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Synthesis of 2,3-Dihydro-1,3-Thiazin-4(1*H*)-ones and Their Remarkably Facile Recyclization to 2,3-Dihydropyrimidin-4(1*H*)-ones

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ABSTRACT: *Functionalized 2,3-dihydro-1,3-thiazin-4(1H)-one derivatives have been synthesized by cyclocondensation of 3-alkyl(aryl)amino-2-cyano-3-mercaptoacrylamides with aldehydes and ketones under acidic catalysis. 6-Alkyl(aryl)amino-5-cyano-2,3-dihydro-1,3-thiazin-4(1H)-ones, when treated with a dilute solution of potassium hydroxide, are converted into the potassium salts of isomeric compounds, 1-alkyl-(aryl)-5-cyano-6-mercapto-2,3-dihydropyrimidin-4(1H)-ones. Alkylation of the latter with dimethyl sulfate in situ furnishes 1-alkyl(aryl)-6-alkylthio-5-cyano-2,3-dihydropyrimidin-4(1H)-ones, whereas boiling them in ethanol with an excess of hydrochloric acid leads to starting 2,3-dihydro-1,3-thiazin-4(1H)-ones*. © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:426–436, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20129

INTRODUCTION

3-Mercaptoacrylamide derivatives noted for several reaction centers in their structure are used in syntheses of functionalized heterocyclic systems including pyrimidines [1,2], 1,3-thiazines [3], pyridines [4], pyrazoles [5,6], thiazoles [7], isothiazoles [8,9], and thiophenes [10,11]. Based on the condensation of 3-alkylthio-2-cyano-3-mercaptoacrylamide with carbonyl compounds (aldehydes and ketones) under acidic conditions, Yokoyama found a convenient synthetic route to 2,5,6-substituted 2,3-dihydro-1,3-thiazin-4(1*H*)-ones [12]. However, the reaction of the related compound, 2-cyano-3-mercapto-3-phenylaminoacrylamide, with acetaldehyde, benzaldehyde, and acetone provided a product for which unequivocal structural determination failed (Goerdeler and Keuser [13]). Though the compounds obtained were presumably 2,3-dihydropyrimidin-4(1*H*)-ones, the alternative 2,3-dihydro-1,3-thiazin-4(1*H*)-one structure could not be ruled out completely.

In the course of our research on new efficient accesses to 2,3-dihydro-1,3-azin-4(1*H*)-ones [14,15], we have reproduced and substantially extended Goerdeler's experiments aiming at accurate structural determination of the cyclocondensation products and study of their chemical behavior.

RESULTS AND DISCUSSION

We have established that 3-alkyl(aryl)amino-2-cyano-3-mercaptoacrylamides **1a–d** react with a variety of carbonyl compounds **2a–l** on boiling in ethanol for 2 h in the presence of catalytic amounts of *p*-toluenesulfonic acid (*p*-TSA) to give

Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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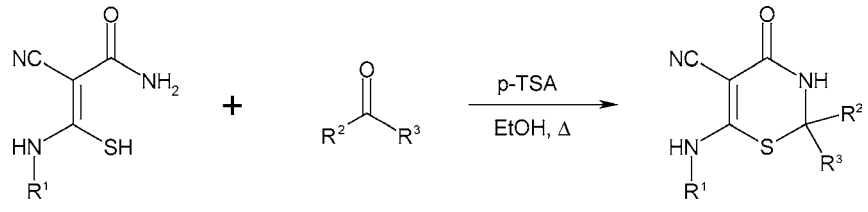


1 **2** **3**

1: R^1 = Me (a), Et (b), Bn (c), Ph (d)

2: R^2 = H, R^3 = Me (a), 6′,6′-dimethylbicyclo[3.1.1]hept-2′-en-2′-yl (b), Ph (c), 4-$MeOC_6H_4$ (d), 4-$NO_2C_6H_4$ (e), (R)-2′,3′-dihydro-1,4-benzodioxin-6′-yl (f); R^2 = R^3 = Me (g); R^2 = Me, R^3 = i-Pr (h); R^2,R^3 = cyclopentyliden (k); R^2,R^3 = adamantyliden (l)

SCHEME 1

6-alkyl(aryl)amino-5-cyano-2,3-dihydro-1,3-thiazin-4(1*H*)-ones **3a–o** in excellent yields (Scheme 1, Table 1). High yields of products **3** also result from boiling the reagents not long in glacial acetic acid. These conditions, however, are not appropriate for the reaction of sterically hindered aliphatic ketones such as pinacolone and menthone. Acetophenone, cycloheptanone, and 2,5-dimethylheptan-4-one proved not to enter the cyclocondensation even under more severe conditions (on boiling the reagents in *i*-PrOH or heating them without a solvent in the presence of *p*-TSA). Nor were the desired products furnished by an attempted reaction with carbonyl compounds activated by electron-acceptor substituents (ethylpyruvate, isatine, and phenylglyoxal).

The structure of compounds **3** is reliably supported by elemental analysis, IR, ^{1}H NMR, and ^{13}C

TABLE 1 Elemental Analytical Data of Compounds **3**

Compound Number	*R^1*	*R^2*	*R^3*	*Formula*	*Calcd (Found)*			
					C	*H*	*N*	*S*
3a	Me	H	Ph	$C_{12}H_{11}N_3OS$ 245.30	58.76 (58.99)	4.52 (4.62)	17.13 (16.91)	13.07 (13.20)
3b	Et	H	Ph	$C_{13}H_{13}N_3OS$ 259.33	60.21 (60.48)	5.05 (4.88)	16.20 (16.03)	12.36 (12.14)
3c	Et	Me	Me	$C_9H_{13}N_3OS$ 211.29	51.16 (50.89)	6.20 (6.27)	19.89 (20.08)	15.18 (15.40)
3d	Bn	H	4-$MeOC_6H_4$	$C_{19}H_{17}N_3OS$ 351.43	64.94 (64.70)	4.88 (5.04)	11.96 (12.23)	9.12 (9.37)
3e	Ph	H	Me	$C_{12}H_{11}N_3OS$ 245.30	58.76 (58.50)	4.52 (4.40)	17.13 (12.27)	13.07 (12.81)
3f	Ph	H	6′,6′-Dimethylbicyclo-[3.1.1]hept-2-en′-2′-yl	$C_{20}H_{21}N_3OS$ 351.47	68.35 (68.41)	6.02 (6.18)	11.96 (12.27)	6.12 (5.94)
3g	Ph	H	Ph	$C_{17}H_{13}N_3OS$ 307.38	66.43 (66.20)	4.26 (4.22)	13.67 (13.38)	10.43 (10.70)
3h	Ph	H	4-$NO_2C_6H_4$	$C_{17}H_{12}N_4O_3S$ 352.37	57.95 (58.27)	3.43 (3.57)	15.90 (16.18)	9.10 (9.33)
3k	Ph	H	2′,3′-Dihydro-1,4-benzodioxin-6′-yl	$C_{19}H_{15}N_3O_3S$ 365.41	62.45 (62.59)	4.14 (3.96)	11.50 (11.22)	8.77 (9.00)
3l	Ph	Me	Me	$C_{13}H_{13}N_3OS$ 259.33	60.21 (60.07)	5.05 (4.89)	16.20 (16.33)	12.36 (12.11)
3m	Ph	Me	*i*-Pr	$C_{15}H_{17}N_3OS$ 287.39	62.69 (62.94)	5.96 (6.10)	14.62 (14.41)	11.16 (11.38)
3n	Ph		—$(CH_2)_4$—	$C_{15}H_{15}N_3OS$ 285.37	63.13 (62.83)	5.30 (5.42)	14.72 (14.95)	11.24 (11.51)
3o	Ph		Adamantyliden	$C_{20}H_{21}N_3OS$ 351.47	68.35 (68.62)	6.02 (5.81)	11.96 (12.04)	9.12 (9.46)

NMR spectroscopy as well as by X-ray diffraction. The IR spectra display the absorption bands at 3230 (NH), 2220 (CN), and 1660 cm^{-1} (C=O). The ^1H NMR spectra are characterized by the signals from the exocyclic NH protons at 9.94–10.15 ($R^1 = Ph$) or 8.18–8.85 ppm ($R^1 = Alk$). A resonance of the endocyclic NH proton is found in the region 7.89–8.45 ppm and easily identified at $R^2 = H$ by the spin–spin coupling with the proton at position 2 of the thiazine ring (the spin–spin coupling constant J amounts to 1–4 Hz). The thiazine moiety gives rise to a characteristic doublet at 4.95–6.06 ppm with the same value of J or to a doublet of quartets ($R^3 = Me$).

If R^2 and R^3 are different substituents, a chiral center appears in the 2,3-dihydro-1,3-thiazin-4(1*H*)-one structure of compounds **3** and therefore the signal from the CH_2 group in the substituent R^1 is split into the ABM ($R^1 = Bn$) or $ABMX_3$ system ($R^1 = Et$). Compounds **3** are also characterized by the ^{13}C NMR signals from the carbon atoms of the thioaminal fragment, with their chemical shifts ranging from 51.90 to 71.82 ppm.

Peculiarities of molecular and crystal structure of **3m** have been studied by X-ray diffraction method. The perspective view of molecule **3m** and selected geometrical parameters are given in Fig. 1. The S(1)N(1)C(1–4) six-membered heterocycle is essentially nonplanar (deviations from the least-squares plane exceed 0.38 Å) and has a *half-chair* conformation. The C(10–15) benzene ring is twisted out of this plane by 66.4°. In the solid state, the molecules of **3m** are joined in the chains by the N(2)—H···O(3) hydrogen bonds (N···2.860(4) Å, O···H 2.09(4) Å, NHO 148(3)°) (see Fig. 2).

Methylation of 2,3-dihydro-1,3-thiazin-4(1*H*)-ones **3** with dimethyl sulfate under basic conditions led to an unexpected result. The reaction proved to involve the sulfur atom thus affording 1-alkyl(aryl)-6-methylthio-5-cyano-2,3-dihydropyrimidin-4(1*H*)-ones **4a–c,e–k,n** in high yields. Alkylation with benzyl chloride in ethanol in the presence of triethylamine provides the analogous products, viz. 1-alkyl(aryl)-6-benzylthio-5-cyano-2,3-dihydropyrimidin-4(1*H*)-ones **4d,l,m** (Scheme 2, Table 2). Treating compounds **3b** and **3h** with a dilute KOH solution, we isolated, in the individual state, the salts of the corresponding thiols **6a** and **6b** forming as intermediates in the alkylation of thiazines **3**. They

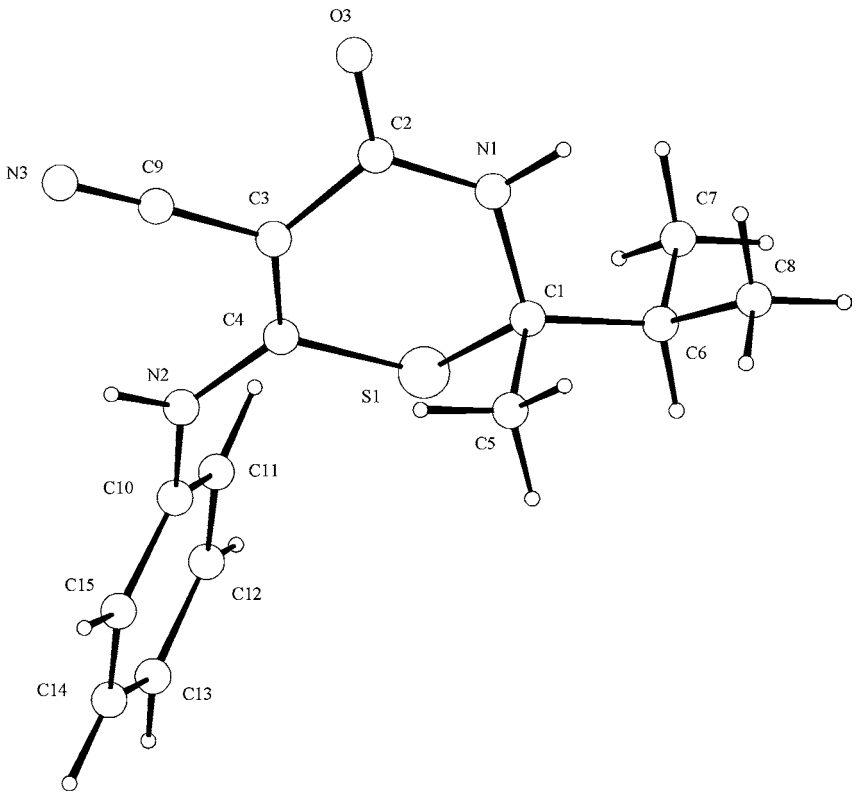


FIGURE 1 Perspective view and labeling scheme for the molecule **3m**. Selected bond lengths (Å) and angles (°): S(1)–C(1) 1.863(5), S(1)–C(4) 1.753(4), N(1)–C(1) 1.446(6), N(1)–C(2) 1.339(6), N(2)–C(4) 1.336(5), C(2)–C(3) 1.453(6), C(3)–C(4) 1.383(5), C(1)S(1)C(4) 97.5(2), C(1)N(1)C(2) 125.4(4), S(1)C(1)N(1) 107.5(3), N(1)C(2)C(3) 117.2(4), C(2)C(3)C(4) 125.9(4), C(4)C(3)C(9) 119.2(4).

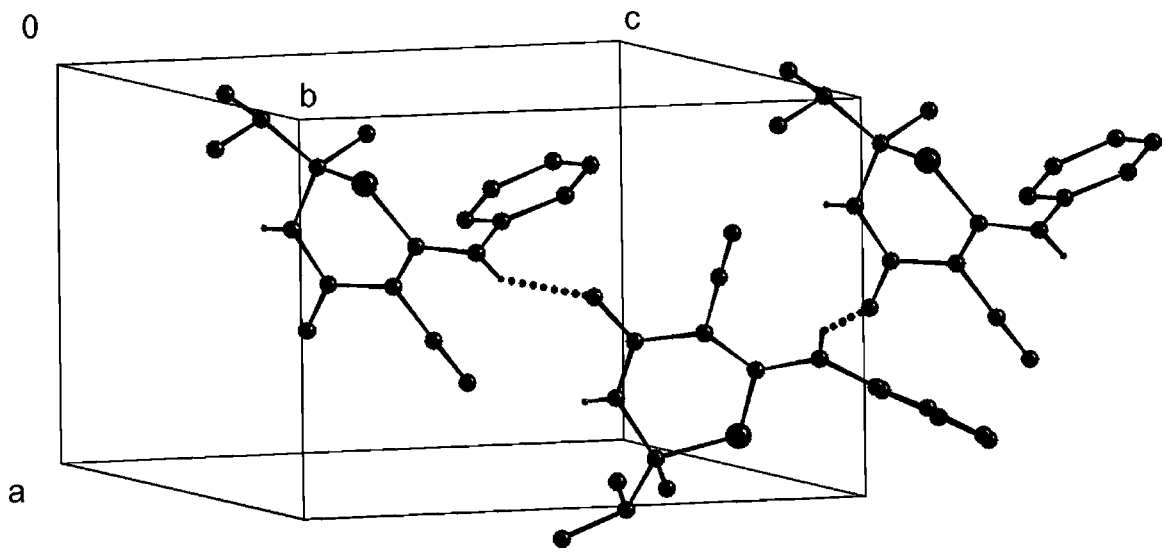
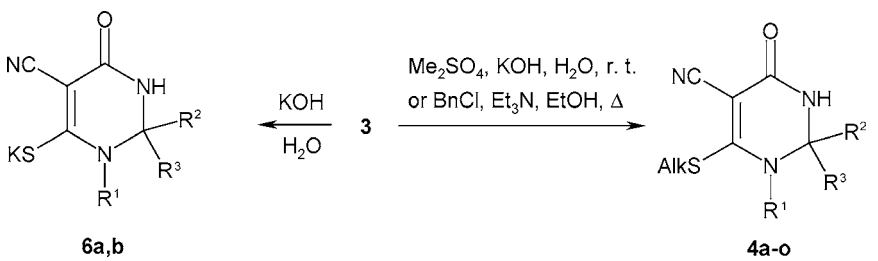


FIGURE 2 Crystal packing of the compound **3m**.

crystallize from water and are stable to aqueous acetic acid; at the same time, they are quantitatively converted into starting thiazines **3**, if heated in ethanol with an excess of hydrochloric acid.

Formation of the pyrimidine structure was corroborated by chemical conversions. Compound **4l** was hydrolyzed in the mixture of dioxane and concentrated hydrochloric acid to produce mainly 3-benzylthio-2-cyano-3-phenylaminoacrylamide **5a** readily obtainable via reverse synthesis, i.e., benzylation of 2-cyano-3-mercapto-3-phenylaminoacrylamide **1d** (Scheme 3). The two samples of compound **5a** thus prepared were proved to be identical by elemental analysis as well as by IR and ^{1}H NMR spectroscopy. Methylation of the derivative **3o** under similar conditions resulted in the mixture of 2-cyano-3-methylthio-3-phenylaminoacrylamide **5b** and adamantanone. As expected, methylation of the obtained mixture of diastereomers **3f** provided the mixture of diastereomeric 2,3-dihydropyrimidin-4(1*H*)-ones **4f** so that the product ratio was 65:35, according to the ^{1}H NMR data.

The interconversions described can be accounted for by the following mechanism (Scheme 4). A base causes proton abstraction from the nitrogen atom in position 3 and the thiazine ring opening. Then the resulting intermediate **A** cyclizes to the stable thiolate **B** and alkylation of the latter in situ yields products **4**. In the case of derivative **3o**, the pyrimidine ring closure cannot occur in the intermediate **A** (presumably due to steric hindrances) and the subsequent methylation leads to the hydrolysis product **5b**. The mechanism suggested is consistent with the fact that compounds **5** provide no cyclic products in the reaction with carbonyl compounds **2** both in acidic and basic media. The reverse recyclization of unstable 2,3-dihydropyrimidin-4(1*H*)-ones **C** to the corresponding 2,3-dihydro-1,3-thiazin-4(1*H*)-ones **3** proceeds via N-alkylidene derivatives **D** which are also likely to be intermediately form in the reaction

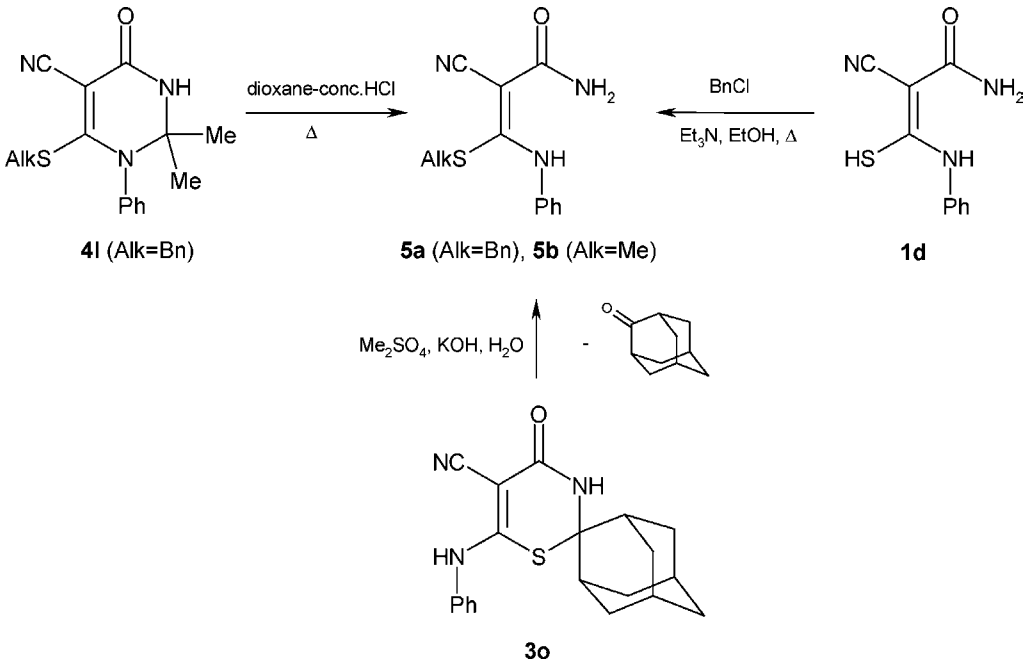


6a,b **4a-o**

SCHEME 2

TABLE 2 Elemental Analytical Data of Compounds **4** and **6**

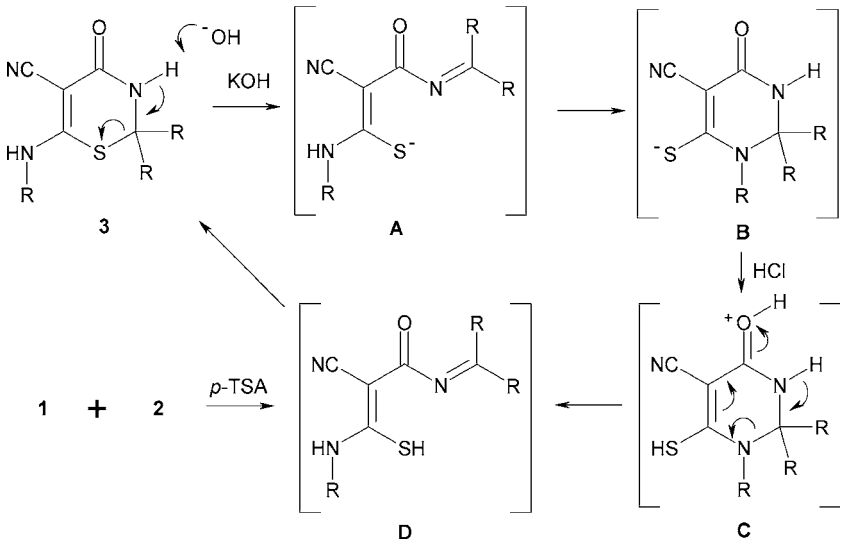
Compound Number	R^1	R^2	R^3	R^4	Formula	Calcd (Found) C	H	N	S
4a	Me	H	Ph	Me	$C_{13}H_{13}N_3OS$ 259.33	60.21 (60.48)	5.05 (4.93)	16.20 (15.87)	12.36 (12.51)
4b	Et	H	Ph	Me	$C_{14}H_{15}N_3OS$ 273.36	61.51 (61.79)	5.53 (5.44)	15.37 (15.21)	11.73 (12.03)
4c	Et	Me	Me	Me	$C_{10}H_{15}N_3OS$ 225.31	53.31 (53.60)	6.71 (6.79)	18.65 (18.65)	14.23 (14.00)
4d	Bn	H	4-$MeOC_6H_4$	Bn	$C_{26}H_{23}N_3O_2S$ 441.56	70.72 (70.46)	5.25 (5.37)	9.52 (9.27)	7.26 (7.39)
4e	Ph	H	Me	Me	$C_{13}H_{13}N_3OS$ 259.33	60.21 (60.44)	5.05 (5.21)	16.20 (16.04)	12.36 (12.62)
4f	Ph	H	6′,6′-Dimethylbicyclo-[3.1.1]hept-2-en-2-yl	Me	$C_{21}H_{23}N_3OS$ 365.50	69.01 (68.67)	6.34 (6.42)	11.50 (11.77)	8.77 (8.48)
4g	Ph	H	Ph	Me	$C_{18}H_{15}N_3OS$ 321.40	67.27 (67.48)	4.70 (4.80)	13.07 (12.84)	9.98 (10.36)
4h	Ph	H	4-$NO_2C_6H_4$	Me	$C_{18}H_{14}N_4O_3S$ 366.40	59.01 (59.21)	3.85 (3.82)	15.29 (15.54)	8.75 (8.43)
4k	Ph	H	2′,3′-Dihydro-1,4-benzodioxin-6′-yl	Me	$C_{20}H_{17}N_3O_3S$ 379.44	63.31 (63.05)	4.52 (4.39)	11.07 (11.41)	8.45 (8.18)
4l	Ph	Me	Me	Bn	$C_{20}H_{19}N_3OS$ 349.46	68.74 (69.05)	5.48 (5.57)	12.02 (12.31)	9.18 (9.47)
4m	Ph	Me	*i*-Pr	Bn	$C_{22}H_{23}N_3OS$ 377.51	70.00 (70.08)	6.14 (6.26)	11.13 (11.31)	8.49 (8.14)
4n	Ph		—$(CH_2)_4$—	Me	$C_{16}H_{17}N_3OS$ 299.40	64.19 (64.47)	5.72 (5.65)	14.03 (14.20)	10.71 (10.96)
6a	Et	H	Ph	Potassium salt	$C_{13}H_{12}KN_3OS$ 297.43	52.50 (52.77)	4.07 (3.90)	14.13 (14.30)	10.78 (11.05)
6b	Ph	H	4-$NO_2C_6H_4$	Potassium salt	$C_{17}H_{11}KN_4O_3S$ 390.47	52.29 (52.01)	2.84 (2.97)	14.35 (14.15)	8.21 (8.04)



4l (Alk=Bn) **5a** (Alk=Bn), **5b** (Alk=Me) **1d**

3o

SCHEME 3



SCHEME 4

between compounds **1** and **2** leading to thiazines **3**. The possibility of interconversions between partially hydrogenated 1,3-thiazines and pyrimidines was previously demonstrated with the examples of 2-arylimino-2,3,5,6-tetrahydro-1,3-thiazin-4(1*H*)-ones [16], 4,4,6-trimethyl-1,4-dihydropyrimidin-2(3*H*)-ones [17], and 2-thioxo-2,3,5,6-tetrahydro-1,3-thiazin-4(1*H*)-ones [18].

Compounds **4** and **6** were characterized spectroscopically by the IR, ^{1}H NMR, and ^{13}C NMR methods. A distinction between the thiazine and pyrimidine structural types is clearly manifested in the ^{13}C NMR spectra: the resonances of the aminal carbon atoms in compounds **4** (δ 68.99–82.84 ppm) are shifted downfield from those of the thioaminal carbon atoms in compounds **3**. Importantly, the difference in chemical shift between two diastereotopic protons in the methylene group of the substituent R^{1}is much larger for S-methylated pyrimidine **4b** and the corresponding salt **6a** (0.27 and 1.54 ppm, respectively) than for thiazine **3b** (0.05 ppm, multiplet). This effect points to the spatial approach of the methylene group and the chiral center of the molecule in going from the thiazine to pyrimidine structure.

Thus, we have developed an efficient method to synthesize 6-alkyl(aryl)amino-5-cyano-2,3-dihydro-1,3-thiazin-4(1*H*)-ones and studied their conversion into the derivatives of isomeric 1-alkyl(aryl)-5-cyano-6-mercapto-2,3-dihydropyrimidin-4(1*H*)-ones.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer in KBr tablets. ^{1}H NMR spectra were registered in the mixture $(CD_3)_2SO$:CCl_4 (2:1) on a Varian-Gemini spectrometer (300 MHz) using TMS as internal standard. ^{13}C NMR spectra were registered in $(CD_3)_2SO$ on a Varian-Gemini spectrometer (75.5 MHz) using TMS as internal standard.

X-ray Structure Determination of **3m**

Crystal data: $C_{15}H_{17}N_3OS$, $M = 287.4$, orthorombic, $a = 8.075(5)$, $b = 15.190(8)$, $c = 11.971(8)$ Å, $V = 1468(2)$ Å^3, $Z = 4$, $d = 1.30$ g cm^{-1}, space group $Pna2_1$ (N 33), $\mu = 2.20$ cm^{-1}, $F(000) = 608.0$, crystal size ca. $0.19 \times 0.28 \times 0.49$ mm. All crystallographic measurements were performed at 20°C on a CAD-4-Enraf-Nonius diffractometer operating in the ω-2θ scan mode (the ratio of the scanning rates $\omega/2\theta = 1.2$). The intensity data were collected within the range $2 < \theta < 25°$ ($0 < h < 9$, $0 < k < 18$, $0 < l < 14$ plus Friedel equivalents) using graphite monochromated Mo K_α radiation ($\lambda = 0.71069$ Å). Intensities of 3028 reflections (1351 unique reflection, R_{int} 0.020) were measured. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scan data [19] was applied. The structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation using the CRYSTALS program package [20]. In the refinement 972 reflections with $I > 3\sigma(I)$ were used. All hydrogen atoms were located in the different Fourier maps and included in the final refinement with fixed positional and thermal parameters (only the H(1) and H(2) atoms were refined isotropically). Convergence was obtained at $R = 0.033$ and $R_w = 0.034$, GOF = 1.205

(189 refined parameters; obs./variabl. 5.1; the largest and minimal peaks in the final difference map, 0.22 and −0.17 e/Å^3). Chebushev weighting scheme [21] with parameters 0.77, 0.25, 0.81, 0.08, and 0.25 was used. The Flack test [22] was applied for the absolute configuration determination (the enantiopole parameter was refined to 0.1(1) using 1878 reflections with the nonavereged Friedel equivalents).

Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this materials should quote the full literature citation and reference number CCDC252077.

3-Alkyl(aryl)amino-2-cyano-3-mercaptoacrylamides **1a–d**

To a stirred and ice-water cooled mixture of cyanoacetamide (0.1 mol) and the corresponding alkyl(aryl)isothiocyanate (0.1 mol) in DMF (150 mL), 40% aqueous KOH (15 mL) was added dropwise. Then the reaction mixture was held on a water bath for 1 h. On cooling down, the solution was diluted with water (150 mL) and filtered; the filtrate was acidified with concentrated HCl to pH 2–3. A resulting precipitate was filtered off, washed with water, dried, and used in further reactions without additional purification.

General Procedure for Preparation of 6-Alkyl (aryl)amino-5-cyano-2,3-dihydro-1,3-thiazin-4(1H)-ones **3a–o**

Method A. A mixture of compound **1** (0.01 mol), the corresponding carbonyl compound **2** (0.01 mol), and *p*-TSA (0.002 mol) in ethanol (20 mL) was boiled for 2 h. On cooling the solution, a resulting precipitate was filtered off, washed with ethanol, dried, and recrystallized from ethanol.

Method B. A mixture of compound **1** (0.01 mol) and the corresponding carbonyl compound **2** (0.01 mol) in glacial acetic acid (20 mL) was boiled for 0.5 h. On cooling the solution, a resulting precipitate was filtered off, washed with ethanol, dried, and recrystallized from ethanol.

5-Cyano-6-methylamino-2-phenyl-2,3-dihydro-1,3-thiazin-4(1H)-one **3a**. Yield 71% (method A); mp 245–247°C; IR (ν/cm^{-1}): 3300 (NH), 2220 (CN), 1660 (C=O); ^{1}H NMR δ 2.90 d (3H, CH_3, $J = 3.0$ Hz), 6.06 d (1H, CH, $J = 2.0$ Hz), 7.25–7.41 m (3H, H_{arom}), 7.47–7.53 m (2H, H_{arom}), 8.20–8.22 m (2H, 2 NH); ^{13}C NMR δ 31.59 (CH_3), 58.05 (CH), 73.04 (C^5), 117.24 (CN), 127.31, 128.66, 129.12, 136.74 (C_{arom}), 165.64 (C=O), 168.20 (C^6).

5-Cyano-6-ethylamino-2-phenyl-2,3-dihydro-1,3-thiazin-4(1H)-one **3b**. Yield 75% (method A); mp 236–238°C; IR (ν/cm^{-1}): 3280 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 1.12 t (3H, CH_3, $J = 7.2$ Hz), 3.28 m (2H, CH_2), 6.06 d (1H, CH, $J = 2.5$ Hz), 7.35–7.51 m (5H, H_{arom}), 8.20 d (1H, NH, $J = 2.5$ Hz), 8.25 t (1H, NH, $J = 5.4$ Hz); ^{13}C NMR δ 15.28 (CH_3), 40.16 (CH_2), 57.97 (CH), 73.29 (C^5), 117.28 (CN), 127.32, 128.65, 129.11, 136.65 (C_{arom}), 165.74 (C=O), 166.78 (C^6).

5-Cyano-2,2-dimethyl-6-ethylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3c**. Yield 76% (method A); mp 238–240°C; IR (ν/cm^{-1}): 3310 (NH), 2220 (CN), 1660 (C=O); ^{1}H NMR δ 1.14 t (3H, CH_3, $J = 6.9$ Hz), 1.64 s (6H, 2 CH_3), 3.31 dqua (2H, CH_2, $J_1 = 6.9$ Hz, $J_2 = 5.4$ Hz),7.89 s (1H, NH), 8.18 t (1H, NH, $J = 5.4$ Hz); ^{13}C NMR δ 15.19 (CH_3), 29.50 ($2CH_3$), 61.12 (C^2), 72.00 (C^5), 117.18 (CN), 164.59 (C=O), 166.26 (C^6).

6-Benzylamino-5-cyano-2-(4-methoxyphenyl)-2,3-dihydro-1,3-thiazin-4(1H)-one **3d**. Yield 88% (method A); mp 209–211°C; IR (ν/cm^{-1}): 3320, 3180 (NH), 2220 (CN), 1670 (C=O); ^{1}H NMR δ 3.77 s (3H, OCH_3), 4.45 dd (1H, $C\underline{H}^AH^B$, $J_1 = 15.9$ Hz, $J_2 = 6.0$ Hz), 4.55 dd (1H, $CH^A\underline{H}^B$, $J_1 = 15.9$ Hz, $J_2 = 6.0$ Hz), 6.00 d (1H, CH, $J = 1.8$ Hz), 6.92 d (2H, H_{arom}, $J = 8.1$ Hz), 7.18–7.45 m (7H, H_{arom}), 8.17 d (1H, NH, $J = 1.8$ Hz), 8.85 t (1H, NH, $J = 6.0$ Hz); ^{13}C NMR δ 48.04 (CH_2), 55.22 (OCH_3), 58.10 (CH), 73.99 (C^5), 116.06 (CN), 113.96, 127.04, 127.35, 127.95,128.53, 128.77, 137.92, 159.77 (C_{arom}), 165.51 (C=O), 167.38 (C^6).

5-Cyano-2-methyl-6-phenylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3e**. Yield 90% (method A); mp 268–270°C (lit. 275°C [13]); IR (ν/cm^{-1}): 3340 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 1.46 d (3H, CH_3, $J = 6.6$ Hz), 4.95 dqua (1H, CH, $J_1 = 6.6$ Hz, $J_2 = 2.2$ Hz), 7.18–7.40 m (5H, H_{arom}), 8.08 d (1H, NH, $J = 2.2$ Hz), 10.07 s (1H, NH); ^{13}C NMR δ 18.93 (CH_3), 51.90 (CH), 77.11 (C^5), 116.51 (CN), 125.74, 126.88, 128.96, 138.13 (C_{arom}), 165.26 (C=O), 166.77 (C^6).

(RR,RS)-5-Cyano-2-(6′,6′-dimethylbicyclo[3.1.1]-hept-2′-en-2′-yl)-6-phenylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3f**. Yield 80% (method A); mp 230–232°C; IR (ν/cm^{-1}): 3310 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 0.73 s (3H, CH_3), 1.05–1.33 m (4H, H_{aliph}), 1.98–2.41 m (5H, H_{aliph}), 5.19 s (0.5H,

CH), 5.30 s (0.5H, CH), 5.54 s (0.5H, CH), 5.68 s (0.5H, CH), 7.16–7.45 m (5H, H_{arom}), 8.07 s (0.5H, NH), 8.16 s (0.5H, NH), 9.94 s (0.5H, NH), 10.00 s (0.5H, NH); ^{13}C NMR δ 20.50, 20.93 (CH_3), 25.74 (CH_3), 30.62 (CH_2), 31.01, 31.12 (CH_2), 37.51 (C_{quat}), 39.82 (CH), 42.51, 42.85 (CH), 57.35, 58.61 (CH), 77.20, 77.48 (C^5), 116.41 (CN), 120.16, 121.98 (CH), 125.29, 125.35, 126.60, 128.76, 128.84, 137.74, 138.01 (C_{arom}), 142.35, 143.37 (C_{quat}), 164.25, 164.82, 165.03, 165.32 (C=O, C^6).

5-Cyano-2-phenyl-6-phenylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3g**. Yield 85% (method A), 80% (method B); mp 264–266°C (lit 267–268°C [13]); IR (ν/cm^{-1}): 3350, 3260 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 6.06 d (1H, CH, $J = 2.5$ Hz), 7.18–7.55 m (10H, H_{arom}), 8.45 d (1H, NH, $J = 2.5$ Hz), 10.15 s (1H, NH); ^{13}C NMR δ 58.18 (CH), 77.50 (C^5), 116.43 (CN), 125.62, 127.34, 128.97, 136.38, 137.87 (C_{arom}), 165.51 (C=O), 165.60 (C^6).

5-Cyano-2-(4-nitrophenyl)-6-phenylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3h**. Yield 84% (method A), 77% (method B); mp 255–257°C; IR (ν/cm^{-1}): 3330, 3250 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 6.22 d (1H, CH, $J = 2.0$ Hz), 7.15–7.41 m (5H, H_{arom}), 7.70 d (2H, H_{arom}, $J = 9$ Hz), 8.23 d (2H, H_{arom}, $J = 9$ Hz), 8.62 d (1H, NH, $J = 2.0$ Hz), 10.15 s (1H, NH); ^{13}C NMR δ 56.40 (CH), 77.47 (C^5), 116.07 (CN), 123.76, 125.66, 127.06, 128.28, 129.04, 137.72, 145.23, 147.53 (C_{arom}), 164.63 (C=O), 164.96 (C^6).

5-Cyano-(2′,3′-dihydro-1,4-benzodioxin-6′-yl)-6-phenylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3k**. Yield 79% (method A), 69% (method B); mp 240–242°C; IR (ν/cm^{-1}): 3360, 3250 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 4.22 s (4H, $2CH_2$), 5.93 d (1H, CH, $J = 2.2$ Hz), 6.75–7.01 m (3H, H_{arom}), 7.17–7.43 m (5H, H_{arom}), 8.34 d (1H, NH, $J = 2.2$ Hz), 10.12 (1H, NH); ^{13}C NMR δ 57.86 (CH), 64.05, 64.10 ($2CH_2$), 77.35 (C^5), 116.40 (CN), 116.18, 117.19, 120.33, 125.56, 126.86, 128.92, 137.87, 143.16, 143.16, 144.06 (C_{arom}), 165.44 (C=O), 165.69 (C^6).

5-Cyano-2,2-dimethyl-6-phenylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3l**. Yield 85% (method A); mp 249–251°C (lit. 254–255°C [13]); IR (ν/cm^{-1}): 3230 (NH), 2230 (CN), 1670 (C=O); ^{1}H NMR δ 1.62 s (6H, $2CH_3$), 7.17–7.42 m (5H, H_{arom}), 8.11 s (1H, NH), 10.02 s (1H, NH); ^{13}C NMR δ 29.38 ($2CH_3$), 61.24 (C^2), 76.32 (C^5), 116.38 (CN), 125.79, 126.84, 128.95, 137.86 (C_{arom}), 164.36 (C^6), 165.21 (C=O).

5-Cyano-2-isopropyl-2-methyl-6-phenylamino-2,3-dihydro-1,3-thiazin-4(1H)-one **3m**. Yield 70% (method A); mp 211–213°C; IR (ν/cm^{-1}): 3320 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 0.93 d (3H, CH_3, $J = 6.4$ Hz), 0.96 d (3H, CH_3, $J = 6.4$ Hz), 1.48 s (3H, CH_3), 2.29 sept (1H, CH, $J = 6.4$ Hz), 7.17–7.40 m (5H, H_{arom}), 8.11 s (1H, NH), 9.96 s (1H, NH); ^{13}C NMR δ 16.82, 18.30 ($2CH_3$), 23.01 (CH_3), 36.50 (CH), 68.75 (C^2), 76.58 (C^5), 116.32 (CN), 125.58, 126.72, 128.95, 138.01 (C_{arom}), 164.10 (C=O), 164.70 (C^6).

5-Cyano-6-phenylamino-2,2-cyclopentyliden-2,3-dihydro-1,3-thiazin-4(1H)-one **3n**. Yield 75% (method A); mp 232–324°C; IR (ν/cm^{-1}): 3200 (NH), 2230 (CN), 1660 (C=O); ^{1}H NMR δ 1.57–1.81 m (4H, $2CH_2$), 1.95–2.06 m (4H, $2CH_2$), 7.17–7.46 m (5H, H_{arom}), 8.26 s (1H. NH), 10.03 s (1H, NH); ^{13}C NMR δ 22.52 ($2CH_2$), 39.91 ($2CH_2$), 69.93 (C^2), 77.10 (C^5), 116.34 (CN), 125.51, 126.65, 128.91, 138.06 (C_{arom}), 164.77 (C=O), 165.68 (C^6).

5-Cyano-6-phenylamino-2,2-adamantyliden-2,3-dihydro-1,3-thiazin-4(1H)-one **3o**. Yield 66% (method A); mp 260–262°C; IR (ν/cm^{-1}): 3300 (NH), 2230 (CN), 1650 (C=O); ^{1}H NMR δ 1.47–181 m (8H, H_{aliph}), 1.90–1.94 m (2H, H_{aliph}), 2.21–2.32 m (4H, H_{aliph}), 7.17–7.41 m (5H, H_{arom}), 7.93 s (1H, NH), 10.01 (1H, NH); ^{13}C NMR δ 25.83, 26.05, 31.91, 33.62, 35.87, 37.29 (C_{aliph}), 71.82 (C^2), 76.88 (C^5), 116.45 (CN), 125.27, 126.62, 128.97, 138.27 (C_{arom}), 161.14 (C^6), 164.25 (C=O).

General Procedure for Preparation of 1-Alkyl-(aryl)-5-cyano-6-methylthio-2,3-dihydropyrimidin-4(1H)-ones **4a–c,e–k,n**

To a stirred 0.75 N aqueous KOH solution (20 mL), compound **3a–c,e–k,n** (0.01 mol) and dimethyl sulfate (1.9 mL, 0.02 mol) were added successively. A resulting precipitate was filtered off, washed with water, dried, and recrystallized from ethanol.

5-Cyano-1-methyl-6-methylthio-2-phenyl-2,3-dihydropyrimidin-4(1H)-one **4a**. Yield 60%; mp; IR (ν/cm^{-1}): 3210 (NH), 2230 (CN), 1650 (C=O); ^{1}H NMR δ 2.56 s (3H, SCH_3), 3.47 s (3H, CH_3), 5.87 d (1H, CH, $J = 3.9$ Hz), 7.30–7.45 m (5H, H_{arom}), 8.49 d (1H, NH, $J = 3.9$ Hz); ^{13}C NMR δ 16.78 (SCH_3), 40.50 (CH_3), 71.43 (CH), 82.06 (C^5), 117.33 (CN), 125.59, 128.57, 128.65, 138.72 (C_{arom}), 161.76 (C=O), 165.63 (C^6).

5-Cyano-1-ethyl-6-methylthio-2-phenyl-2,3-dihydropyrimidin-4(1H)-one **4b**. Yield 73%; mp 179–181°C; IR (ν/cm^{-1}): 3300 (NH), 2230 (CN), 1670 (C=O); ^{1}H NMR δ 1.7 t (3H, CH_3, $J = 7.2$ Hz), 2.59 s (3H, SCH_3), 3.75 sex (1H, $C\underline{H}^AH^B$, $J = 7.2$ Hz), 4.02

sex (1H, $CH^A\underline{H}^B$, $J = 7.2$ Hz), 5.93 d (1H, CH, $J = 3.6$ Hz), 7.28–7.47 m (5H, H_{arom}), 8.58 d (1H, NH, $J = 3.6$ Hz); ^{13}C NMR δ 14.89, 16.92 ($2CH_3$), 48.29 (CH_2), 68.99 (CH), 84.45 (C^5), 117.02 (CN), 125.40, 125.52, 128.48, 139.30 (C_{arom}), 161.79 (C=O), 165.48 (C^6).

5-Cyano-1-ethyl-6-methylthio-2-phenyl-2,3-dihydropyrimidin-4(1H)-one **4c**. Yield 67%; mp 170–172°C; IR (ν/cm^{-1}): 3300 (NH), 2230 (CN), 1670 (C=O); ^{1}H NMR δ 1.20 t (3H, CH_3, $J = 7.0$ Hz), 1.50 s (6H, $2CH_3$), 2.65 s (3H, SCH_3), 3.75 qua (2H, CH_2, $J = 7.0$ Hz), 7.81 s (1H, NH); ^{13}C NMR δ 16.30 (CH_3), 18.01 (SCH_3), 25.61 ($2CH_3$), 42.28 (CH_2), 72.94 (C^2), 81.65 (C^5), 117.58 (CN), 161.67 (C=O), 165.21 (C^6).

5-Cyano-2-methyl-6-methylthio-1-phenyl-2,3-dihydropyrimidin-4(1H)-one **4e**. Yield 69%; mp 224–226°C; IR (ν/cm^{-1}): 3310, 3200 (NH), 2230 (CN), 1680 (C=O); ^{1}H NMR δ 1.46 d (3H, CH_3, $J = 6.6$ Hz), 2.13 s (3H, SCH_3), 5.01 m (1H, CH), 7.27–7.61 m (5H, H_{arom}), 8.10 d (1H, NH, $J = 1.8$ Hz); ^{13}C NMR δ 15.88, 19.94 ($2CH_3$), 69.15 (CH), 86.61 (C^5), 116.48 (CN), 126.50, 127.87, 129.50, 141.81 (C_{arom}), 160.67 (C=O), 164.74 (C^6).

(RR,RS)-5-Cyano-2-(6′,6′-dimethylbicyclo[3.1.1]hept-2′-en-2′-yl)-6-methylthio-1-phenyl-2,3-dihydro-1,3-thiazin-4(1H)-one **4f**. Yield 65%; mp 210–215°C; IR (ν/cm^{-1}): 3360 (NH), 2230 (CN), 1680 (C=O); ^{1}H NMR δ 0.80 s (1.5H, CH_3), 0.82 s (1.5H, CH_3), 1.13 m (1H, CH), 1.32 s (3H, CH_3), 2.04–2.49 m (9H, H_{aliph}), 5.16 s (0.35H, CH), 5.23 s (0.65H, CH), 5.55 d (0.35H, CH, $J = 4.8$ Hz), 5.60 d (0.65H, CH, $J = 4.8$ Hz), 7.27–7.52 m (5H, H_{arom}), 8.39 d (0.65H, NH, $J = 4.8$ Hz), 8.45 d (0.35H, NH, $J = 4.8$ Hz); ^{13}C NMR δ 15.18, 15.30 (SCH_3), 20.73 (CH_3), 25.87, 26.07 (CH_3), 30.71 (CH_2), 31.50, 31.62 (CH_2), 37.52, 37.77 (C_{quat}), 39.50 (CH), 42.00, 42.11 (CH), 73.89, 74.16 (CH), 89.45, 89.85 (C^5), 115.83, 116.02 (CN), 119.42, 121.19 (CH), 124.78, 125.07, 127.22, 129.69, 144.39 (C_{arom}), 143.39, 143.48 (C_{quat}), 160.04, 160.30 (C=O), 163.65, 164.00 (C^6).

5-Cyano-1,2-diphenyl-6-methylthio-2,3-dihydropyrimidin-4(1H)-one **4g**. Yield 78%; mp 217–219°C; IR (ν/cm^{-1}): 3310, 3200 (NH), 2230 (CN), 1680 (C=O); ^{1}H NMR δ 2.16 s (3H, SCH_3), 6.03 d (1H, CH, $J = 4.8$ Hz), 7.36–7.55 m (10H, H_{arom}), 8.81 d (1H, NH, $J = 4.8$ Hz); ^{13}C NMR δ 15.39 (SCH_3), 73.98 (CH), 89.74 (C^5), 115.87 (CN), 125.47, 126.08, 127.54, 128.68, 128.75, 129.80, 138.80, 143.03 (C_{arom}), 160.59 (C=O), 164.95 (C^6).

5-Cyano-6-methylthio-2-(4′-nitrophenyl)-1-phenyl-2,3-dihydropyrimidin-4(1H)-one **4h**. Yield 70%; mp 253–255°C; IR (ν/cm^{-1}): 3290 (NH), 2230 (CN), 1680 (C=O); ^{1}H NMR δ 2.18 s (3H, SCH_3), 6.20 d (1H, CH, $J = 6.9$ Hz), 7.38–7.54 m (5H, H_{arom}), 7.73 d (2H, H_{arom}, $J = 9.0$ Hz), 8.30 d (2H, H_{arom}, $J = 9.0$ Hz), 9.02 d (1H, NH, $J = 6.9$ Hz); ^{13}C NMR δ 15.30 (SCH_3), 73.31 (CH), 90.12 (C^5), 115.48 (CN), 123.91, 125.46, 127.54, 127.70, 129.83, 142.82, 146.30, 147.66 (C_{arom}), 160.23 (C=O), 165.43 (C^6).

5-Cyano-2-(2′,3′-dihydro-1,4-benzodioxin-6′-yl)-6-methylthio-1-phenyl-2,3-dihydropyrimidin-4(1H)-one **4k**. Yield 72%; mp 178–180°C; IR (ν/cm^{-1}): 3300 (NH), 2230 (CN), 1670 (C=O); ^{1}H NMR δ 2.14 s (3H, SCH_3), 4.25 s (4H, $2CH_2$), 5.89 d (1H, CH, $J = 3.9$ Hz), 6.81–6.92 m (3H, H_{arom}), 7.26–7.60 m (5H, H_{arom}), 8.76 d (1H, NH, $J = 3.9$ Hz); ^{13}C NMR δ 15.38 (SCH_3), 64.11 ($2CH_2$), 73.53 (CH), 89.54 (C^5), 115.92 (CN), 114.92, 117.28, 118.80, 125.41, 127.47, 129.75, 131.75, 142.93, 143.32, 143.65 (C_{arom}), 160.50 (C=O), 164.75 (C^6).

5-Cyano-6-methylthio-1-phenyl-2,2-cyclopentyliden-2,3-dihydro-1,3-thiazin-4(1H)-one **4n**. Yield 67%; mp 198–200°C; IR (ν/cm^{-1}): 3290, 3200 (NH), 2230 (CN), 1670 (C=O); ^{1}H NMR δ 1.59–1.85 m (8H, $4CH_2$), 2.32 s (3H, SCH_3), 7.28–7.33 m (2H, H_{arom}), 7.44–7.50 m (3H, H_{arom}), 8.37 s (1H, NH); ^{13}C NMR δ 16.93 (SCH_3), 21.48 ($2CH_2$), 36.49 ($2CH_2$), 82.84 (C^2), 86.30 (C^5), 116.65 (CN), 128.96, 129.30, 129.33, 139.87 (C_{arom}), 161.77 (C=O), 167.34 (C^6).

1-Alkyl(aryl)-6-benzylthio-5-cyano-2,3-dihydropyrimidin-4(1H)-ones **4d,l,m**

A mixture of compound **3d,l,m** (0.01 mol), benzyl chloride (1.39 g, 0.011 mol), and triethylamine (2.1 mL, 0.015 mol) in ethanol (20 mL) was boiled for 2 h. On cooling the solution, resulting crystals were filtered off, dried, and recrystallized from ethanol.

5-Cyano-1-benzyl-6-benzylthio-2-(4′-methoxyphenyl)-2,3-dihydropyrimidin-4(1H)-one **4d**. Yield 69%; mp 169–171°C; IR (ν/cm^{-1}): 3300, 3180 (NH), 2220 (CN), 1660 (C=O); ^{1}H NMR δ 3.75 s (3H, OCH_3), 4.19 d (1H, $C\underline{H}^AH^B$, $J = 13$ Hz), 4.36 d (1H, $CH^A\underline{H}^B$, $J = 13$ Hz), 4.65 d (1H, $C\underline{H}^AH^B$, $J = 16$ Hz), 5.34 d (1H, $CH^A\underline{H}^B$, $J = 16$ Hz), 5.68 d (1H, CH, $J = 3.6$ Hz), 6.90 d (2H, H_{arom}, $J = 10$ Hz), 7.10–7.41 m (12H, H_{arom}), 8.36 d (1H, NH, $J = 3.6$ Hz); ^{13}C NMR δ 38.22 (SCH_2), 55.10 (NCH_2), 55.17 (OCH_3), 69.21 (CH), 85.93 (C^5), 117.30 (CN), 113.94, 127.27, 127.84, 128.88, 130.31, 135.95, 136.41, 159.46 (C_{arom}), 161.36 (C=O), 162.29 (C^6).

5-Cyano-6-benzylthio-2,2-dimethyl-1-phenyl-2,3-dihydropyrimidin-4(1H)-one **4l**. Yield 69%; mp 233–235°C; IR (ν/cm^{-1}): 3300, 3190 (NH), 2230 (CN), 1670 (C=O); ^{1}H NMR δ 1.26 s (6H, 2CH$_3$), 4.05 s (2H, CH$_2$), 6.98–7.03 m (2H, H$_{arom}$), 7.14–7.18 m (2H, H$_{arom}$), 7.24–7.42 m (6H, H$_{arom}$), 8.11 s (1H, NH); ^{13}C NMR δ 26.68 (2CH$_3$), 37.77 (SCH$_2$), 73.43 (C^2), 86.08 (C^5), 117.09 (CN), 127.67, 128.50, 129.39, 135.85, 138.97 (C$_{arom}$), 161.11 (C=O), 161.62 (C^6).

5-Cyano-6-benzylthio-2-isopropyl-2-methyl-1-phenyl-2,3-dihydropyrimidin-4(1H)-one **4m**. Yield 63%; mp 234–236°C; IR (ν/cm^{-1}): 3300, 3200 (NH), 2230 (CN), 1670 (C=O); ^{1}H NMR δ 0.89–0.95 m (9H, 3CH$_3$), 2.49 m (1H, CH), 3.94 d (1H, C$\underline{\text{H}}^{\text{A}}H^{\text{B}}$, J = 12.9 Hz), 4.12 d (1H, CH$^{\text{A}}\underline{\text{H}}^{\text{B}}$, J = 12.9 Hz), 6.82 d (1H, H$_{arom}$, J = 7.5 Hz), 7.00–7.10 m (2H, H$_{arom}$), 7.25–7.53 m (7H, H$_{arom}$), 8.31 s (1H, NH); ^{13}C NMR δ 17.01, 17.57 (2CH$_3$), 20.58 (CH$_3$), 33.89 (CH), 37.38 (CH$_2$), 78.88 (C^2), 88.91 (C^5), 116.62 (CN), 127.71, 128.56, 128.75, 128.82, 129.32, 130.21, 135.36, 140.16 (C$_{arom}$), 160.29 (C=O), 162.92 (C^6).

3-Benzylthio-2-cyano-3-phenylaminoacrylamide **5a**

Method A. A mixture of compound **1d** (2.19 g, 0.01 mol), benzyl chloride (1.39 g, 0.011 mol), and triethylamine (2.1 mL, 0.015 mol) in ethanol (20 mL) was boiled for 2 h. On cooling the solution, a resulting precipitate was filtered off, dried, and recrystallized from ethanol. Yield 77%; mp 138–140°C; IR (ν/cm^{-1}): 3410, 3210 (NH), 2220 (CN), 1670 (C=O); ^{1}H NMR δ 3.83 s (2H, CH$_2$), 6.95 br s (1H, NH$_2$), 7.10–7.49 m (11H, H$_{arom}$, NH$_2$), 12.54 s (1H, NH).

Method B. 1.74 g (0.05 mol) of compound **4l** in 10 mL of the mixture of dioxane and concentrated HCl (1:1) was boiled for 2 h. On cooling the solution a mixture was diluted with 20 mL of water, a resulting precipitate was filtered off, dried, and recrystallized from ethanol. Yield 31%.

3-Methylthio-2-cyano-3-phenylaminoacrylamide **5b**

To a stirred 0.75 N aqueous KOH solution (20 mL), compound **3o** (0.01 mol) and dimethyl sulfate (1.9 mL, 0.02 mol) were added successively. A resulting precipitate was filtered off, washed with water, dried, and recrystallized from ethanol. Yield 32%; mp 151–153°C; ^{1}H NMR δ 2.13 s (3H, SCH$_3$), 7.12 br s (1H, NH$_2$), 7.24–7.43 m (6H, H$_{arom}$, NH$_2$), 12.55 s (1H, NH).

General Procedure for Preparation of 1-Alkyl(aryl)-5-cyano-6-mercapto-2,2-dimethyl-1-phenyl-2,3-dihydropyrimidin-4(1H)-one Potassium Salts **6a,b**

Compound **3b**,**h** (0.01 mol) was dissolved in 0.75 N aqueous KOH (20 mL) at heating. On cooling the solution, a resulting precipitate was filtered off, washed with water, and dried.

5-Cyano-1-ethyl-6-mercapto-2-phenyl-2,3-dihydropyrimidin-4(1H)-one **6a**. Yield 82%; mp 240–242°C; IR (ν/cm^{-1}): 3350 (NH), 2210 (CN), 1610 (C=O); ^{1}H NMR δ 1.04 t (3H, CH$_3$, J = 6.9 Hz), 3.03 sex (1H, C$\underline{\text{H}}^{\text{A}}H^{\text{B}}$, J = 6.9 Hz), 4.57 sex (1H, CH$^{\text{A}}\underline{\text{H}}^{\text{B}}$, J = 6.9 Hz), 5.59 (1H, CH, J = 3.9 Hz), 7.19–7.46 m (6H, H$_{arom}$, NH); ^{13}C NMR δ 13.61 (CH$_3$), 44.37 (CH$_2$), 69.03 (CH), 78.60 (C^5), 123.68 (CN), 126.11, 127.61, 128.15, 141.94 (C$_{arom}$), 164.10 (C=O), 184.37 (C^6).

5-Cyano-6-mercapto-1-phenyl-2-(4′-nitrophenyl)-2,3-dihydropyrimidin-4(1H)-one **6b**. Yield 75%; mp 270–274°C; IR (ν/cm^{-1}): 3380 (NH), 2210 (CN), 1620 (C=O); ^{1}H NMR δ 5.90 d (1H, CH, J = 4.0 Hz), 7.15–7.31 m (5H, H$_{arom}$), 7.62 d (2H, H$_{arom}$, J = 8.0 Hz), 7.86 d (1H, NH, J = 4.0 Hz), 8.27 d (2H, H$_{arom}$, J = 8.0 Hz); ^{13}C NMR δ 71.52 (CH), 83.37 (C^5), 122.37 (CN), 123.42, 125.21, 126.99, 127.63, 128.07, 145.50, 147.04, 149.52 (C$_{arom}$), 163.35 (C=O), 184.90 (C^6).

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