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1,3-Oxazines and Related Compounds. VI.[1] Synthesis and Some Reactions of 2,6-Disubstituted 4*H*-1,3-Thiazin-4-ones[2]

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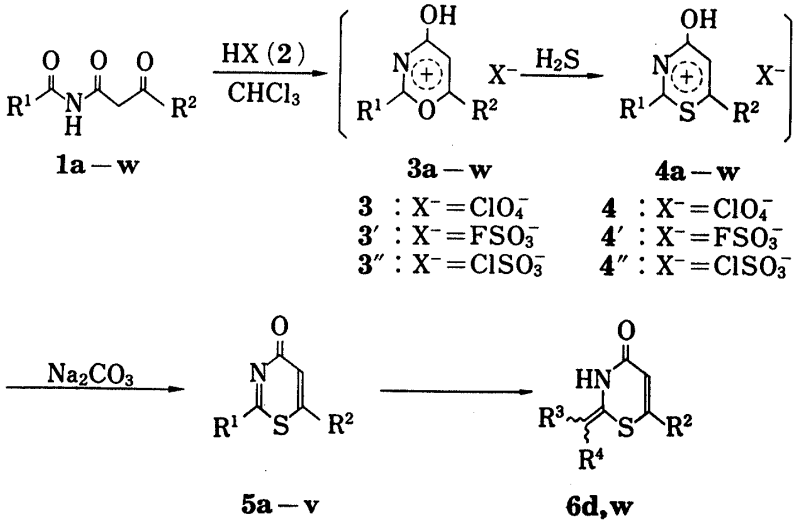
Various of 2,6-disubstituted 4*H*-1,3-thiazin-4-ones (**5**) were synthesized by successive treatment of *N*-acylacetylcarboxamides with acid (such as 70% perchloric acid or fluorosulfonic acid) and hydrogen sulfide. Reactions of **5** were investigated; ammonolysis with ethanolic ammonia gave the corresponding pyrimidin-4-ones; hydrolysis of 2-alkyl-1,3-thiazine derivatives yielded ring-opened *N*-acyl-*β*-mercaptocrotonamides; reduction with $NaBH_4$ or $LiAlH_4$ afforded 3,4-dihydro-2*H*-1,3-thiazin-4-one derivatives.

Keywords——1,3-thiazin-4-one; 3,4-dihydro-2*H*-1,3-thiazin-4-one; pyrimidin-4-one; 1,3-oxazinium salt; 1,3-thiazinium salt; *N*-acylacetylcarboxamide; *N*-acyl-*β*-mercaptocrotonamide

In a preliminary communication,[2] the synthesis of 1,3-thiazin-4-one derivatives *via* 1,3-oxazinium salts was reported. We wish to describe herein details of the synthesis of 1,3-thiazin-4-ones bearing various substituents at the 2- and 6-positions and some of their reactions, such as ammonolysis to pyrimidin-4-ones, ring-opening by hydrolysis, and reduction with



	R¹(R³,R⁴)	R²
a	Me	Me
b	Et	Me
c	*n*-Pr	Me
d	iso-Pr(Me,Me)	Me
e	*tert*-Bu	Me
f	Ph	Me
g	Ph	Et
h	Ph	iso-Pr
i	Ph	$PhCH_2$
j	Ph	$BrCH_2$
k	Me	Et
l	Me	iso-Pr
m	Me	$PhCH_2$
n	2-Py	Me
o	3-Py	Me
p	4-Py	Me
q	2-Py	Et
r	3-Py	Et
s	4-Py	Et
t	2-Py	$PhCH_2$
u	3-Py	$PhCH_2$
v	4-Py	$PhCH_2$
w	$PhCH_2$(Ph,H)	Me

Chart 1

metal hydrides to 3,4-dihydro-2*H*-1,3-thiazin-4-one derivatives.

Synthesis of 1,3-Thiazin-4-ones (5) from *N*-Acylacetylcarboxamides (1)

N-Acylacetylcarboxamides (**1**)[1] were readily converted into the corresponding 1,3-thiazin-4-one derivatives (**5**) by successive treatment with acid (**2**) and hydrogen sulfide (H_2S). For example, *N*-acetoacetylbenzamide (**1f**) in chloroform ($CHCl_3$) was treated with 70% perchloric acid ($HClO_4$, **2a**) in the presence of acetic anhydride, then with H_2S, leading to 6-methyl-2-phenyl-4*H*-1,3-thiazin-4-one (**5f**) (method A).

A probable pathway to **5** from **1** involves the sequential steps shown in Chart 1; this pathway is supported by the isolation of 1,3-oxazinium (**3f**) and 1,3-thiazinium (**4f**) salts, which are important key intermediates, and their identification on the basis of the spectral data (described in Experimental), although purification of **3f** was impeded by high sensitivity to moisture.

Similar treatment of *N*-acetoacetyl-isobutyramide (**1d**) and -phenylacetamide (**1w**) gave rise to 2-isopropylidene- (**6d**) and 2-benzylidene-1,3-thiazine derivatives (**6w**), respectively, which were formed by isomerization of the corresponding 2-isopropyl- (**5d**) and 2-benzyl-1,3-thiazine derivatives (**5w**). The 1,3-thiazine **5d** was isolated by recrystallization of the crude product in a freezer, whereas isolation of **5w** was unsuccessful. **5d** was isomerized easily to **6d** on being allowed to stand overnight at room temperature.

The structures of **5** and **6** were confirmed on the basis of spectroscopic and analytical data (Table II). ^{1}H-Nuclear magnetic resonance (^{1}H-NMR) spectra of **5** and **6** showed characteristic signals due to the proton at the 5-position on the 1,3-thiazine ring at δ 6.4—6.6 in **5** and at δ 5.8 in **6**.

Method A was found to be less effective for the synthesis of 2-pyridyl-1,3-thiazine derivatives (**5n—v**) from 2-, 3-, and 4-pyridinecarboxamides (**1n—v**). Hence, modification of method A was attempted by using a variety of acids in place of 70% $HClO_4$ solution. The employment of fluorosulfonic acid (FSO_3H, **2b**) gave better results, as shown in Table I. Thus, *N*-propionylacetylnicotinamide (**1r**), for instance, was treated with FSO_3H and then worked up by a procedure similar to that described in method A, giving 6-ethyl-2-(3-pyridyl)-4*H*-1,3-thiazin-4-one (**5r**) in a satisfactory yield (method B). Table II summarizes the results of the preparation of **5** (and **6**) and shows the availability of these methods for products with a variety of substituents at the 2- and 6-positions; attempts to prepare 6-phenyl-1,3-thiazine derivatives from *N*-benzoylacetylcarboxamides such as *N*-benzoylacetyl-acetamide, -benzamide, and -nicotinamide, however, resulted in the quantitative recovery of the starting carboxamides. On the other hand, 1,3-thiazine derivatives (**5a—c, k—m**) having an alkyl group at the 2-position such as methyl, ethyl, and *n*-propyl were found readily to undergo dimerization on being allowed to stand at room temperature. This dimerization will be the subject of a subsequent paper.[3]

Ammonolysis of 5 and 6 to Pyrimidin-4-ones (7)

1,3-Thiazin-4-one derivatives (**5** and **6**) smoothly underwent ammonolysis with ethanolic

TABLE I. Overall Yields of **5r** from **1r**

		Yield (%) of **5r**
2a	$HClO_4$–Ac_2O	18
2b	FSO_3H	52
2c	$ClSO_3H$	20
2d	CF_3SO_3H	40
2e	HBF_4·Et_2O	31
2f	BF_3·Et_2O	10
2g	CF_3COOH	Trace

TABLE II. Preparation of 1, 3-Thiazin-4-ones (**5a—v, 6d, w**)

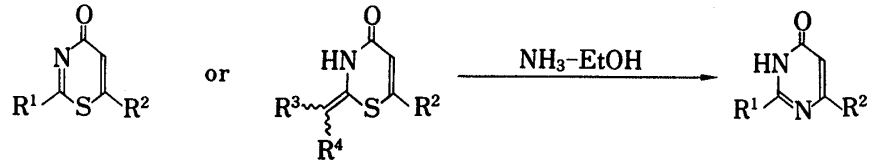
Compd.	Yield(%) (Method)	mp (°C) (Solvent) or bp (°C) (Torr)	IR (KBr) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ: 5-H	Formula	Analysis (%) Calcd (Found) C	H	N
5a	63 (A)	68—70 (0.04)	1640[a]	6.50	C_6H_7NOS[b]	—	—	—
5b	67 (A)	100—102 (0.02)	1650[a]	6.48	C_7H_9NOS[b]	—	—	—
5c	60 (A)	100—105 (0.05)	1640[a]	6.47	$C_8H_{11}NOS$[b]	—	—	—
5d	52 (A)	51—52 (Et_2O)[c]	1640	6.47	$C_8H_{11}NOS$	56.77 (56,48	6.55 6.48	8.28 8.58)
5e	71 (A)	70 (0.04)	1650[a]	6.40	$C_9H_{13}NOS$	58.98 (59.08	7.15 7.04	7.64 7.37)
5f	72 (A)	125—126 (AcOEt)	1640	6.53	$C_{11}H_9NOS$	64.95 (65.25	4.46 4.37	6.89 6.62)
5g	60 (A)	83—84 (Et_2O)	1645	6.58	$C_{12}H_{11}NOS$	66.33 (66.59	5.10 5.12	6.45 6.27)
5h	59 (A)	79—81 (Et_2O-P.E.)[d]	1640	6.63	$C_{13}H_{13}NOS$	67.50 (67.28	5.67 5.48	6.06 6.08)
5i	64.5 (A)	122—123 (AcOEt)	1640	6.63	$C_{17}H_{13}NOS$	73.09 (73.31	4.69 4.59	5.01 4.91)
5j	62 (A)	148—149 (acetone)	1635	6.83	$C_{11}H_8BrNOS$	46.83 (46.60	2.86 2.99	4.96 5.07)
5k	58 (A)	45—47 (0.15)	1650[a]	6.50	C_7H_9NOS[b]	—	—	—
5l	62 (A)	120 (0.5)	1650[a]	6.40	$C_8H_{11}NOS$[b]	—	—	—
5m	63 (A)	60—63 (0.1)	1650[a]	6.55	$C_{12}H_{11}NOS$[b]	—	—	—
5n	73.5 (B)	204—205 (acetone)	1650	6.60	$C_{10}H_8N_2OS$	58.81 (58.85	3.95 4.01	13.72 13.66)
5o	42 (B)	143—145 (C_6H_6)	1640	6.61	$C_{10}H_8N_2OS$	58.81 (58.83	3.95 3.82	13.72 13.64)
5p	48 (B)	113—114 (C_6H_6)	1650	6.63	$C_{10}H_8N_2OS$	58.81 (58.80	3.95 3.73	13.72 13.51)
5q	68.5 (B)	107—108 (C_6H_6-Et_2O)	1660	6.60	$C_{11}H_{10}N_2OS$	60.53 (60.61	4.62 4.41	12.83 12.72)
5r	52 (B)	94—95 (C_6H_6-Et_2O)	1650	6.62	$C_{11}H_{10}N_2OS$	60.53 (60.78	4.62 4.62	12.83 12.58)
5s	41 (B)	62—64 (Et_2O)	1650	6.67	$C_{11}H_{10}N_2OS$	60.53 (60.41	4.62 4.38	12.83 13.06)
5t	46 (B)	117—118 (Et_2O)	1640	6.63	$C_{16}H_{12}N_2OS$	68.55 (68.51	4.31 4.26	9.99 9.65)
5u	44 (B)	114—115 (CH_2Cl_2-Et_2O)	1645	6.63	$C_{16}H_{12}N_2OS$	68.55 (68.82	4.31 4.26	9.99 9.78)
5v	58.5 (B)	117—118 (C_6H_6-Et_2O)	1650	6.66	$C_{16}H_{12}N_2OS$	68.55 (68.26	4.31 4.49	9.99 10.12)
6d	63 (A)	153—155 (C_6H_6)	1650	5.80[e]	$C_8H_{11}NOS$	56.77 (56.79	6.55 6.53	8.28 7.99)
6w	73 (A)	160—161 (C_6H_6)	1660	5.80[f]	$C_{12}H_{11}NOS$	66.33 (66.62	5.10 5.04	6.45 6.23)

a) Taken neat.
b) These compounds readily underwent dimerization on being allowed to stand at room temperature, and their formulae were obtained by mass spectroscopy.
c) **5d** was obtained by recrystallization in a freezer.
d) P.E.=petroleum ether.
e) Other signals; 1.73 (6H,s,$(C\underline{H}_3)_2C$=C), 2.07 (3H,s,$C\underline{H}_3$), and 8.00(1H,br,N$\underline{H}$).
f) In $CDCl_3$-DMSO-d_6 (10:1).
Other signals; 2.07 (3H,s,$C\underline{H}_3$), 6.06 (1H,s,PhC$\underline{H}$=C),7.1—7.3(5H,m,$C_6\underline{H}_5$), and 9.83(1H,br,N$\underline{H}$).

ammonia leading to the corresponding pyrimidin-4-one derivatives (**7**) in high yields. The experimental data are summarized in Table III.

Hydrolysis: Ring-opening Reaction

2-Alkyl-1,3-thiazine derivatives (**5a—e, k—m, 6d, w**) were found to be hydrolyzed under mild conditions into ring-opened compounds, *N*-acyl-β-mercaptocrotonamides (**8**). Thus, **5a**



5a,f,g,i,n **6d** **7a—f**

Chart 2

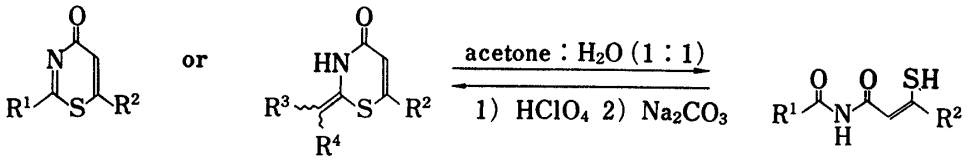
TABLE III. 2,6-Disubstituted Pyrimidin-4-ones (**7a—f**)

Compd.	R^1	R^2	Yield (%)	mp (°C) (Solvent)	Lit. mp (°C) or formula	IR (KBr) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ	
							5-H	NH[a]
7a	Me	Me	77.5	197—198 (Acetone)	195—195.5[4]	1660	6.13	13.56
7b	iso-Pr	Me	79	173—175 (Acetone)	172—173[4]	1680	6.13	12.33
7c	Ph	Me	76	216—218 (Acetone)	214—215[4]	1660	6.13	13.70
7d	Ph	Et	80	168—169 (Et_2O)	$C_{12}H_{12}N_2O$	1655	6.28	13.10
7e	Ph	$PhCH_2$	74	178—180.5 (C_6H_6)	$C_{17}H_{14}N_2O$	1650	6.13	12.93
7f	2-Py	Me	72	101—102 (C_6H_6)	96—97[5]	1685 1660	6.33	11.70

a) Exchageable with deuterium oxide.

in acetone–water (1 : 1) solution was allowed to stand at room temperature for 30 min to give *N*-acetyl-β-mercaptocrotonamide (**8a**). The other 2-alkyl-1,3-thiazines (**5b—e, k, m, 6w**) were similarly hydrolyzed. The results obtained are shown in Table IV. Prolongation of the reaction time caused further hydrolysis to yield *N*-acylacetylcarboxamide (**1**) accompanied with loss of H_2S. In contrast, the 1,3-thiazines (**5f—j, n—v**) possessing an aryl group such as phenyl or pyridyl at the 2-position were not affected under such conditions, even under reflux.

Recyclization of **8** took place very easily on successive treatment with 70% $HClO_4$ and sodium carbonate solution to give the corresponding 1,3-thiazines **5** in high yields.



5a—c,e,k,m **6d,w** **8a—h**

Chart 3

Reduction of 5 with $NaBH_4$ or $LiAlH_4$ to 3,4-Dihydro-1,3-thiazin-4-ones (9)

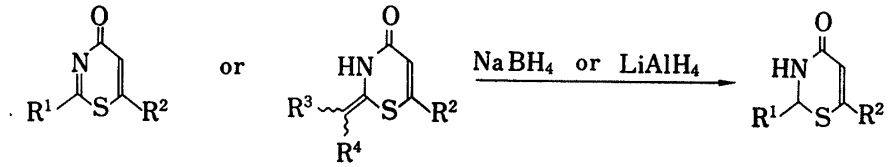
Reductions of 1,3-thiazin-4-ones **5** with sodium borohydride ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$) were carried out. In both cases, only the C=N double bond on the 1,3-thiazine ring was reduced to afford 3,4-dihydro-2*H*-1,3-thiazin-4-one derivatives **9** in good yields. Compound **9** was also obtained as a sole product, even when **5** was treated with excess $LiAlH_4$ in tetrahydrofuran (THF) under reflux. Table V summarizes the results of the reduction of **5** and **6** with $NaBH_4$.

TABLE IV. *N*-Acyl-β-mercaptocrotonamide Derivatives (**8a—h**)

Compd.	R^1	R^2	Yield (%)	mp (°C) (Solvent)	IR (KBr) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ		
						SH[a]	CH=C	NH[a]
8a	Me	Me	63	99 (Hexane)	1710 (sh) 1660	5.80	6.43	9.50
8b	Et	Me	60	98—99 (Hexane)	1710 (sh) 1660	5.77	6.57	9.16
8c	*n*-Pr	Me	66	92—92.5 (Hexane)	1700 (sh) 1660	5.80	6.60	9.20
8d	iso-Pr	Me	72	83—84 (Hexane)	1720 1650	5.73	6.87	9.33
8e	*tert*-Bu	Me	67	122—123 (Hexane)	1720 1650	5.93	7.20	7.87
8f	$PhCH_2$	Me	78	114—115 (Et_2O)	1730 1660	5.80	7.23	8.33
8g	Me	Et	62	76—77 (Hexane)	1710 1660	6.13	6.47	9.30
8h	Me	$PhCH_2$	75	118—120 (Et_2O)	1730 1660	5.67	6.47	9.37

a) Exchangeable with deuterium oxide.

Structural determination of **9** was accomplished on the basis of the spectral and analytical evidence. In the ^{1}H-NMR spectra of **9**, characteristic signals due to the proton at the 5-position on the 1,3-thiazine ring were observed at δ 5.9—6.0.



5a,k,f,i,n,r,s **6w** **9a—h**

Chart 4

TABLE V. 3,4-Dihydro-2*H*-1,3-thiazin-4-ones (**9a—h**)

Compd.	R^1	R^2	Yield (%)	mp (°C) (Solvent)	IR (KBr) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ		
						2-H	5-H	NH[a]
9a	Me	Me	72	132—134 (Et_2O)	1680 1660	4.93	5.90	7.43
9b	Me	Et	69	83—84 (Et_2O)	1660 1650	4.95	5.95	7.80
9c	$PhCH_2$	Me	75	179—180 (Acetone)	1660	5.03	5.93	6.70
9d	Ph	Me	80	166—168 (C_6H_6·Et_2O)	1660	5.93	6.00	6.35
9e	Ph	$PhCH_2$	83	175—176 (C_6H_6)	1655	4.95	5.95	7.80
9f	2-Py	Me	79	135—136 (C_6H_6)	1645	6.10	6.03	7.30
9g	3-Py	Et	78	133—134.5 (C_6H_6)	1650	5.95	6.00	7.76
9h	4-Py	Et	81	159—160 (C_6H_6)	1650	5.80	5.95	8.10

a) Exchangeable with deuterium oxide.

Experimental

Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube, and are uncorrected. Infrared (IR) spectra were taken on a Shimadzu IR-400 or IR-430 spectrometer. ^{1}H-NMR spectra were measured on a JEOL JNM-PMX 60 instrument. Chemical shifts are reported in δ values downfield relative to internal tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulfonate. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broad.

1,3-Oxazinium Salt (3f)——A 70% $HClO_4$ solution (1.5 ml, 17.5 mmol) was added dropwise to an ice-cooled solution of *N*-acetoacetylbenzamide (**1f**, 3 g, 15 mmol) and acetic anhydride (14 g, 137 mmol) in $CHCl_3$ (30 ml) with stirring. After a few minutes, 4-hydroxy-6-methyl-2-phenyl-1,3-oxazinium perchlorate (**3f**, 3.5 g) separated out as a colorless powder. An attempt to purify **3f** was unsuccessful, since **3f** was highly sensitive to moisture and underwent hydrolysis to give the starting **1f**. **3f** was also obtained by similar treatment of 6-methyl-2-phenyl-4*H*-1,3-oxazin-4-one[6] with 70% $HClO_4$. The ^{1}H-NMR spectrum (DMSO-d_6) of the crude **3f** showed a three-proton singlet at δ 2.35 (CH_3), a one-proton singlet at δ 6.21 ($C_{(5)}$–H), and a five-proton multiplet at δ 7.3—8.5 (C_6H_5) together with the signals of contaminating **1f** in a ratio of **3f**: **1f**=5: 2.

1,3-Thiazinium Salt (4f)——A 70% $HClO_4$ solution (1 ml, 11.7 mmol) was added dropwise to an ice-cooled solution of **1f** (2 g, 10 mmol) and acetic anhydride (5 g, 49 mmol) in $CHCl_3$ (20 ml) with stirring. H_2S was passed into the reaction mixture for 30 min at room temperature. The yellow precipitate was collected and recrystallized from acetonitrile to give **4f** (2.3 g, 76%), mp 135—140°C (dec.). The salt **4f** was also prepared by a similar treatment of **3f** with H_2S. IR ν_{max}^{KBr} cm^{-1}: 3400, 3000, 1590. ^{1}H-NMR (DMSO-d_6) δ: 2.43 (3H, s, CH_3), 6.63 (1H, s, $C_{(5)}$–H), 7.4—8.1 (5H, m, C_6H_5). *Anal.* Calcd for $C_{11}H_9NOS\cdot HClO_4$ (**4f**): C, 43.50; H, 3.30; N, 4.61. Found: C, 43.91; H, 3.59; N, 4.43. As the analytical result was not satisfactory, 4-hydroxy-6-methyl-2-phenyl-1,3-thiazinium chlorosulfonate (**4″f**), mp 138—142°C (dec.) (CH_3CN), was likewise prepared from **1f** and H_2S by using chlorosulfonic acid instead of 70% $HClO_4$ and acetic anhydride. *Anal.* Calcd for $C_{11}H_9NOS\cdot ClSO_3H$ (**4″f**): C, 41.32; H, 2.82; N, 4.38. Found: C, 41.39; H, 2.62; N, 4.44. IR ν_{max}^{KBr} cm^{-1}: 3400, 3000, 1590. ^{1}H-NMR (DMSO-d_6) δ: 2.40 (3H, s, CH_3), 6.68 (1H, s, $C_{(5)}$–H), 7.5—8.1 (5H, m, C_6H_5).

General Procedure for Synthesis of 5——Method A: A 70% $HClO_4$ solution (1 ml, 11.7 mmol) was added dropwise to an ice-cooled solution of *N*-acylacetylcarboxamide (**1**, 10 mmol) and acetic anhydride (5 g, 49 mmol) in $CHCl_3$ (70 ml) with stirring. After completion of the addition, the cooling bath was removed and stirring was continued for 30 min at room temperature. Subsequently, H_2S was passed into the reaction mixture for 30 min at room temperature. The resulting mixture was treated with saturated sodium carbonate (Na_2CO_3) solution and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over anhydrous potassium carbonate (K_2CO_3), and concentrated under reduced pressure. The resultant product was purified either by distillation or by recrystallization from the solvent indicated in Table II.

Method B: A typical procedure for **5n—v** in Table II was as follows. A solution of FSO_3H (1.1 g, 11 mmol) in $CHCl_3$ (70 ml) was added dropwise to an ice-salt cooled solution of *N*-propionylacetylnicotinamide (**1r**, 1.1 g, 5 mmol) with stirring. After completion of the addition, stirring was continued for 30 min at room temperature. H_2S was passed into the reaction mixture. The resulting solution was worked up by the procedure described above for method A. The crude product **5** was purified by recrystallization from the solvent indicated in Table II.

Ammonolysis into 2,6-Disubstituted Pyrimidin-4-ones (7)——A solution of **5** (5 mmol) or **6** (5 mmol) in ethanolic ammonia (10 ml of 95% ethanol and 10 ml of 28% ammonia aqueous solution) was heated for 20 min under reflux. A further 10 ml of 28% ammonia solution was added and heating was continued for another 20 min under reflux. The reaction mixture was concentrated under an aspirator-generated vacuum, followed by extraction with $CHCl_3$. The $CHCl_3$ layer was dried over K_2CO_3, filtered, and concentrated under reduced pressure. Recrystallization of the remaining crude product **7** was carried out from the solvent shown in Table III.

Hydrolysis of 5 and 6: Ring-opening Reaction——A solution of **5** (2 mmol) or **6** (2 mmol) in 10 ml of acetone–water (1: 1) was stirred for 30 min at room temperature. The reaction mixture was concentrated under reduced pressure. The residue was extracted with $CHCl_3$. The $CHCl_3$ layer was dried over anhydrous sodium sulfate, filtered, and then concentrated, to give crude **8**, which was purified by recrystallization from the solvent shown in Table IV.

Treatment of a solution of **8** and acetic anhydride in $CHCl_3$ with 70% $HClO_4$, followed by saturated Na_2CO_3 solution afforded the corresponding **5** or **6** in high yields.

Reduction of 5 and 6 to 3,4-Dihydro-2*H*-1,3-thiazin-4-one (9)——a) A solution of **5** (1 mmol) or **6** (1 mmol) in methanol (5 ml) was added dropwise to an ice-cooled solution of $NaBH_4$ (0.02 g, 0.53 mmol) in methanol (10 ml) with stirring. The reaction mixture was stirred for 1 h at room temperature, concentrated under reduced pressure, and then extracted with $CHCl_3$. The $CHCl_3$ layer was dried over K_2CO_3, filtered, and concentrated. The residue **9** was purified by recrystallization from the solvent indicated in Table V.

Experimental data are summarized in Table V.

b) A solution of $LiAlH_4$ (0.015 g, 0.4 mmol) and **5** (1 mmol) in THF (20 ml) was stirred for 30 min at room temperature. Water (30 ml) was added. The reaction mixture was concentrated under an aspirator-generated vacuum, followed by extraction with $CHCl_3$. The $CHCl_3$ layer was dried over K_2CO_3, filtered, and concentrated under reduced pressure to give crude **9**, which was purified by recrystallization from the solvent indicated in Table V. The yields were excellent.

TABLE VI. Elemental Analysis Data for New Compounds (**7d,e**, **8a—h**, **9a—h**)

Compd.	Formula	Analysis (%)					
		Calcd			Found		
		C	H	N	C	H	N
7d	$C_{12}H_{12}N_2O$	71.98	6.04	13.99	72.20	6.31	14.11
7e	$C_{17}H_{14}N_2O$	77.84	5.38	10.68	78.01	5.52	10.81
8a	$C_6H_9NO_2S$	45.26	5.70	8.80	45.20	5.65	8.77
8b	$C_7H_{11}NO_2S$	48.53	6.40	8.09	48.55	6.37	8.07
8c	$C_8H_{13}NO_2S$	51.31	7.00	7.48	51.37	7.11	7.22
8d	$C_8H_{13}NO_2S$	51.31	7.00	7.48	51.50	7.10	7.77
8e	$C_9H_{15}NO_2S$	53.70	7.51	6.96	53.41	7.20	7.00
8f	$C_{12}H_{13}NO_2S$	61.26	5.57	5.95	61.22	5.68	6.14
8g	$C_7H_{11}NO_2S$	48.53	6.40	8.09	48.62	6.69	7.90
8h	$C_{12}H_{13}NO_2S$	61.26	5.57	5.95	61.56	5.75	5.93
9a	C_6H_9NOS	50.33	6.34	9.78	50.60	6.61	10.01
9b	$C_7H_{11}NOS$	53.47	7.05	8.91	53.16	7.23	9.03
9c	$C_{12}H_{13}NOS$	65.72	5.98	6.39	65.67	5.95	6.30
9d	$C_{11}H_{11}NOS$	64.36	5.40	6.82	64.64	5.35	6.69
9e	$C_{17}H_{15}NOS$	72.59	5.37	4.98	72.90	5.39	4.74
9f	$C_{10}H_{10}N_2OS$	58.23	4.89	13.58	58.50	4.85	13.59
9g	$C_{11}H_{12}N_2OS$	59.98	5.45	12.72	59.67	5.41	12.48
9h	$C_{11}H_{12}N_2OS$	59.98	5.45	12.72	60.06	5.44	12.45

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