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HETEROCYCLIZATION OF 1,3-BUTADIENETHIOLATES

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Condensation of derivatives of ethoxymethylenecyanoacetic acid with cyanothioacetamide with base catalysis gave butadienethiolates and mercaptopyridines. On interaction with alkyl halides, butadienethiolates are cyclized into alkylthiopyridines, but their reactions with phenacyl bromides give substituted thiazoles.

Keywords: 1,3-butadienethiolates, nicotinamide, pyrido[2,3-*d*]pyrimidine, derivatives of ethoxymethylenecyanoacetic acid, thiazole, X-ray crystallography.

We have developed a synthesis of substituted 1,3-butadienethiolates by nucleophilic vinyl substitution (S_NVin) and we have shown their use in the preparation of substituted heterocycles – pyridines and thienopyridines [1]. The practicability of this synthetic route is based on the ability of alkyl functionalized butadienes to undergo intramolecular cyclization with participation of the nitrile group.

In this work we have explored new synthetic possibilities for 1,3-butadienethiolates, prepared by the interaction of derivatives of ethoxymethylenecyanoacetic acid **1a-e** with cyanothioacetamide (**2**) in the presence of bases. It was found that the products of the S_NVin reaction (**3**), which could not be isolated, formed the 1,3-butadienethiolates **4a-c** in the presence of N-methylmorpholine. Note that stabilization enaminocarbonyl compounds **4a-c** resulted from direct polar donor-acceptor conjugation of the functional groups [2, 3].

Increasing the basicity of the medium in this reaction facilitated intramolecular cyclization of compounds **3** into the mercaptopyridines **5a,b**. Compounds **4** reacted readily with the alkyl halides **6a-d** to give the alkylthiopyridines **7a-d** (Tables 1, 2, experimental). Introduction of phenacyl bromide in this reaction gave the thiazole **8** as a result of the Hantzsch synthesis.

Compound **8** occurs as a mixture of *E*- and *Z*-isomers according to the spectroscopic data. In the IR spectrum there are 3 nitrile stretching bands at 2170, 2188, and 2232 cm^{-1}. In the ^1H NMR spectrum a doubling of the signals for the protons of the ethoxycarbonyl and methyne protons was observed (Experimental). Since the butadienethiolate **4a** exists as one of the π-diastereomers [1], it may be proposed that it is possible that rotation about the $C_{(3)}$–$C_{(4)}$ of the butadiene occurs during the formation of the thiazole **8** to give an equal mixture of two π-diastereomers (Scheme 1).

The pyridylthiones **5** reacted with amyl iodide to give the sulfides **9**, the study of the chemical properties of which showed they are capable of undergoing a variety of chemical transformations. In particular they were brominated with bromine in benzene to give the derivative **10.** On refluxing in acetic anhydride 2-methylpyrido[2,3-*d*]pyrimidine **11** was obtained, and on reaction with triethyl orthoformate (see [4]) 2-unsubstituted pyrido[2,3-*d*]pyrimidines **12a,b** were obtained.

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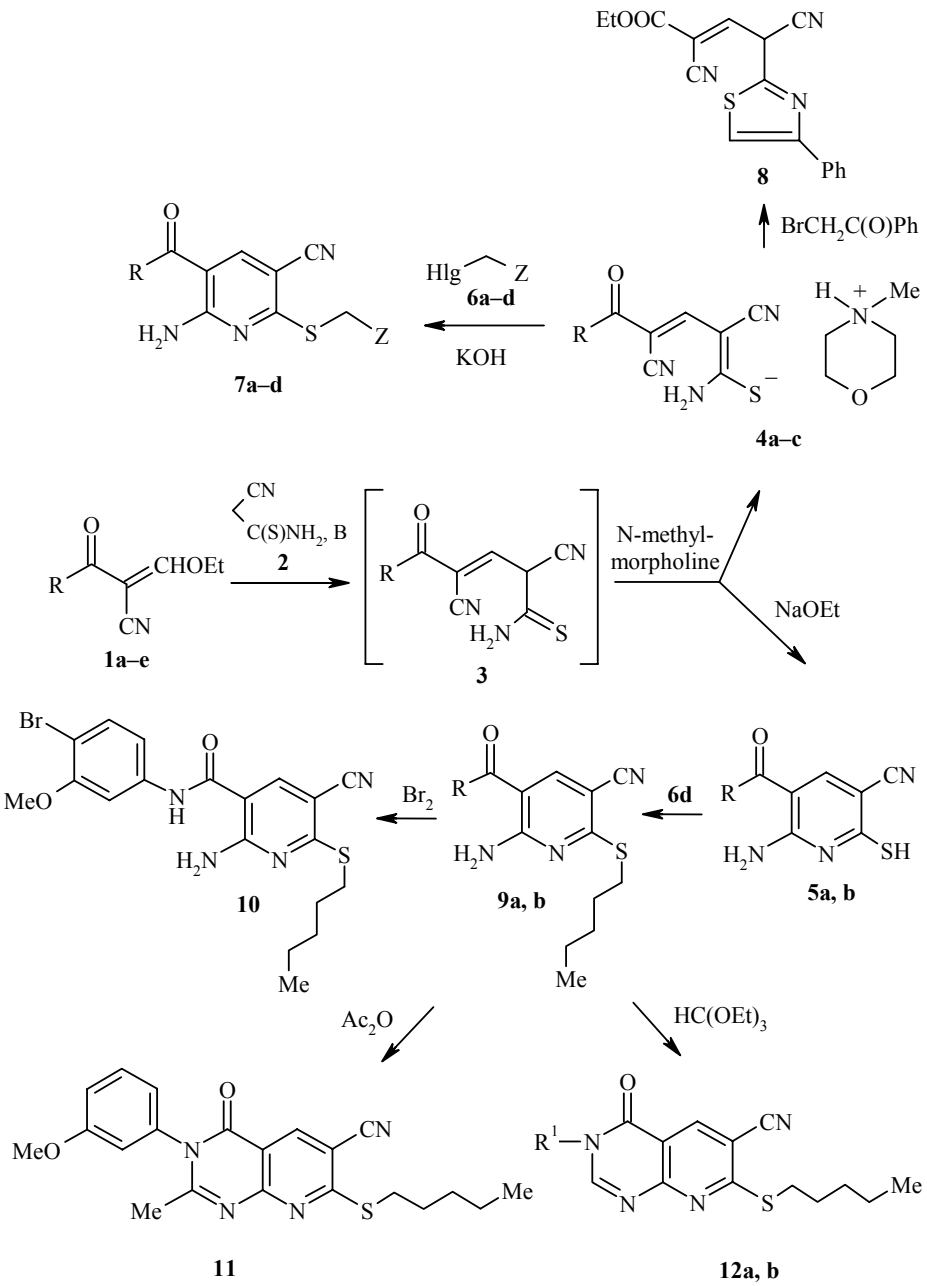
Scheme 1



1a R = EtO, **b** R = α-naphthylamino, **c** R = *o*-MeC_6H_4NH, **d** R = *o*-$MeOC_6H_4NH$, **e** R = *m*-$MeOC_6H_4NH$; **4a** R = EtO, **b** R = α-naphthylamino, **c** R = *o*-MeC_6H_4NH; **5, 9 a** R = *o*-$MeOC_6H_4NH$, **b** R = *m*-$MeOC_6H_4NH$; **6 a–c** Hal = Br, **a** Z = C(O)Ph, **b** Z = $CH{=}CH_2$, **c** Z = CH_2Me; **d** Hal = I, Z = $(CH_2)_3Me$; **7 a,b** R = EtO, **a** Z = C(O)Ph, **b** Z = $(CH_2)_3Me$, **c** R = α-naphthylamino, Z = $CH{=}CH_2$, **d** R = *o*-MeC_6H_4NH, Z = CH_2Me; **12 a** R^1 = *o*-$MeOC_6H_4$, **b** R^1 = *m*-$MeOC_6H_4$; B = N-methylmorpholine, NaOEt

To establish unambiguously the regioselectivity of the cyclization of olefin **3**, and also by alkylation of the thioles formed, an X-ray crystallographic investigation of 6-amino-3-cyano-5-(*o*-methoxyphenylcarbamoyl)-2-pentylthiopyridine (**9a**) was carried out. The general shape of the molecule is shown in Fig. 1, and the basic bond lengths and angles are shown in Table 3. Atoms $N_{(2)}$ and $N_{(4)}$ have planar trigonal arrangement of the

TABLE 1. Characteristics of Compounds **4b,c, 5a,b, 7a-d**, and **9a,b**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
4b	$C_{22}H_{23}N_5O_2S$	62.34 / 62.69	5.65 / 5.50	16.88 / 16.62	328-330	73
4c	$C_{19}H_{23}N_5O_2S$	58.98 / 59.20	6.12 / 6.01	18.09 / 18.17	178-180	82
5a	$C_{14}H_{12}N_4O_2S$	55.51 / 55.98	3.89 / 4.03	18.42 / 18.66	305-307	90
5b	$C_{14}H_{12}N_4O_2S$	55.69 / 55.98	4.25 / 4.03	18.91 / 18.66	172-174	68
7a	$C_{17}H_{15}N_3O_3S$	59.99 / 59.81	4.29 / 4.43	12.27 / 12.31	199-201	74
7b	$C_{14}H_{19}N_3O_2S$	57.63 / 57.31	6.74 / 6.53	14.89 / 14.32	105-107	85
7c	$C_{20}H_{16}N_4OS$	66.57 / 66.64	4.39 / 4.48	15.47 / 15.55	200-202	68
7d	$C_{17}H_{18}N_4OS$	62.69 / 62.55	5.55 / 5.56	17.23 / 17.17	158-160	70
9a	$C_{19}H_{22}N_4O_2S$	61.49 / 61.60	6.11 / 5.99	15.34 / 15.12	140-142	85
9b	$C_{19}H_{22}N_4O_2S$	61.45 / 61.60	5.88 / 5.99	15.02 / 15.12	153-155	81

bonds (sum of the bond angles 359.8 and 360.0°). The $N_{(2)}H_2$ group is practically coplanar with the ring $N_{(1)}C_{(1-5)}$ (the interfacial angle is only 3.6°), which is favorable for effective conjugation between the lone electron pair of atom $N_{(2)}$ and the pyridine π-system. The conformation is also suitable for the conjugation $n(N_{(4)})$–$\pi(C_{(6)}=O_{(1)})$ and $n(N_{(4)})$–$\pi(C_{(7\text{-}12)})$ – the torsion angles $O_{(1)}C_{(6)}N_{(4)}C_{(7)}$ and $C_{(6)}N_{(4)}C_{(7)}C_{(8)}$ are 2.2 and 4.7° respectively.

As a result of these electronic interactions the bonds $N_{(2)}$–$C_{(5)}$ 1.338(11), $N_{(4)}$–$C_{(6)}$ 1.360(10), and $N_{(4)}$–$C_{(7)}$ 1.402(11) A are considerably shorter than the standard value for a N(sp^2)–C(sp^2) bond of 1.45 A [5]. A characteristic of the structure of molecule **9a** is the presence of a very strong hydrogen bond (strengthened by resonance [6]) $N_{(2)}$–$H_{(2)}\cdots O_{(1)}$ ($N_{(2)}$–$H_{(2)}$ 0.70(10), $N_{(2)}\cdots O_{(1)}$ 2.662(8), $O_{(1)}\cdots H_{(2)}$ 2.09(9) A, $N_{(2)}H_{(2)}O_{(1)}$ 133(6)°) which closes the six-membered ring $O_{(1)}C_{(6)}C_{(4)}C_{(5)}N_{(2)}H_{(2)}$. We note that the statistical average distance for N···O in hydrogen bonds of the type N–H···O is 2.89 A [7].

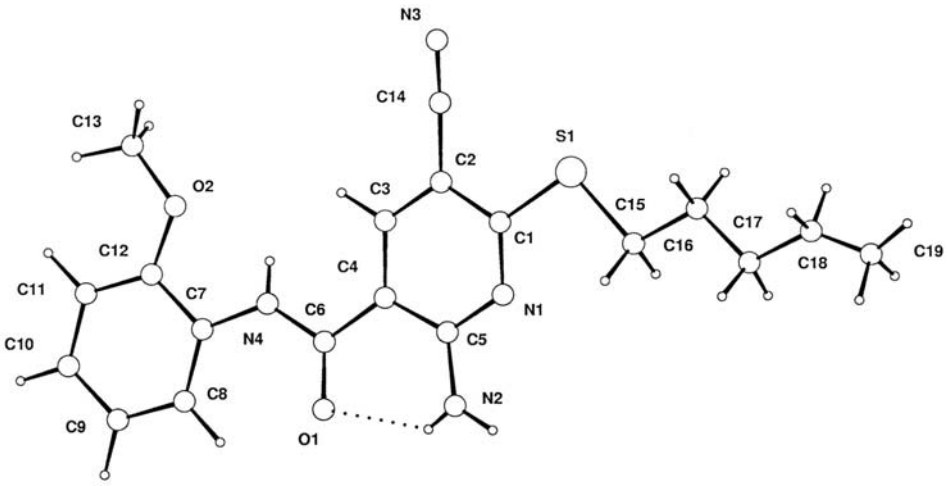


Fig. 1. Overall view of compound **9a** with numbering of the atoms.

TABLE 2. Spectral Characteristic of Compounds **4b,s, 5a,b, 7a-d**, and **9a,b**

Com-pound	IR spectrum, ν, cm^{-1}			^1H NMR spectrum, δ, ppm (*J*, Hz)				
	NH_2	C=O	C≡N	CONH, s or OCH_2, q	$H_{(4)}$, s or –CH=, s	NH_2, br. s	Ar or $\underline{CH_3}CH_2$, t	other signals
1	2	3	4	5	6	7	8	9
4b	3214, 3336, 3446	1666	2202, 2232	10.22	8.57	7.63	7.55-6.92 (7H, m)	3.85 (4H, m, CH_2OCH_2); 3.28 (4H, m, CH_2NCH_2); 2.79 (3H, s, CH_3)
4c	3256, 3312, 3430	1648	2180, 2196	9.10	8.68	7.93	7.92-6.94 (4H, m)	3.76 (4H, m, CH_2OCH_2); 3.09 (4H, m, CH_2NCH_2); 2.75 (3H, s, CH_3); 2.28 (3H, s, Ar$\underline{CH_3}$)
5a	3336, 3364	1650	2208	8.98	8.34	7.31	7.67 (1H, d, *J* = 7.1), 7.07-6.87 (3H, m)	11.62 (1H, s, SH); 3.85 (3H, s, OCH_3)
5b	3294, 3356	1658	2208	9.62	8.02	7.33	7.34 (1H, s), 7.22 (1H, d, *J* = 7.5), 7.12 (1H, dd), 6.54 (1H, d, *J* = 8.0)	3.75 (3H, s, OCH_3)*
7a	3322, 3428	1696	2206	4.29 (*J* = 7.1)	8.17	7.69	1.36 (*J* = 7.1)	8.07 (2H, d, *J* = 7.9, C_6H_5); 7.60 (2H, dd, C_6H_5); 7.53 (1H, dd, *J* = 7.0, C_6H_5); 4.89 (2H, s, SCH_2)

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9
7b	3238, 3378	1694	2208	4.30 (J = 7.1)	8.14	7.99	1.38 (J = 7.1)	3.22 (2H, t, J = 7.0, SCH_2); 1.65 (2H, m, $SCH_2\underline{CH_2}$); 1.41 (4H, m, $SCH_2CH_2\underline{CH_2CH_2}$); 0.94 (3H, t, J = 7.0, CH_3)
7c	3234, 3320	1664	2222	10.28	8.62	7.78	8.10-7.47 (7H, m)	5.93 (1H, m, CH=); 5.39 (1H, d, J_{trans} = 18.6, $=CH_2$); 5.13 (1H, d, J_{cis} = 8.3, $=CH_2$); 3.92 (2H, d, J = 6.7, SCH_2)
7d	3360, 3450	1656	2210	9.69	8.42	7.88	7.23 (1H, d, J = 7.1), 7.22 (1H, d), 7.17 (1H, dd, J = 7.2), 7.13 (1H, dd, J = 7.1)	3.18 (2H, t, J = 7.0, SCH_2); 2.22 (3H, s, $Ar\underline{CH_3}$); 1.72 (2H, m, $SCH_2\underline{CH_2}$); 1.05 (3H, t, J = 7.3, $S(CH_2)_2\underline{CH_3}$)
9a	3328, 3418	1648	2214	9.28	8.36	7.84	7.59 (1H, d, J = 7.8), 7.09 (1H, dd, J = 7.2), 6.94 (1H, d, J = 7.2), 6.87 (1H, dd)	3.82 (3H, s, OCH_3); 3.17 (2H, t, J = 7.1, SCH_2); 1.66 (2H, m, $SCH_2\underline{CH_2}$); 1.37 (4H, m, $SCH_2CH_2\underline{CH_2CH_2}$); 0.90 (3H, t, J = 6.9, $S(CH_2)_4\underline{CH_3}$)
9b	3280, 3388, 3440	1658	2214	9.91	8.41	7.92	7.36 (1H, s), 7.24 (1H, d, J = 7.6), 7.16 (1H, dd), 6.59 (1H, d, J = 8.0)	3.78 (3H, s, OCH_3); 3.24 (2H, t, J = 7.1, SCH_2); 1.65 (2H, m, $SCH_2\underline{CH_2}$); 1.41 (4H, m, $SCH_2CH_2\underline{CH_2CH_2}$); 0.93 (3H, t, J = 6.7, $S(CH_2)_4\underline{CH_3}$)

* Signals of the SH protons were not observed, probably as a result of fast exchange with protons of water molecules.

TABLE 3. Basic Bond Lengths (Å) and Bond Angles (deg) in the Molecule **9a**

Bond	*d*, Å	Angle	ω, deg.
$S_{(1)}$–$C_{(1)}$	1.763(8)	$C_{(1)}$–$S_{(1)}$–$C_{(15)}$	103.0(4)
$S_{(1)}$–$C_{(15)}$	1.815(8)	$C_{(1)}$–$N_{(1)}$–$C_{(5)}$	118.3(7)
$N_{(1)}$–$C_{(1)}$	1.320(8)	$C_{(6)}$–$N_{(4)}$–$C_{(7)}$	130.0(8)
$N_{(1)}$–$C_{(5)}$	1.350(10)	$O_{(1)}$–$C_{(6)}$–$N_{(4)}$	120.2(9)
$N_{(2)}$–$C_{(5)}$	1.338(11)	$O_{(1)}$–$C_{(6)}$–$C_{(4)}$	123.0(8)
$N_{(4)}$–$C_{(6)}$	1.360(10)		
$N_{(4)}$–$C_{(7)}$	1.402(11)		
$C_{(6)}$–$O_{(1)}$	1.222(8)		

EXPERIMENTAL

Melting points were recorded on a Kofler block. IR spectra of nujol mulls were recorded with a IKS-40 spectrometer. ^{1}H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were recorded on a Gemini-200 (199 MHz) spectrometer. Mass spectra were recorded with a Kratos MS-890 (70 eV) machine. The course of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates with 3:5 acetone–hexane as eluant and iodine vapor as detector.

X-ray Crystallographic Investigation of a Monocrystal of Compound 9a with linear dimensions 0.14×0.37×0.49 mm was carried out at room temperature with an Enraf-Nonius CAD-4 automatic four-circle diffractometer (MoKα radiation, relative rate of scanning $2\theta/\omega = 1.2$, $\theta_{max} = 27°$, segment of a sphere $0 \le h \le 16$, $0 \le k \le 8$, $-29 \le l \le 29$). A total of 4858 reflexions were collected, of which 4243 were symmetrically independent ($R_{int} = 0.018$). Crystals of compound **9a** are monoclinic, $a = 12.962(5)$, $b = 6.777(2)$, $c = 23.015(8)$ Å; $\beta = 105.84(3)°$; $V = 1944.8(1.1)$ Å^3; M = 370.47; $Z = 4$; $d_{calc} = 1.265$ g/cm^3; $\mu = 1.78$ cm^{-1}; $F(000) = 784.56$; space group $P2_1/c$. The structure was solved by direct methods and refined by least squares in the full matric anisotropic approximation using the CRYSTALS suite of programs [8]. In the refinement 1229 reflexions with $I > 3(I)$ (244 parameters refined, 5.0 reflexions per parameter). About half of the hydrogen atoms were revealed in the difference syntheses of the electron density, the positions of the rest were calculated. The hydrogen atoms on $N_{(2)}$ and $N_{(4)}$ were refined isotropically, the remaining hydrogen atoms were included in the refinement with fixed positions and thermal parameters. Calculation of absorption in the crystal was carried with the help azimuthal scanning [9]. The weighting scheme $w = 1 / [0.01Fo^2 + 12.0\sigma|Fo|^2 + 1.0]$. The final values for the residual factors were $R = 0.068$ and $R_w = 0.066$. The residual electron densities from a Fourier difference synthesis were 0.26 and -0.33 e/Å^3. Coordinates of the non-hydrogen atoms can be obtained from the authors.

N-Methylmorpholinium 1-Amino-2,4-dicyano-4-ethoxycarbonyl-1,3-butadiene-1-thiolate (4a) was characterized elsewhere [1].

N-Methylmorpholinium 1-Amino-4-arylcarbamoyl-2,4-dicyano-1,3-butadiene-1-thiolates 4b,c. N-Methylmorpholine (2.20 ml, 20 mmol) was added to a suspension of cyanothioacetamide **2** (1.00 g, 10 mmol) in ethanol (15 ml) at 20°C and the mixture was stirred until solution occurred. Then the corresponding ethoxymethylene derivative of cyanoacetic acid **1b,c** (10 mmol) was added and stirring was continued for 10 min to give a dark solution with a precipitate. The mixture was kept for a day. The precipitate was filtered off and washed with ethanol and hexane (Tables 1 and 2).

Nitriles of 6-Amino-5-arylcarbamoyl-2-mercaptonicotinic Acids 5a,b were obtained analogously to salts **4** from the olefins **1d,e**. Sodium ethoxide (0.68 g, 10 mmol) was used as the base (Tables 1,2).

Nitriles of 6-Amino-5-arylcarbamoyl(ethoxycarbonyl)-2-(*Z*-methylthio)nicotinic Acids 7a-d and 9a,b (General Method). A 10% aqueous solution of KOH (2.80 ml, 5 mmol) was added to a suspension of salt **4** or mercaptopyridine **5** (5 mmol) in DMF (10 ml). The corresponding alkyl halide **6** (5 mmol) was added to the solution formed. The mixture heated spontaneously to 40-45°C and was stirred for 1 h. The precipitate which formed was filtered off and washed ethanol and hexane (Tables 1 and 2). Mass spectrum of compound **7d**, *m/z* (I_{rel},%): 326 $[M]^+$ (32), 220 (100), 178 (70), 107 (98).

2-(1,3-Dicyano-3-ethoxycarbonylprop-2-ene)-4-phenylthiazole (8). Phenacyl bromide (1.99 g, 10 mmol) was added to a solution of salt **4a** (3.24 g, 10 mmol) in DMF (5 ml) and the mixture was stirred for 1 h. The precipitate formed was filtered off and washed with ethanol and hexane. Yield 2.55 g (79%); mp 183-185°C. IR spectrum, ν, cm^{-1}: 1684, 1698 (C=O), 2170, 2188, 2232 (C≡N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.18 (1H, s, $H_{(5)}$ thiazole); 7.86 and 7.78 (1H, both d, *J* = 7.0, =CH–); 7.73-7.38 (5H, m, C_6H_5); 4.38 and 4.13 (2H, both q, *J* = 7.1, $\underline{CH_2}CH_3$); 4.07 (1H, d, *J* = 7.0, CHCN); 1.40 and 1.37 (3H, both t, *J* = 7.1, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 322 $[M - 1]^+$ (80), 276 (100), 250 (80), 134 (40), 102 (25), 82 (28), 73 (28), 44 (30). Found, %: C 63.37; H 3.94; N 13.14. $C_{17}H_{13}N_3O_2S$. Calculated, %: C 63.14; H 4.05; N 12.99.

Nitrile of 6-Amino-3-(4-bromo-3-methoxyphenylcarbamoyl)-2-pentylthionicotinic Acid (10). Br_2 (0.515 ml, 10 mmol) was added dropwise with stirring to a solution of pyridine **9b** (3.71 g, 10 mmol) in DMF (15 ml) and stirring was continued for 1 h. The precipitate formed was washed with ethanol and hexane. Yield 3.99 g (89%); mp 205-207°C. IR spectrum, ν, cm^{-1}: 1664 (C=O), 2216 (C≡N), 3178, 3326, 3384 (NH, NH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.03 (1H, s, CONH); 8.38 (1H, s, $H_{(4)}$); 7.89 (2H, br. s, NH_2); 7.52 (1H, s, H_{arom}); 7.37 (1H, d, *J* = 8.7 , H_{arom}); 7.21 (1H, d, *J* = 8.7 , H_{arom}); 3.85 (3H, s , OCH_3) , 3.20 (2H, t, *J* = 7.1, SCH_2); 1.68 (2H, m, $SCH_2\underline{CH_2}$); 1.38 (4H, m, $SCH_2CH_2\underline{CH_2CH_2}$); 0.90 (3H, t, *J* = 6.9, $S(CH_2)_4\underline{CH_3}$). Found, %: C 50.93; H 4.63; N 12.31. $C_{19}H_{21}BrN_4O_2S$. Calculated, %: C 50.78; H 4.71; N 12.47.

6-Cyano-2-methyl-3-(3-methoyphenyl)-7-pentylthiopyrido[2,3-*d*]pyrimidin-4(3H)-one (11). Pyridine (0.01 ml) was added to a solution thiol **9b** (1.85 g, 5 mmol) in acetic anhydride (5 ml) and the mixture was refluxed for 2 h. It was kept at room temperature for 1 day, the precipitate was filtered off and washed with ethanol. Yield 1.72 g (87%); mp 260-262°C. IR spectrum, ν, cm^{-1}: 1690 (C=O), 2230 (C≡N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.59 (1H, s, $H_{(5)}$); 7.44 (1H, dd, J_1 = 8.1, J_2 =7.6, H_{arom}); 7.04 (1H, d, *J* = 8.1, H_{arom}); 6.94 (1H, s, H_{arom}); 6.87 (1H, d, *J* = 7.6, H_{arom}); 3.83 (3H, s, OCH_3); 3.37 (2H, t, *J* = 7.1, SCH_2); 1.78 (2H, m, $SCH_2\underline{CH_2}$); 1.41 (4H, m, $SCH_2CH_2\underline{CH_2CH_2}$); 0.93 (3H, t, *J* = 7.0, $S(CH_2)_4\underline{CH_3}$). Found, %: C 64.09; H 5.51; N 14.39. $C_{21}H_{22}N_4O_2S$. Calculated, %: C 63.93; H 5.62; N 14.20.

3-Aryl-6-cyano-7-pentylthiopyrido[2,3-*d*]pyrimidin-4(3H)-ones (12a,b). A solution of aminopyridine **9a** or **9b** (1.85 g, 5 mmol) in triethyl orthoformate (1.66 ml, 10 mol) and acetic anhydride (1.42 ml, 15 mmol) was refluxed for 1 h., then kept at room temperature for 1 day. The precipitate was filtered off and washed with ethanol.

Compound 12a. Yield 1.37 g (72%); mp 104-106°C. IR spectrum, ν, cm^{-1}: 1691 (C=O), 2232 (C≡N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.77 (1H, s, $H_{(2)}$); 8.41 (1H, s, $H_{(5)}$); 7.55 (1H, dd, *J* = 7.3,, H_{arom}); 7.43 (1H, d, *J* = 7.8, H_{arom},); 7.25 (1H, d, *J* = 7.6, H_{arom}),7.14 (1H, dd. J_1 = 7.6, J_2 = 7.8, H_{arom}) , 3.84 (3H, s, OCH_3); 3.41 (2H, t, *J* = 7.1, SCH_2); 1.81 (2H, m, $SCH_2\underline{CH_2}$); 1.46 (4H, m, $SCH_2CH_2\underline{CH_2CH_2}$); 0.96 (3H, t, *J* = 7.0, $S(CH_2)_4\underline{CH_3}$). Found, %: C 62.91; H 5.21; N 14.92. $C_{20}H_{20}N_4O_2S$. Calculated,%:C 63.14; H 5.30; N 14.73.

Compound 12b. Yield 1.58 g (83%); mp 116-118°. IR spectrum, ν, cm^{-1}: 1702 (C=O), 2230 (C≡N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.73 (1H, s, $H_{(2)}$); 8.53 (1H, s, $H_{(5)}$); 7.45 (1H, dd, *J* = 7.7, H_{arom}); 7.45 (1H, d, *J* = 7.7, H_{arom}); 7.08-7.02 (3H, m, H_{arom}); 3.85 (3H, s, OCH_3); 3.38 (2H, t, *J* = 7.2, SCH_2); 1.79 (2H, m, $SCH_2\underline{CH_2}$); 1.44 (4H, m, $SCH_2CH_2\underline{CH_2CH_2}$); 0.94 (3H, t, *J* = 7.1, $S(CH_2)_4\underline{CH_3}$). Found, %: C 63.28; H 5.15; N 14.51. $C_{20}H_{20}N_4O_2S$. Calculated,%: C 63.14; H 5.30; N 14.73.

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