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Facile Formation of 1,3-Disubstituted 2,3,5,6-Tetrahydro-2-thioxopyrimidin-4(1*H*)-ones and 2-*N*,3-Disubstituted 2,3,5,6-Tetrahyro-2-imino-1,3-thiazin-4-ones from Thioureas and β-Haloacyl Halides

TADASHI OKAWARA, KENTARO NAKAYAMA and MITSURU FURUKAWA*

Faculty of pharmaceutical Sciences, Kumamoto University, 5-1, Oe-hon-machi, Kumamoto 862, Japan

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The reaction of 1,3-disubstituted thioureas (**1**) with β-haloacyl halides (**2**) was carried out in 5% NaOH-CH_2Cl_2 to afford 1,3-disubstituted 2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-ones (**3**) or 2-*N*,3-disubstituted 2,3,5,6-tetrahydro-2-imino-1,3-thiazin-4-ones (**4**) in yields of 51—63 or 54—68%, respectively.

Keywords——β-haloacyl halide; 1,3-disubstituted thiourea; 2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-one; 2,3,5,6-tetrahydro-2-imino-1,3-thiazin-4-one; cyclization

Thioureas are very versatile materials in the formation of heterocyclic ring systems,[1] and many reactions of thioureas with carboxylic acids and esters and aliphatic halides are known. Recently, we found that α-haloacyl halides and dichloroacetyl chloride readily reacted with thioureas under basic conditions to give 2-iminothiazolidin-5-ones[2] and their dimers, respectively.

In this paper, we newly examined a facile preparation of 1,3-disubstituted 2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-ones (**3**) and 2-*N*,3-disubstituted 2,3,5,6-tetrahydro-2-imino-1,3-thiazin-4-ones (**4**) by the reaction of 1,3-disubstituted thioureas (**1**) with β-haloacyl halides (**2**) in a solution of 5% sodium hydroxide-dichloromethane.

Many methods for the syntheses of 2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-ones[1,4] and 2,3,5,6-tetrahydro-2-imino-1,3-thiazin-4-ones[1,4,5] have already been reported. Unfortunately, most of these methods required anhydrous conditions. On the other hand, our method using a biphasic system (organic solvent and water) as the solvent in the presence of a phase transfer catalyst is convenient and has the advantage of making the work-up easier.

The reaction was successfully carried out by slowly adding **2** to a stirred solution of **1** in 5% NaOH-CH_2Cl_2, followed by stirring for 12 h at room temperature to afford **3** in 51—63% yields or **4** in 54—68% yields. The results are summarized in Table I.

In this reaction, the direction of cyclization was affected by the substituent at the α-position in β-haloacyl halide **2**. In the case of $R^3=CH_3$, the compounds **3** were obtained from the CH_2Cl_2 layer, and acidification of the aqueous solution with 6N HCl gave thioureido acids (**5**), which were readily converted to **3** in quantitative yields by refluxing with 6N HCl for 1 h.[6] On the other hand, in the case of $R^3=Br$, the compound **4**, in which the sulfur atom was involve in the heterocyclic ring, were obtained.

In the reaction of **1** with **2** (X=Cl, $R^3=CH_3$), the formation of 2,3,5,6-tetrahydro-1,3-thiazin-4-one (**6**) and the isomeric 6-one (**7**) along with **3** is also possible. The infrared spectra (IR) of the product showed thioureido and carbonyl absorptions at 1480—1505 and 1708—1716 cm^{-1}, respectively, and did not exhibit the imino absorptions. These data supported the assigned structure of **3**. The isomeric compound **8**, in which R^1 and R^2 are attached to N^1 and N^2 in the ring, respectively, is also possible.

In order to confirm the structure of **3**, the 2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-one (**3a**) prepared from 1-benzyl-3-phenylthiourea was hydrolyzed with 47% HBr, and 3-anilino-2,2-dimethylpropionic acid (**9**) was obtained in 60% yield. On the bases of this result it is evident

that the benzyl and phenyl groups are attached to the N^1 and N^3 atoms, respectively.

The reaction course is presumed to be as follows: the acyl halide **2** undergoes attack of the electron-rich nitrogen atom carrying the R^1 group, followed by cyclization at the electron-poor nitrogen atom carrying the R^2 group.

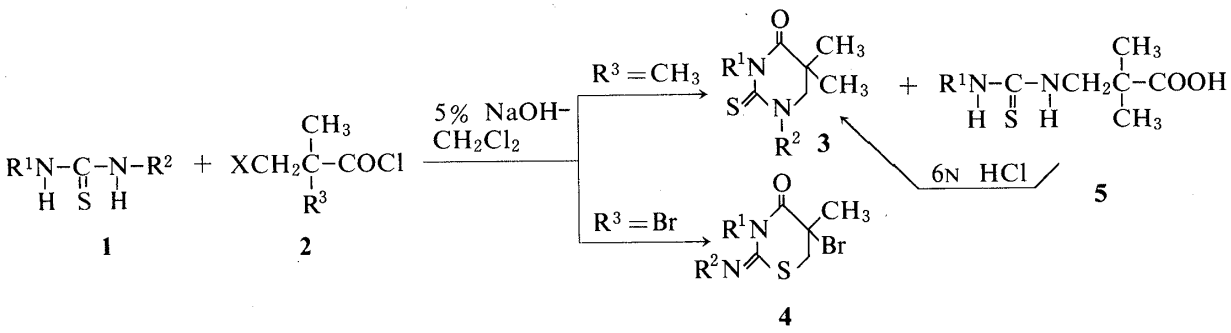


Chart 1

TABLE I. Preparations of 2,3,5,6,-Tetrahydro-2-thioxopyrimidin-4(1*H*)-ones (**3**) and 2,3,5,6,-Tetrahydro-2-imino-1,3-thiazin-4-ones (**4**)

	R^1	R^2	R^3	mp (°C)	Yield (%)
3a	$PhCH_2$	Ph	CH_3	88—89	51
3b	CH_3	Ph	CH_3	119—120	45
3c[a]	CH_3	$PhCH_2$	CH_3	Oil	55
3d[b]	(*S*)$PhCH_2CH(EtOOC)$	Ph	CH_3	118—119	63
4a	$PhCH_2$	Ph	Br	100—101	54
4b	CH_3	Ph	Br	106—107	57
4c[a]	CH_3	$PhCH_2$	Br	Oil	61
4d	Ph	Ph	Br	103—104	64
4e[b]	(*S*)$PhCH_2CH(EtOOC)$	Ph	Br	106—107	68

a) Another isomer (R^1=$PhCH_2$, R^2=CH_3) was contained in compounds **3c** and **4c**.
b) Hydrolysis of the ester was not observed under these reaction conditions.
3d: $[\alpha]_D^{18}$=−88.50°(*c*=2.0, $CHCl_3$). **4e**: $[\alpha]_D^{18}$=−20.94°(*c*=2.0, $CHCl_3$).

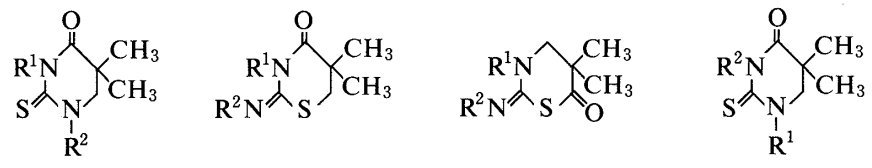


Chart 2

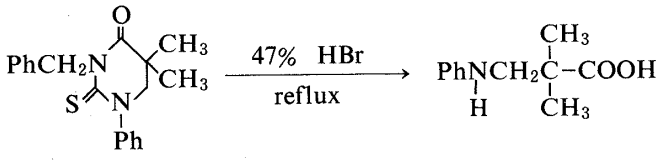
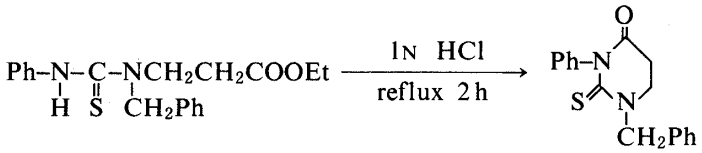


Chart 3

In this context, 1-benzyl-3-phenyl-2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-one (**11**) was prepared from 3-benzyl-3-ethoxycarbonylethyl-1-phenylthiourea (**10**), which was easily obtained from phenyl isothiocyanate and ethyl 3-benzylaminopropionate.

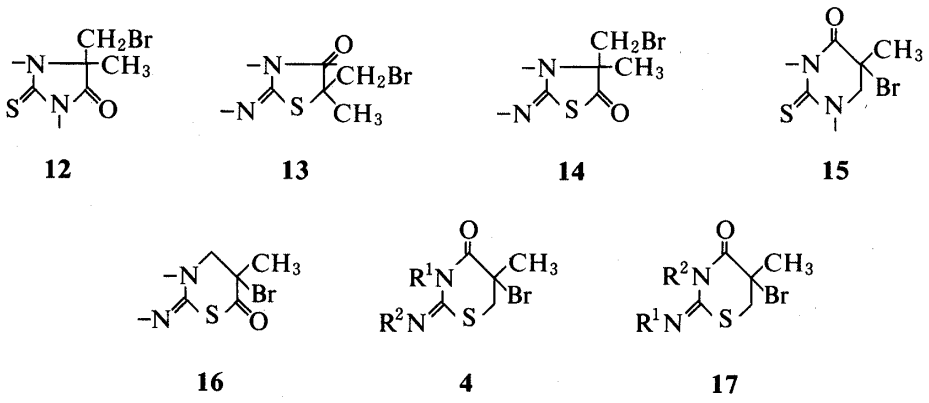


10 **11**

Chart 4

The cyclization of **10** was successfully achieved by treating it with 1N HCl under reflux to give **11** in 61% yield, whereas treatment with sodium ethoxide in ethanol was unsuccessful, giving ethyl *N*-phenyl thiocarbamate. The IR spectrum of **11** showed the thioureido and carbonyl absorptions at 1503 and 1708 cm^{-1}, respectively, and the ^{1}H-NMR spectrum exhibited the *N*-benzylic methylene signal at 5.30 ppm. This result also provides further support for the assigned structure of **3**.

In the reaction of **1** with **2** ($X=R^3=Br$), six isomeric compounds could be formed. They are the five-membered ring compounds, thiohydantoin (**12**), thiazolidin-4-one (**13**), and thiazolidin-5-one (**14**), and the six-membered ring compounds, 2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-one (**15**), 2,3,5,6-tetrahydro-1,3-thiazin-6-one (**16**), and 2,3,5,6-tetrahyro-1,3-thiazin-4-one (**4**).



12 **13** **14** **15**

16 **4** **17**

Chart 5

The IR spectra of the products showed absorptions of carbonyl and imino groups at 1725—1740 and 1620—1640 cm^{-1}, respectively. These data limited the possible structures to four, **13**, **14**, **16**, and **4**. In order to clarify the actual structure, compound **4a** ($R^1=PhCH_2$, $R^2=Ph$) obtained from 1-benzyl-3-phenylthiourea (**1**) and 2,3-dibromo-2-methylpropionyl chloride (**2**, $X=R^3=Br$) was subjected to hydrolysis by refluxing it in 15% NaOH–EtOH to afford 1-benzyl-3-phenylurea. Accordingly, **4** and **13** are possible structures of the product. In the ^{1}H-NMR spectra of the products, the methylene hydrogens showed doublet or quartet signals. These couplings seem to be attributable to the nonequivalent geminal hydrogens at C^6 in **4**, whereas the equivalent geminal hydorgens of the methylene group in **13** are expected to show a singlet signal. Therefore, the structure **13** is excluded, and the assigned structure **4** for the product is considered to be correct. Although the IR spectra of **4** showed the carbonyl absorption at considerably higher frequency (1725—1740 cm^{-1}) than ordinary carbonyl absorption, this is presumed to be due to a repulsion between the carbony group and bromine atom.

The reaction of **1** with **2** (X=R^3=Br) was assumed to proceed *via* *N*-acylation at the electron-rich nitrogen, followed by *S*-alkylation.

In the reaction of 1-benzyl-3-methylthiourea (**1**) with **2** (X=Cl, $R^3=CH_3$), both **3c** and the isomeric compound **8** ($R^1=PhCH_2$, $R^2=CH_3$) were formed, and the ratio was found from the ^{1}H-NMR spectra to be 69:31. Similarly, in the reaction with **2** (X=R^3=Br), **4c** and the isomeric compound **17** ($R^1=PhCH_2$, $R^2=CH_3$) were obtained as a mixture in the ratio of 57:43. Unfortunately, attempts to separate these isomeric compounds by silica-gel column chromatography resulted in failure.

The use of a phase transfer catalyst (benzyltriethylammonium chloride) in the reaction of **1** with **2** did not provide improved yields of **3** and **4**. When saturated $NaHCO_3$ instead of 5% NaOH was used, the yield of **4** was 46—64%, though the yield of **3** was rather lower than 11%.

Further applications and extensions of these reactions for the preparation of other heterocyclic compounds are being investigated.

Experimental

All the melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded with a JASCO IRA-1 grating infrared spectrometer. Nuclear magnetic resonance (^{1}H-NMR) spectra were determined with a JEOL-60 H high resolution NMR instrument. Mass spectra were measured with a JEOL-01 SG mass spectrometer.

1,3-Disubstituted Thioureas (1)———These compounds were prepared from isothiocyanates and amines in fairly good yields.[7] $R^1=PhCH_2$, $R^2=Ph$: mp 155—156°C. $R^1=CH_3$, $R^2=Ph$: mp 108—109°C. $R^1=PhCH_2$, $R^2=CH_3$: mp 70—71°C. $R^1=R^2=Ph$: 153—154°C. $R^1=(S)PhCH_2CHCOOEt$, $R^2=Ph$: mp 142—143°C. IR ν_{max}^{KBr} cm^{-1}: 3360 (NH), 3260 (NH), 1720 (C=O),1590 (Ph), 1530 (NCN). *Anal.* Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.63; H, 6.39; N,8.59.

2,3-Dibromo-2-methylpropionyl Chloride (2, X=R^3=Br) and 3-Chloro-2,2-dimethylpropionyl Chloride (2, X=Cl, $R^3=CH_3$)———These compounds were obtained from 2,3-dibromo-2-methylpropionic acid and 3-chloro-2,2-dimethylpropionic acid.[8]

General Procedure for Preparation of 1,2-Disubstituted 2,3,5,6-Tetrahydro-2-thioxopyrimidin-4(1*H*)-one (3) and 2-*N*,3-Disubstituted 2,3,5,6-Tetrahydro-2-imino-1,3-thiazin-4-one (4)———A β-haloacyl halide **2** (5 mmol) was added dropwise to a stirred solution of thiourea ***1*** (5 mmol) in 5% NaOH (5 ml) and CH_2Cl_2 (30 ml) under cooling with ice-water, and the solution was kept alkaline by adding 5% NaOH. When the addition was over, 5 ml of 5% NaOH was further added to the reaction mixture, and stirring was continued for 12 h at room temperature. The CH_2Cl_2 layer was separated, washed with H_2O (15 ml×2), dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by recrystallization from EtOH or by silica-gel column chro ›graphy (benzene:AcOEt=2:1). The melting points, yields, IR, ^{1}H-NMR and mass spectral data, and elemental analyses are listed in Tables I and II.

1,3-Disubstituted 3-(2-Carboxy-2-methylpropyl)thiourea (5)———In the case of $R^3=CH_3$, the aqueous layer separated as described above was acidified with 6N HCl. The precipitated compound was filtered off, and the filtrate was extracted with CH_2Cl_2 (15 ml). The extract was washed with H_2O (10 ml), dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue and the precipitate were combined and recrystallized from EtOH. $R^1=PhCH_2$, $R^2=Ph$: mp 162—163°C. Yield 17%. IR ν_{max}^{KBr} cm^{-1}: 3350 (NH), 1705 (C=O), 1600 (Ph), 1513 (NCN). NMR (δ) ($CDCl_3$): 1.30 (s, CH_3×2, 6H),4.73 (s, CH_2, 2H), 4.83 (s, CH_2, 2H), 5.67 (br, NH, 1H), 7.22 (s, Ph, 5H), 7.24 (s, Ph, 5H). Ms *m/e*: 342 (M^+). *Anal.* Calcd for $C_{19}H_{22}N_2O_2S$: C, 66.64; H, 6.48; N, 8.18. Found: C, 66.52; H, 6.63; N, 8.08. $R^1=CH_3$, $R^2=Ph$: mp 159—160°C. Yield 26%. IR ν_{max}^{KBr} cm^{-1}: 3280 (NH), 1695 (C=O), 1595 (Ph), 1510 (NCN). NMR (δ) ($CDCl_3$): 1.28 (s, CH_3×2, 6H), 3.02 (d, NCH_3, 3H, J=2.5Hz), 4.66 (s, CH_2, 2H), 7.07—7.33 (m, Ph, 5H), 7.83 (br, NH, 1H). *Anal.* Calcd for $C_{13}H_{18}N_2O_2S$: C, 58.62; H, 6.81; N, 10.52. Found: C, 58.64; H, 6.61; N,10.36.

3-Anilino-2,2-dimethylpropionic Acid (9)———Compound **3a** (200 mg, 0.6 mmol) was refluxed with 47% HBr (8 ml) for 4 h. The mixture was extracted with ether (5 ml), and the aqueous layer was evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of water and the solution was applied to an IR 120 column (H^+ form). The column was eluted with 1.5N aqueous ammonia and the desired fraction was evaporated to dryness under reduced pressure. The residue was recrystallized from EtOH to give **7**: Yield 71 mg (60%). mp 83—84°C. IR ν_{max}^{KBr} cm^{-1}: 3280 (NH), 1705 (C=O), 1595 (Ph). NMR (δ) ($CDCl_3$): 1.30 (s, CH_3×2,

TABLE II. 1,3-Disubstituted 2,3,5,6,-Tetrahydro-2-thioxopyrimidin-4(1*H*)-ones (**3**) and 2-*N*,3-Disubstituted 2,3,5,6,-Tetrahydro-2-imino-1,3-thiazin-4-ones (**4**)

	IR $\nu_{max}^{KBr(film)}$ (cm^{-1})	^{1}H-NMR(δ) in $CDCl_3$	$m/e(M^+)$	Analysis (%) Calcd (Found) C	H	N
3a	1710(C=O) 1490(NCN, ‖ S)	1.38 (s, CH_3×2, 6H), 3.66 (s, CH_2, 2H), 5.64 (s, Ph$\underline{CH_2}$, 2H), 7.17—7.57 (m, Ph×2, 10H)	324	70.34 (70.16	6.21 6.17	8.63 8.34)
3b	1716(C=O) 1490(NCN, ‖ S)	1.33 (s, CH_3×2, 6H), 3.60 (s, CH_3N, 3H), 3.64 (s, CH_2, 2H), 7.17—7.47 (m, Ph, 5H)	248	62.87 (62.80	6.50 6.48	11.28 11.17)
3c[a]	1710(C=O) 1505(NCN, ‖ S)	1.05 (s, CH_3×2, 6H), 3.20 (s, CH_2, 2H), 3.56 (s, CH_3N, 3H), 5.26 (s, Ph$\underline{CH_2}$, 2H), 7.34 (s, $\underline{Ph}CH_2$, 5H)	262	64.09 (63.86	6.91 6.90	10.68 10.33)
3d	1738(C=O) 1708(C=O) 1480(NCN, ‖ S)	1.23 (d, CH_3×2, 6H, J=2.0 Hz), 1.38 (t, $\underline{CH_3}CH_2O$, 3H, J=4.0 Hz), 3.12 (s, CH_2N, 2H), 3.53 (d, Ph$\underline{CH_2}$, 2H, J=4.0 Hz), 4.23 (q, $CH_3\underline{CH_2}$, 2H, J=4.0 Hz), 6.62 (t, CH, 1H, J=4.0 Hz) 6.90—7.42 (m, Ph, 5H), 7.25 (s $\underline{Ph}CH_2$, 5H)	410	67.29 (67.41	6.38 6.55	6.82 6.67)
4a	1740(C=O) 1640(C=N)	1.89 (s, CH_3, 3H), 3.80 (q, CH_2, 2H, J=11 Hz), 4.53 (s, CH_2N, 2H), 7.23 (s, Ph, 5H), 7.40 (s, $\underline{Ph}CH_2$, 5H)	390 388	55.53 (55.39	4.40 4.36	7.19 7.16)
4b	1730(C=O) 1625(C=N)	1.73 (s, CH_3 3H), 3.30 (s, CH_3N, 3H), 3.66 (q, CH_2, 2H, J=10 Hz), 6.90—7.43 (m, Ph, 5H)	314 312	46.02 (46.26	4.18 4.29	8.94 8.79)
4c[b]	1725(C=O) 1644(C=N)	1.71 (s, CH_3, 3H), 3.35 (s, CH_3N, 3H), 3.67 (s, CH_2, 2H), 4.43 (s, Ph$\underline{CH_2}$, 2H), 7.27 (s, Ph, 5H)	328 326	47.72 (47.72	4.62 4.63	8.56 8.25)
4d	1728(C=O) 1620(C=N)	1.85 (s, CH_3, 3H), 3.76 (q, CH_2, 2H, J=5.0Hz), 6.87—7.40 (m, Ph, 5H), 7.43 (s, Ph, 5H)	376 374	54.41 (54.36	4.03 4.20	7.46 7.58)
4e	1735(C=O) 1720(C=O) 1623(C=N)	1.25 (t, $\underline{CH_3}CH_2O$, 3H, J=3.5 Hz), 1.70 and 1.83 (s, CH_3, 3H), 2.93 and 3.17 (d, CH_2, 2H, J=2.5 Hz), 3.67 (m, CH, 1H), 4.13 (m, CH, 1H), 4.16 (q, CH_2O, 2H, J=3.5 Hz), 7.19 (s, Ph$\underline{CH_2}$, 5H), 7.12—7.50 (m, Ph, 5H)	476 474	55.58 (55.44	4.88 4.84	5.89 5.87)

a) ^{1}H-NMR shifts of the isomer (R^1=$PhCH_2$, R^2=CH_3): 1.21 (s, CH_3×2, 6H), 3.33 (s, CH_2, 2H), 3.53 (s, CH_3N, 3H), 5.53 (s, $PhCH_2$, 2H), 7.24 (s, Ph, 5H).

b) ^{1}H-NMR shifts of the isomer (R^1=$PhCH_2$, R^2=CH_3): 1.69 (s, CH_3, 3H), 3.06 (s, CH_3N, 3H), 3.63 (s, CH_2, 2H), 4.83 (s, Ph$\underline{CH_2}$, 2H), 7.23 (s, Ph, 5H).

6H), 3.23 (s, CH_2, 2H), 6.57 and 6.70 (s, $PhNH_2^+$, 2H), 7.05—7.33 (m, Ph, 5H). MS m/e: 193 (M^+). *Anal.* Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.32; H, 7.50; N, 7.27.

1-Benzyl-1-ethoxycarbonylethyl-3-phenylthiourea (10)———Phenyl isothiocyanate (2.1 g, 10 mmol) was gradually added to a stirred solution of ethyl 3-benzylaminopropionate (1.4 g, 10 mmol) in anhydrous Et_2O (20 ml) under cooling with ice-water. When the addition was over, the mixture was stirred for 1 h at room temperature then for 3 h under reflux, and allowed to stand overnight. The resulting precipitate was recrystallized from EtOH to give **8**. Yield 3.1 g (91%). mp 78—79°C. IR ν_{max}^{KBr} cm^{-1}: 3190 (NH), 1700 (C=O), 1590 (Ph), 1480 (NCN, ‖ S). NMR (δ) ($CDCl_3$): 1.22 (t, $\underline{CH_3}CH_2$, 3H, J=3.5 Hz), 2.69 (t, $N\underline{CH_2}CH_2$, 2H, J=3.0 Hz), 3.96 (t, CH_2CO, 2H, J=3.0 Hz), 4.12 (q, $O\underline{CH_2}CH_3$, 2H, J=3.5 Hz), 5.08 (s, $N\underline{CH_2}Ph$, 2H), 7.13—7.41 (m, Ph, 5H), 7.31 (s, $\underline{Ph}CH_2$, 5H), 8.48 (br, NH, 1H). *Anal.* Calcd for $C_{19}H_{22}N_2O_2S$: C, 66.64; H, 6.48; N, 8.18. Found: C, 66.31; H, 6.48; N, 8.01.

1-Benzyl-3-phenyl-2,3,5,6-tetrahydro-2-thioxopyrimidin-4(1*H*)-one (9)———Compound **8** (1.0 g, 3 mmol) was refluxed with 1 N HCl (10 ml) for 2 h. On cooling the reaction mixture with ice-water, **9** separated. It was filtered off, and recrystallized from EtOH. Yield 0.35 g (61%). mp 163—164°C. IR ν_{max}^{KBr} cm^{-1}: 1708 (C=O), 1599 (Ph), 1503 (NCN, ‖ S). NMR (δ) ($CDCl_3$): 2.80 (t, CH_2, H, J=3.5 Hz), 3.63 (t, CH_2, 2H, J=3.5 Hz),

5.30 (s, $PhCH_2$, 2H), 7.06—7.50 (m, Ph, 5H), 7.33 (s, $PhCH_2$, 5H). MS *m/e*: 296 (M^+). *Anal.* Calcd for $C_{17}H_{16}N_2OS$: C, 68.89; H, 5.44; N, 9.45. Found: C, 68.84; H, 5.49; N, 9.30.

1-Benzyl-3-phenylurea from 3-Benzyl-5-bromo-5-methyl-2-phenylimino-2,3,5,6-tetrahydro-1,3-thiazin-4-one (4a)———Compound **4a** (200 mg, 0.5 mmol) was refluxed with 15% NaOH (5 ml) and EtOH (15 ml) for 10 h. The mixture was allowed to stand overnight. The separated crystals were recrystallized from EtOH. Yield 90 mg (80%). mp 168—169°C. IR ν_{max}^{KBr} cm^{-1}: 3330 (NH), 3280 (NH), 1625 (C=O), 1600 (Ph). MS *m/e*: 226 (M^+). *Anal.* Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.76; H, 6.38; N, 12.30.

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