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STUDIES ON FUNCTIONALLY-SUBSTITUTED AZINES. 8.* SYNTHESIS AND TRANSFORMATIONS OF 1-ARYLSULFONYLAMIDO-4-METHOXY-6-METHYLPYRIMIDINES

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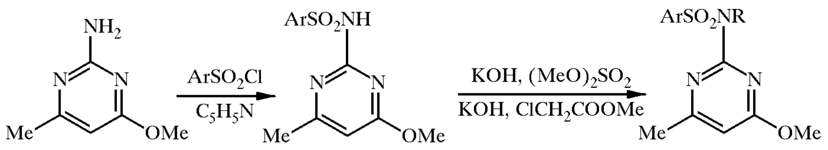
The action of arylsulfonyl chlorides on 2-amino-4-methoxy-6-methylpyrimidine in pyridine gave 2-arylsulfonylamido-4-methoxy-6-methylpyrimidines, which were alkylated at the amide fragment, while the action of hydrazine hydrate led to nucleophilic replacement of the methoxy group. The resultant hydrazinopyrimidines were converted into azidopyrimidines and N-pyrimidinyldithiocarbazinates. Potassium salt of 2-p-toluenesulfonylamido-4-methoxy-6-methylpyrimidine dithiocarbazinate reacted with dimethyl sulfate to give the S-methyl derivative, while the reaction with chloroacetonitrile gave thiazolidinylaminopyrimidine. The chlorination using N-chlorosuccinimide yielded only 5-chloropyrimidines.

Keywords: azidopyrimidines, 2-arylsulfonylamidopyrimidines, dithiocarbazinates, S-methyl derivatives, and S-cyanomethyl derivatives.

Functionally-substituted pyrimidines, which have found use in the production of drugs and pesticides, may serve as synthones in the preparation of new physiologically active compounds. Definite interest in this regard is found in 1-arylsulfonylamido-4-methoxy-6-methylpyrimidines **2a-d**, whose transformations are described in the present work.

Pyrimidines **2a-d** were synthesized by the reaction of 2-amino-4-methoxy-6-methylpyrimidine (**1**) with arylsulfonyl chlorides in pyridine and are NH-acids, which form salts with alkali. These salts readily undergo N-alkylation.



2a Ar = Ph; **2b** Ar = *p*-MeC_6H_4; **2c** Ar = *p*-ClC_6H_4; **2d** Ar = *o*-ClC_6H_4; **3a** Ar = Ph, R = Me;
3b Ar = *p*-MeC_6H_4, R = Me; **3c** Ar = *o*-ClC_6H_4, R = Me; **3d** Ar = Ph, R = CH_2COOMe;
3e Ar = *p*-MeC_6H_4, R = CH_2COOMe; **3f** Ar = *o*-ClC_6H_4, R = CH_2COOMe

* Communication 7, see ref. [1].

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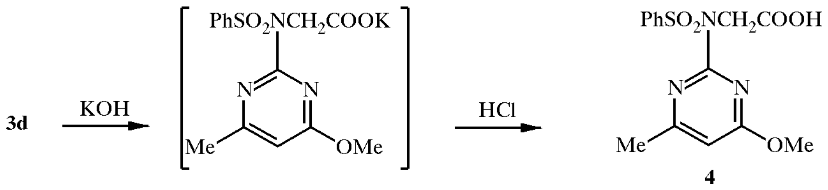
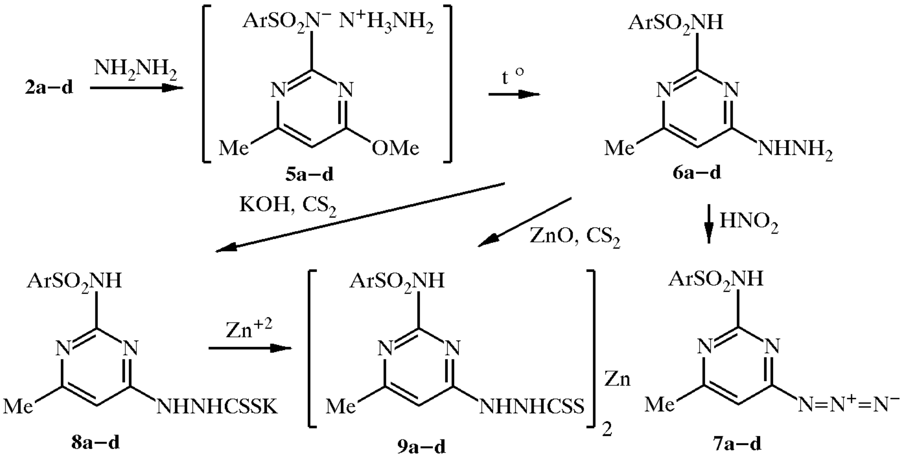
Pyrimidines **2a-d** and **3a-f** are extremely stable in aqueous or ethanolic alkali even upon heating. This stability should be attributed to steric factors due to the bulky arylsulfonyl group, which hinders dissociation of the S–N bond. Similar N-alkyl-N-acetylamidopyrimidines (*sym*-triazines) undergo extremely facile deacetylation even in dilute aqueous alkali at room temperature to give N-alkyl derivatives [2].

The action of alkali on **3d** leads, as expected, to hydrolysis of the ester group and formation of a water-soluble salt, which is converted to the free acid upon acidification:



Hydrazine hydrate is sometimes used as a deacetylating agent for amides and imides [3-5] but the action of hydrazine on compounds **2a-d** gives hydrazinium salts **5a-d**, which are converted upon heating into products of the nucleophilic replacement of the methoxy group by hydrazine. Treatment of the resultant 4-hydrazinopyrimidines **6a-d** with nitrous acid leads to the corresponding azidopyrimidines **7a-d**, while treatment of **6a-d** with a mixture of CS_2 and KOH or ZnO leads to potassium N-pyrimidinyldithiocarbazinates **8a-d** or their zinc analogs **9a-d**.



5–9 a Ar = Ph, **b** Ar = *p*-MeC_6H_4, **c** Ar = *p*-ClC_6H_4, **d** Ar = *o*-ClC_6H_4

The action of dimethyl sulfate on potassium salt **8b** gives S-methyldithiocarbazinate **10**, while the action of chloroacetonitrile leads to the product of the intramolecular heterocyclization, namely, thiazolidinylaminopyrimidine **12** instead of S-cyanomethyl derivative **11**.

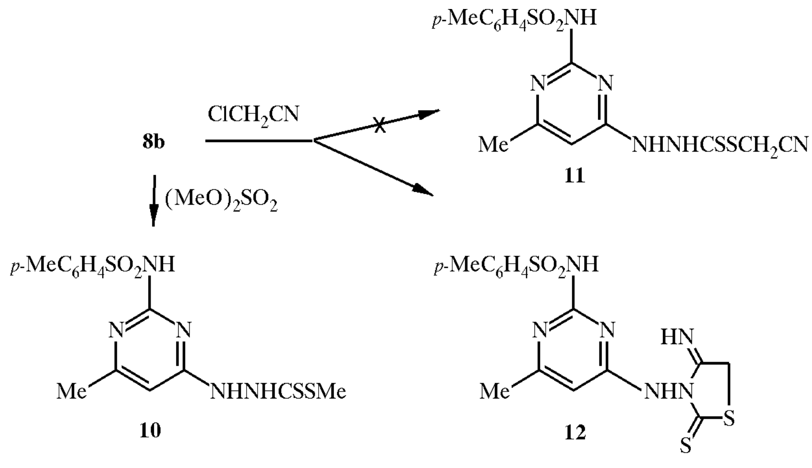


TABLE 1. Characteristics of Compounds **3a-f, 15a,** and **15b**

Compound	Ar	R	R′	Empirical formula	Found, % / Calculated, % C	H	N	S	Cl	¹H NMR spectrum, δ, ppm (CDCl₃)	mp, °C	Yield, %
3a	C_6H_5	CH_3	H	$C_{13}H_{15}N_3SO_3$	53.17 / 53.23	5.22 / 5.15	14.48 / 14.32	11.05 / 10.93	—	2.20 (3H, s, CH_3); 3.62 (3H, s, NCH_3); 3.62 (3H, s, OCH_3); 6.03 (1H, s, CH); 7.25-8.06 (5H, m, C_6H_5)	114-116	85
3b	*p*-$CH_3C_6H_4$	CH_3	H	$C_{14}H_{17}N_3SO_3$	54.66 / 54.70	5.70 / 5.57	13.54 / 13.67	10.36 / 10.43	—	2.20 (3H, s, CH_3); 2.36 (3H, s, CH_3); 3.56 (3H, s, NCH_3); 3.62 (3H, s, OCH_3); 6.10 (1H, s, CH); 7.23-8.23 (4H, m, C_6H_4)	89-91	68
3c	*o*-$C1C_6H_4$	CH_3	H	$C_{13}H_{14}N_3SO_3Cl$	47.65 / 47.63	4.43 / 4.30	12.62 / 12.82	10.08 / 9.78	10.75 / 10.82	2.41 (3H, s, CH_3); 3.60 (6H, s, NCH_3 and OCH_3); 5.90 (1H, s, CH); 7.22-8.53 (4H, m, C_6H_4)	133-135	53
3d	C_6H_5	CH_2COOCH_3	H	$C_{15}H_{17}N_3SO_5$	51.26 / 51.27	5.04 / 4.88	12.25 / 11.96	9.07 / 9.13	—	2.2 (3H, s, CH_3); 3.6 (3H, s, OCH_3); 3.73 (3H, s, OCH_3); 4.96 (2H, s, NCH_2); 6.06 (1H, s, CH); 7.20-8.33 (5H, m, C_6H_5)	99-101	80
3e	*p*-$CH_3C_6H_4$	CH_2COOCH_3	H	$C_{16}H_{19}N_3SO_5$	52.73 / 52.59	5.27 / 5.24	11.35 / 11.50	9.03 / 8.77	—	2.2 (3H, s, CH_3); 2.38 (3H, s, CH_3); 3.66 (3H, s, OCH_3); 3.72 (3H, s, OCH_3); 4.93 (2H, s, NCH_2); 6.06 (1H, s, CH); 7.1-8.2 (4H, m, C_6H_4)	128-130	75
3f	*o*-$C1C_6H_4$	CH_2COOCH_3	H	$C_{15}H_{16}N_3SO_5Cl$	46.61 / 46.69	4.17 / 4.18	11.13 / 10.89	8.28 / 8.31	9.42 / 9.19	2.23 (3H, s, CH_3); 3.6 (3H, s, OCH_3); 3.7 (3H, s, OCH_3); 4.93 (2H, s, NCH_2); 5.93 (1H, s, CH); 7.33-8.51 (4H, m, C_6H_4)	141-143	68
15a	*p*-$CH_3C_6H_4$	CH_3	Cl	$C_{14}H_{16}N_3SO_3Cl$	49.15 / 49.19	4.77 / 4.72	12.17 / 12.29	9.62 / 9.38	10.55 / 10.37	2.36 (6H, s, $2CH_3$); 3.60 (3H, s, NCH_3); 3.83 (3H, s, OCH_3); 7.16-8.22 (4H, m, C_6H_4)	134-135	93
15b	*p*-$CH_3C_6H_4$	CH_2COOCH_3	Cl	$C_{16}H_{18}N_3SO_5Cl$	48.11 / 48.06	4.47 / 4.54	10.63 / 10.51	8.21 / 8.02	8.79 / 8.87	2.33 (3H, s, CH_3); 2.4 (3H, s, CH_3); 3.76 (6H, s, $2OCH_3$); 4.93 (2H, s, NCH_2); 7.23-8.20 (4H, m, C_6H_4)	152-154	82

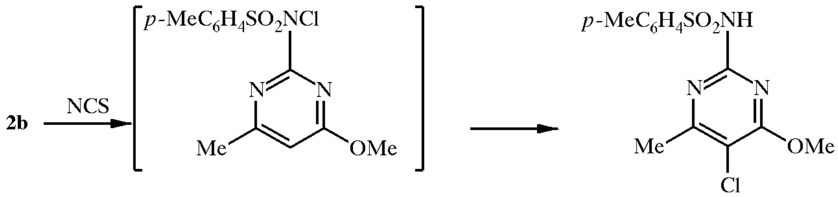
TABLE 2. Characteristics of Compounds **6a-d** and **7a-d**

Com-pound	Ar	R	Empirical formula	Found, % / Calculated, % C	H	N	S	Cl	IR spectrum, cm^{-1}	^1H NMR spectrum, δ, ppm Solvent	mp, °C	Yield, %
6a	C_6H_5	$NHNH_2$	$C_{11}H_{13}N_5SO_2$	47.27 / 47.30	4.83 / 4.69	25.01 / 25.07	11.35 / 11.48	—	1530, 1600 (C=C, C=N); 3200 (NH); 3520, 3600 (NH_2)	—	234-236	98
6b	*p*-$CH_3C_6H_4$	$NHNH_2$	$C_{12}H_{15}N_5SO_2$	49.24 / 49.13	5.16 / 5.15	23.74 / 23.87	11.13 / 10.93	—	1520, 1600 (C=C, C=N); 3150 (NH); 3500, 3570 (NH_2)	—	265-267	99
6c	*p*-ClC_6H_4	$NHNH_2$	$C_{11}H_{12}N_5SO_2Cl$	42.14 / 42.11	3.78 / 3.85	22.51 / 22.32	10.52 / 10.22	11.18 / 11.30	1530, 1605 (C=C, C=N); 3180 (NH); 3530, 3600 (NH_2)	—	242-244	97
6d	*o*-ClC_6H_4	$NHNH_2$	$C_{11}H_{12}N_5SO_2Cl$	41.94 / 42.11	3.83 / 3.85	22.44 / 22.32	10.41 / 10.22	11.26 / 11.30	1530, 1600 (C=C, C=N); 3180 NH); 3520, 3605 (NH_2)	—	255-257	83
7a	C_6H_5	N_3	$C_{11}H_{10}N_6SO_2$	45.53 / 45.51	3.65 / 3.47	29.17 / 28.95	11.13 / 11.04	—	1520, 1600 (C=C, C=N); 2140 ($–N=N^+=N^-$); 3100 (NH)	2.23 (3H, s, CH_3); 6.20 (1H, s, CH); 7.32-8.1 (6H, m, C_6H_5 and NH). CD_3OD	155-157	88
7b	*p*-$CH_3C_6H_4$	N_3	$C_{12}H_{12}N_6SO_2$	47.12 / 47.36	3.82 / 3.97	27.68 / 27.62	10.23 / 10.54	—	1510, 1600 (C=C, C=N); 2140 ($–N=N^+=N^-$); 3080 (NH)	2.33 (3H, s, CH_3); 2.36 (3H, s, CH_3); 6.2 (1H, s, CH); 7.0 (1H, br. s, NH); 7.22-8.13 (4H, m, C_6H_4). $CDCl_3$.	126-128	71
7c	*p*-ClC_6H_4	N_3	$C_{11}H_9N_6SO_2Cl$	40.73 / 40.68	2.71 / 2.79	25.84 / 25.88	9.65 / 9.87	11.12 / 10.92	1520, 1605 (C=C, C=N); 2150 ($–N=N^+=N^-$); 3100 (NH)	2.50 (3H, s, CH_3); 5.96 (1H, s, CH); 7.23-8.1 (5H, m, C_6H_4 and NH). $CDCl_3$.	164-166	62
7d	*o*-ClC_6H_4	N_3	$C_{11}H_9N_6SO_2Cl$	40.82 / 40.68	2.74 / 2.79	26.03 / 25.88	9.85 / 9.87	10.83 / 10.92	1520, 1600 C=C, C=N); 2130 ($–N=N^+=N^-$); 3110 (NH)	2.30 (3H, s, CH_3); 6.0 (1H, s, CH); 7.26-8.5 (5H, m, C_6H_4 and NH). $CDCl_3$.	153-155	93

TABLE 3. Characteristics of Compounds **8a-d** and **9a-d**

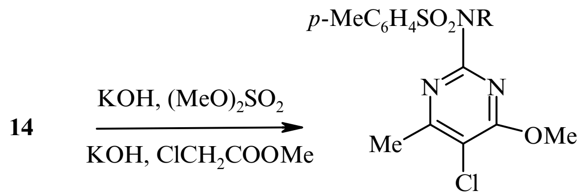
Compound	Ar	Cation	Empirical formula	Found, % / Calculated, % C	H	N	S	Cl	M^+
8a	C_6H_5	K	$C_{12}H_{12}N_5S_3O_2K$	36.57 / 36.63	3.15 / 3.07	17.84 / 17.80	24.28 / 24.45	—	394
8b	*p*-$CH_3C_6H_4$	K	$C_{13}H_{14}N_5S_3O_2K$	38.25 / 38.32	3.49 / 3.46	17.30 / 17.19	23.53 / 23.61	—	408
8c	*p*-ClC_6H_4	K	$C_{12}H_{11}N_5S_3O_2ClK$	33.54 / 33.69	2.78 / 2.59	16.43 / 16.37	22.61 / 22.48	8.43 / 8.29	428
8d	*o*-ClC_6H_4	K	$C_{12}H_{11}N_5S_3O_2ClK$	33.59 / 33.68	2.64 / 2.59	16.27 / 16.37	22.62 / 22.48	8.34 / 8.29	428
9a	C_6H_5	Zn	$C_{24}H_{24}N_{10}S_6O_4Zn$	37.36 / 37.23	3.30 / 3.12	18.35 / 18.09	24.67 / 24.85	—	774
9b	*p*-$CH_3C_6H_4$	Zn	$C_{26}H_{28}N_{10}S_6O_4Zn$	38.86 / 38.92	3.48 / 3.52	17.55 / 17.46	23.82 / 23.98	—	802
9c	*p*-ClC_6H_4	Zn	$C_{24}H_{22}N_{10}S_6O_4Cl_2Zn$	34.22 / 34.19	2.57 / 2.63	16.68 / 16.61	22.75 / 22.82	8.34 / 8.41	843
9d	*o*-ClC_6H_4	Zn	$C_{24}H_{22}N_{10}S_6O_4Cl_2Zn$	34.15 / 34.19	2.68 / 2.63	16.54 / 16.61	22.94 / 22.82	8.35 / 8.41	843

Since several halopyrimidines such as Bromacil, Terbacil, and Kastriks are highly active pesticides [6, 7], definite interest was found in the preparation of the chlorination products of pyrimidines **2b, 3b,** and **3e**. The use of N-chlorosuccinimide for this purpose, as expected, provides high regioselectivity of the chlorination and formation of only 5-chloro derivatives **14** [8]:



13 **14**

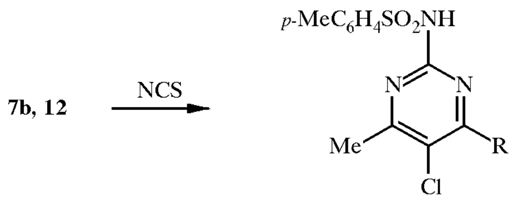
The hypothesis that the chlorination of **2b** proceeds through intermediate chlorosulfonylamidopyrimidine **13** is based on the failure of compounds **3b**,**e**, the formation of chloramides **13** from which is impossible, to undergo chlorination under these conditions. Thus, chloro derivatives **15a**,**b** are obtained from N-alkylated derivatives **3a**,**e** through an alternative pathway, namely, N-alkylation of compound **14**:



15a,**b**

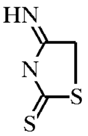
15 a R = Me, **b** R = CH_2COOMe

Despite possessing labile groups sensitive to oxidizing agents, **7b** and **12** are also smoothly chlorinated under similar conditions to give 5-chloro derivatives **16a**,**b**.



16a,b

16a R = $N{=}N^{+}{=}N^{-}$, **b** R =



EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Bruker AC-300 spectrometer with TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer in vaseline oil. The mass spectra were taken on an MKh 1321A spectrometer. The purity of the products was established by thin-layer chromatography on Silufol UV-254 plates using 1:1 hexane–acetone, 1:2 hexane–acetone*, or 5:1 2-butanone–hexane*[2] as the solvent system with development by 2% $AgNO_3$ + 0.4% BFS + 4% citric acid.

2-Benzenesulfonylamido-4-methoxy-4-methylpyrimidine (2a). A solution of pyrimidine **1** (1.4 g, 10 mmol) and benzenesulfonic acid (1.8 g, 10 mmol) in pyridine (5 ml) was maintained for 48 h at 20°C. Then, water (10 ml) was added and the precipitate formed was filtered off, washed several times with water, and recrystallized from

2-propanol to give pyrimidine **2a** (1.55 g, 55%); mp 172-174°C, R_f* 0.43. IR spectrum: 1510, 1620 (C=C, C=N), 3100 cm^{-1} (NH). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm: 2.20 (3H, s, CH_3); 3.67 (3H, s, OCH_3); 6.12 (1H, s, CH); 7.53-7.93 (5H, m, C_6H_5); 12.20 (1H, br. s, NH). Found, %: C 51.75; H 5.0; N 14.88; S 11.63. $C_{12}H_{13}N_3O_3S$. Calculated, %: C 51.60; H 4.69; N 15.04; S 11.48.

4-Methoxy-6-methyl-2-*p*-toluenesulfonylamidopyrimidine (2b) was obtained analogously to **2a** from pyrimidine **1** (1.4 g, 10 mmol) and *p*-toluenesulfonyl chloride (1.9 g, 10 mmol) in pyridine (5 ml). Yield of **2b** 1.5 g (51%); mp 173-175°C, R_f 0.45. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 (3H, s, 6-CH_3); 2.36 (3H, s, CH_3); 3.60 (3H, s, OCH_3); 6.06 (1H, s, CH); 7.16-8.16 (4H, m, C_6H_4); 8.72 (1H, s, NH). Found, %: C 53.16; H 5.24; N 14.27; S 11.04. $C_{13}H_{15}N_3O_3S$. Calculated, %: C 53.23; H 5.15; N 14.32; S 10.93.

2-(4-Chlorobenzenesulfonylamido)-4-methoxy-6-methylpyrimidine (2c) was obtained analogously to **2a** from (1.4 g, 10 mmol) pyrimidine **1** and 4-chlorobenzenesulfonyl chloride (2.1 g, 10 mmol) in pyridine (5 ml). Yield of **2c** 1.35 g (43%); mp 158-160°C, R_f 0.52. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 (3H, s, CH_3); 3.71 (3H, s, OCH_3); 5.93 (1H, s, CH); 7.16-8.10 (5H, m, C_6H_4 and NH). Found, %: C 45.88; H 3.82; N 13.12; S 9.96; Cl 11.43. $C_{12}H_{12}N_3SO_3Cl$. Calculated, %: C 45.94; H 3.85; N 13.39; S 10.22; Cl 11.30.

2-(2-Chlorobenzenesulfonylamido)-4-methoxy-6-methylpyrimidine (2d) has been obtained according to Gesing et al. [9], but was synthesized in our laboratory analogously to **2a**. Yield of **2d** 1.5 g (49%); mp 208-210°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.46 (3H, s, CH_3); 3.03 (3H, s, OCH_3); 5.93 (1H, s, CH); 7.23 (1H, s, NH); 7.25-8.50 (4H, m, C_6H_4). Found, %: C 45.75; H 3.90; N 13.08; S 10.0; Cl 11.17. $C_{12}H_{12}SO_3N_3Cl$. Calculated, %: C 45.94; H 3.85; N 13.39; S 10.22; Cl 11.30.

5-Chloro-4-methoxy-6-methyl-2-*p*-toluenesulfonylamidopyrimidine (14). A mixture of pyrimidine **2b** (2.9 g, 10 mmol) and N-chlorosuccinimide (1.3 g, 10 mmol) in chloroform (10 ml) was heated for 3-4 h at 55-60°C. The solvent was evaporated. The residue was washed with warm water and recrystallized from ethanol to give chloropyrimidine **14** (3.2 g, 97%); mp 162-163°C, R_f 0.5. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.33 (3H, s, CH_3); 2.36 (3H, s, CH_3); 3.80 (3H, s, OCH_3); 7.06-8.0 (4H, m, C_6H_4); 8.66 (1H, br. s, NH). Found, %: C 47.57; H 4.35; N 12.67; S 9.84; Cl 11.04. $C_{13}H_{14}N_3SO_3Cl$. Calculated, %: C 47.63; H 4.30; N 12.82; S 9.78; Cl 10.82.

Methylation of Compounds 2a,b,d and 14. A sample of dimethyl sulfate (1.5 g, 12 mmol) was added dropwise to a suspension of potassium salt of pyrimidine **2** (or **14**) in acetone (10-15 ml) obtained from KOH (0.7 g, 10 mmol) and pyrimidine (10 mmol). The temperature of the suspension was maintained at 20°C. Then, the mixture obtained was heated at 50-55°C for 3-4 h. After evaporation of the solvent, the residue was recrystallized from ethanol (**3a,c,** and **15a**) or 2:1 ethanol–water (compound **3b**) (Table 1).

N-Carbomethoxymethylation of Compounds 2a,b,d and 14. To a solution of potassium salt of pyrimidine **2** (or **14**) (10 mmol) in DMF (10 ml) methyl ester of chloroacetic acid (1.3 g, 12 mmol) and NaI (1.8 g, 12 mmol) were added. The mixture was stirred for 5-6 h at 55-60°C. After cooling, water (20 ml) was added. The precipitate was filtered and recrystallized from ethanol (compounds **3d-f**, **15b**) (Table 1).

2-(N-Carboxymethyl)benzenesulfonylamido-4-methoxy-6-methylpyrimidine (4). A mixture of pyrimidine **3d** (3.5 g, 10 mmol) and NaOH (0.8 g, 20 mmol) in water (10 ml) was heated with stirring at 65-70°C for 3 h, cooled, and neutralized by adding acetic acid. The precipitate was filtered off and washed twice with water to give pyrimidine **4** (3 g, 89%); mp 178-180°C, R_f*[2] 0.53. IR spectrum, cm^{-1}: 1510, 1600 (C=C, C=N), 1710 (C=O), 3400 (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 (3H, s, CH_3); 3.61 (2H, s, OCH_3); 4.82 (2H, s, CH_2); 6.20 (1H, s, CH); 7.43-8.26 (5H, m, C_6H_5); 11.60 (1H, br. s, OH). Found, %: C 49.9; H 4.52; N 12.08; S 9.75. $C_{14}H_{15}N_3O_3S$. Calculated, %: C 49.84; H 4.48; N 12.46; S 9.50.

2-Arylsulfonylamido-4-hydrazino-6-methylpyrimidines (6a-d). A mixture of pyrimidine **2** (10 mmol) and concentrated hydrazine hydrate (1 ml) in dry dioxane (15 ml) was heated with stirring at 100-110°C for 6-7 h. After cooling, the precipitate was filtered off and twice washed with water (Table 2).

2-Arylsulfonylamido-4-azido-6-methylpyrimidines (7a-d). A sample of pyrimidine **6** (10 mmol) was dissolved in a solution of conc. hydrochloric acid (1 ml) in water (10 ml). Then, a solution of $NaNO_2$ (1 g, 15 mmol) in water (5 ml) was added dropwise with stirring at 0-5°C. Stirring was continued for an additional 4-5 h at 20°C. The crystalline precipitate was filtered off and washed with cold water (Table 2).

Potassium N-(2-Arylsulfonylamido-6-methyl-4-pyrimidinyl)dithiocarbazinates (8a-d) and Zinc N-(2-Arylsulfonylamido-6-methyl-4-pyrimidinyl)dithiocarbazinates (9a-d). A sample of CS_2 (0.9 g, 20 mmol) was added with stirring to a solution of pyrimidine **6** (10 mmol) and KOH (0.7 g, 10 mmol) or ZnO (0.8 g, 10 mmol) in ethanol (10 ml) at 65-70°C. Stirring was continued under these conditions for 6-8 h. The reaction mixture was cooled and filtered. The product was washed with ethanol (Table 3).

Methylation of Dithiocarbazinate 8b to 10. A sample of dimethyl sulfate (1.5 g, 12 mmol) was added dropwise to a solution of potassium dithiocarbazinate **8b** (4 g, 10 mmol) in DMF (7 ml). The mixture obtained was heated at 65-70°C for 4-5 h. After cooling, water (20 ml) was added. The crystalline precipitate was filtered off and washed with water to give compound **10** (3.5 g, 91%); mp 85°C (dec). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.31 (3H, s, CH_3); 2.42 (3H, s, CH_3); 2.60 (3H, s, SCH_3); 6.42 (1H, s, CH); 7.23-7.83 (4H, m, C_6H_4). Found, %: C 43.77; H 4.50; N 18.27; S 24.87. $C_{14}H_{17}N_5O_2S_3$. Calculated, %: C 43.85; H 4.47; N 18.26; S 25.08.

4-N-(4-Imino-2-thioxo-1,3-thiazolidin-3-yl)-6-methyl-2-*p*-toluenesulfonylamidopyrimidine (12). A sample of chloroacetonitrile (0.9 g, 12 mmol) was added dropwise with stirring to a solution of potassium dithiocarbazinate **8b** (4 g, 10 mmol) in water (5 ml) at 0-5°C. After 30 min, stirring was continued at 20°C for 4-5 h. The crystalline precipitate was filtered off and washed with cold water to give pyrimidine **12** (4 g, 99%); mp 161-162°C. IR spectrum, cm^{-1}: 1520, 1600 (C=C, C=N), 3200 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.36 (3H, s, CH_3); 2.40 (3H, s, CH_3); 3.56 (2H, s, CH_2); 4.22 (2H, s, 2NH); 6.70 (1H, s, CH); 7.33-8.0 (4H, m, C_6H_4). Found, %: C 44.34; H 4.15; N 20.76; S 23.58. $C_{15}H_{16}N_6O_2S_3$. Calculated, %: C 44.10; H 3.95; N 20.57; S 23.55.

Chlorination of 7b and 12. Products **16a** and **16b** were obtained analogously to **14** from **7b** or **12** (10 mmol) and N-chlorosuccinimide (1.3 g, 10 mmol) in chloroform (10 ml).

Chloropyrimidine 16a was obtained in 96% yield (2.9 g); mp 191-193°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.4 (3H, s, CH_3); 2.43 (3H, s, CH_3); 7.2-8.16 (4H, m, C_6H_4). Found, %: C 42.51; H 3.29; N 24.67; S 9.61; Cl 10.35. $C_{12}H_{11}N_6SO_2Cl$. Calculated, %: C 42.54; H 3.27; N 24.81; S 9.46; Cl 10.46.

Chloropyrimidine 16b was obtained in 56% yield (2.5 g); mp 176-178°C, R_f*[2] 0.68. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.06 (3H, s, CH_3); 2.16 (3H, s, CH_3); 4.26 (2H, s, CH_2); 7.40 (3H, s, 3NH); 7.03-8.60 (4H, m, C_6H_4). Found, %: C 40.57; H 3.33; N 19.14; S 21.57; Cl 7.93. $C_{15}H_{15}N_6S_3O_2Cl$. Calculated, %: C 40.67; H 3.41; N 18.97; S 21.71; Cl 8.00.

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