NEW PREPARATION OF 2-N-ALKYL(ARYL)AMINO-5-METHYL-4*H*-1,3-THIAZIN-4-ONES AND 3,4-DIHYDRO-5-METHYL-2,4-DIOXO-2*H*-1,3-THIAZINE

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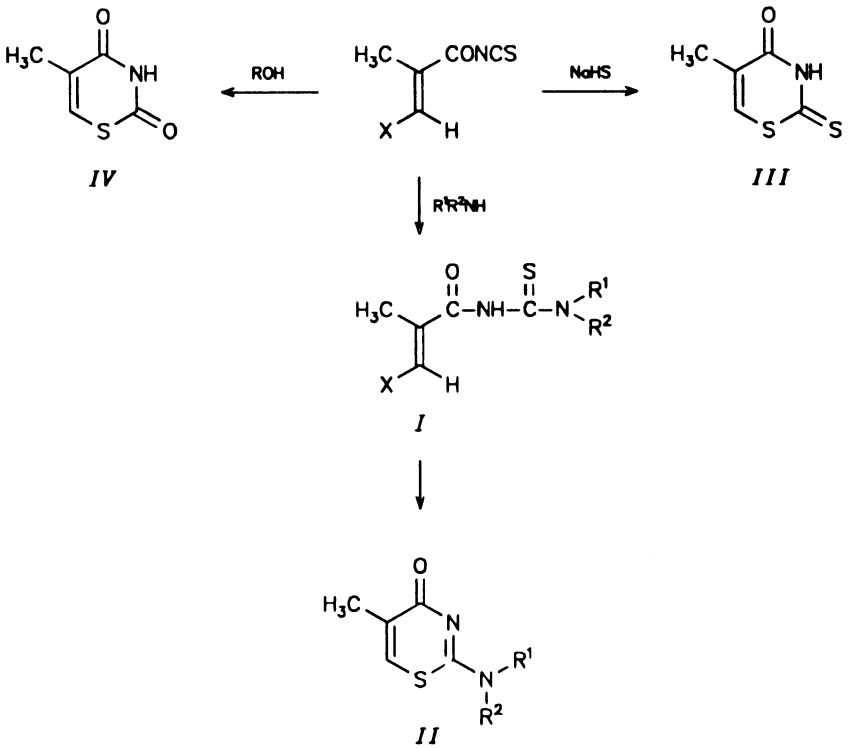
Addition-cyclization reactions of 3-bromo- and 3-chloro-2-methylpropenoylisothiocyanates with primary and secondary amines and alcohols have been studied. The formed addition products, thioureas, underwent cyclization on heating with ethanolic KOH or in dimethylformamide in the presence of lithium hydride. This method represents a new approach to 2-dialkyl(aryl)amino-5-methyl-4*H*-1,3-thiazin-4-ones. Addition reactions with alcohols afforded 3,4-dihydro-5-methyl-2,4-dioxo-2*H*-1,3-thiazine as the sole product. The structure of the synthesized compounds was confirmed by ^{1}H NMR, ^{13}C NMR, IR and mass spectroscopy.

The synthesis of 1,3-thiazines has been extensively studied[1 - 7]. A great number of references covering this subject have been compiled by Cain and Warrener[8]. Analogous syntheses of 2-amino-4*H*-1,3-thiazin-4-ones and their pyrimidine analogs were studied by Schroth[9] and other authors[10 - 12]. Aiming at the synthesis of biologically active compounds we tried to utilize our previous knowledge in the study of synthesis of thiazine and pyrimidine heterocycles.

As starting compounds we used 3-chloro- and 3-bromo-2-methylpropenoyl isothiocyanates obtained by reaction of 3-chloro- and 3-bromo-2-methylpropenoyl chlorides with potassium thiocyanate in acetone or with lead thiocyanate in heptane. These isothiocyanates react with amines to give thioureas *Ia – Ik* (Table I), with alcohols they afford directly 3,4-dihydro-5-methyl-2,4-dioxo-2*H*-1,3-thiazine (*IV*) and with sodium hydrogen sulfide 3,4-dihydro-5-methyl-2-thio-2*H*-1,3-thiazin-4-one (*III*) (Scheme 1). Because of the ambidental character of the thiocarbamoyl group (–CSNH–) in the thioureas *Ia – Ik*, the substitution of the bromine or chlorine atom in position 6 may proceed either with formation of thiazines (S-nucleophilicity) or pyrimidines (N-basicity), depending on the reaction conditions. In spite of the different electronegativity of chlorine and bromine bonded to the sp^2 carbon atom, we observed no differences in reactivity and stability of the corresponding chloro and bromo derivatives in the series *Ia – Ik*. The cyclization-elimination reaction of the thioureas *Ia – Ik* took place already on heating in chloroform or ethanol. With diphenylamine as nucleophile we isolated



I	X	R^1	R^2
a	Br	H	H
b	Br	H	C_2H_5
c	Br	H	4-BrC_6H_4
d	Br	H	4-$NO_2C_6H_4$
e	Br	H	4-Cl-2-$CH_3C_6H_3$
f	Br	$(CH_2)_2O(CH_2)_2$	

I	X	R^1	R^2
g	Cl	H	H
h	Cl	H	C_2H_5
i	Cl	H	4-ClC_6H_4
j	Cl	H	4-BrC_6H_4
k	Cl	$(CH_2)_2O(CH_2)_2$	
l	–	H	H

II	R^1	R^2
m	H	C_2H_5
n	H	4-BrC_6H_4
o	H	4-$NO_2C_6H_4$
p	H	4-Cl-2-$CH_3C_6H_3$
r	$(CH_2)_2O(CH_2)_2$	
s	C_6H_5	C_6H_5

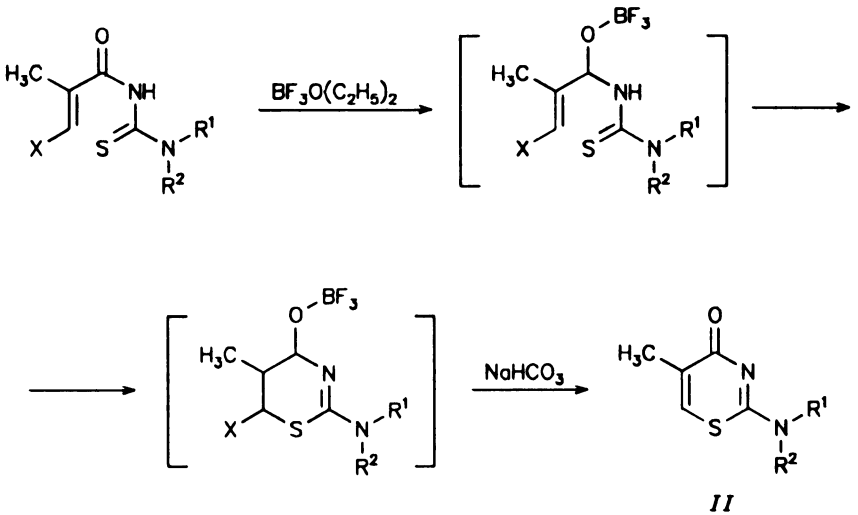
SCHEME 1

only hydrohalide of 1,3-thiazine *IIs* instead of the corresponding thiourea *Is*. Complete cyclization of these thioureas was achieved by treatment with KOH in ethanol (method *A*), with LiH in dimethylformamide (method *B*) or with boron trifluoride etherate (method *C*). Attempted Dimroth rearrangement of 1,3-thiazines to pyrimidines was unsuccessful. It is assumed[13] that the rearrangement of 1,3-thiazines to pyrimidines takes place only in the presence of hydrogen in position alpha (Scheme 2). The reaction mechanism is in accord with the investigations of Schroth. A pericyclic process is assumed in which the chlorine is substituted in an electrocyclic reaction or in an intramolecular variant of polar cycloaddition[9,13].

TABLE I
Physicochemical properties of N-alkyl(aryl)-N'-3-bromo(chloro)-2-methylpropenoylthioureas

Compound	Formula (M. w.)	M. p., °C (Yield, %)	Calculated/Found		
			% C	% H	% N
Ia	$C_5H_7N_2OSBr$ (223.1)	132 – 135 (85[a])	26.99 27.10	3.13 3.16	12.55 12.61
Ib	$C_7H_{11}N_2OSBr$ (251.1)	60 – 62 (76[b])	28.68 28.70	4.38 4.90	11.15 11.19
Ic	$C_{11}H_{10}N_2OSBr_2$ (378.1)	130 – 132 (81[b])	34.92 34.88	2.64 2.57	7.40 7.38
Id	$C_{11}H_{10}N_3O_3SBr$ (344.2)	129 – 132 (83[b])	38.37 38.42	2.90 2.88	12.20 12.15
Ie	$C_{12}H_{12}N_2OSBrCl$ (347.7)	147 – 149 (72[b])	41.49 41.38	3.45 3.41	8.06 8.09
If	$C_9H_{13}N_2O_2SBr$ (293.2)	172 – 174 (76[b])	36.86 36.80	4.43 4.39	9.55 9.61
Ig	$C_5H_7N_2OSCl$ (178.6)	128 – 130 (82[a])	33.70 33.81	3.93 3.90	15.73 15.69
Ih	$C_7H_{11}N_2OSCl$ (206.7)	71 – 73 (75[b])	40.77 41.02	5.33 5.36	13.59 13.61
Ii	$C_{11}H_{10}N_2OSCl_2$ (289.2)	124 – 126 (84[b])	45.67 45.70	3.46 3.48	9.68 9.72
Ij	$C_{11}H_{10}N_2OSBrCl$ (333.6)	110 – 112 (80[b])	39.63 39.70	3.00 3.02	8.40 8.46
Ik	$C_9H_{13}N_2O_3SCl$ (248.7)	131 – 132 (73[b])	43.54 43.60	5.24 5.28	11.29 11.31

Solvent: [a] $(CH_3)_2SO$; [b] $CHCl_3$.



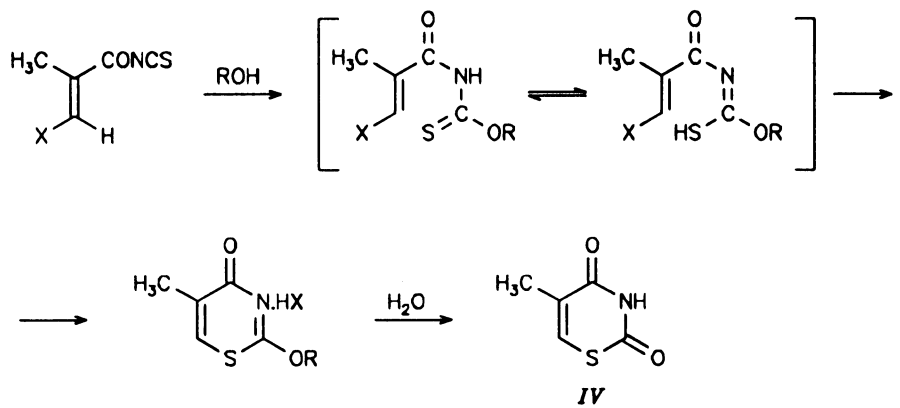
II

X = Cl; Br

R^1 = H; R^2 = 4-BrC_6H_4

SCHEME 2

On standing with alcohols for 24 h at room temperature, the synthesized isothiocyanates afford directly 3,4-dihydro-5-methyl-2,4-dioxo-2*H*-1,3-thiazine *IV* (Scheme 3).



IV

X = Cl; Br

R = CH_3; C_2H_5; $CH_2C_6H_5$; C_3H_7

SCHEME 3

The presence of moisture in the alcohols used is sufficient for the cleavage of the ether bond.

The above-mentioned isocyanates react with NaHS to give 3,4-dihydro-5-methyl-2-thio-2*H*-1,3-thiazin-4-one; even in the presence of methanol as solvent, the reaction with the sodium hydrogen sulfide is preferential.

In the IR spectra, thioureas *Ia – Ik* exhibit a characteristic broad thioamide band due to ν(NHCS) in the region 1 495 – 1 525 cm^{-1}, depending on the substituent. Their ^1H NMR spectra display characteristic signals of CH_3 and (–CH=) protons the position of which again depends on the substituents. In ^{13}C NMR spectra there are characteristic signals of CO carbon atoms at 165.4 – 167.13 δ (ppm) and CS carbon atoms at 177.8 – 183.45 δ (ppm) (Table II). In the IR spectra of thiazines *III – IIs* the ν(CO) band appears at lower values (1 600 – 1 625 cm^{-1}) (Table III) which is due to the –CO–N=C– conjugated system in the thiazine skeleton. Bands due to ν(C=N) vibrations in the synthesized 1,3-thiazines are in the region 1 475 – 1 535 cm^{-1} (Table IV). In accord with the suggested structure of thiazines *III*, *IIm*, *IIo*, and *IIs* are also their mass spectra which exhibit identical fragments *m/z* = 28, 72 and 100 that correspond to characteristic fragmentation of 2-N-alkyl(aryl)-amino-5-methyl-4*H*-1,3-thiazin-4-ones. These fragments are also characteristic of the thiazine types *III* and *IV*.

TABLE II
Spectral data for N-alkyl(aryl)-N′-3-bromo(chloro)-2-methylpropenoylthioureas

Compound	IR[a], cm^{-1}		^1H NMR, δ ppm		^{13}C NMR, δ ppm				
	ν(C=O)	ν(NH–C=S)	–CH=	$-CH_3$	=C=	–CH=	$-CH_3$	C=O	C=S
Ia[b]	1 675	1 525	8.1	2.27	137.25	120.94	16.24	167.07	183.31
Ib[b]	1 685	1 520	7.4	2.12	135.83	121.31	15.83	165.55	179.32
Ic[c]	1 675	1 500	7.58	2.13	135.46	120.08	15.75	165.43	177.83
Id[c]	1 680	1 495	7.85	2.21	136.18	121.43	16.11	166.12	179.93
Ie[c]	1 680	1 505	7.55	2.16	136.43	120.44	15.83	167.11	180.51
If[c]	1 685	1 510	7.37	2.05	134.93	121.03	16.18	166.41	179.13
Ig[b]	1 680	1 525	7.35	1.95	134.16	131.01	14.31	167.13	183.45
Ih[c]	1 675	1 500	7.25	2.10	132.66	131.21	13.44	165.77	179.36
Ii[c]	1 670	1 510	7.40	2.13	132.11	132.22	13.12	165.52	177.81
Ij[c]	1 670	1 500	7.30	2.06	132.14	132.29	13.07	165.66	177.83
Ik[c]	1 700	1 510	8.00	2.25	132.52	131.83	13.51	165.90	178.15

[a] In KBr; [b] NMR spectra measured in $(CD_3)_2SO$; [c] NMR spectra measured in $CDCl_3$.

EXPERIMENTAL

Infrared spectra were recorded on an IR-75 (Karl Zeiss, Jena) spectrometer in the region 400 – 4 000 cm^{-1}. Compounds *Ia – Ik* were measured in chloroform solutions, compounds *III – IIs* by the KBr technique. Proton NMR spectra were taken on a Tesla BS 487 A instrument at 80 MHz in $CDCl_3$ or $(CD_3)_2SO$, ^{13}C NMR spectra were obtained with a Tesla BS 567 A spectrometer at 25 MHz. In both cases TMS was used as internal standard. Mass spectra were measured on a Jeol IMS 100 D spectrometer at ionizing electron energy 70 eV. Elemental analyses were performed on a CHN Perkin–Elmer 2400 analyzer.

3-Bromo- and 3-chloro-2-methylpropenoic acids were prepared according to the published procedures[14 - 17], 3-bromo-2-methylpropenoyl chloride was synthesized as described in ref.[18]. The chloride is a yellow liquid boiling at 22 °C/399 Pa, in accord with the literature. 3-Chloro-2-methylpropenoyl chloride is a colourless liquid, b.p. 17 °C/399 Pa (again in accord with the published values[19]). In both cases the chlorides were the *Z*-isomers.

Preparation of 3-Bromo- and 3-Chloro-2-methylpropenoyl Isothiocyanates

Lead isothiocyanate (23.17 g, 0.072 mol) was added to 3-bromo-2-methylpropenoyl chloride (10 g, 0.055 mol) or 3-chloro-2-methylpropenoyl chloride (10 g, 0.072 mol) in heptane (40 ml) and the mixture was refluxed for 40 min. The hot solution was filtered, the solvent evaporated in vacuo and the residue distilled under reduced pressure.

3-Bromo-2-methylpropenoyl isothiocyanate, yield 8.7 g (78%), yellowish liquid b.p. 55 – 57 °C/399 Pa. IR spectrum, cm^{-1}: 1 595 (C=C), 1 680 (C=O), 1 950 (N=C=S). ^1H NMR spectrum: 2.08 s (CH_3), 8.05 s (CH). For C_5H_4BrNOS (206.2) calculated: 29.26% C, 1.95% H, 6.82% N; found: 29.11% C, 1.99% H, 6.79% N.

3-Chloro-2-methylpropenoyl isothiocyanate, yield 8.35 g (72%), b.p. 49 – 51 °C/399 Pa. IR spectrum, cm^{-1}: 1 600 (C=C), 1 680 (C=O), 1 955 (N=C=S). ^1H NMR spectrum: 2.07 s (CH_3), 7.8 s (CH). For C_5H_4ClNOS (161.8) calculated: 35.92% C, 2.39% H, 8.39% N; found: 35.86% C, 2.41% H, 8.40% N.

Preparation of N-Alkyl(aryl)-N'-3-bromo(chloro)-2-methylpropenoylthioureas *Ia – Ik*

The corresponding amine (0.01 mol) was added slowly to a stirred solution of 3-bromo-2-methylpropenoyl isothiocyanate (2.06 g, 0.01 mol) or 3-chloro-2-methylpropenoyl isothiocyanate (1.615 g, 0.01 mol) in dry diethyl ether (100 ml) under cooling to 0 °C. After addition, the reaction mixture was stirred for 2 h at room temperature, hexane (30 ml) was slowly added and the crystalline product was collected. The products were not crystallized because they were very unstable and easily underwent cyclization.

2-(N,N-Diphenylamino)-5-methyl-4*H*-1,3-thiazin-4-one (*IIs*)

A solution of diphenylamine (1.693 g, 0.01 mol) in diethyl ether was added to a stirred and cooled solution of 3-bromo-2-methylpropenoyl isothiocyanate (2.06 g, 0.01 mol) or 3-chloro-2-methylpropenoyl isothiocyanate (1.615 g, 0.01 mol) in diethyl ether (100 ml). The formed thiazine hydrohalide was filtered, dissolved in dimethylformamide (10 ml) and the solution was heated to 60 °C for 30 min.. After cooling, the product was precipitated with water, collected and crystallized from chloroform–hexane or acetone–hexane. Yield 1.85 g (63%), m.p. 133 – 134 °C. Mass spectrum, *m/z* (rel. int. %): 28 (33.4), 39 (15.9), 51 (23.2), 72 (11.6), 77 (42.0), 100 (8.7), 145 (17.4), 167 (10.1), 194 (63.8), 294 (100).

2-N-Alkyl(aryl)amino-5-methyl-4*H*-1,3-thiazin-4-ones *III – IIr*

Method A. N-Alkyl(aryl)-N'-3-bromo(chloro)-2-methylpropenoylthiourea (0.01 mol) was dissolved in a minimum volume of hot ethanol, potassium hydroxide (0.84 g, 0.015 mol) was added and the mixture was

TABLE III
Physicochemical data and analyses for 2-N-alkyl(aryl)amino-5-methyl-4*H*-1,3-thiazin-4-ones

Compound	Formula (M. w.)	Yield, % (Method[a])	M. p., °C	Calculated/Found		
				% C	% H	% N
IIl	$C_5H_6N_2OS$	49	224 – 226[b]	42.25	4.22	19.71
	(142.2)	(A)		42.20	4.14	19.76
IIm	$C_7H_{10}N_2OS$	47	131 – 133[c]	49.41	5.88	16.47
	(170.2)	(A)		49.51	6.01	16.51
IIn	$C_{11}H_9N_2OSBr$	97	186 – 188[b]	44.44	3.03	9.42
	(297.2)	(C)		44.52	3.06	9.51
IIo	$C_{11}H_9N_3O_3S$	78	254 – 256[b]	50.19	3.42	15.96
	(263.3)	(A)		50.20	3.49	15.88
IIp	$C_{12}H_{11}N_2OSCl$	42	175 – 177[b]	54.13	4.13	10.52
	(266.8)	(A)		54.20	4.11	10.61
IIr	$C_9H_{12}N_2O_2S$	58	82 – 84[b]	50.99	5.66	13.20
	(212.3)	(A)		50.91	5.48	13.31
IIs	$C_{17}H_{14}N_2OS$	63	133 – 134[c]	69.38	4.76	9.52
	(294.4)	–		69.41	4.79	9.60

[a] Method with highest yield; [b] $(CH_3)_2SO$; [c] $CHCl_3$.

TABLE IV
Spectral data for 2-N-alkyl(aryl)amino-5-methyl-4*H*-1,3-thiazin-4-ones

Compound	IR[a], cm^{-1}		^1H NMR, δ ppm		^{13}C NMR, δ ppm				
	ν(C=O)	ν(C=N)	–CH=	$-CH_3$	=C=	–CH=	C=O	C=N	$-CH_3$
IIl[b]	1 625	1 500	7.60	2.20	126.85	124.99	168.43	164.18	17.48
IIm[c]	1 605	1 535	7.08	2.12	127.37	125.14	168.47	162.39	18.30
IIn[b]	1 600	1 480	7.10	2.10	129.28	125.10	166.46	155.93	17.89
IIo[b]	1 610	1 505	7.93	2.16	128.89	125.60	166.33	160.36	17.95
IIp[b]	1 605	1 475	7.12	2.13	128.44	125.16	164.20	150.80	17.54
IIr[c]	1 620	1 500	7.11	2.13	127.36	125.53	169.43	163.57	18.89
IIs[c]	1 610	1 480	7.00	2.16	127.80	125.79	169.09	167.90	18.14

[a] In KBr; [b] NMR spectra measured in $(CD_3)_2SO$; [c] NMR spectra measured in $CDCl_3$.

refluxed for 30 min. After cooling, water (15 ml) was added and the mixture was slightly acidified with dilute (1 : 1) hydrochloric acid. The precipitate was filtered, washed with water (20 ml), dried and crystallized from an appropriate solvent.

Method B. A solution of N-alkyl(aryl)-N'-3-bromo(chloro)-2-methylpropenoylthiourea (0.01 mol) in dimethylformamide (10 ml) was heated at 60 °C for 15 min. Lithium hydride (0.08 g, 0.01 mol) was then added with stirring. After cooling, water (15 ml) was added and the mixture was slightly acidified with dilute (1 : 1) hydrochloric acid. The precipitate was collected, washed with water, dried and crystallized from an appropriate solvent.

Method C. N-Alkyl(aryl)-N'-3-bromo(chloro)-2-methylpropenoylthiourea (0.01 mol) was dissolved in a minimum amount of warm chloroform and stirred with boron trifluoride etherate (0.01 mol) for 15 min at room temperature. The mixture was then shaken for 10 min with sodium carbonate (2.12 g, 0.02 mol) in water (50 ml), the solid was filtered off, washed with water, dried and crystallized from a mixture of solvents.

2-Amino-5-methyl-4H-1,3-thiazin-4-one (IIIi), prepared by methods *A* and *B*, yield 0.7 g (49%) and 0.58 g (41.2%), respectively. M.p. 224 – 226 °C. Mass spectrum, *m/z* (rel. int. %): 28 (100), 32 (33.3), 43 (15.3), 45 (24.4), 55 (14.4), 57 (17.7), 72 (51.1), 100 (72.2), 115 (13.0), 142 (14.5).

2-N-Ethylamino-5-methyl-4H-1,3-thiazin-4-one (IIIm), prepared by method *A*, yield 0.8 g (47%). M.p. 131 – 133 °C. Mass spectrum, *m/z* (rel. int. %): 28 (100), 32 (37.7); 43 (29.5), 55 (13.3), 57 (12.2), 72 (79.3), 100 (58.4), 130 (11.0), 155 (25.5), 170 (62.2).

2-N-4-Bromophenylamino-5-methyl-4H-1,3-thiazin-4-one (IIIn), prepared by methods *B* and *C*, yield 2.02 g (68%) and 2.88 g (97%), respectively. M.p. 186 – 188 °C.

2-N-4-Nitrophenylamino-5-methyl-4H-1,3-thiazin-4-one (IIIo), prepared by methods *A* and *B*, yield 2.05 g (78%) and 1.77 g (67%), respectively. M.p. 254 – 256 °C. Mass spectrum, *m/z* (rel. int. %): 28 (100), 39 (23.7), 45 (20.3), 72 (94.9), 90 (22.0), 100 (93.2), 101 (98.0), 263 (89.8).

2-N-4-Chloro-2-methylphenylamino-5-methyl-4H-1,3-thiazin-4-one (IIIp), prepared by method *A*, yield 1.12 g (42%), m.p. 175 – 177 °C.

2-N-4-Morpholino-5-methyl-4H-1,3-thiazin-4-one (IIIr), prepared by method *A*, yield 1.23 g (58%), m. p. 82 – 84 °C.

3,4-Dihydro-5-methyl-2-thio-2*H*-1,3-thiazin-4-one (*III*)

3-Bromo- or 3-chloro-2-methylpropenoyl isothiocyanate (2.06 g or 1.615 g, 0.01 mol) was added dropwise to a stirred solution of NaHS (1.15 g, 0.02 mol) in dry acetone or methanol (25 ml). After addition, the reaction mixture was stirred for 15 min and then heated at 50 °C. The solvent was evaporated in vacuo, water (25 ml) was added and dilute hydrochloric acid (1 : 1) was added to neutral reaction. The precipitate was collected on filter, washed with water (20 ml) and dried, yield 0.76 g (48%). M.p. 177 – 178 °C. For $C_5H_5NOS_2$ (159.2) calculated: 37.73% C, 3.14% H, 8.80% N; found: 37.81% C, 3.12% H, 8.85% N. IR spectrum (KBr), cm^{-1}: 1 765 (CO), 1 540 (NH–C=S). ^1H NMR spectrum ($(CD_3)_2SO$): 7.8 s (–CH=), 2.2 t (CH_3). ^{13}C NMR spectrum: 136.52 (=C=), 126.70 (–CH=), 161.08 (C=O), 133.52 (C=S), 17.00 (CH_3). Mass spectrum, *m/z* (rel. int. %): 28 (61.6), 39 (35.4), 45 (40.4), 59 (14.1), 71 (60.6), 72 (100), 100 (69.7), 159 (80.8).

3,4-Dihydro-5-methyl-2,4-dioxo-2*H*-1,3-thiazine (*IV*)

A solution of 3-bromo-2-methylpropenoyl isothiocyanate (2.06 g, 0.01 mol) or 3-chloro-2-methylpropenoyl isothiocyanate (1.615 g, 0.01 mol) in methanol or ethanol (10 ml) was allowed to stand at room temperature for 24 h. The crystals were filtered, dissolved in hot dimethylformamide (10 ml) and after cooling the product was precipitated by addition of water (10 ml), yield 1.19 g (83%), m.p. 220 – 222 °C (reported[17] m.p. 222 – 223 °C). For $C_5H_5NO_2S$ (143.2) calculated: 41.95% C, 3.49% H, 9.79% N; found:

42.01% C, 3.51% H, 9.82% N. IR spectrum (KBr), cm^{-1}: 1 635 (NH–C=O), 1 650 (S–C=O). ^1H NMR spectrum: 7.8 s (–CH=), 2.25 s (CH_3). ^{13}C NMR: 132.12 (=C=), 124.95 (–C=), 164.59 (C=O), 164.59 (S–C=O), 16.89 (CH_3).

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