methanol was added to the residue, and the mixture was heated to the boiling point. The undissolved material (compound **XII**) was filtered off and dried. The mother liquor was evaporated, and the solid residue (compound **XIII**) was recrystallized from 60% aqueous ethanol.

Compound **XII**. Yield 33%, mp >300°C. IR spectrum, ν, cm^{-1}: 3390–3360 (N–H); 1670, 1655 (C=O). ^1H NMR spectrum, δ, ppm: 3.62 d (2H, CH_2, J = 4.8 Hz), 7.86 t (1H, NH, J = 4.8 Hz), 8.11 s (1H, 3-H),

11.83 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 46.11 (CH_2), 106.98 (C^{3a}), 132.48 br.s (S^3), 145.97 br.s (C^{8a}), 165.00 (C^4), 169.16 (C^7). Found, %: C 43.06; H 3.77; N 33.90. *m*/*z* 167 $[M + 1]^+$. $C_6H_6N_4O_2$. Calculated, %: C 43.38; H 3.64; N 33.72. *M* 166.14.

Compound **XIII**. Yield 24%, mp 180–181°C. IR spectrum, ν, cm^{-1}: 3315–3270 (N–H); 1730, 1655 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.81–1.29 m (5H, C_6H_{11}), 1.41–1.88 m (6H, C_6H_{11}), 3.63 s (3H, OCH_3), 3.64–3.75 m (2H, CH_2), 3.82–3.97 m (2H, CH_2), 6.17 s (2H, NH_2), 7.65 s (1H, 3-H), 8.16 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 25.17 (CH_2), 25.93 (CH_2), 29.79 (CH_2), 37.17 (CH), 39.80 (CH_2), 51.54 (OCH_3), 51.83 (CH_2), 95.85 (C^4), 136.27 (C^3), 149.35 (C^5), 164.46 (C=O, amide), 170.92 (C=O, ester). Found, %: C 56.78; H 7.91; N 18.79. *m*/*z* 295 $[M + 1]^+$. $C_{14}H_{23}N_4O_3$. Calculated, %: C 56.93; H 7.85; N 18.97. *M* 294.36.

1-Substituted 5,6,7,8-tetrahydropyrazolo[3,4-*e*]-[1,4]diazepin-4(1*H*)-ones XIVa–XIVi (*general procedures***).** *a*. Compound **Va**–**Vc** or **VIIIa**–**VIIIf**, 10 mmol, was added in portions under stirring to a suspension of 0.38 g (10 mmol) of sodium tetrahydridoborate in 50 ml of anhydrous propan-2-ol, and the mixture was stirred for 24 h. Anhydrous methanol, 20 ml, was then added, and the mixture was stirred for 1 h, acidified to pH 3–4 with 10% hydrochloric acid, and evaporated under reduced pressure (water-jet pump). The solid residue was dissolved in 10 ml of water, the solution was made alkaline by adding 10% aqueous sodium hydroxide to pH 9–10 and extracted with methylene chloride (3×20 ml), the extracts were combined and evaporated, and the residue was recrystallized from acetonitrile.

b. Compound **Xa**–**Xc**, 20 mmol, was added in portions under stirring to a suspension of 0.756 g (20 mmol) of $LiAlH_4$ in 150 ml of THF, and the mixture was heated for 4 h under reflux. The mixture was then treated in succession with 5 ml of methanol, 10 ml of 20% aqueous sodium hydroxide, and 10 ml of 40% aqueous ammonia. The undissolved material was filtered off, the filtrate was evaporated, and the residue was recrystallized from acetonitrile.

1-Methyl-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]-diazepin-4(1*H*)-one (XIVa). Yield 52% (*a*), 58% (*b*); mp 251–252°C. IR spectrum, ν, cm^{-1}: 3370–3280 (NH), 1620 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.11–3.27 m (2H, CH_2), 3.27–3.41 m (2H, CH_2), 3.49 s (3H, CH_3), 6.73 br.s (1H, NH), 7.29 br.s (1H, NH), 7.41 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 34.52 (NCH_3), 42.08 (C^6), 45.57 (C^7), 99.29 (C^{3a}), 139.94 (C^3), 146.31 (C^{8a}), 165.38 (C=O). Found, %: C 50.21; H 5.94; N 33.89. *m*/*z* 167 $[M + 1]^+$. $C_7H_{10}N_4O$. Calculated, %: C 50.59; H 6.07; N 33.71. *M* 166.18.

1-Benzyl-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]-diazepin-4(1*H*)-one (XIVb). Yield 61% (*a*), 62% (*b*); mp 202–203°C. IR spectrum, ν, cm^{-1}: 3390–3270 (NH), 1615 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.19–3.26 m (2H, CH_2), 3.26–3.33 m (2H, CH_2), 5.11 s (2H, CH_2), 6.94 s (1H, NH), 7.10–7.16 m (2H, H_{arom}), 7.22–7.28 m (1H, H_{arom}), 7.28–7.33 m (2H, H_{arom}), 7.34 s (1H, NH), 7.50 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 42.14 (C^6), 45.52 (C^7), 50.04 (Ph**C**H_2), 99.22 (C^{3a}), 127.03 ($C^{3'}$), 127.21 ($C^{4'}$), 128.38 ($C^{2'}$), 137.19 ($C^{1'}$), 140.94 (C^3), 146.39 (C^{8a}), 165.42 (C=O). Found, %: C 64.18; H 5.97; N 23.32. *m*/*z* 243 $[M + 1]^+$. $C_{13}H_{14}N_4O$. Calculated, %: C 64.45; H 5.82; N 23.12. *M* 242.28.

1-Phenyl-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]-diazepin-4(1*H*)-one (XIVc). Yield 54% (*a*), 56% (*b*); mp 260–262°C. IR spectrum, ν, cm^{-1}: 1615 (C=O), 3240–3370 (NH). ^{1}H NMR spectrum, δ, ppm: 3.22–3.35 m (4H, CH_2), 6.69 s (1H, NH), 7.37–7.47 m (2H, H_{arom}, NH), 7.50–7.57 m (4H, H_{arom}), 7.69 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 41.95 (C^6), 45.87 (C^7), 99.98 (C^{3a}), 124.15 ($C^{2'}$), 127.31 ($C^{4'}$), 129.34 ($C^{3'}$), 138.28 ($C^{1'}$), 142.36 (C^3), 146.04 (C^{8a}), 165.16 (C=O). Found, %: C 62.87; H 5.38; N 24.29. *m*/*z* 229 $[M + 1]^+$. $C_{12}H_{12}N_4O$. Calculated, %: C 63.15; H 5.30; N 24.55. *M* 228.26.

1-Methyl-7-phenyl-5,6,7,8-tetrahydropyrazolo-[3,4-*e*][1,4]diazepin-4(1*H*)-one (XIVd). Yield 69% (*a*), mp 254–256°C. IR spectrum, ν, cm^{-1}: 3370–3210 (NH), 1610 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.27–3.39 m (1H, CH), 3.49–3.58 m (1H, CH), 3.58 s (3H, CH_3), 4.65–4.74 m (1H, CH), 7.06–7.17 m (2H, NH), 7.21–7.39 m (5H, H_{arom}), 7.42 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 34.80 (NCH_3), 46.30 (CH_2), 58.05 (CH), 99.10 (C^{3a}), 127.46 ($C^{2'}$), 127.01($C^{4'}$), 128.24 ($C^{3'}$), 139.61 (C^3), 141.65 ($C^{1'}$), 145.76 (C^{8a}), 165.48 (C=O). Found, %: C 64.71; H 5.66; N 23.32. *m*/*z* 243 $[M + 1]^+$. $C_{13}H_{14}N_4O$. Calculated %: C 64.45; H 5.82; N 23.12. *M* 242.28.

7-(4-Chlorophenyl)-1-methyl-5,6,7,8-tetrahydro-pyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (XIVe). Yield 57% (*a*), mp 242–243°C. IR spectrum, ν, cm^{-1}: 1625 (C=O), 3215–3380 (NH). ^{1}H NMR spectrum, δ, ppm: 3.30–3.38 m (1H, CH), 3.49–3.58 m (1H, CH), 3.57 s (3H, NCH_3), 4.71–4.78 m (1H, CH), 7.09 s (1H, NH), 7.19 s (1H, NH), 7.27 d (2H, H_{arom}, *J* = 8.3 Hz),

7.39 d (2H, H_{arom}, J = 8.3 Hz), 7.40 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 34.80 (NCH_3), 45.81 (CH_2), 57.17 (CH), 99.09 (C^{3a}), 128.14 and 128.37 ($C^{2'}$, $C^{3'}$), 131.52 ($C^{4'}$), 139.61 (C^3), 140.65 ($C^{1'}$), 145.53 (C^{8a}), 165.45 (C=O). Found, %: C 56.17; H 4.70; N 20.07. *m/z* 277 $[M + 1]^+$. $C_{13}H_{13}ClN_4O$. Calculated, %: C 56.43; H 4.74; N 20.25. *M* 276.73.

7-(4-Methoxyphenyl)-1-methyl-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (XIVf). Yield 72% (*a*), mp 217–218°C. IR spectrum, ν, cm^{-1}: 3390–3285 (NH), 1615 (C=O). ^1H NMR spectrum, δ, ppm: 3.25–3.35 m (1H, CH), 3.45–3.56 m (1H, CH), 3.57 s (3H, NCH_3), 3.73 s (3H, OCH_3), 4.59–4.65 m (1H, CH), 6.90 d (2H, H_{arom}, J = 8.6 Hz), 7.03 s (1H, NH), 7.10 s (1H, NH), 7.20 d (2H, H_{arom}, J = 8.6 Hz), 7.41 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 34.79 (NCH_3), 46.57 (CH_2), 55.06 (OCH_3), 57.62 (CH), 99.09 (C^{3a}), 113.68 ($C^{3'}$), 127.59 ($C^{2'}$), 133.64 ($C^{1'}$), 139.61 (C^3), 145.76 (C^{8a}), 158.38 ($C^{4'}$), 165.45 (C=O). Found, %: C 61.51; H 6.05; N 20.18. *m/z* 273 $[M + 1]^+$. $C_{14}H_{16}N_4O_2$. Calculated, %: C 61.75; H 5.92; N 20.57. *M* 272.31.

1-Benzyl-7-phenyl-5,6,7,8-tetrahydropyrazolo-[3,4-*e*][1,4]diazepin-4(1*H*)-one (XIVg). Yield 72% (*a*), mp 198–200°C. IR spectrum, ν, cm^{-1}: 3350–3200 (NH), 1635 (C=O). ^1H NMR spectrum, δ, ppm: 3.32–3.44 m (1H, CH), 3.47–3.62 m (1H, CH), 4.65–4.78 m (1H, CH), 5.15–5.32 m (2H, CH_2), 7.01–7.43 m (12H, H_{arom}, NH), 7.51 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 46.06 (CH_2), 50.35 (CH_2), 57.60 (CH), 99.10 (C^{3a}); 126.42, 126.90, 127.06, 128.23, 128.38, 129.42, 137.34, 140.67 (C_{arom}); 141.52 (C^3), 145.87 (C^{8a}), 165.64 (C=O). Found, %: C 71.75; H 5.60; N 17.38. *m/z* 319 $[M + 1]^+$. $C_{19}H_{18}N_4O$. Calculated, %: C 71.68; H 5.70; N 17.60. *M* 318.38.

1,7-Diphenyl-5,6,7,8-tetrahydropyrazolo[3,4-*e*]-[1,4]diazepin-4(1*H*)-one (XIVh). Yield 51% (*a*), mp 131–132°C. IR spectrum, ν, cm^{-1}: 3380–3220 (NH), 1610 (C=O). ^1H NMR spectrum, δ, ppm: 3.40–3.49 m (1H, CH), 3.60–3.71 m (1H, CH), 4.69–4.78 m (1H, CH), 7.12 s (1H, NH), 7.20–7.29 m (4H, H_{arom}, NH), 7.30–7.37 m (2H, H_{arom}), 7.38–7.44 m (1H, H_{arom}), 7.49–7.61 m (4H, H_{arom}), 7.68 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 45.68 (CH_2), 57.86 (**C**HPh), 99.65 (C^{3a}); 124.61, 126.29, 126.80, 127.50, 128.23, 129.39, 138.29, 141.52 (C_{arom}); 142.00 (C^3), 145.51 (C^{8a}), 165.33 (C=O). Found, %: C 70.83; H 5.11; N 18.62. *m/z* 305 $[M + 1]^+$. $C_{18}H_{16}N_4O$. Calculated, %: C 71.04; H 5.30; N 18.41. *M* 304.35.

7-(4-Fluorophenyl)-1-phenyl-5,6,7,8-tetrahydropyrazolo[3,4-*e*][1,4]diazepin-4(1*H*)-one (XIVi). Yield 60% (*a*), mp 135–136°C. IR spectrum, ν, cm^{-1}: 3370–3225 (NH), 1605 (C=O). ^1H NMR spectrum, δ, ppm: 3.38–3.49 m (1H, CH), 3.60–3.69 m (1H, CH), 4.71–4.79 m (1H, CH), 7.09–7.32 m (6H, H_{arom}, NH), 7.38–7.45 m (1H, H_{arom}), 7.49–7.61 m (4H, H_{arom}), 7.68 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 45.53 (CH_2), 57.20 (C^7), 99.66 (C^{3a}), 114.96 d ($C^{3''}$, J_{CF} = 21.4 Hz), 124.36 ($C^{2'}$), 127.55 ($C^{4'}$), 128.27 d ($C^{2''}$, J_{CF} = 8.0 Hz), 129.41 ($C^{3'}$), 137.67 d ($C^{1''}$, J_{CF} = 2.5 Hz), 138.26 ($C^{1'}$) 142.00 (C^3), 145.36 (C^{8a}), 161.15 d ($C^{4''}$, J_{CF} = 242.3 Hz), 165.36 (C=O). Found, %: C 67.33; H 4.80; N 17.12. *m/z* 323 $[M + 1]^+$. $C_{18}H_{15}FN_4O$. Calculated, %: C 67.07; H 4.69; N 17.38. *M* 322.34.

1-Substituted 1,4,5,6,7,8-hexahydropyrazolo-[3,4-*e*][1,4]diazepines XVa–XVd (*general procedure*). Lithium tetrahydridoaluminate, 3.78 g (100 mmol), was dispersed in 150 ml of tetrahydrofuran, 10.86 g (100 mmol) of chloro(trimethyl)silane was added under stirring in an argon atmosphere, and 20 mmol of compound **Xa**–**Xc** (*a*) or **XIVa**–**XIVc** or **XIVg** (*b*) was then added in portions. The mixture was heated for 40–45 h under reflux, treated in succession with 15 ml of propan-2-ol, 10 ml of 20% aqueous sodium hydroxide, and 10 ml of 40% aqueous ammonia, the inorganic material was filtered off, and the filtrate was evaporated. In the reactions with **Xb**, **XIVb**, and **XIVg**, the residue was dissolved in 20 ml of ethanol, the solution was acidified to pH 3–4 with concentrated hydrochloric acid, the mixture was evaporated under reduced pressure (water-jet pump), and the solid residue was recrystallized from propan-2-ol.

1-Methyl-1,4,5,6,7,8-hexahydropyrazolo[3,4-*e*]-[1,4]diazepine (XVa). Oily substance. Yield 48% (*a*), 53% (*b*). IR spectrum: ν 3340–3250 cm^{-1} (NH). ^1H NMR spectrum, δ, ppm: 2.78–2.85 m (2H, CH_2), 2.91–2.99 m (2H, CH_2), 3.40–3.54 m (2H, CH_2), 3.52 s (3H, CH_3), 5.53 br.s (1H, NH), 6.90 s (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 34.54 (CH_3), 45.09 (CH_2), 49.11 (CH_2), 52.75 (CH_2), 107.16 (C^{3a}), 135.34 (C^3), 146.97 (C^{8a}). Found, %: C 55.38; H 8.06; N 36.58. *m/z* 153 $[M + 1]^+$. $C_7H_{12}N_4$. Calculated, %: C 55.24; H 7.95; N 36.81. *M* 152.20.

1-Benzyl-1,4,5,6,7,8-hexahydropyrazolo[3,4-*e*]-[1,4]diazepine dihydrochloride (XVb). Yield 45% (*a*), 48% (*b*); mp 138–139°C. IR spectrum: ν 3370–3260 cm^{-1} (NH). ^1H NMR spectrum, δ, ppm: 3.21–3.39 m (4H, CH_2), 3.95–4.09 m (2H, CH_2), 5.27 s (2H, CH_2), 6.30 br.s (1H, NH), 7.13–7.24 m (2H, H_{arom}), 7.24–7.38 m (3H, H_{arom}), 7.42 s (1H, 3-H), 9.34 br.s (2H, NH_2^+). ^{13}C NMR spectrum, δ_C, ppm: 41.67 (CH_2),

42.51 (CH_2), 49.69 (CH_2), 50.13 (CH_2), 97.81 (C^{3a}), 127.21 ($C^{3'}$), 127.25 ($C^{4'}$), 128.32 ($C^{2'}$), 137.43 ($C^{1'}$), 137.62 (C^3) , 147.98 (C^{8a}). Found, %: C 52.10; H 6.23; Cl 23.97; N 18.05. *m*/*z* 229 $[M + 1]^+$. $C_{13}H_{18}Cl_2N_4$. Calculated, %: C 51.84; H 6.02; Cl 23.54; N 18.60. *M* 228.30.

1-Benzyl-7-phenyl-1,4,5,6,7,8-hexahydropyrazolo[3,4-*e*][1,4]diazepine dihydrochloride (XVc). Yield 46% (*a*), 56% (*b*), mp 174–175°C. IR spectrum: ν 3240–3360 cm^{-1} (NH). ^1H NMR spectrum, δ, ppm: 3.32–3.47 m (2H, CH_2), 3.86–3.98 m (1H, CH), 4.31–4.42 m (1H, CH), 4.57–4.67 m (1H, CH), 5.31–5.46 m (2H, CH_2), 6.30 br.s (1H, NH), 7.12–7.20 m (2H, H_{arom}), 7.25–7.47 m (8H, H_{arom}), 7.53 s (1H, 3-H), 9.40–9.57 m and 9.95–10.13 m (2H, NH_2^+). ^{13}C NMR spectrum, δ_C, ppm: 41.14 (CH_2), 50.27 (CH_2), 54.32 (CH_2), 56.86 (CH), 99.40 (C^{3a}); 127.06, 127.17, 127.49, 128.34, 128.49, 128.76 (C_{arom}); 136.97 (C_{arom}, C^3), 139.37 (C_{arom}), 146.77 (C^{8a}). Found, %: C 60.27; H 5.61; Cl 18.91; N 14.64. *m*/*z* 305 $[M + 1]^+$. $C_{19}H_{22}Cl_2N_4$. Calculated, %: C 60.48; H 5.88; N 14.85; Cl 18.79. *M* 304.40.

1-Phenyl-1,4,5,6,7,8-hexahydropyrazolo[3,4-*e*]-[1,4]diazepine (XVd). Yield 63% (*a*), 66% (*b*); mp 153–155°C. IR spectrum: ν 3150–3250 cm^{-1} (NH). ^1H NMR spectrum, δ, ppm: 2.77–2.89 m (2H, CH_2), 2.91–3.05 m (2H, CH_2), 3.52–3.67 m (2H, CH_2), 5.44 br.s (1H, NH), 7.22 s (1H, 3-H), 7.30–7.40 m (1H, H_{arom}), 7.40–7.56 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 44.75 (CH_2), 49.25 (CH_2), 52.43 (CH_2), 108.63 (C^{3a}), 123.71 ($C^{2'}$), 126.60 ($C^{4'}$), 129.15 ($C^{3'}$), 138.31 (C^3), 139.01 ($C^{1'}$), 146.72 (C^{8a}). Found, %: C 67.01; H 6.73; N 26.00. *m*/*z* 215 $[M + 1]^+$. $C_{12}H_{14}N_4$. Calculated, %: C 67.27; H 6.59; N 26.15. *M* 214.27.

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