ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 2, pp. 286–291. © Pleiades Publishing, Ltd., 2010.
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Synthesis of Arylamino-Substituted Pyrazolo[3,4-*d*][1,2,4]triazolo[4,3-*a*]pyrimidinones, Pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-a]pyrimidinones, and Their Thermal Isomerization

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Received May 27, 2009

Abstract—The reaction of 1-(4-oxo-1-R-5*H*-pyrazolo[3,4-*d*]pyrimidin-6-yl)-4-arylthiosemicarbazides with methyl iodide gave rise to 1,2,4-triazolo-pyrazolopyrimidinones of linear structure, and with dicyclohexylcarbodiimide the products had angular and linear structure. The heating of compounds obtained higher than their melting point resulted in their isomerization into 7-aryl-amino-1-R-1,8-dihydro-4*H*-pyrazolo[3,4-*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidin-4-ones.

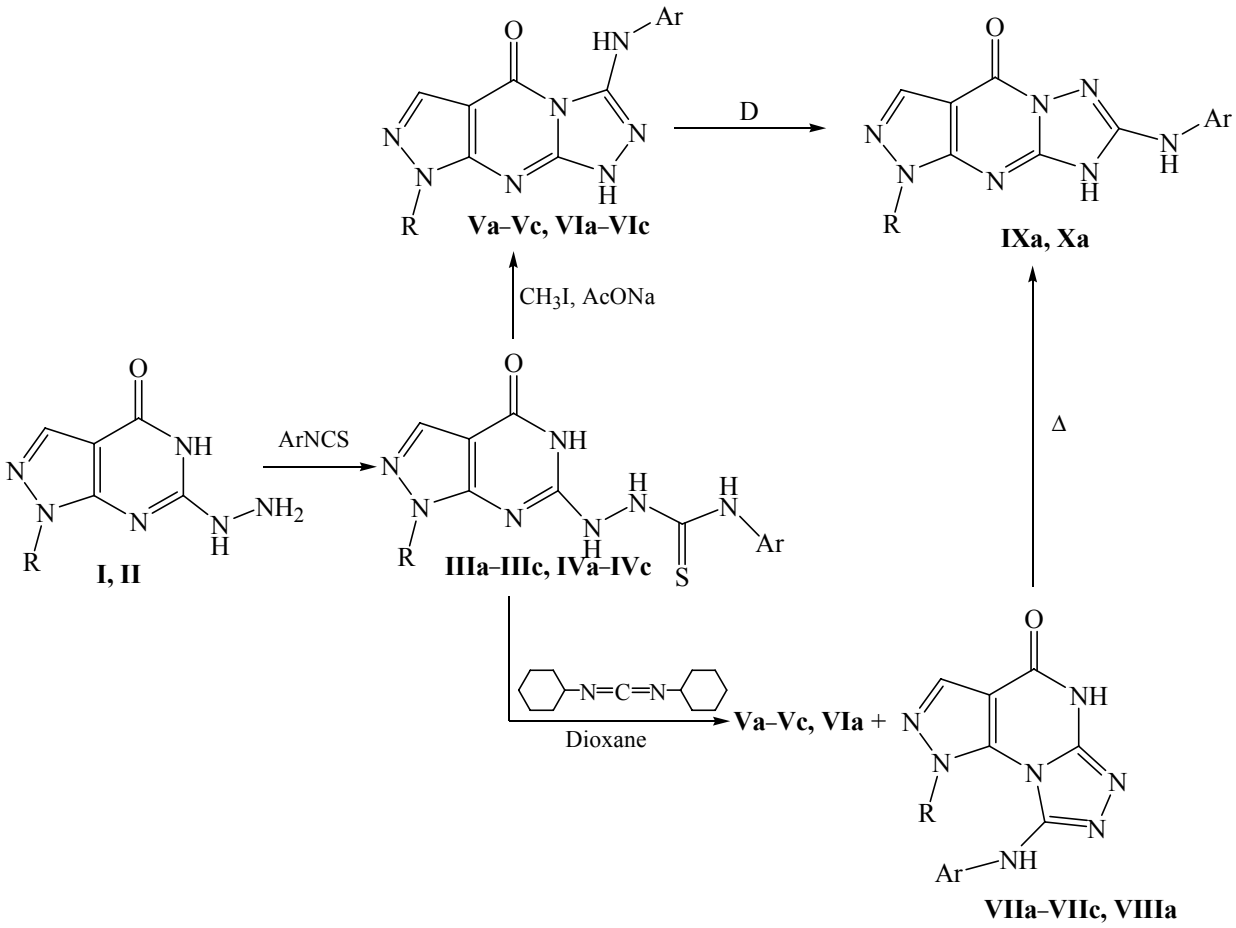
DOI: 10.1134/S1070428010020235

It was formerly reported that the cyclization of 1-(4,6-dimethylpyrimidin-2-yl)-4-arylthiosemicarbazides under the action of methyl iodide and sodium acetate in ethanol resulted in the products of Dimroth rearrangement, 2-aryl-amino-5,7-dimethyl-1,2,4-triasolo[1,5-*a*]pyrimidines [1]. In the presence of dicyclohexylcarbodiimide the cyclization was accompanied by the formation of unrearranged compounds, 3-arylamino-5,7-dimethyl-1,2,4-triazolo[1,5-*a*]-pyrimidines which further under alkaline conditions suffered the Dimroth rearrangement [2]. At the same time 1-(6-methyl-4-oxo-3,4-dihydropyrimidin-2-yl)-4-arylthio-semicarbazides in reactions with methyl iodide and sodium acetate provided 3-arylamino-7-methyl-5-oxo-1-hydro-1,2,4-triazolo[4,3-*a*]pyrimidines which did not suffer the catalytic Dimroth rearrangement [1].

Aiming at a deeper understanding of the cyclization regiochemistry of 1-hetaryl-4-arylthiosemicarbazides under the action of methyl iodide and dicyclohexylcarbo-diimide we tested 1-(4-oxo-1-R-5*H*-pyrazolo[3,4-*d*]-pyrimidin-6-yl)-4-arylthiosemicarbazides **IIIa–IIIc, IVa–IVc** obtained from the corresponding 6-hydrazino-substituted pyrazolopyrimidines **I** and **II** (see the scheme). In compounds **IIIa–IIIc, IVa–IVc** the pyrimidine ring is fused with a pyrazole cycle providing a possibility to vary the substituent at N^1 atom and also to study the effect of the π-excessive pyrazole ring on the regio-chemistry of the triazole ring formation.

In the reaction of thiosemicarbazides **IIIa–IIIc, IVa–IVc** with methyl iodide and sodium acetate in ethanol the closure of the triazole ring occurred only at the N^5 atom of the pyrazolopyrimidine framework with the formation of pyrazolo[3,4-*d*][1,2,4]triazolo[4,3-*a*]-pyrimidinones of linear structure **Va–Vc, VIa–VIc**. The similar cyclization regiochemistry we previously established by the XRD method for thiosemicarbazides containing in the position *1* a pyrimidinone ring [1, 3].

Compounds **IIIa–IIIc** reacted with dicyclohexyl-carbodiimide in dioxane nonselectively. We isolated in 37–60% yield and identified pyrazolo[4,3-*e*][1,2,4]triazolo-[4,3-*a*]pyrimidinones of angular structure **VIIa–VIIc**. Besides in 15–40% yields compounds of linear structure **Va–Vc** formed and were present in the filtrate. It should be noted that the yield of the compound **VIIb** of the angular structure was considerably lower, and the yield of compound **Vb** of the linear structure greater in the case of Ar = 4-$CH_3OC_6H_4$. It was also established that at the cyclization of compound **IVa** effected by dicyclohexylcarbodiimide the yield of the product of the



R = H (**I, III, V, VII, IX**), Ph (**II, IV, VI, VIII, X**); Ar = C_6H_5 (**a**), 4-$CH_3OC_6H_4$ (**b**), 4-$C_2H_5O_2CC_6H_4$ (**c**).

angular structure **VIIIa** was twice less than in the case of cyclization of compound **IIIa**.

We investigated the ability to rearrange of compounds V–VII at heating in alcohol solutions of sodium acetate and alkaline DMSO solutions. It turned out that under catalytic conditions the Dimroth rearrangement [4–6] products did not form, and the isolated only initial compounds. Therefore we attempted to perform the Dimroth rearrangement at heating [6, 7]. For instance, at heating compounds **Va** and **VIa** over their melting points (320 and 360°C respectively) we obtained rearrangement products **IXa** and **Xa**. Yet compound **VIIa** of the angular structure underwent the rearrangement into compound **IXa** only at the temperature over 400°C.

The composition and structure of synthesized compounds **V–X** were confirmed by elemental analysis, IR and ^{1}H NMR spectra.

In the ^{1}H NMR spectra of compounds with the angular **VIIa–VIIc, VIIIa** and linear **Va–Vc, VIa–VIc**, **IXa, Xa** structure the difference was observed in the chemical sifts of protons at the nitrogen atoms. For instance, the singlet of the proton of the NHAr group in the compounds of linear structure was observed in the region 9.29–9.90 ppm, and in the compounds of the angular structure, at 8.31–9.05 ppm. The singlet of the NH proton of the pyrimidine fragment in the spectra of compounds of the angular structur appeared at 12.02–12.50 ppm, and in the spectra of compounds of the linear structure the singlet of the triazole proton of the NH group was located in the region 12.84–13.63 ppm.

In the IR spectra of the cyclization products the stretching vibrations of the carbonyl group in the compounds of the linear structure **Va, IXa** were found at 1720, 1730 cm^{-1}, and for the angular compound **VIIa**, in the region 1690 cm^{-1}.

Thus we established that the cyclization of thiosemicarbazides **IIIa–IIIc, IVa–IVc** effected by methyl iodide and sodium acetate in ethanol proceeded

regioselectively at the N^5 atom of the pyrazolopyrimidine framework, and under the action of dicyclohexylcarbodiimide it occurred at the atoms N^7 and N^5 of the pyrazolopyrimidine system. The heating of pyrazolotriazolopyrimidines of the linear (**V, VI**) and angular (**VII**) structure higher than their melting points resulted in their isomerization into 7-arylamino-1-R-1,8-dihydro-4*H*-pyrazolo[3,4-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-4-ones.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20 from pellets with KBr. ^{1}H NMR spectra were registered on a spectrometer VXR-300 (300 MHz) in DMSO-d_6 with internal reference TMS.

1-(4-Oxo-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]-pyrimidin-6-yl)-4-arylthiosemicarbazides IIIa–IIIc. A mixture of 0.83 g (5 mmol) of reagent I and 7 mmol of an appropriate isothiocyanate in 50 ml of ethanol was boiled at stirring for 4 h, then the solution was cooled, the separated precipitate was filtered off and washed with ethanol. To purify the precipitate obtained it was boiled for 10 min with 0.61 ml (5 mmol) of acetylenedicarboxylic ester in 40 ml of dioxane. The reaction mixture was cooled, the precipitate was filtered off, washed with dioxane and with ether.

1-(4-Oxo-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]-pyrimidin-6-yl)-4-phenyl-thiosemicarbazide (IIIa). Yield 0.84 γ (56%), mp >360°C. IR spectrum, ν, cm^{-1}: 3200, 3050 (NH), 1700 (C=O), 1610, 1460, 1360, 960. ^{1}H NMR spectrum, δ, ppm: 7.15 t (1H$_{arom}$, *J* 7.5 Hz), 7.33 t (2H$_{arom}$, *J* 7.8 Hz), 7.51 d (2H$_{arom}$, *J* 7.8 Hz), 7.85 s (1H$_{arom}$), 8.66 br.s (1H, NH), 9.68 s (1H, NH), 9.92 s (1H, NH), 10.90 s (1H, NH), 13.24 s (1H, NH). Found, %: C 47.64; H 3.61; N 32.33; S 10.47. $C_{12}H_{11}N_7OS$. Calculated, %: C 47.83; H 3.68; N 32.54; S 10.64.

1-(4-Oxo-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]-pyrimidin-6-yl)-4-(4-methoxyphenyl)thiosemicarbazide (IIIb). Yield 1.01 g (61%), mp >360°C. IR spectrum, ν, cm^{-1}: 3200, 3020 (NH), 1700 (C=O), 1620, 1530, 1360, 1300, 1250, 1040, 960. ^{1}H NMR spectrum, δ, ppm: 3.75 s (3H, OCH$_3$), 6.89 d (2H$_{arom}$, *J* 8.7 Hz), 7.34 d (2H$_{arom}$, *J* 8.7 Hz), 7.85 s (1H$_{arom}$), 8.63 br.s (1H, NH), 9.58 s (1H, NH), 9.81 s (1H, NH), 10.86 s (1H, NH), 13.25 s (1H, NH). Found, %: C 46.93; H 3.83; N 29.39; S 9.51. $C_{13}H_{13}N_7O_2S$. Calculated, %: C 47.12; H 3.95; N 29.59; S 9.68.

1-(4-Oxo-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]-pyrimidin-6-yl)-4-(4-ethoxycarbonyl-phenyl)-thiosemicarbazide (IIIc). Yield 0.88 g (47%), mp >360°C. IR spectrum, ν, cm^{-1}: 3200, 3120, 2980 (NH), 1710 (C=O), 1620, 1550, 1370, 1280, 1180, 1110, 1020, 960, 930. ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, CH$_3$, *J* 6.9 Hz), 4.30 q (2H, CH$_2$, *J* 7.2 Hz), 7.78 d (2H$_{arom}$, *J* 8.4 Hz), 7.82–7.93 m (3H$_{arom}$), 8.70 br.s (1H, NH), 9.91 br.s (1H, NH), 10.13 br.s (1H, NH), 10.96 br.s (1H, NH), 13.24 br.s (1H, NH). Found, %: C 47.98; H 3.97; N 26.12; S 8.44. $C_{15}H_{15}N_7O_3S$. Calculated, %: C 48.25; H 4.05; N 26.26; S 8.59.

1-(4-Oxo-1-phenyl-4,5-dihydro-1*H*-pyrazolo-[3,4-*d*]pyrimidin-6-yl)-4-arylthiosemicarbazides IVa–IVc. A mixture of 1.21 g (5 mmol) of reagent **II** and 7 mmol of an appropriate isothiocyanate in 50 ml of ethanol was boiled at stirring for 1 h, then the solution was cooled, the separated precipitate was filtered off and washed with ethanol and ether.

1-(4-Oxo-1-phenyl-4,5-dihydro-1*H*-pyrazolo-[3,4-*d*]pyrimidin-6-yl)-4-phenylthiosemicarbazide (IVa). Yield 1.26 g (67%), mp 187–189°C (decomp.). IR spectrum, ν, cm^{-1}: 3270 (NH), 1670 (C=O), 1630, 1600, 1540, 1510, 1450, 1430, 1410, 1370, 1300, 1260, 1120, 960. ^{1}H NMR spectrum, δ, ppm: 7.15 t (1H$_{arom}$, *J* 7.2 Hz), 7.29–7.35 m (3H$_{arom}$), 7.46–7.51 m (4H$_{arom}$), 8.12 s (1H$_{arom}$), 8.20 d (2H$_{arom}$, *J* 8.1 Hz), 9.07 br.s (1H, NH), 9.67 s (1H, NH), 9.98 br.s (1H, NH), 11.33 s (1H, NH). Found, %: C 57.07; H 3.95; N 25.71; S 8.41. $C_{18}H_{15}N_7OS$. Calculated, %: C 57.28; H 4.01; N 25.98; S 8.50.

4-(4-Methoxyphenyl)-1-(4-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazolo[3,4-*d*]pyrimidin-6-yl)-thiosemicarbazide (IVb). Yield 1.63 g (80%), mp 155–157°C (decomp.). IR spectrum, ν, cm^{-1}: 3230 (NH), 1690 (C=O), 1620, 1520, 1300, 1250, 1030, 970. ^{1}H NMR spectrum, δ, ppm: 3.74 s (3H, OCH$_3$), 6.88 d (2H$_{arom}$, *J* 9.0 Hz), 7.32–7.36 m (3H$_{arom}$), 7.50 t (2H$_{arom}$, *J* 7.8 Hz), 8.13 s (1H$_{arom}$), 8.22 d (2H$_{arom}$, *J* 8.7 Hz), 9.09 br.s (1H, NH), 9.59 br.s (1H, NH), 9.85 br.s (1H, NH), 11.31 s (1H, NH). Found, %: C 55.92; H 4.07; N 23.95; S 7.65. $C_{19}H_{17}N_7O_2S$. Calculated, %: C 56.01; H 4.21; N 24.06; S 7.87.

1-(4-Oxo-1-phenyl-4,5-dihydro-1*H*-pyrazolo-[3,4-*d*]pyrimidin-6-yl)-4-(4-ethoxycarbonyl-phenyl)thiosemicarbazide (IVc). Yield 1.62 g (72%), mp 166–169°C (decomp.). IR spectrum, ν, cm^{-1}: 3280, 3190 (NH), 1700 (C=O), 1650, 1600, 1550, 1510, 1340, 1290, 1230, 1180, 1120, 1020, 960. ^{1}H NMR spectrum, δ, ppm: 1.31 t (3H, CH$_3$, *J* 7.2 Hz), 4.29 q (2H, CH$_2$, *J* 7.2 Hz), 7.33 t (1H$_{arom}$, *J* 7.2 Hz), 7.48 t (2H$_{arom}$,

J 7.2 Hz), 7.77 d (2H$_{arom}$, *J* 8.4 Hz), 7.90 d (2H$_{arom}$, *J* 8.7 Hz), 8.13 s (1H$_{arom}$), 8.17 d (2H$_{arom}$, *J* 7.8 Hz), 9.19 br.s (1H, NH), 9.91 br.s (1H, NH), 10.20 br.s (1H, NH), 11.47 br.s (1H, NH). Found, %: C 56.05; H 4.16; N 21.77; S 7.06. $C_{21}H_{19}N_7O_3S$. Calculated, %: C 56.11; H 4.26; N 21.81; S 7.13.

3-Arylamino-1,8-dihydro-5*H*-pyrazolo[3,4-*d*]-[1,2,4]triazolo[4,3-*a*]-pyrimidin-5-ones Va–Vc, VIa–VIc. A mixture of 2 mmol of an appropriate thiosemicarbazide **IIIa–IIIc, IVa–IVc**, 0.25 g (3 mmol) of sodium acetate, and 0.19 ml (3 mmol) of methyl iodide in 50 ml of ethanol was boiled at stirring for 1 h, then the solution was cooled to room temperature, the separated precipitate was filtered off and washed on the filter with ethanol and ether.

3-Phenylamino-1,8-dihydro-5*H*-pyrazolo[3,4-*d*]-[1,2,4]triazolo[4,3-*a*]-pyrimidin-5-one (Va). Yield 0.46 g (86%), mp 308–310°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3310, 3070 (NH), 1720 (C=O), 1660, 1600, 1570, 980, 920, 870, 820, 760. ^{1}H NMR spectrum, δ, ppm: 7.03 t (1H$_{arom}$, *J* 7.5 Hz), 7.38 t (2H$_{arom}$, *J* 7.8 Hz), 7.60 d (2H$_{arom}$, *J* 7.8 Hz), 8.05 s (1H$_{arom}$), 9.57 s (1H, NH), 13.00 s, 13.11 s (2H, 2NH). Found, %: C 53.74; H 3.22; N 36.47. $C_{12}H_9N_7O$. Calculated, %: C 53.93; H 3.39; N 36.69.

3-(4-Methoxyphenylamino)-1,8-dihydro-5*H*-pyrazolo[3,4-*d*][1,2,4]triazolo[4,3-*a*]pyrimidin-5-one (Vb). Yield 0.52 g (87%), mp 310–312°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3310, 3070, 2920, 2840 (NH), 1740 (C=O), 1670, 1620, 1570, 1530, 1240, 1180, 1120, 1030, 970. ^{1}H NMR spectrum, δ, ppm: 3.74 s (3H, OCH_3), 6.94 d (2H$_{arom}$, *J* 8.4 Hz), 7.52 d (2H$_{arom}$, *J* 8.7 Hz), 8.01 s (1H$_{arom}$), 9.33 s (1H, NH), 12.84 s (1H, NH), 13.05 s (1H, NH). Found, %: C 52.45; H 3.67; N 32.83. $C_{13}H_{11}N_7O_2$. Calculated, %: C 52.52; H 3.73; N 32.98.

3-(4-Ethoxycarbonylphenylamino)-1,8-dihydro-5*H*-pyrazolo[3,4-*d*][1,2,4]-triazolo[4,3-*a*]-pyrimidin-5-one (Vc). Yield 0.52 g (77%), mp 322–324°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3180 (NH), 1730 (C=O), 1670, 1620, 1560, 1430, 1370, 1320, 1290, 1180, 1100, 1050, 1020, 960, 920. ^{1}H NMR spectrum, δ, ppm: 1.33 t (3H, CH_3, *J* 6.9 Hz), 4.29 q (2H, CH_2, *J* 7.2 Hz), 7.71 d (2H$_{arom}$, *J* 9.3 Hz), 7.96 d (2H$_{arom}$, *J* 8.1 Hz), 8.06 s (1H$_{arom}$), 9.90 s (1H, NH), 13.17 m (2H, 2NH). Found, %: C 52.98; H 3.71; N 28.66. $C_{15}H_{13}N_7O_3$. Calculated, %: C 53.10; H 3.86; N 28.90.

8-Phenyl-3-phenylamino-1,8-dihydro-5*H*-pyrazolo[3,4-*d*][1,2,4]triazolo[4,3-*a*]pyrimidin-5-one (VIa). Yield 0.67 g (98%), mp 341–343°C (decomp.) (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3320, 3100, 3060 (NH), 1730 (C=O), 1690, 1620, 1590, 1560, 1520, 1470, 1420, 1300, 1250, 1190, 1080, 1060, 990, 920. ^{1}H NMR spectrum, δ, ppm: 7.05 t (1H$_{arom}$, *J* 7.5 Hz), 7.34–7.41 m (3H$_{arom}$), 7.54–7.64 m (4H$_{arom}$), 8.10 d (2H$_{arom}$, *J* 7.5 Hz), 8.32 s (1H$_{arom}$), 9.51 s (1H, NH), 13.43 s (1H, NH). Found, %: C 62.79; H 3.77; N 28.43. $C_{18}H_{13}N_7O$. Calculated, %: C 62.97; H 3.82; N 28.56.

3-(4-Methoxyphenylamino)-8-phenyl-1,8-dihydro-5*H*-pyrazolo[3,4-*d*]-[1,2,4]triazolo[4,3-*a*]-pyrimidin-5-one (VIb). Yield 0.68 g (91%), mp 309–311°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3100, 2800 (NH), 1720 (C=O), 1680, 1620, 1580, 1550, 1520, 1250, 1180, 1030, 980. ^{1}H NMR spectrum, δ, ppm: 3.73 s (3H, OCH_3), 6.94 d (2H$_{arom}$, *J* 9.0 Hz), 7.35 t (1H$_{arom}$, *J* 7.8 Hz), 7.52–7.58 m (4H$_{arom}$), 8.09 d (2H$_{arom}$, *J* 8.7 Hz), 8.30 s (1H$_{arom}$), 9.29 s (1H, NH), 13.33 s (1H, NH). Found, %: C 60.95; H 3.98; N 26.17. $C_{19}H_{15}N_7O_2$. Calculated, %: C 61.12; H 4.05; N 26.26.

8-Phenyl-3-(4-ethoxycarbonylphenylamino)-1,8-dihydro-5*H*-pyrazolo-[3,4 *d*][1,2,4]triazolo-[4,3-*a*]pyrimidin-5-one (VIc). Yield 0.71 g (85%), mp 316–318°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3180, 2980 (NH), 1740, 1710 (C=O), 1680, 1620, 1550, 1510, 1430, 1290, 1180, 1110, 980, 910. ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, CH_3, *J* 7.2 Hz), 4.28 q (2H, CH_2, *J* 7.2 Hz), 7.37 t (1H$_{arom}$, *J* 7.8 Hz), 7.57 t (2H$_{arom}$, *J* 7.8 Hz), 7.72 d (2H$_{arom}$, *J* 8.7 Hz), 7.96 d (2H$_{arom}$, *J* 9.0 Hz), 8.10 d (2H$_{arom}$, *J* 7.8 Hz), 8.35 s (1H$_{arom}$), 9.83 s (1H, NH), 13.63 s (1H, NH). Found, %: C 60.66; H 4.02; N 23.47. $C_{21}H_{17}N_7O_3$. Calculated, %: C 60.72; H 4.13; N 23.60.

8-Arylamino-1*H*-pyrazolo[4,3-*e*][1,2,4]triazolo-[4,3-*a*]pyrimidin-4(5*H*)-ones VIIa–VIIc. To a solution of 0.52 g (2.5 mmol) of dicyclohexylcarbodiimide in 20 ml of dioxane was added 2 mmol of an appropriate thiosemicarbazide **IIIa–IIIc**, and the mixture was boiled for 40 min on an oil bath (115–120°C). The reaction mixture was cooled to 30–40°C, the separated precipitate was filtered off, washed on the filter with dioxane and ether.

8-Phenylamino-1*H*-pyrazolo[4,3-*e*][1,2,4]-triazolo[4,3-*a*]pyrimidin-4(5*H*)-one (VIIa). Yield 0.32 g (60%), mp >360°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3370, 3100 (NH), 1690 (C=O), 1630, 1580, 1500, 1440, 1400, 1370, 1250, 1220. ^{1}H NMR spectrum, δ, ppm:

6.95 t (1H_{arom}, *J* 6.6 Hz), 7.33 t (2H_{arom}, *J* 6.9 Hz), 7.55 d (2H_{arom}, *J* 6.9 Hz), 8.39 s (1H_{arom}), 8.69 s (1H, NH), 12.16 br.s (1H, NH), 13.98 s (1H, NH). Found, %: C 53.67; H 3.23; N 36.54. $C_{12}H_9N_7O$. Calculated, %: C 53.93; H 3.39; N 36.69.

8-(4-Methoxyphenylamino)-1*H*-pyrazolo[4,3-*e*]-[1,2,4]triazolo[4,3-*a*]pyrimidin-4(5*H*)-one (VIIb). Yield 0.22 g (37%), mp >360°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3370, 3100 (NH), 1700 (C=O), 1640, 1590, 1520, 1440, 1410, 1370, 1250, 1210, 1120, 1040, 820, 760. ^{1}H NMR spectrum, δ, ppm: 3.73 s (3H, OCH_3), 6.91 d (2H_{arom}, *J* 9.3 Hz), 7.53 d (2H_{arom}, *J* 9.0 Hz), 8.13 s (1H_{arom}), 8.68 s (1H, NH), 12.02 br.s (1H, NH), 13.97 s (1H, NH). Found, %: C 52.39; H 3.63; N 32.83. $C_{13}H_{11}N_7O_2$. Calculated, %: C 52.52; H 3.73; N 32.98.

8-(4-Ethoxycarbonylphenylamino)-1*H*-pyrazolo[4,3-*e*][1,2,4]triazolo-[4,3 *a*]pyrimidin-4(5*H*)-one (VIIc). Yield 0.39 g (57%), mp >360°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3370, 3100, 3000 (NH), 1750, 1730 (C=O), 1660, 1640, 1600, 1530, 1460, 1440, 1420, 1380, 1290, 1260, 1230, 1190, 1110. ^{1}H NMR spectrum, δ, ppm: 1.33 t (3H, CH_3, *J* 6.9 Hz), 4.29 q (2H, CH_2, *J* 7.2 Hz), 7.52 d (2H_{arom}, *J* 8.7 Hz), 7.90 d (2H_{arom}, *J* 9.0 Hz), 8.68 s (1H_{arom}), 9.03 s (1H, NH), 12.21 br.s (1H, NH), 13.97 br.s (1H, NH). Haθ-dενO, %: C 52.98; H 3.57; N 28.78. $C_{15}H_{13}N_7O_3$. Calculated, %: C 53.10; H 3.86; N 28.90.

1-Phenyl-8-phenylamino-1*H*-pyrazolo[4,3-*e*]-[1,2,4]triazolo[4,3-*a*]pyrimidin-4(5*H*)-one (VIIIa). To a solution of (2.5 mmol) of dicyclohexylcarbodiimide in 20 ml of dioxane was added 0.75 g (2 mmol) of thiosemicarbazide **IVa**. The mixture was boiled for 40 min on an oil bath (115–120°C). The reaction mixture was the cooled, the separated precipitate was filtered off and treated with a solution of 0.17 g (3 mmol) of KOH in 30 ml of water, the insoluble product was separated, and the filtrate (compound VIIIa) was acidified with acetic acid, the separated precipitate was filtered off and washed with water on the filter. Yield 0.18 g (26%), mp 339–341°C (decomp.) (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3060 (NH), 1730 (C=O), 1610, 1520, 1460, 1410, 1350, 1270, 1180. ^{1}H NMR spectrum, δ, ppm: 6.44 d (2H_{arom}, *J* 7.8 Hz), 6.75 t (1H_{arom}, *J* 7.8 Hz), 7.02 t (2H_{arom}, *J* 7.8 Hz), 7.23–7.34 m (3H_{arom}), 7.40 s (1H_{arom}), 7.46 d (2H_{arom}, *J* 7.2 Hz), 8.31 s (1H, NH), 12.50 s (1H, NH). Found, %: C 62.83; H 3.73; N 28.45. $C_{18}H_{13}N_7O$. Calculated, %: C 62.97; H 3.82; N 28.56.

7-Phenylamino-1,8-dihydro-4*H*-pyrazolo[3,4-*d*]-[1,2,4]triazolo[1,5-*a*]-pyrimidin-4-one (IXa). *a*. Compound **Va** (0.27 g, 1 mmol) was heated for 5 min on a sand bath (320°C). The obtained crystalline product was cooled, transferred to a filter and washed with ethanol and ether.

b. Compound **VIIa** (0.27 g, 1 mmol) was heated in a test tube in the flame of a burner till the formation of a porous mass that was treated with water, and the precipitate was filtered.

Yield 0.26 g (96%) (*a*), 0.22 g (81%) (*b*), mp > 360°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3160, 2970 (NH), 1730 (C=O), 1620, 1590, 1460, 1320, 1250, 1210, 1190, 1060, 1030, 980, 930, 830, 750. ^{1}H NMR spectrum, δ, ppm: 6.90 t (1H_{arom}, *J* 7.5 Hz), 7.31 t (2H_{arom}, *J* 7.8 Hz), 7.69 d (2H_{arom}, *J* 7.5 Hz), 8.70 s (1H_{arom}), 9.55 s (1H, NH), 13.08 s (1H, NH), 13.70 s (1H, NH). Found, %: C 53.74; H 3.27; N 36.58. $C_{12}H_9N_7O$. Calculated, %: C 53.93; H 3.39; N 36.69.

1-Phenyl-7-phenylamino-1,8-dihydro-4*H*-pyrazolo[3,4-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-4-one (Xa). Compound **VIa** (0.34 g, 1 mmol) was heated for 5 min on a sand bath (360°C). The obtained crystalline product was cooled, transferred to a filter and washed with ethanol and ether. Yield 0.29 g (85%), mp > 360°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3380 (NH), 1730 (C=O), 1600, 1540, 1510, 1420, 1250, 1170, 1060, 930, 860, 760. ^{1}H NMR spectrum, δ, ppm: 7.03 t (1H_{arom}, *J* 7.5 Hz), 7.35–7.40 m (3H_{arom}), 7.57 t (2H_{arom}, *J* 7.8 Hz), 7.67 d (2H_{arom}, *J* 7.5 Hz), 8.13 d (2H_{arom}, *J* 7.5 Hz), 8.33 s (1H_{arom}), 9.88 s (1H, NH), 13.43 br.s (1H, NH). Found, %: C 62.84; H 3.76; N 28.43. $C_{18}H_{13}N_7O$. Calculated, %: C 62.97; H 3.82; N 28.56.

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