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Cyclofunctionalization of 6-Alkenylsulfanylpyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-ones with Arenesulfenyl Chlorides

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Abstract—Reactions of 6-allylsulfanylpyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one with arenesulfenyl chlorides in chloroform gave products of addition of the latter at the exocyclic double bond, while analogous reactions in acetic acid in the presence of $LiClO_4$ were accompanied by intramolecular electrophilic cyclization involving the N^7 atom. 6-Cinnamylsulfanylpyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one reacted with arenesulfenyl chlorides in acetic acid in the absence of electrolyte to produce fused pyrazolo[4′,3′:5,6]pyrimido[2,1-*b*][1,3]thiazine derivatives. Introduction of a bulky phenyl group into position *1* of the pyrazolo[3,4-*d*]pyrimidine system reduces the yield of the corresponding intramolecular cyclization product at N^7 as a result of concurrent formation of acyclic addition product.

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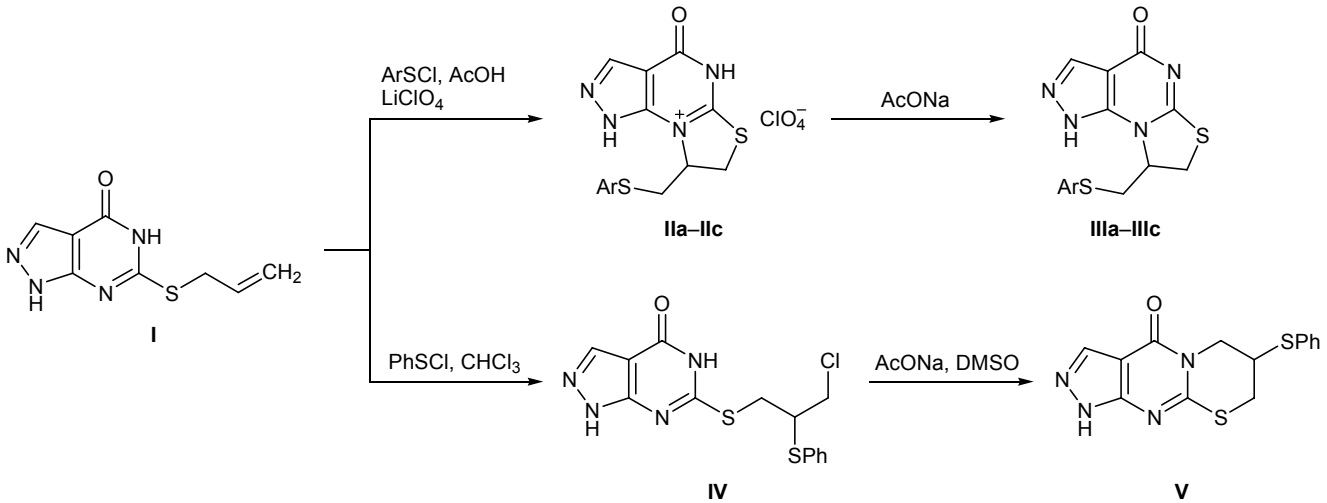
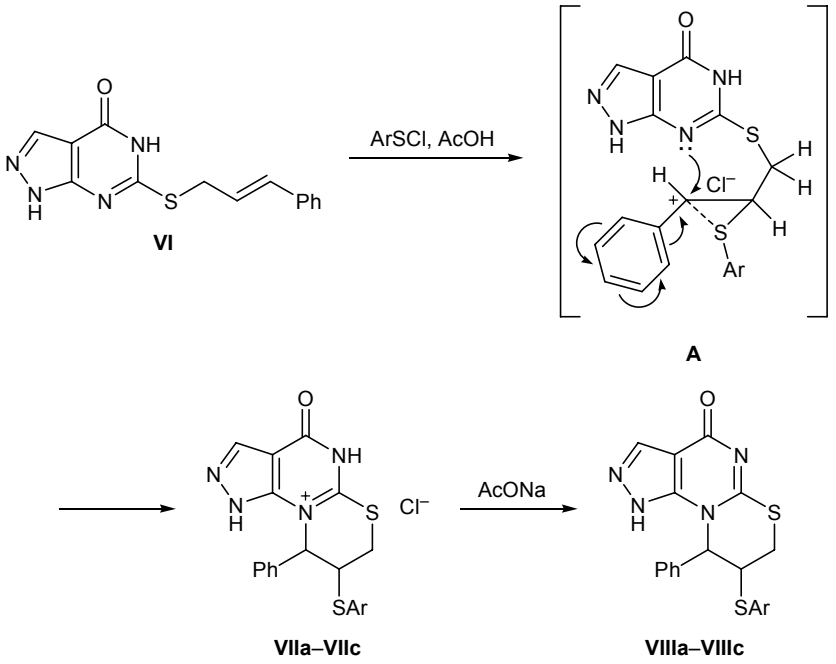
Intramolecular electrophilic cyclization of unsaturated functionally substituted compounds by the action of sulfenyl chlorides provides a convenient synthetic route to heterocyclic systems [1, 2]. Sulfenyl chlorides are known to react with olefins in weakly ionizing medium to form weakly polar intermediates (sulfurane or contact ion pair), and the final products were mainly Ad_E adducts. Addition of salts, e.g., lithium perchlorate, to the reaction mixture favors formation of more polar intermediates, such as solvent-separated ion pairs and solvated ions, which are responsible for non-addition reaction pathways, including intramolecular electrophilic cyclization [3]. Reactions of arenesulfenyl chlorides with alkenylsulfanyl-substituted quinazolinones and thieno[2,3-*d*]pyrimidinones afforded mainly angular intramolecular electrophilic cyclization products, whereas 2-alkenylsulfanylpyrimidin-4(3*H*)-ones under analogous conditions gave rise to mixtures of isomeric cyclization products at the N^1 and N^3 atoms of the pyrimidine ring [4, 5].

Scheme 1.



Ar = 4-$O_2NC_6H_4$ (**a**), Ph (**b**), 4-MeC_6H_4 (**c**).

Scheme 2.



Ar = 4-$O_2NC_6H_4$ (**a**), Ph (**b**), 4-MeC_6H_4 (**c**).

In continuation of these studies, in the present work we examined reactions of arenesulfenyl chlorides (4-$O_2NC_6H_4SCl$, PhSCl, and 4-MeC_6H_4SCl) with 6-alkenylsulfanylpyrazolo[3,4-*d*]pyrimidin-4(5*H*)-ones **I**, **VI**, and **IX**. The goal of this work was to elucidate how the structure of the initial compounds (specifically, the presence of a substituent in the pyrazole ring and the nature of the exocyclic alkenyl group) is related to chemo- and regioselectivity of their reactions with arenesulfenyl chlorides.

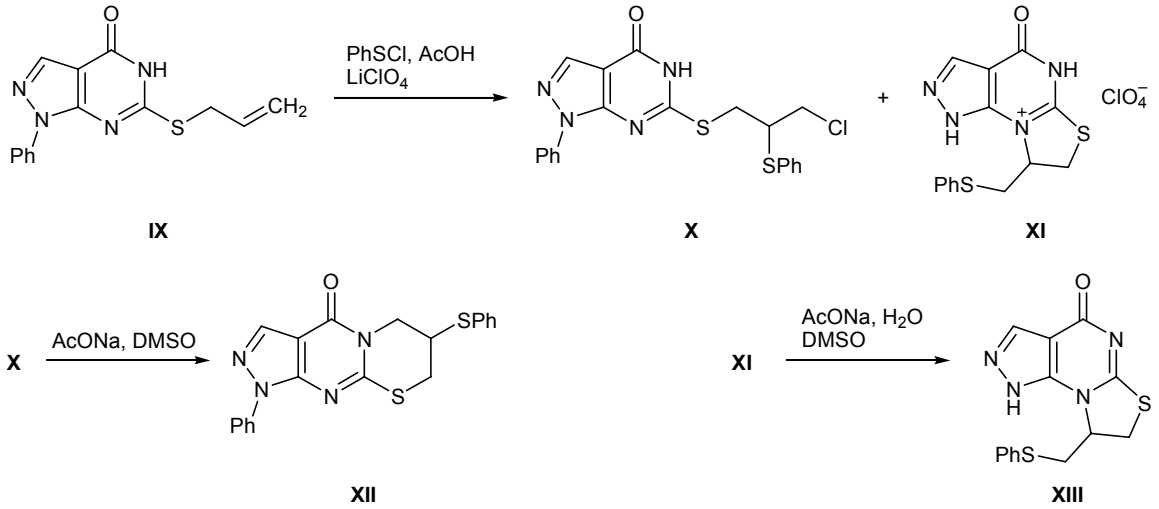
The reactions of 6-allylsulfanylpyrazolo[3,4-*d*]-pyrimidin-4(5*H*)-one (**I**) with arenesulfenyl chlorides in acetic acid in the presence of $LiClO_4$ gave the corresponding cyclization products, 8-arylsylfanylmethyl-4-oxo-4,5,7,8-tetrahydro-1*H*-pyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-9-ium perchlorates **IIa**–**IIc**, in 62–84% yield, depending on the substituent in the *para* position of benzene ring in the initial arenesulfenyl chloride (Scheme 1). Perchlorates **IIa**–**IIc** were converted into the corresponding bases **IIIa**–**IIIc** by the action of sodium acetate. As followed from the ^{1}H NMR and IR data, closure of dihydrothiazole ring involves the N^7 atom in the pyrazolopyrimidine system. The 8-H signal in the ^{1}H NMR spectra of salts **IIa**–**IIc** and bases **IIIa**–**IIIc** appeared as a multiplet in the region δ 5.33–5.43 and 5.09–5.30 ppm, respectively. The IR spectra of **IIIa**–**IIIc** contained an absorption band at 1635–1630 cm^{-1} due to stretching vibrations of the carbonyl group [6, 7].

Compound **I** reacted with benzenesulfenyl chloride in chloroform to give acyclic addition product, pyrazolopyrimidinone **IV**. The regioselectivity of the addition of PhSCl at the allyl fragment of **I** was confirmed by subsequent intramolecular cyclization of compound **IV** by the action of sodium acetate in dimethyl sulfoxide, which afforded linearly fused pyrazolopyrimidothiazine **V**. In this case, the cyclization involved the N^5 atom of the pyrazolopyrimidine system, as clearly followed from the presence of carbonyl absorption band at 1715 cm^{-1} in the IR spectrum of **V** [6, 8].

Unlike allylsulfanyl derivative **I**, in the reactions of 6-cinnamylsulfanylpyrazolo[3,4-*d*]pyrimidinone **VI** with arenesulfenyl chlorides in acetic acid intramolecular cyclization products **VIIa**–**VIIc** were formed in the absence of $LiClO_4$ (Scheme 2). The presence of a phenyl group at the terminal carbon atom of the allylic fragment of **VI** stabilizes carbocation intermediate **A**, so that internal nucleophilic center of the substrate (N^7 atom) successfully competes with external nucleophile (chloride ion) generated from arenesulfenyl chloride.

The structure of pyrazolopyrimidothiazines **VIIa**–**VIIc** and **VIIIa**–**VIIIc** follows from their ^{1}H NMR and IR spectra. In the ^{1}H NMR spectra of **VIIa**–**VIIc**,

Scheme 3.



methylene protons in the thiazine ring resonated in the region δ 3.15–3.42 ppm, and the 8-H and 9-H signals were located at δ 4.60–5.11 and 5.97–6.17 ppm; the corresponding signals in the spectra of **VIIIa**–**VIIIc** were observed at δ 3.05–3.30, 4.53–5.02, and 5.92–6.09 ppm, respectively. Stretching vibrations of the carbonyl group in salts **VIIa**–**VIIc** and bases **VIIIa**–**VIIIc** give rise to IR absorption bands at 1730 and 1630 cm^{-1}, respectively [6, 7].

We then examined the behavior of 6-allylsulfanyl-1-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (**IX**) in analogous reactions with arenesulfenyl chlorides. The presence of a bulky phenyl group on the N^1 atom of the pyrazolopyrimidine system should hinder intramolecular cyclization at the N^7 atom. In fact, compound **IX** reacted with benzenesulfenyl chloride in acetic acid in the presence of lithium perchlorate to give a mixture of two products at a ratio of 2:1 (according to the ^{1}H NMR data). The major product was compound **X** resulting from addition of PhSCl at the exocyclic double bond, and the minor one was angular intramolecular cyclization product **XI** (Scheme 3). We failed to isolate perchlorate **XI** as individual substance, and it was converted into free base **XIII** by the action of sodium acetate.

The structure of compounds **X** and **XIII** was determined on the basis of the ^{1}H and IR data. Adduct **X** displayed in the ^{1}H NMR spectrum signals in the region δ 3.53–4.01 ppm from protons in the two methylene groups and one CH proton (PhSC**H**). The ^{1}H NMR spectrum of **XIII** contained signals at δ 2.92–3.08 (2H, CH_2), 3.27–3.31 (1H, CH), 3.80–3.86 (1H, CH), and 4.76–4.83 ppm (1H, CH). In the IR spectra of **X** and **XIII**, the carbonyl stretching vibration band was observed at 1690 and 1650 cm^{-1}, respectively.

The structure of compound **X** was also confirmed by its transformation into pyrazolopyrimidothiazine **XII** by the action of sodium acetate in DMSO. Judging by the position of the carbonyl absorption band in the IR spectrum (1700 cm^{-1}), compound **XII** is a linearly fused heterocyclic system [6, 8].

Thus the chemoselectivity of reactions of 6-allylsulfanylpyrazolo[3,4-*d*]pyrimidinone **I** with arenesulfenyl chlorides strongly depends on the conditions. The reactions in chloroform give the corresponding acyclic addition products, while intramolecular electrophilic cyclization at the N^7 atom occurs in acetic acid in the presence of $LiClO_4$. Closure of thiazine ring in the reaction of cinnamylsulfanyl-substituted pyrazolopyrimidinone **VI** in the reaction with ArSCl in acetic acid does not require the presence of electrolyte. Introduction of a bulky phenyl substituent into position *1* of the pyrazolopyrimidine system leads to reduced yield of the corresponding intramolecular cyclization product at N^7 because of concurrent formation of the acyclic addition product. Appreciable effect of $LiClO_4$ on the reaction direction should also be noted.

EXPERIMENTAL

The IR spectra were recorded in KBr on a UR-20 spectrometer. The ^{1}H NMR spectra were measured from solutions in DMSO-d_6 on Varian VXR-300 instrument (300 MHz) using TMS as internal reference.

Perchlorates IIa–IIc (*general procedure***).** A solution of 0.22 g (2 mmol) of lithium perchlorate in 10 ml

of acetic acid was added at 15–20°C under stirring to a suspension of 0.42 g (2 mmol) of compound **I** in 10 ml of acetic acid, a solution of 2.1 mmol of arenesulfenyl chloride in 10 ml of acetic acid was added dropwise, and the mixture was stirred for 5–6 h and left to stand for 12 h. The precipitate was filtered off and washed on a filter with petroleum ether.

8-(4-Nitrophenylsulfanylmethyl-4-oxo-4,5,7,8-tetrahydro-1*H*-pyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]-pyrimidin-9-ium perchlorate (IIa). Yield 0.57 g (62%), mp 294–296°C. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1600, 1560, 1520, 1430, 1380, 1340, 1260, 1170, 1100 (ClO_4^-). ^1H NMR spectrum, δ, ppm: 3.69–3.87 m (3H, CH_2, CH), 4.01–4.08 m (1H, CH), 5.40 m (1H, CH), 7.68 d (2H, H_{arom}, J = 8.4 Hz), 8.07 d (2H, H_{arom}, J = 8.4 Hz), 8.62 s (1H, 3-H), 14.32 br.s (1H, NH). Found, %: C 36.34; H 2.58; Cl 7.63; N 15.59; S 13.91. $C_{14}H_{12}ClN_5O_7S_2$. Calculated, %: C 36.41; H 2.62; Cl 7.68; N 15.61; S 13.88.

4-Oxo-8-(phenylsulfanylmethyl)-4,5,7,8-tetrahydro-1*H*-pyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-9-ium perchlorate (IIb). Yield 0.53 g (64%), mp 123–125°C. IR spectrum, ν, cm^{-1}: 1720 (C=O), 1610, 1560, 1440, 1385, 1340, 1265, 1120, 1090 (ClO_4^-). ^1H NMR spectrum, δ, ppm: 3.56–3.61 m (1H, CH), 3.73–3.80 m (3H, CH_2, CH), 5.33–5.43 m (1H, CH), 7.17–7.23 m (3H, H_{arom}), 7.33–7.04 m (2H, H_{arom}), 8.59 s (3-H), 14.18 br.s (1H, NH). Found, %: C 40.30; H 3.11; Cl 8.44; N 13.42; S 15.36. $C_{14}H_{13}ClN_4O_5S_2$. Calculated, %: C 40.34; H 3.14; Cl 8.50; N 13.44; S 15.38.

8-(4-Methylphenylsulfanylmethyl)-4-oxo-4,5,7,8-tetrahydro-1*H*-pyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]-pyrimidin-9-ium perchlorate (IIc). Yield 0.72 g (84%), mp 183–185°C. IR spectrum, ν, cm^{-1}: 1720 (C=O), 1600, 1560, 1440, 1380, 1260, 1110 (ClO_4^-). ^1H NMR spectrum, δ, ppm: 2.23 s (3H, CH_3), 3.48–3.54 m (1H, CH), 3.75–3.82 m (2H, CH_2), 4.03–4.10 m (1H, CH), 5.35–5.40 m (1H, CH), 6.97 d (2H, H_{arom}, J = 8.1 Hz), 7.23 d (2H, H_{arom}, J = 8.1 Hz), 8.62 s (1H, 3-H), 14.22 br.s (1H, NH). Found, %: C 41.78; H 3.50; Cl 8.21; N 12.96; S 14.90. $C_{15}H_{15}ClN_4O_5S_2$. Calculated, %: C 41.81; H 3.51; Cl 8.23; N 13.00; S 14.88.

Compounds IIIa–IIIc (*general procedure*). Perchlorate **IIa**–**IIc**, 1 mmol, was dissolved in 10 ml of DMSO, 5 ml of 20% aqueous sodium acetate was added, and the precipitate was filtered off and washed with water.

8-(4-Nitrophenylsulfanylmethyl)-7,8-dihydro-1*H*-pyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-4-one (IIIa). Yield 0.34 g (95%), mp 284–286°C. IR spectrum, ν, cm^{-1}: 1635 (C=O), 1585, 1555, 1510, 1435, 1380, 1340, 1260, 1230, 1165, 1095. ^1H NMR spectrum, δ, ppm: 3.52–3.56 m (1H, CH), 3.69–3.81 (2H, CH_2), 3.89–3.96 m (1H, CH), 5.22–5.30 m (1H, CH), 7.67 d (2H, H_{arom}, J = 9.0 Hz), 8.06 d (2H, H_{arom}, J = 9.0 Hz), 8.38 s (1H, 3-H), 13.75 s (1H, NH). Found, %: C 46.51; H 3.02; N 19.34; S 17.77. $C_{14}H_{11}N_5O_3S_2$. Calculated, %: C 46.53; H 3.07; N 19.38; S 17.74.

8-(Phenylsulfanylmethyl)-7,8-dihydro-1*H*-pyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-4-one (IIIb). Yield 0.28 g (90%), mp 245–247°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 1590, 1555, 1435, 1385, 1260, 1170, 1080. ^1H NMR spectrum, δ, ppm: 3.51–3.64 m (3H, CH_2, CH), 3.87–3.93 m (1H, CH), 5.12–5.23 m (1H, CH), 7.15–7.28 m (3H, H_{arom}), 7.41 d (2H, H_{arom}, J = 7.5 Hz), 8.35 s (1H, 3-H), 13.69 s (1H, NH). Found, %: C 53.11; H 3.80; N 17.65; S 20.29. $C_{14}H_{12}N_4OS_2$. Calculated, %: C 53.15; H 3.82; N 17.71; S 20.27.

8-(4-Methylphenylsulfanylmethyl)-7,8-dihydro-1*H*-pyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-4-one (IIIc). Yield 0.25 g (75%), mp 288–290°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 1590, 1555, 1435, 1385, 1265, 1180. ^1H NMR spectrum, δ, ppm: 2.25 s (3H, CH_3), 3.51–3.58 m (3H, CH, CH_2), 3.85–3.92 m (1H, CH), 5.09–5.18 m (1H, CH), 7.05 d (2H, H_{arom}, J = 8.4 Hz), 7.29 d (2H, H_{arom}, J = 8.1 Hz), 8.35 s (1H, 3-H), 13.67 s (1H, NH). Found, %: C 54.47; H 4.25; N 16.91; S 19.44. $C_{15}H_{14}N_4OS_2$. Calculated, %: C 54.52; H 4.27; N 16.96; S 19.41.

6-[3-Chloro-2-(phenylsulfanyl)propylsulfanyl]-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (IV). A solution of 2.1 mmol of benzenesulfanyl chloride in 10 ml of chloroform was added drpwise under stirring at 15–20°C to a suspension of 0.42 g (2 mmol) of compound **I** in 10 ml of chloroform. The mixture was stirred for 5–6 h and left to stand for 12 h. The precipitate was filtered off and washed on a filter with chloroform and petroleum ether. Yield 0.66 g (93%), mp 149–151°C. IR spectrum, ν, cm^{-1}: 1710 (C=O), 1590, 1400, 1245, 1160. ^1H NMR spectrum, δ, ppm: 3.54–3.70 m (2H, CH_2), 3.88–4.02 m (3H, CH, CH_2), 7.32–7.48 m (3H, H_{arom}), 7.54–7.62 m (2H, H_{arom}), 8.14 s (1H, 3-H), 12.39 s (1H, NH). Found, %: C 47.62; H 3.67; Cl 10.07; N 15.85; S 18.18. $C_{14}H_{13}ClN_4OS_2$. Calculated, %: C 47.65; H 3.71; Cl 10.05; N 15.88; S 18.17.

7-Phenylsulfanyl-7,8-dihydro-6*H*-pyrazolo-[3′,4′:4,5]pyrimido[2,1-*b*][1,3]thiazin-4(1*H*)-one (V). A mixture of 0.35 g (1 mmol) of compound **IV** and 1.1 mmol of anhydrous sodium acetate in 10 ml of DMSO was heated for 1 h at 60°C. Water was then added dropwise until a colorless solid separated. The precipitate was filtered off and washed with water. Yield 0.21 g (68%), mp 105–107°C. IR spectrum, ν, cm^{-1}: 1715 (C=O), 1595, 1575, 1490, 1230, 1140, 1100. ^{1}H NMR spectrum, δ, ppm: 3.25–3.44 m (1H, CH), 3.58–3.63 m (1H, CH), 4.04–4.37 m (3H, CH, CH_2), 7.33–7.51 m (5H. H_{arom}), 8.03 s (1H, 3-H_{arom}), 13.51 s (1H, NH). Found, %: C 53.11; H 3.80; N 17.69; S 20.29. $C_{14}H_{12}N_4OS_2$. Calculated, %: C 53.15; H 3.82; N 17.71; S 20.27.

Chlorides VIIa–VIIc (*general procedure*). A solution of 2.1 mmol of the corresponding arenesulfenyl chloride in 10 ml of acetic acid was added dropwise under stirring at 15–20°C to a suspension of 0.57 g (2 mmol) of compound **VI** in 20 ml of acetic acid. The mixture was stirred for 5–6 h and was left to stand for 12 h, and the precipitate was filtered off and washed on a filter with petroleum ether.

8-(4-Nitrophenylsulfanyl)-4-oxo-9-phenyl-1,4,5,7,8,9-hexahydropyrazolo[4′,3′:5,6]pyrimido-[2,1-*b*][1,3]thiazin-10-ium chloride (VIIa). Yield 0.75 g (79%), mp 290–292°C. IR spectrum, ν, cm^{-1}: 1740 (C=O), 1590, 1520, 1340, 1250, 1180. ^{1}H NMR spectrum, δ, ppm: 3.29–3.42 m (2H, CH_2), 5.09–5.11 m (1H, CH), 6.17 m (1H, CH), 7.40–7.46 m (5H, H_{arom}), 7.83 d (2H, H_{arom}, J = 8.7 Hz), 8.23 d (2H, H_{arom}, J = 9.0 Hz), 8.61 s (1H, 3-H), 14.12 br.s (1H, NH). Found, %: C 50.67; H 3.37; Cl 7.44; N 14.75; S 13.55. $C_{20}H_{16}ClN_5O_3S_2$. Calculated, %: C 50.68; H 3.40; Cl 7.48; N 14.78; S 13.53.

4-Oxo-9-phenyl-8-phenylsulfanyl-1,4,5,7,8,9-hexahydropyrazolo[4′,3′:5,6]pyrimido[2,1-*b*][1,3]-thiazin-10-ium chloride (VIIb). Yield 0.82 g (96%), mp 271–274°C. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1630, 1590, 1540, 1420, 1390, 1300, 1250, 1180, 1070. ^{1}H NMR spectrum, δ, ppm: 3.15–3.28 m (2H, CH_2), 4.65–4.71 m (1H, CH), 5.97–6.01 d (1H, CH), 7.21–7.28 m (2H, H_{arom}), 7.30–7.52 m (6H, H_{arom}), 7.55–7.63 m (2H, H_{arom}), 8.47 s (1H, 3-H), 13.83 s (1H, NH). Found, %: C 55.97; H 3.94; Cl 8.22; N 13.01; S 14.98. $C_{20}H_{17}ClN_4OS_2$. Calculated, %: C 56.00; H 3.99; Cl 8.26; N 13.06; S 14.95.

8-(4-Methylphenylsulfanyl)-4-oxo-9-phenyl-1,4,5,7,8,9-hexahydropyrazolo[4′,3′:5,6]pyrimido-[2,1-*b*][1,3]thiazin-10-ium chloride (VIIc). Yield 0.83 g (94%), mp 258–260°C. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1630, 1600, 1540, 1390, 1250, 1180. ^{1}H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3), 3.23 d (2H, CH_2, J = 2.4 Hz), 4.60–4.63 m (1H, CH), 5.97 d (1H, CH, J = 2.1 Hz), 7.20–7.49 m (9H, H_{arom}), 8.60 s (1H, 3-H), 14.07 br.s (1H, NH). Found, %: C 56.91; H 4.27; Cl 7.96; N 12.62; S 14.51. $C_{21}H_{19}ClN_4OS_2$. Calculated, %: C 56.94; H 4.32; Cl 8.00; N 12.65; S 14.48.

Compounds VIIIa–VIIIc (*general procedure*). Compound **VIIa–VIIc**, 1 mmol, was dissolved in 10 ml of DMSO, 5 ml of 20% aqueous sodium acetate was added, and the precipitate was filtered off and washed with water.

8-(4-Nitrophenylsulfanyl)-9-phenyl-8,9-dihydro-7*H*-pyrazolo[4′,3′:5,6]pyrimido[2,1-*b*][1,3]thiazin-4(1*H*)-one (VIIIa). Yield 0.34 g (78%), mp 310–312°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 1600, 1540, 1430, 1390, 1340, 1255, 1185, 1100. ^{1}H NMR spectrum, δ, ppm: 3.21–3.30 m (2H, CH_2), 5.02 m (1H, CH), 6.09 m (1H, CH), 7.31–7.49 m (5H, H_{arom}), 7.82 d (2H, H_{arom}, J = 8.7 Hz), 8.23 d (2H, H_{arom}, J = 9.0 Hz), 8.40 s (1H, 3-H), 13.64 s (1H, NH). Found, %: C 54.86; H 3.42; N 16.00; S 14.64. $C_{20}H_{15}N_5O_3S_2$. Calculated, %: C 54.91; H 3.46; N 16.01; S 14.66.

9-Phenyl-8-phenylsulfanyl-8,9-dihydro-7*H*-pyrazolo[4′,3′:5,6]pyrimido[2,1-*b*][1,3]thiazin-4(1*H*)-one (VIIIb). Yield 0.30 g (76%), mp 317–318°C. IR spectrum, ν, cm^{-1}: 1650 (C=O), 1625, 1595, 1555, 1430, 1395, 1260, 1180. ^{1}H NMR spectrum, δ, ppm: 3.07–3.25 m (2H, CH_2), 4.59–4.66 m (1H, CH); 5.94 m (1H, CH), 7.17 d (2H. H_{arom}, J = 7.2 Hz), 7.31–7.47 m (6H, H_{arom}), 7.58 d (2H, H_{arom}, J = 6 Hz), 8.38 s (1H, 3-H), 13.61 s (1H, NH). Found, %: C 54.86; H 3.42; N 16.00; S 14.64. Calculated, %: C 54.91; H 3.46; N 16.01; S 14.66.

8-(4-Methylphenylsulfanyl)-9-phenyl-8,9-dihydro-7*H*-pyrazolo[4′,3′:5,6]pyrimido[2,1-*b*][1,3]thiazin-4(1*H*)-one (VIIIc). Yield 0.30 g (74%), mp 306–308°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 1610, 1540, 1425, 1390, 1255, 1185. ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, CH_3), 3.05–3.23 m (2H, CH_2), 4.53–4.55 m (1H, CH), 5.92 d (1H, CH), 7.15–7.24 m (4H, H_{arom}), 7.32–7.49 m (5H, H_{arom}), 8.40 s (1H, 3-H), 13.58 br.s (1H, NH). Found, %: C 62.01; H 4.42; N 13.73; S 15.75. $C_{21}H_{18}N_4OS_2$. Calculated, %: C 62.05; H 4.46; N 13.78; S 15.77.

Compounds X and XIII. A solution of 0.22 g (2 mmol) of lithium perchlorate in 10 ml of acetic acid

was added under stirring at 15–20°C to a suspension of 0.57 g (2 mmol) of compound **IX** in 10 ml of acetic acid, a solution of 2.1 mmol of benzenesulfenyl chloride in 10 ml of acetic acid was then added dropwise, and the mixture was stirred for 5–6 h and left to stand for 12 h. The precipitate of compound **X** was filtered off and washed on a filter with acetic acid and petroleum ether. The filtrate was evaporated, and the residue was washed with water and ground in acetone. The crystalline product (compound **XI** with an impurity of **X**) was filtered off and dissolved in 5 ml of DMSO, 3 ml of 20% aqueous sodium acetate was added, and the precipitate (compound **XIII**) was filtered off and washed with water.

6-[3-Chloro-2-(phenylsulfanyl)propylsulfanyl]-1-phenyl-1*H*-pyrazolo[3,4-*d*]pyrimidin-4(5*H*)-one (X). Yield 0.36 g (42%), mp 180–182°C. IR spectrum, ν, cm^{-1}: 1690 (C=O), 1570, 1400, 1220, 990, 960. ^{1}H NMR spectrum, δ, ppm: 3.53–4.01 m (5H, $2CH_2$, CH), 7.30–7.53 m (8H, H_{arom}), 8.06 d (2H, H_{arom}, J = 8.4 Hz), 8.26 s (1H, 3-H), 12. 80 s (1H, NH). Found, %: C 55.98; H 3.95; Cl 8.24; N 13.03; S 14.96. $C_{20}H_{17}ClN_4OS_2$. Calculated, %: C 56.00; H 3.99; Cl 8.26; N 13.06; S 14.95.

1-Phenyl-8-(phenylsulfanylmethyl)-7,8-dihydropyrazolo[4,3-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-4(1*H*)-one (XIII). Yield 0.15 g (19%), mp 225–227°C. IR spectrum, ν, cm^{-1}: 1650 (C=O), 1580, 1560, 1470, 1410, 1240. ^{1}H NMR spectrum, δ, ppm: 2.92–3.08 m (2H, CH_2), 3.27–3.31 m (1H, CH), 3.80–3.86 m (1H, CH), 4.76–4.83 m (1H, CH), 7.07–7.24 m (5H, H_{arom}), 7.52–7.73 m (5H, H_{arom}), 8.05 s (1H, 3-H). Found, %: C 61.17; H 4.09; N 14.25; S 16.33. $C_{20}H_{16}N_4OS_2$. Calculated, %: C 61.20; H 4.11; N 14.27; S 16.34.

1-Phenyl-7-phenylsulfanyl-7,8-dihydro-6*H*-pyrazolo[3′,4′:4,5]pyrimido[2,1-*b*][1,3]thiazin-4(1*H*)-one (XII). Compound **X**, 0.43 g (1 mmol), was dissolved in 5 ml of DMSO, 1.1 mmol of dry sodium acetate was added, and the mixture was heated for 1 h at 60°C. The mixture was diluted with 10 ml of water, and the precipitate was filtered off, washed with water and alcohol, and recrystallized from ethanol. Yield 0.33 g (85%), mp 173–174°C (from ethanol). IR spectrum, ν, cm^{-1}: 1700 (C=O), 1595, 1560–1540, 1510, 1470, 1440, 1400, 1380, 1310, 1210, 1190, 1110, 1090. ^{1}H NMR spectrum, δ, ppm: 3.29–3.36 m (1H, CH), 3.62–3.67 m (1H, CH), 4.00–4.15 m (1H, CH), 4.19–4.29 m (1H, CH), 4.35–4.40 m (1H, CH), 7.33–7.61 m (8H, H_{arom}), 8.00–8.02 m (2H, H_{arom}), 8.30 s (1H, 3-H). Found, %: C 61.18; H 4.07; N 14.26; S 16.32. $C_{20}H_{16}N_4OS_2$. Calculated, %: C 61.20; H 4.11; N 14.27; S 16.34.

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