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Reactions of 2-(2-Propynylsulfanyl)-5,6,7,8-tetrahydrobenzo[*b*]thieno[2,3-*d*]pyrimidin-4(3*H*)-one with Arylsulfenyl Chlorides

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Abstract—2-(2-propynylsulfanyl)-5,6,7,8-tetrahydrobenzo[*b*]thieno[2,3-*d*]pyrimidin-4(3*H*)-one with arylsulfenyl chlorides in chloroform gave products of anti-Markownikoff Ad_E-addition. The use of nitromethane as solvent in the presence of lithium perchlorate additives favored intramolecular electrophilic cyclization into 1-arylsulfanyl-1,2,6,7,8,9-hexahydro-4*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo[3,2-*a*]-pyrimidin-5-one.

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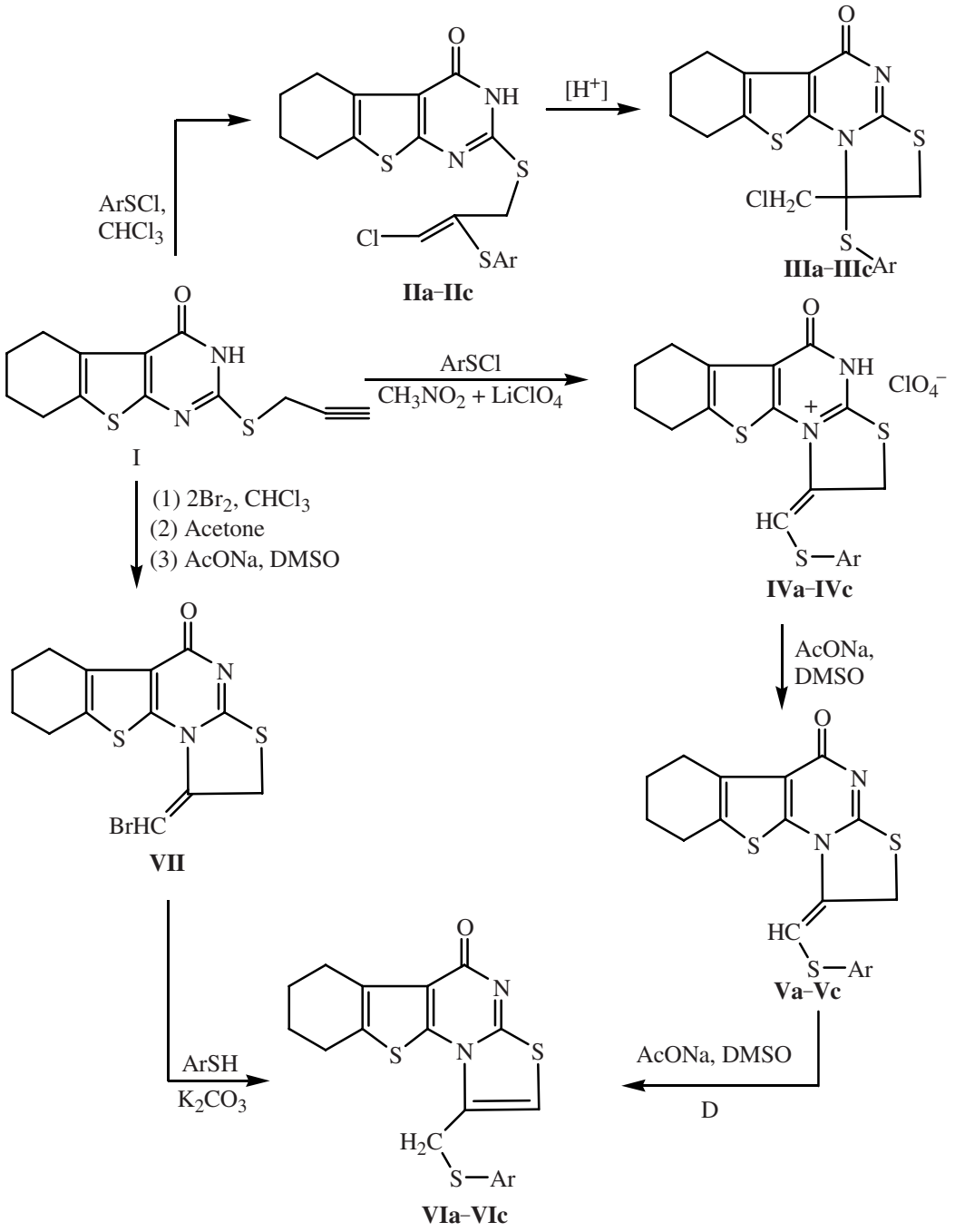
Reactions of alkenes with electrophilic reagents are among the most widely spread and well understood reactions in the organic chemistry, and it is well known that if in an appropriated position with respect to the double bond a nucleophilic site is present then the electrophilic intramolecular cyclization is in competition with the Ad_E-addition. The acetylenes reactivity in addition reactions and consequently also in cyclizations is considerably lower that that of compounds with a double C=C bond. However the cyclization was successfully carried out in functionally substituted alkynes by the action of mercury salts [1, 2], palladium [3, 4], halosuccinimides [5], phenylselenylphthalimide [6], selenyl and sulfenyl chlorides [7, 8].

We showed formerly by an example of S-alkenyl-substituted pyrimidinones that the character of the sulfenyl chloride and the substituents at the double bond of the olefin significantly affected the composition and ratio of the reaction products [9, 10]. In extension of our studies we attempted to reveal the behavior in this process of alkynylsulfanyl-substituted substrates. As a model compound 2-(2-propynylsulfanyl)-5,6,7,8-tetrahydrobenzo-[*b*]-thieno[2,3-*d*]pyrimidin-4(3*H*)-one (**I**) was selected, and its reactions were studied with *p*-tolyl-, phenyl-, *p*-nitro-phenylsulfenyl chlorides.

Compound **I** with ArSCl in chloroform formed products of Ad_E-addition against the Markownikoff rule **IIa–IIc**. At the use of *p*-tolylsulfenyl chloride alongside the product **IIa** we isolated from the reaction mixture 16% of cyclic compound **IIIa**. Evidently the primarily formed adduct **IIa** underwent the cyclization at the action of hydrogen chloride appeared in a small amount in the reaction mixture through the decomposition of unreacted sulfenyl chloride. The treatment of addition products **IIa–IIc** with hydrogen chloride in $CHCl_3$ led to the formation of thiazolinothienopyrimidinones **IIIa–IIIc** in confirmation of the above assumption.

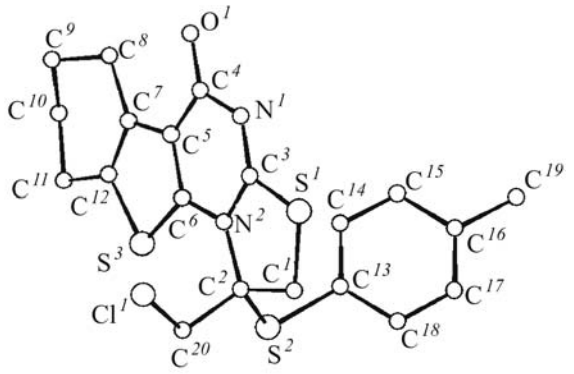
The structure of compound **IIIa** was unambiguously established by X-ray diffraction analysis. The location of substituents at the thiazoline ring of compound **IIIa** suggests that the preceding compound **IIa** is the product of anti-Markownikoff addition of arylsulfenyl chloride to alkyne **I**. The general view of molecule **IIIa** and its main bond distances and bond angles are presented on the figure. The central heterocyclic system $S^1S^3N^1N^2C^{1–7}C^{12}$ is virtually planar: the deviations of atoms from the mean-square plain do not exceed 0.132 Å; the dihedral angles between the central five-membered ring $N^1N^2C^{3–6}$ and heterocycles $S^3C^{5–7}C^{12}$ and $S^1N^2C^{1–3}$ are only 1.3 and 3.4°. Due to sterical reasons the benzene ring $C^{13–18}$ is turned with respect to the central tricyclic system by 63.7°. The N^2 atom has a planary trigonal configuration of bonds, the corresponding sum of bond angles at this atom is 360.0(6)°.



Ar = 4-$CH_3C_6H_4$ (**a**), C_6H_5 (**b**), 4-$NO_2C_6H_4$ (**c**).

The reaction of S-propargyl-substituted thienopyrimidinone **I** with ArSCl under conditions of "doping addition" (nitromethane as solvent with $LiClO_4$ additive) led to the formation in 53–60% yield of intramolecular cyclization products of angular structure **IVa–IVc**. At the use of 4-$NO_2C_6H_4SCl$ alongside the cyclic compound **IVc** formed 12% of adduct **IIc**. Perchlorates **IVa–IVc** were converted into the corresponding bases **Va–Vc** by treating with sodium acetate in DMSO. At heating compounds **Va–Vc** with sodium acetate the exocyclic double bond migrated into the thiazole ring giving compounds **VIa–VIc**.

To confirm the structure of compounds **VIa–VIc** and to establish the position of the multiple bond in cyclization products **Va–Vc** an independent synthesis was performed. In the first stage by treating compound **I** with



General view of compound **IIIa** molecule. Bond distances (Å) and bond angles (deg): C^1–C^2 1.538(3), C^2–N^2 1.469(3), N^2–C^3 1.363(3), C^3–S^1 1.740(2), S^1–C^1 1.806(3), S^3–C^{12} 1.737(3), C^{12}–C^7 1.351(3), C^7–C^5 1.440(3), C^5–C^6 1.368(3), C^6–S^3 1.722(2), C^5–C^4 1.456(3), O^1–C^4 1.221(3), C^4–N^1 1.403(3), N^1–C^3 1.293(3), C^6–N^2 1.386(3), Cl^1–C^{20} 1.782(3), C^2–S^2 1.840(2), S^2–C^{13} 1.771(2); $C^2N^2C^3$117.64(18), $C^2N^2C^6$126.61(18), $C^6N^2C^3$115.74(19), $C^3S^1C^1$ 92.86(11), $C^2S^2C^{13}$102.66(11), $C^3N^1C^4$119.7(2), $C^{12}S^3C^6$ 90.74(12).

bromine we obtained bromomethylidene-substituted thiazolinothienopyrimidinone **VII** that was subjected to reaction with thiophenol and *para*-thiocresol. The bromine in compound **VII** is not labile, and its substitution is accompanied by a simultaneous migration of the multiple bond into the thiazole ring [11]. Therefore on bromine substitution with a thioaryl moiety formed compounds **VI** and not products **V** with an exocyclic double bond.

The difference in the reactivity of sulfenyl chlorides and bromine should be emphasized. Whereas the bromine reacted with compound **I** in chloroform forming a cyclization product **VII**, the arylsulfenyl chlorides under similar conditions yielded addition products **II** and only the use of a polar solvent and introducing into the reaction medium of "doping-additives" led to the formation of cyclic compounds **IVa–IVc**.

In the IR spectra of compounds **IVa–IVc** the carbonyl absorption band appeared at 1720–1710 cm^{-1}, besides the vibrations of the perchlorate anion were observed in the range 1120–1100 cm^{-1}. The carbonyl absorption band in the spectra of compounds **Va–Vc** was observed at 1645–1640 cm^{-1}, in those of their isomers **VIa–VIc,** at 1620 cm^{-1}. The absorption band of the carbonyl group appeared in the spectra of acyclic **IIa–IIc** at 1670–1665 cm^{-1}, and of isomeric cyclic structures **IIIa–IIIc**, at 1650–1640 cm^{-1}.

In the ^{1}H NMR spectra of compounds **Va–Vc** the signal of the methylene group of the thiazoline ring appeared as a doublet in the region 4.42–4.49 ppm with a coupling constant 2.0 Hz. The methine proton =C<u>H</u>SAr gave rise to a triplet at 6.69–6.80 ppm (*J* 2.0 Hz).

In the ^{1}H NMR spectra of compounds **VIa–VIc** the singlet of C<u>H</u>$_2$SAr group appeared in the region 4.49–4.82 ppm, and the singlet of methine proton of the thiazole ring, in the range 6.89–7.24 ppm.

EXPERIMENTAL

IR spectra of compounds **II–VII** were recorded on a spectrophotometer UR-20 from pellets with KBr. ^{1}H NMR spectra from solutions of compounds **II–VII** in DMSO-d_6 were registered on a spectrometer Varian VXR-300 (300 MHz), internal reference TMS.

X-ray diffraction study on a single crystal of compound **IIIa** of linear dimensions 0.24×0.37×0.58 mm was carried out at room temperature on an automatic CCD diffractometer Bruker Apex II (MoK_α-radiation, λ 0.71069 Å, θ_{max} 26°, $-16 \le h \le 16$, $-17 \le k \le 15$, $-25 \le l \le 25$). 24403 reflections were collected (2551 independent reflections, R_{int} 0.027). Crystals of compound **IIIa** rhombic, *a* 13.3526(2), *b* 14.3976(3), *c* 20.7577(4) Å, *V* 3990.6(1) Å^3, *M* 435.03, *Z* 8, d_{calc} 1.45 g/cm^3, μ 5.19 cm^{-1}, *F*(000) 1808, space group *Pbca* (N 61). The structure was solved by the direct method and refined by the least-squares procedure in a full-matrix anisotropic approximation using software CRYSTALS [12]. In the refinement 2551 reflections were used with $I > 3\sigma(I)$ (244 refined parameters, 10.5 reflections per parameter). All hydrogen atoms were revealed from the difference synthesis of the electron density and were involved in the refinement with the fixed position and thermal parameters. In the refinement weight Chebyshev scheme was used [13] with five parameters: 1.81, 0.203, 2.06, 0.0604, and 0.665. The final values of divergence factors are *R* 0.033 and R_W 0.035, GOF 1.125. The residual electron density from the difference Fourier series was –0.29 and 0.39 e/Å^3. The complete set of X-ray data for compound **IIIa** was deposited into Cambridge Structural Database (CCDC 604010).

2-(2-Propynylsulfanyl)-5,6,7,8-tetrahydro-benzo[*b*]-thieno[2,3-*d*]pyrimidin-4(3*H*)-one (**I**) was obtained by procedure [14].

Reaction of compound I with ArSCl in chloroform. To a dispersion of 0.55 g (2 mmol) of compound **I** in 10 ml of chloroform at 15–20°C while stirring was added dropwise a solution of 2.1 mmol of ArSCl in 10 ml of chloroform. The mixture was stirred for 12–16 h, then

additionally was added 0.3 mmol of arylsulfenyl chloride, and the stirring was continued for 10 h. The separated precipitate of compounds **IIa–IIc** was filtered off, and washed on the filter with ether. Additional portion of compounds **IIa–IIc** was obtained by removing the solvent. At the use of *p*-$CH_3C_6H_4SCl$ a mixture formed of substances **IIa** and **IIIa** which was separated by fractional crystallization from ethanol. Compound **IIa** crystallized first, and after evaporation of filtrate 0.14 g (16%) of compound **IIIa** was obtained.

2-[2-(4-Tolylsulfanyl)-3-chloro-2-propenylsulfanyl]-5,6,7,8-tetrahydrobenzo[*b*]thieno[2,3-*d*]pyrimidin-4(3*H*)-one (IIa). Yield 0.62 g (71%), mp 217–219°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 1680 (C=O), 1570, 1510, 1420, 1340. ^1H NMR spectrum, δ, ppm: 1.77 m (4H, $2CH_2$), 2.26 s (3H, CH_3), 2.70–2.82 m (4H, $2CH_2$), 4.13 s (2H, CH_2), 6.88 s (1H, CH), 7.15 d ($2H_{arom}$, *J* 8.1 Hz), 7.25 d ($2H_{arom}$, *J* 8.4 Hz), 12.60 s (1H, NH). Found, %: C 55.12; H 4.31; Cl 8.11; N 6.37; S 22.06. $C_{20}H_{19}ClN_2OS_3$. Calculated, %: C 55.22; H 4.40; Cl 8.15; N 6.44; S 22.11.

2-(2-Phenylsulfanyl-3-chloro-2-propenylsulfanyl)-5,6,7,8-tetrahydrobenzo[*b*]thieno[2,3-*d*]pyrimidin-4(3*H*)-one (IIb). Yield 0.63 g (75%), mp 208–210°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 1670 (C=O), 1560, 1410. ^1H NMR spectrum, δ, ppm: 1.77 m (4H, $2CH_2$), 2.72–2.84 m (4H, $2CH_2$), 4.19 s (2H, CH_2), 6.99 s (1H, CH), 7.37 m ($5H_{arom}$), 12.63 s (1H, NH). Found, %: C 54.03; H 4.05; Cl 8.34; N 6.51; S 22.73. $C_{19}H_{17}ClN_2OS_3$. Calculated, %: C 54.21; H 4.07; Cl 8.42; N 6.65; S 22.85.

2-[2-(4-Nitrophenylsulfanyl)-3-chloro-2-propenylsulfanyl]-5,6,7,8-tetrahydrobenzo[*b*]-thieno[2,3-*d*]-pyrimidin-4(3*H*)-one (IIc). Yield 0.78 g (84%), mp 237–239°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 1665 (C=O), 1560, 1520, 1420, 1360. ^1H NMR spectrum, δ, ppm: 1.75 m (4H, $2CH_2$), 2.67–2.78 m (4H, $2CH_2$), 4.33 s (2H, CH_2), 7.34 s(1H, CH), 7.44 d ($2H_{arom}$, *J* 9.3 Hz), 8.06 d ($2H_{arom}$, *J* 9.3 Hz), 12.56 s (1H, NH). Found, %: C 48.81; H 3.29; Cl 7.58; N 9.03; S 20.49. $C_{19}H_{16}ClN_3O_3S_3$. Calculated, %: C 48.97; H 3.46; Cl 7.61; N 9.02; S 20.64.

1-Arylsulfanyl-1-chloromethyl-1,2,6,7,8,9-hexahydro-5*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo-[3,2-*a*]pyrimidin-5-ones IIIa–IIIc. A solution of 1 mmol of an appropriate compound **IIa–IIc** in 10 ml of chloroform at 15–20°C was saturated while stirring with dry hydrogen chloride for 30 min, then the mixture was stirred for 12 h, and afterwards chloroform was removed in a vacuum. The residue was treated with 10 ml of acetone, filtered off, and washed with ether on the filter.

1-(4-Tolylsulfanyl)-1-chloromethyl-1,2,6,7,8,9-hexahydro-5*H*-benzo-[4,5]thieno[3,2-*e*][1,3]thiazolo-[3,2-*a*]pyrimidin-5-one (IIIa). Yield 0.28 g (64%), mp 190–192°C (acetone). IR spectrum, ν, cm^{-1}: 1640 (C=O), 1570, 1530, 1440, 1370. ^1H NMR spectrum, δ, ppm: 1.74–1.86 m (4H, $2CH_2$), 2.31 s (3H, CH_3), 2.78–2.89 m (4H, $2CH_2$), 3.72 d (1H, CH, *J* 13.2 Hz), 4.01 d (1H, CH, *J* 13.5 Hz), 4.48 d (1H, CH, *J* 14.4 Hz), 4.68 d (1H, CH, *J* 12.6 Hz), 7.19–7.25 m ($4H_{arom}$). Found, %: C 55.13; H 4.34; Cl 8.09; N 6.33; S 22.07. $C_{20}H_{19}ClN_2OS_3$. Calculated, %: C 55.22; H 4.40; Cl 8.15; N 6.44; S 22.11.

1-Phenylsulfanyl-1-chloromethyl-1,2,6,7,8,9-hexahydro-5*H*-benzo[4,5]-thieno[3,2-*e*][1,3]thiazolo-[3,2-*a*]pyrimidin-5-one (IIIb). Yield 0.31 g (74%), mp 169–171°C (acetone). IR spectrum, ν, cm^{-1}: 1640 (C=O), 1570, 1535, 1470, 1435, 1370. ^1H NMR spectrum, δ, ppm: 1.71–1.87 m (4H, $2CH_2$), 2.78–2.90 m (4H, $2CH_2$), 3.74 d (1H, CH, *J* 13.5 Hz), 4.04 d (1H, CH, *J* 13.2 Hz), 4.53 d (1H, CH, *J* 12.6 Hz), 4.70 d (1H, CH, *J* 12.9 Hz), 7.32 d ($2H_{arom}$, *J* 6.9 Hz), 7.43 t ($2H_{arom}$, *J* 7.5 Hz), 7.54 t ($1H_{arom}$, *J* 7.5 Hz). Found, %: C 54.06; H 4.02; Cl 8.37; N 6.49; S 22.77. $C_{19}H_{17}ClN_2OS_3$. Calculated, %: C 54.21; H 4.07; Cl 8.42; N 6.65; S 22.85.

1-(4-Nitrophenylsulfanyl)-1-chloromethyl-1,2,6,7,8,9-hexahydro-5*H*-benzo[4,5]thieno[3,2-*e*]-[1,3]thiazolo[3,2-*a*]pyrimidin-5-one (IIIc). Yield 0.32 g (69%), mp 220–221°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 1650 (C=O), 1580, 1540, 1440, 1380, 1350. ^1H NMR spectrum, δ, ppm: 1.79 m (4H, $2CH_2$), 2.77–2.89 m (4H, $2CH_2$), 3.76 d (1H, CH, *J* 13.8 Hz), 4.10 d (1H, CH, *J* 15.0 Hz), 4.59 d (1H, CH, *J* 12.6 Hz), 4.65 d (1H, CH, *J* 12.9 Hz), 7.62 d ($2H_{arom}$, *J* 8.4 Hz), 8.24 d ($2H_{arom}$, *J* 9.3 Hz). Found, %: C 48.86; H 3.34; Cl 7.56; N 8.94; S 20.56. $C_{19}H_{16}ClN_3O_3S_3$. Calculated, %: C 48.97; H 3.46; Cl 7.61; N 9.02; S 20.64.

Reaction of compound I with ArSCl in nitroethane with lithium perchlorate additive. To a dispersion of 0.55 g (2 mmol) of compound **I** in 10 ml nitromethane at 15–20°C was added while stirring a solution of 0.22 g (2 mmol) of $LiClO_4$ in 10 ml of nitromethane, then a solution of 2.1 mmol of ArSCl in 10 ml of nitromethane. The mixture was stirred for 5–6 h and left standing for 12 h. The separated precipitate was filtered off and washed with water on the filter.

1-(4-Tolylsulfanylmethylidene)-1,2,6,7,8,9-hexahydro-4*H*-benzo[4,5]thieno[3,2-*e*]-[1,3]thiazolo-

[3,2-*a*]pyrimidin-5-one perchlorate (IVa). Yield 0.53 g (53%), mp 215–217°C. IR spectrum, ν, cm^{-1}: 1720 (C=O), 1650, 1580, 1540, 1510, 1420, 1380, 1100 (ClO_4^-). ^{1}H NMR spectrum, δ, ppm: 1.76 m (4H, $2CH_2$), 2.31 C (3H, CH_3), 2.72–2.86 m (4H, $2CH_2$), 4.42 d (2H, CH_2, *J* 2.7 Hz), 6.71 m (1H, CH), 7.23 d ($2H_{arom}$, *J* 8.1 Hz), 7.35 d ($2H_{arom}$, *J* 8.4 Hz). Found, %: C 48.03; H 3.71; Cl 7.09; N 5.54; S 19.06. $C_{20}H_{19}ClN_2O_5S_3$. Calculated, %: C 48.14; H 3.84; Cl 7.10; N 5.61; S 19.28.

1-Phenylsulfanylmethylidene-1,2,6,7,8,9-hexahydro-4*H*-benzo[4,5]thieno[3,2-*e*]-[1,3]thiazolo-[3,2-*a*]pyrimidin-5-one perchlorate (IVb). Yield 0.58 g (60%), mp 191–193°C. IR spectrum, ν, cm^{-1}: 1710 (C=O), 1660, 1580, 1540, 1480, 1430, 1370, 1120 (ClO_4^-). ^{1}H NMR spectrum, δ, ppm: 1.76 m (4H, $2CH_2$), 2.72–2.86 m (4H, $2CH_2$), 4.45 d (2H, CH_2, *J* 2.4 Hz), 6.74 t (1H, CH, *J* 2.1 Hz), 7.29–7.47 m ($5H_{arom}$). Found, %: C 47.01; H 3.67; Cl 7.23; N 5.67; S 19.77. $C_{19}H_{17}ClN_2O_5S_3$. Calculated, %: C 47.05; H 3.53; Cl 7.31; N 5.78; S 19.83.

1-Arylsulfanylmethylidene-1,2,6,7,8,9-hexahydro-5*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo-[3,2-*a*]pyrimidin-5-ones Va and Vb. To a solution of 1 mmol of compound **IVa** or **IVb** in 10 ml of DMSO was added 5 ml of 20% water solution of sodium acetate and was the mixture left standing for 2–3 h. The separated precipitate was filtered off, washed with water, and recrystallized from an appropriated solvent.

1-(4-Tolylsulfanylmethylidene)-1,2,6,7,8,9-hexahydro-5*H*-benzo[4,5]-thieno[3,2-*e*][1,3]thiazolo-[3,2-*a*]pyrimidin-5-one (Va). Yield 0.32 g (80%), mp 226–228°C (ethanol). IR spectrum, ν, cm^{-1}: 1640 (C=O), 1580, 1550, 1495, 1430, 1380. ^{1}H NMR spectrum, δ, ppm: 1.76 m (4H, $2CH_2$), 2.31 s (3H, CH_3), 2.72–2.86 m (4H, $2CH_2$), 4.42 d (2H, CH_2, *J* 2.1 Hz), 6.69 t (1H, CH, *J* 2.1 Hz), 7.23 d ($2H_{arom}$, *J* 8.1 Hz), 7.35 d ($2H_{arom}$, *J* 8.4 Hz). Found, %: C 60.14; H 4.47; N 7.01; S 24.09. $C_{20}H_{18}N_2OS_3$. Calculated, %: C 60.27; H 4.55; N 7.03; S 24.14.

1-Phenylsulfanylmethylidene-1,2,6,7,8,9-hexahydro-5*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo-[3,2-*a*]pyrimidin-5-one (Vb). Yield 0.31 g (81%), mp 206–208°C. IR spectrum, ν, cm^{-1}: 1645 (C=O), 1570, 1540, 1480, 1430, 1380, 1340. ^{1}H NMR spectrum, δ, ppm: 1.76 m (4H, $2CH_2$), 2.72–2.86 m (4H, $2CH_2$), 4.44 d (2H, CH_2, *J* 1.8 Hz), 6.73 t (1H, CH, *J* 2.1 Hz), 7.28–7.46 m ($5H_{arom}$). Found, %: C 59.26; H 4.10; N 7.17; S 25.00. $C_{19}H_{16}N_2OS_3$. Calculated, %: C 59.34; H 4.19; N 7.28; S 25.02.

1-(4-Nitrophenylsulfanylmethylidene)-1,2,6,7,8,9-hexahydro-5*H*-benzo[4,5]thieno[3,2-*e*]-[1,3]thiazolo-[3,2-*a*]pyrimidin-5-one (Vc). To a dispersion of 0.55 g (2 mmol) of compound **I** in 10 ml of nitromethane at 15–20°C was added while stirring a solution of 0.22 g (2 mmol) of $LiClO_4$ in 10 ml of nitromethane, then a solution of 0.40 g (2.1 mmol) of *p*-nitrophenylsulfenyl chloride in 10 ml of nitromethane. The mixture was stirred for 5–6 h and left standing for 12 h. The solvent was removed, and the residue was dissolved in DMSO and treated with 5 ml of 20% water solution of sodium acetate. The separated precipitate was filtered off, washed with water, and recrystallized from dimethyl sulfoxide. Yield 0.74 g (86%), mp 252–254°C (DMSO). IR spectrum, ν, cm^{-1}: 1645 (C=O), 1585, 1550, 1440, 1390, 1340. ^{1}H NMR spectrum, δ, ppm: 1.79 m (4H, $2CH_2$), 2.76–2.89 m (4H, $2CH_2$), 4.49 d (2H, CH_2, *J* 2.7 Hz), 6.80 t (1H, CH, *J* 2.4 Hz), 7.65 d ($2H_{arom}$, *J* 9.0 Hz), 8.20 d ($2H_{arom}$, *J* 9.3 Hz). Found, %: C 53.05; H 3.48; N 9.72; S 22.33. $C_{19}H_{15}N_3O_3S_3$. Calculated, %: C 53.13; H 3.52; N 9.78; S 22.40.

1-Arylsulfanylmethyl-6,7,8,9-tetrahydro-5*H*-benzo[4,5]thieno[3,2-*e*]-[1,3]thiazolo[3,2-*a*]-pyrimidin-5-ones VIa–VIc. *a*. To a solution of 1 mmol of an appropriate compound **Va–Vc** in 15 ml of DMSO was added a solution of 0.16 g (2 mmol) of sodium acetate in 2 ml of water, and the mixture was heated on a water bath at 70°C for 1 h, then 10 ml of water was added, the separated precipitate was filtered off, washed with water, and recrystallized.

b. A solution of 0.36 g (1 mmol) of compound **VII**, 0.28 g (2 mmol) of potassium hydrogen carbonate, and 1.5 mmol of the corresponding thiol in 20 ml of DMF was heated at stirring on a water bath at 60°C for 1 h. The mixture was cooled, 10 ml of water was added, the separated precipitate was filtered off, washed on the filter with ethanol and ether.

1-(4-Tolylsulfanylmethyl)-6,7,8,9-tetrahydro-5*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo[3,2-*a*]-pyrimidin-5-one (VIa). Yield 0.34 g (85%) (*a*), 0.23 g (58%) (*b*), mp 253–255°C (ethanol). IR spectrum, ν, cm^{-1}: 1620 (C=O), 1570, 1530, 1465, 1415, 1380, 1330. ^{1}H NMR spectrum, δ, ppm: 1.76–1.84 m (4H, $2CH_2$), 2.29 s (3H, CH_3), 2.79–2.95 m (4H, $2CH_2$), 4.49 s (2H, CH_2), 6.89 s (1H, CH), 7.16 d ($2H_{arom}$, *J* 7.8 Hz), 7.27 d ($2H_{arom}$, *J* 8.1 Hz). Found, %: C 60.16; H 4.43; N 7.04; S 24.11. $C_{20}H_{18}N_2OS_3$. Calculated, %: C 60.27; H 4.55; N 7.03; S 24.14.

1-Phenylsulfanylmethyl-6,7,8,9-tetrahydro-5*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo[3,2-*a*]-pyrimidin-5-one (VIb). Yield 0.35 g (91%) (*a*), 0.28 g (73%) (*b*), mp 234–236°C (ethanol). IR spectrum, ν, cm^{-1}: 1620 (C=O), 1570, 1530, 1465, 1415, 1380. ^1H NMR spectrum, δ, ppm: 1.75–1.88 m (4H, $2CH_2$), 2.79–2.97 m (4H, $2CH_2$), 4.56 s (2H, CH_2), 6.96 s (1H, CH), 7.28–7.43 m ($5H_{arom}$). Found, %: C 59.29; H 4.13; N 7.21; S 24.97. $C_{19}H_{16}N_2OS_3$. Calculated, %: C 59.34; H 4.19; N 7.28; S 25.02.

1-(4-Nitrophenylsulfanylmethyl)-6,7,8,9-tetrahydro-5*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo-[3,2-*a*]pyrimidin-5-one (VIc). Yield 0.38 g (88%) (*a*), mp 267–269°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 1620 (C=O), 1570, 1520, 1460, 1420, 1380, 1340. ^1H NMR spectrum, δ, ppm: 1.72–1.86 m (4H, $2CH_2$), 2.77–2.95 m (4H, $2CH_2$), 4.82 s (2H, CH_2), 7.24 m (1H, CH), 7.69 d ($2H_{arom}$, *J* 8.4 Hz), 8.16 d ($2H_{arom}$, *J* 8.7 Hz). Found, %: C 53.02; H 3.49; N 9.77; S 22.36. $C_{19}H_{15}N_3O_3S_3$. Calculated, %: C 53.13; H 3.52; N 9.78; S 22.40.

1-Bromomethylidene-6,7,8,9-tetrahydro-5*H*-benzo[4,5]thieno[3,2-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-5-one (VII). To a dispersion of 0.55 g (2 mmol) of compound **I** in 20 ml of chloroform at 15–20°C was added while stirring a solution of 0.24 ml (4 mmol) of bromine in 10 ml of chloroform. The mixture was stirred for 6–8 h and left standing for 12 h. The separated precipitate was filtered off, washed on the filter with ether, then treated with 15 ml of acetone and stirred for 1 h. The formed precipitate was filtered off and washed on the filter with acetone, then it was dissolved in 20 ml of DMSO, and 5 ml of 20% water solution of sodium acetate was added. The separated precipitate was filtered off, washed on the filter with ethanol and ether. Yield 0.43 g (61%), mp 207–209°C. IR spectrum, ν, cm^{-1}: 1640 (C=O), 1580, 1550. ^1H NMR spectrum, δ, ppm: 1.70–1.87 m (4H, $2CH_2$), 2.74–2.85 m (4H, $2CH_2$), 4.34 d (2H, CH_2, *J* 2.1 Hz), 6.95 t (1H, CH, *J* 2.1 Hz). Found, %: C 43.87; H 3.03; Br 22.42; N 7.76; S 17.97. $C_{13}H_{11}BrN_2OS_2$. Calculated, %: C 43.95; H 3.12; Br 22.49; N 7.89; S 18.05.

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