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LETTERS TO THE EDITOR

Synthesis of 2-Aryl-6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidine-7-thione and 2-Aryl-6*H*,7*H*-[1,3]thiazolo[5,4-*d*]pyrimidine-7-thione Using 2-Aroylaminomalonodiamide

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Oxazolo- and thiazolopyrimidines have a biological significance, since they are the structural analogs and antagonists of purine bases. Among them substances were found, which inhibit enzymes [1, 2] and possess fungicidal [3] and antiviral [4] activity.

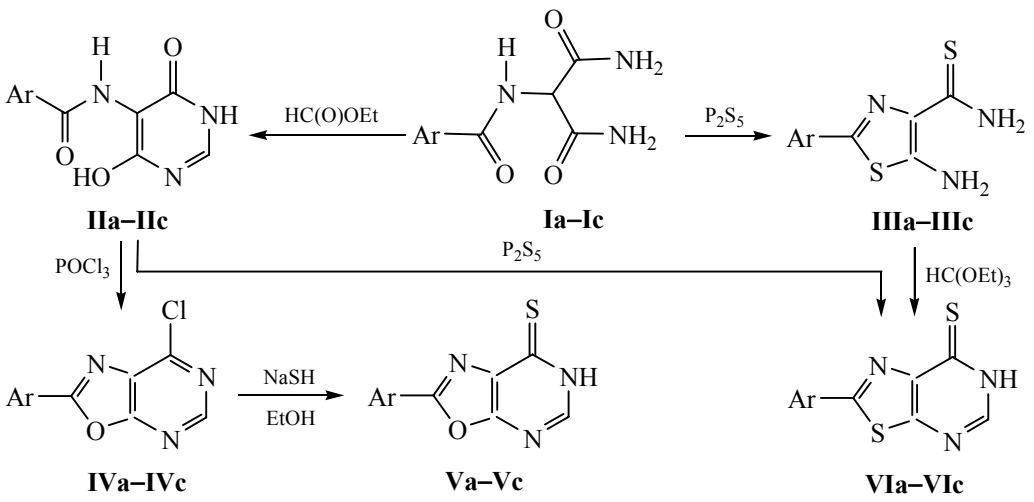
There are two strategic approaches to construct the azolopyrimidine system: via cyclization of the pyrimidine ring on an azole or by fusion of azole ring with the pyrimidine. In this work we used two approaches using 2-aroylaminomalonodiamides **Ia**–**Ic** as the starting materials [5]. In this case, the target products were 2-aryl-6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidine-7-thiones **Va**–**Vc** and 2-aryl-6*H*,7*H*-[1,3]thiazolo[5,4-*d*]pyrimidine-7-thiones **VIa**–**VIc**. The reactions sequence **I**→**II**→**IV**→**V** has as the initial reaction that of 2-aroylaminomalonodiamides **Ia**–**Ic** with ethyl formate in the presence of sodium ethoxide to form 5-aroylamino-6-hydroxypyrimidin-4-ones **IIa**–**IIc**. The ^{13}C NMR spectra of these compounds contain the characteristic signals of the C^5 and C^6 atoms of the pyrimidine ring in the ranges of 102.87–103.34 and 165.75–165.85 ppm, respectively. In the ^{1}H NMR spectra there are no signals of the primary amide groups, and the singlet of C^2H proton appears in the range of 8.04–8.07 ppm.

The subsequent fusion of the five-membered oxazole ring was performed by boiling 5-aroylamino-6-hydroxypyrimidin-4-ones **IIa**–**IIc** in an excess of phosphorus oxychloride to give 2-aryl-7-chloro[1,3]oxazolo[5,4-*d*]pyrimidines in 57–79% yields. In the ^{13}C NMR spectra the signals of the C^5 and C^6 atoms are shifted downfield to 130.08–130.63 and 165.75–165.85 ppm, respectively. The signal of the pyrimidine carbon atom bonded to the chlorine atom is observed in the range of 153.63–154.02 ppm. The treatment of compounds **IVa**–**IVc** with sodium hydrosulfide in ethanol at 50°C gives rise to 2-aryl-6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidine-7-thiones **Va**–**Vc**. A characteristic feature of the ^{13}C NMR spectra of these compounds is an appearance of the signal of the C=S moiety in the range of 176.33–176.65 ppm.

The boiling of 2-aroylaminomalonodiamides **Ia**–**Ic** with 2 eq of phosphorus pentasulfide in pyridine leads to sulfurization of the amide groups and heterocyclization into 5-amino-2-aryl-1,3-thiazol-4-carboxthioamides **IIIa**–**IIIc**. The structure of the latter was proved by the spectral data (appearance of two singlets of thioamide groups in the range of 8.78–8.94 ppm in the ^{1}H spectra and the presence of the signal of thiourea group at δ_C 183.90–187.29 ppm in the ^{13}C NMR spectra) and their conversion into 2-aryl-6*H*,7*H*-[1,3]thiazolo[5,4-*d*]pyrimidine-7-thiones **VIa**–**VIc** via the boiling in triethylorthoformate.

The ^{1}H and ^{13}C NMR spectra of compounds **VIa**–**VIc** contain the same characteristic signals that in the spectra of 2-aryl-6*H*,7*H*-[1,3]oxazolo-[5,4-*d*]pyrimidine-7-thiones **Va**–**Vc**. Thus, in the ^{1}H NMR spectra there is the signal of the C^2H proton of pyrimidine fragment at 8.24–8.30 ppm, and the ^{13}C NMR spectrum contains the signals of the C=S moiety at δ_C 177.20–177.57 ppm.

Thiazolopyrimidines **VIa**–**VIc** were also obtained by the reaction of phosphorus pentasulfide with 5-



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**).

aroylamino-6-hydroxypyrimidin-4-ones **IIa**–**IIc** in 10–15% yields. The identity of the products **VIa**–**VIc** obtained via the transformations **II**→**VI** and **III**→**VI** was proved by comparing their IR and NMR spectra.

The structure of the obtained compounds is also consistent with the data of elemental analysis and gas chromatography-mass spectrometry. In addition, compounds **IVa**, **Va**, **VIa** have been previously obtained [6, 7].

Thus, we demonstrated that the available 2-aroylaminomalonodiamides can be used in the synthesis of oxazolo- and thiazolo[5,4-*d*]pyrimidines, among which it is possible to look for biologically active compounds.

5-Aroylamino-6-hydroxypyrimidin-4-ones (IIa–IIc). To a solution of 4.60 g (0.20 mol) of sodium in 150 ml of anhydrous ethanol was added 0.10 mol of 2-aroylaminomalonodiamide **Ia**–**Ic** and 18.56 ml (0.23 mol) of ethyl formate. The mixture was heated with stirring for 2 h. Then ethanol was evaporated in a vacuum, and to the residue was added water (100 ml). The unreacted 2-aroylaminomalonodiamide **Ia**–**Ic** was filtered off. The filtrate was acidified with hydrochloric acid to pH 5, the formed precipitate was filtered off, and compounds **IIa**–**c** were analyzed without further purification.

5-Benzoylamino-6-hydroxypyrimidin-4-one (IIa). Yield 58%, mp 217–218°C. ^{1}H NMR spectrum, δ_H, ppm: 7.45–7.98 m (5H, C_6H_5), 8.07 s (1H, CH), 9.24 s (1H, NH), 12.08 br. s (2H, NH, OH). ^{13}C NMR spectrum, δ_C, ppm: 103.15, 128.18, 128.68, 131.82, 134.64, 147.87, 154.18, 162.76, 165.79. Mass spectrum, *m/z*: 232 $[M + 1]^+$. Found, %: C 57.28, H 3.81; N 18.09. $C_{11}H_9N_3O_3$. Calculated, %: C 57.14; H 3.92; N 18.27. *M* 231.

5-(4-Methylbenzoylamino)-6-hydroxypyrimidin-4-one (IIb). Yield 69%, mp 247–248°C. IR spectrum, ν, cm^{-1}: 1537, 1648, 2597, 3050, 3193, 3340, 3394. ^{1}H NMR spectrum, δ_H, ppm: 2.37 s (3H, CH_3), 7.29 d (2H, C_6H_4, *J* 7.5 Hz), 7.86 d (2H, C_6H_4, *J* 7.5 Hz), 8.04 s (1H, CH), 9.13 s (1H, NH). ^{13}C NMR spectrum, d_C, ppm: 21.48, 103.34, 126.11, 128.21, 129.22, 129.96, 131.87, 141.70, 147.72, 168.91. Mass spectrum, *m/z*: 246 $[M + 1]^+$. Found, %: C 58.51; H 4.40; N 17.29. $C_{12}H_{11}N_3O_3$. Calculated, %: C 58.77; H 4.52; N 17.13. *M* 245.

5-(4-Chlorobenzoylamino)-6-hydroxypyrimidin-4-one (IIc). Yield 58%, mp 258°C. IR spectrum, ν, cm^{-1}: 1546, 1648, 2597, 3059, 3332. ^{1}H NMR spectrum, δ_H, ppm: 7.57 d (2H, C_6H_4, *J* 6.8 Hz), 7.97 d (2H, C_6H_4, *J* 6.8 Hz), 8.06 s (1H, CH), 9.31 s (1H, NH), 12.05 br. s (2H, NH, OH). ^{13}C NMR spectrum, δ_C, ppm: 102.87, 128.79, 129.38, 130.09, 133.50, 136.63, 147.93, 162.83, 164.75. Mass spectrum, *m/z*: 266 $[M]^+$. Found, %: C 49.98, H 3.11; Cl 13.21; N 15.66. $C_{11}H_8ClN_3O_3$. Calculated, %: C 49.73; H 3.04; Cl 13.35; N 15.82. *M* 266.

5-Amino-2-aryl-1,3-thiazole-4-carbothioamides (IIIa–IIIc). To a suspension of 4.45 g (0.02 mol) of

phosphorus pentasulfide in 20 ml of anhydrous pyridine was added 0.01 mol of compound **IIa–IIc**. The mixture was refluxed for 2 h, then diluted with water (50 ml) and acidified with hydrochloric acid to pH 5. The formed precipitate was filtered off and suspended in 60 ml of 5% aqueous NaOH. The mixture was refluxed for 3 min and cooled. The precipitate was filtered off. The additional amount of thioamides **IIIa–IIIc** was obtained by acidification of the mother liquor to pH 1. The formed precipitate was filtered off and suspended in 20 ml of ethanol. After reflux for 6 h, the precipitate was filtered off, washed with water, and recrystallized from ethanol.

5-Amino-2-phenyl-1,3-thiazole-4-carbothioamide (IIIa). Yield 69%, mp 194–195°C. IR spectrum, ν, cm^{-1}: 1522, 1564, 1639, 3194, 3275, 3403. ^1H NMR spectrum, δ_H, ppm: 7.33–7.95 m (5H, C_6H_5), 8.75 s (2H, NH_2), 8.84 s [1H, C(S)NH_2], 8.92 s [1H, C(S)NH_2]. ^{13}C NMR spectrum, δ_C, ppm: 123.16, 126.94, 128.35, 129.29, 132.09, 142.73, 150.66, 183.90. Found, %: C 51.29; H 3.92; N 17.61; S 27.40. $C_{10}H_9N_3S_2$. Calculated, %: C 51.04; H 3.85; N 17.86; S 27.25.

5-Amino-2-(4-methylphenyl)-1,3-thiazole-4-carbothioamide (IIIb). Yield 75%, mp 222–223°C. IR spectrum, ν, cm^{-1}: 1500, 1564, 1664, 3197, 3292, 3431 ^1H NMR spectrum, δ_H, ppm: 2.34 s (3H, CH_3), 7.26 d (2H, C_6H_4, *J* 5.6 Hz), 7.75 d (2H, C_6H_4, *J* 5.6 Hz), 8.71 s (2H, NH_2), 8.78 s [1H, C(S)NH_2], 8.87 s [1H, C(S)NH_2]. ^{13}C NMR spectrum, δ_C, ppm: 21.40, 126.05, 126.37, 129.98, 130.72, 139.55, 144.48, 160.20, 187.19. Mass spectrum, *m/z*: 250 $[M + 1]^+$. Found, %: C 52.73; H 4.49; N 16.79; S 25.61. $C_{10}H_9N_3S_2$. Calculated, %: C 52.98; H 4.45; N 16.85; S 25.72. *M* 249.

5-Amino-2-(4-chlorophenyl)-1,3-thiazole-4-carbothioamide (IIIc). Yield 86%, mp 209–210°C. IR spectrum, ν, cm^{-1}: 1521, 1561, 1641, 1910, 3184, 3289, 3431. ^1H NMR spectrum, δ_H, ppm: 7.49 d (2H, C_6H_4, *J* 6.7 Hz), 7.88 d (2H, C_6H_4, *J* 6.7 Hz), 8.78 s (2H, NH_2), 8.89 s [1H, C(S)NH_2], 8.94 s [(1H, C(S)NH_2]. ^{13}C NMR spectrum, d_C, ppm: 126.59, 127.69, 129.43, 132.25, 134.20, 142.80, 160.65, 187.29. Mass spectrum, *m/z*: 270 $[M]^-$. Found, %: C 44.38; H 3.07; Cl 13.19; N 15.45; S 23.82. $C_{10}H_8ClN_3S_2$. Calculated, %: C 44.52; H 2.99; Cl 13.14; N 15.58; S 23.77. *M* 270.

2-Aryl-7-chloro[1,3]oxazolo[5,4-*d*]pyrimidines (IVa–IVc). A mixture of 230 ml (2.48 mol) of phosphorus oxychloride and 0.1 mol of compound **IIa–IIc** was heated for 5 h. Then phosphorus oxychloride was distilled off in vacuum. The residue was poured onto ice and neutralized with sodium hydrogen carbonate to pH 7. The precipitate was filtered off and dried. The substances **IVa–IVc** were analyzed without further purification.

2-Phenyl-7-chloro[1,3]oxazolo[5,4-*d*]pyrimidine (IVa). 57% yield, mp 155–156°C (mp 152°C [6]). IR spectrum, ν, cm^{-1}: 16128, 1713, 1914, 1973, 3060. ^1H NMR spectrum, δ_H, ppm: 7.64–34 m (5H, C_6H_5), 8.93 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 125.33, 128.64, 130.08, 131.14, 134.08, 149.38, 153.87, 163.51, 165.85. Mass spectrum, *m/z*: 232 $[M]^+$. Found, %: C 57.29, H 2.68; Cl 15.17; N 18.22. $C_{11}H_6ClN_3O$. Calculated, %: C 57.04; H 2.61; Cl 15.31; N 18.14. *M* 232.

2-(4-Methylphenyl)-7-chloro[1,3]oxazolo[5,4-*d*]pyrimidine (IVb). Yield 79%, mp 163–164°C. IR spectrum, ν, cm^{-1}: 1600, 1616, 2216, 3038. ^1H NMR spectrum, δ_H, ppm: 2.43 s (3H, CH_3), 7.46 d (2H, C_6H_4, *J* 7.6 Hz), 8.13 d (2H, C_6H_4, *J* 7.6 Hz), 8.88 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 21.79, 122.47, 128.59, 130.63, 131.40, 144.70, 149.06, 153.63, 163.66, 165.75. Mass spectrum, *m/z*: 266 $[M]^+$. Found, %: C 58.83, H 3.35; Cl 14.59; N 17.24. $C_{12}H_5ClN_3O$. Calculated, %: C 58.67, H 3.28; Cl 14.43; N 17.10. *M* 266.

7-Chloro-2-(4-chlorophenyl)[1,3]oxazolo[5,4-*d*]pyrimidine (IVc). Yield 79%, mp 180–181°C. ^1H NMR spectrum, δ_H, ppm: 7.72 d (2H, C_6H_4, *J* 8.3 Hz), 8.24 d (2H, C_6H_4, *J* 8.3 Hz), 8.93 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 124.17, 130.25, 130.35, 131.32, 138.94, 149.54, 154.02, 162.61, 165.78. Mass spectrum, *m/z*: 246 $[M]^+$. Found, %: C 49.81; H 1.85; Cl 26.73; N 15.71. $C_{11}H_5Cl_2N_3O$. Calculated, %: C 49.65; H 1.89; Cl 26.65; N 15.79. *M* 246.

2-Aryl-6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidine-7-thiones (Va–c). To a solution of 0.1 mol of compound **IVa–IVc** in 925 ml of ethanol was added 20.75 g (0.28 mol) of sodium hydrosulfide monohydrate. The mixture was refluxed for 2.5 h. The precipitate was filtered off. Compounds **Va–Vc** were analyzed without further purification.

2-Phenyl-6*H*,7*H*-[1,3]oxazolo[5,4-*d*]pyrimidine-7-thione (Va). Yield 85%, mp 287–288°C (mp 292°C [6]). IR spectrum, ν, cm^{-1}: 1510, 1617, 1684, 1939, 3038, 3111 ^1H NMR spectrum, δ_H, ppm: 7.55–8.21 m (5H, C_6H_5), 8.40 s (1H, CH), 14.37 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 125.95, 127.64, 129.93,

132.83, 134.50, 148.53, 159.82, 160.55. 176.54. Mass spectrum, *m/z*: 230 $[M + 1]^+$. Found, %: C 57.75; H 3.02; N 18.21; S 14.09. $C_{11}H_7N_3OS$. Calculated, %: C 57.63; H 3.08; N 18.33; S 13.99. *M* 229.

2-(4-Methylphenyl)-6*H*,7*H*-[1,3]oxazolo[5,4-*d*]-pyrimidine-7-thione (Vb). Yield 80%, mp 267–268°C. ^{1}H NMR spectrum, δ_H, ppm: 2.39 s (3H, CH_3), 7.39 d (2H, C_6H_4, *J* 7.0 Hz), 7.99 d (2H, C_6H_4, *J* 7.0 Hz), 8.32 s (1H, CH), 14.23 s (1H, NH). ^{13}C NMR spectrum, d_C, ppm: 21.68, 123.11, 127.54, 130.41, 134.47, 143.10, 148.26, 159.59, 160.71, 176.33. Mass spectrum, *m/z*: 244 $[M + 1]^+$. Found, %: C 50.19; H 2.34; Cl 13.40; N 15.99; S 12.22. $C_{11}H_6ClN_3OS$. Calculated, %: C 50.10; H 2.29; Cl 13.44; N 15.93; S 12.16. *M* 243.

2-(4-Chlorophenyl)-6*H*,7*H*-[1,3]oxazolo[5,4-*d*]-pyrimidine-7-thione (Vc). Yield 88%, mp 295–296°C (decomp.). IR spectrum, ν, cm^{-1}: 1537, 1567, 1609, 1904, 2208, 3040, 3084 ^{1}H NMR spectrum, δ_H, ppm: 7.66 d (2H, C_6H_4, *J* 4.8 Hz), 8.11 d (2H, C_6H_4, *J* 4.8 Hz), 8.38 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 124.79, 129.33, 130.03, 137.56, 139.47, 148.65, 159.82, 162.07, 176.65. Found, %: C 50.19; H 2.33; Cl 13.38; N 15.98; S 12.09. $C_{11}H_6ClN_3OS$. Calculated, %: C 50.10; H 2.29; Cl 13.44; N 15.93; S 12.16.

2-Aryl-6*H*,7*H*-[1,3]thiazolo[5,4-*d*]pyrimidine-7-thiones (VIa-VIc). *a*. To 0.1 mol of compound **IIIa–IIIc** was added 260 ml (1.57 mol) of triethylorthoformate and the mixture was refluxed for 8 h. After cooling the formed precipitate was filtered off, washed with diethyl ether, and analyzed without further purification.

b. A mixture of 0.1 mol of compound **IIa–IIc** in 200 ml of anhydrous pyridine and 44.46 g (0.2 mol) of phosphorus pentasulfide was refluxed for 5 h and poured into water. The formed precipitate was filtered off, dried, and recrystallized from an ethanol–DMF mixture (1:1.5). The mixture of two samples of **VIa–VIc** obtained by the methods *a* and *b* did not give the melting point depression.

2-Phenyl-6*H*,7*H*-[1,3]thiazolo[5,4-*d*]pyrimidine-7-thione (VIa). Yield 64% (method *a*), 10% (method *b*), mp 239–240°C (mp 238–245°C [7]). IR spectrum, ν, cm^{-1}: 1522, 1542, 1653, 2865, 3000, 3129, 3245 ^{1}H NMR spectrum, δ_H, ppm: 7.53–8.10 m (5H, C_6H_5), 8.31 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 127.53, 129.94, 132.24, 132.80, 146.65, 148.66, 158.96, 165.31, 177.57. Mass spectrum, *m/z*: 246 $[M + 1]^+$. Found, %: C 53.71; H 2.82; N 17.21; S 26.01. $C_{11}H_7N_3S_2$. Calculated, %: C 53.85; H 2.88; N 17.13; S 26.14. *M* 245.

2-(4-Methylphenyl)-6*H*,7*H*-[1,3]thiazolo[5,4-*d*]-pyrimidine-7-thione (VIb). Yield 73% (method *a*), 15% (method *b*), mp 219–220°C. IR spectrum, ν, cm^{-1}: 1517, 1570, 2836, 3280. ^{1}H NMR spectrum, δ_H, ppm: 2.39 s (3H, CH_3), 7.38 d (2H, C_6H_5, *J* 7.8 Hz), 7.92 d (2H, C_6H_5, *J* 7.8 Hz), 8.29 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 21.57, 129.16, 129.99, 131.51, 136.90, 146.49, 148.59, 159.05, 164.21, 177.20. Mass spectrum, *m/z*: 260 $[M + 1]^+$. Found, %: C 55.70; H 3.44; N 16.27; S 24.84. $C_{12}H_9N_3S_2$. Calculated, %: C 55.57; H 3.50; N 16.20; S 24.73. *M* 259.

2-(4-Chlorophenyl)-6*H*,7*H*-[1,3]thiazolo[5,4-*d*]-pyrimidine-7-thione (VIc). Yield 87% (method *a*), 13% (method *b*), mp 252°C. IR spectrum, ν, cm^{-1}: 1548, 1591, 1679, 1870, 2740, 2845, 2964, 3123. ^{1}H NMR spectrum, δ_H, ppm: 7.62 d (2H, C_6H_4, *J* 6.7 Hz), 8.04 d (2H, C_6H_4, *J* 6.7 Hz), 8.24 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 129.16, 129.99, 131.51, 136.90, 146.49, 148.59, 159.05, 164.21, 177.20. Mass spectrum, *m/z*: 280 $[M]^+$. Found, %: C 47.32; H 2.11; Cl 12.75; N 15.10; S 22.98. $C_{11}H_6ClN_3S_2$. Calculated, %: C 47.22; H 2.16; Cl 12.67; N 15.02; S 22.92. *M* 280.

The NMR spectra were recorded on a Bruker AVANCE DRX-500 spectrometer [500 MHz (^{1}H), 125 MHz (^{13}C)] using DMSO-d_6 as a solvent and TMS as an internal reference. The IR spectra were taken on a Vertex 70 spectrometer from KBr pellets. The melting points were determined on a Fisher Johns instrument. The GC-MS spectra were recorded on a HPLC Agilent 1100 Series chromatograph equipped with a diode matrix with an Agilent LC\MSD SL mass selective detector. The GC-MS (APCI) parameters are as follows: column Zorbax SB-C18 (1.8 μm×4.6×15 mm, PN 821975-932); solvents: A acetonitrile–water (95:5) + 0.1% TFA, B 0.1% aqueous TFA; eluent flow rate 3 ml min^{-1}; injection volume 1 μl; UV detecting at 215, 254, 285 nm; scanning range of *m/z* 80–1000. The reaction progress was monitored by TLC.

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