Synthesis of 2,3,5,6-Tetrahydro-4*H*-1,4-thiazin-3-one 1,1-Dioxides from Methyl (Styrylsulfonyl)acetate

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Methyl (styrylsulfonyl)acetate (**1**) was shown to be a useful building block for the synthesis of 5-phenyl-2,3,5,6-4*H*-tetrahydro-1,4-thiazin-3-one (**2**), its 4-amino **3**, and 4-hydroxy **4** derivatives. Their 2-spirocyclopropanes **9**, **10**, and **11**, and 2,7-diphenyl-6,7-dihydro-8*H*-pyrimido[5,4-*b*][1,4]thiazine 5,5-dioxide (**18**) were also prepared from **1**.

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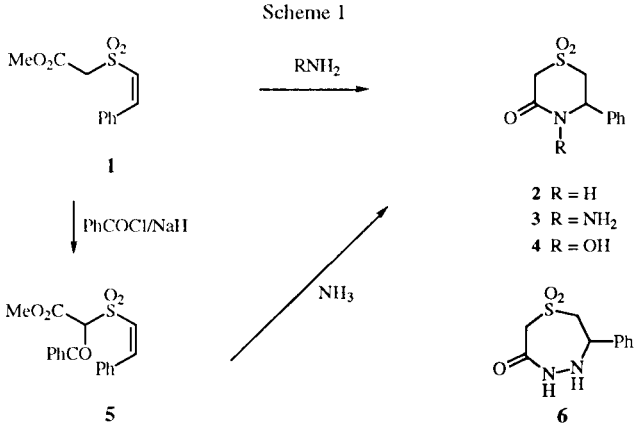
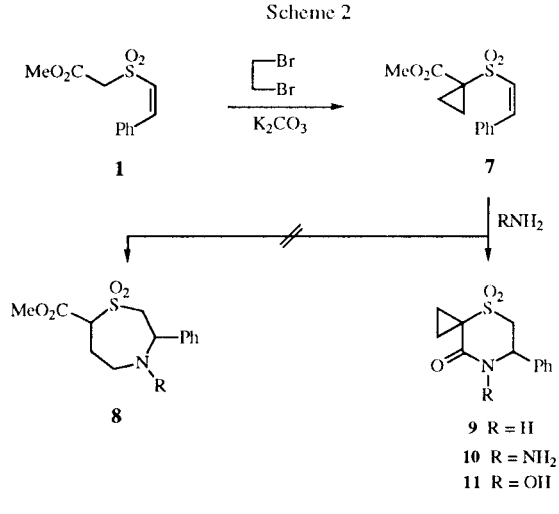
Recently vinyl sulfones [1] have been extensively studied from the view points of cycloaddition reactions [2], conjugate additions [3], and other synthetic tools [4]. However, little is known about vinyl sulfones which have an additional functional group on the sulfone group. In our continuous studies on the synthesis of heterocycles by use of sulfur derivatives, we have shown that methyl (styrylsulfonyl)acetate (**1**), a vinyl sulfone bearing an active methylene group, available readily from phenylacetylene and ethyl thioglycolate, served as a building block for 1,3,4-thiadiazine 1,1-dioxides [5]. In this reaction the cyclization of arylhydrazones of **1** occurred in a fashion of intramolecular conjugate addition to the vinyl sulfone moiety [6]. It is known that divinyl sulfone reacts with alkylamines [7] or *N*-methylhydroxylamine [8] to give 2,3,5,6-tetrahydro-4*H*-1,4-thiazine 1,1-dioxides, while arylamines needed aminomercuration-demercuration process to form the same ring [9]. The present study on the reactivities of the sulfone **1** revealed that simple amines such as ammonia, hydrazine, and hydroxylamine reacted with both vinyl and ester moieties of **1** to give 2,3,5,6-tetrahydro-4*H*-1,4-thiazin-3-one 1,1-dioxides.

Treatment of **1** with concentrated ammonia in methanol or methanolic ammonia at room temperature yielded 5-phenyl-2,3,5,6-tetrahydro-4*H*-1,4-thiazin-3-one 1,1-dioxide (**2**) in 70% yield (Scheme 1). Hydrazine hydrate also reacted at ice-cooled temperature to give 4-amino derivative **3** in 51% yield. A possibility of another structure, 1,4,5-thiadiazepin-3-one derivative **6**, was excluded on the basis of NH_2 resonance in the ^{1}H-nmr spectrum. 4-Hydroxy derivative **4** was produced in 44% yield on treatment of **1** with hydroxylamine at room temperature. However, *N*-substituted amines and hydrazines gave only complex mixtures. In our attempted functionalization of **1** we obtained benzoylated sulfone **5** from **1** and benzoyl chloride in the presence of sodium hydride. Reaction of **5** with ammonia gave also **2** on elimination of the benzoyl group. 2,3,5,6-Tetrahydro-4*H*-1,4-thiazin-3-ones have been prepared from the reaction of 2-aminoethanethiols and 2-chloroacetic acids [10]. However, their 1,1-dioxide derivatives are hardly known, and their pesticidal activities are reported in a patent [11]. Thus, condensation of amines with the ester group of **1** and their simultaneous conjugate addition to the vinylsulfone moiety provide a simple synthesis of 2,3,5,6-tetrahydro-4*H*-1,4-thiazin-3-one 1,1-dioxides.

Scheme 1



Scheme 2

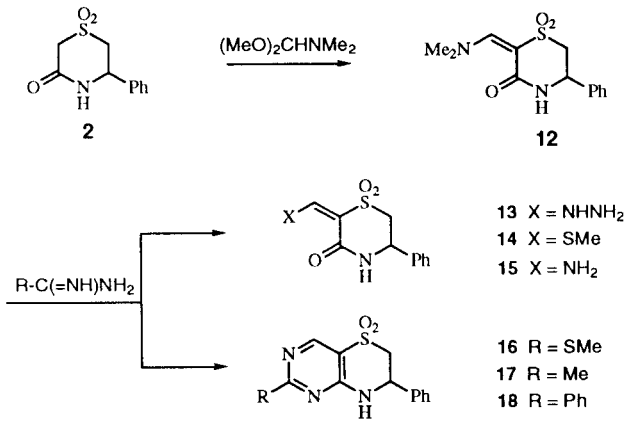


Cyclopropanation of β-sulfonyl ketones [12], β-sulfonyl esters [13], and α-chlorosulfones [14] were pre-

viously reported. On the other hand, activated cyclopropanes having electron-withdrawing groups are known to give ring-opened products by attack of nucleophiles [15]. These reports prompted us to attempt cyclopropanation of **1** and the ring-opening by amines followed by conjugate addition to the vinyl sulfone to afford 1,4-thiazepines **8** (Scheme 2). Cyclopropanation of **1** by 1,2-dibromoethane in the presence of potassium carbonate proceeded smoothly to give methyl 1-(styrylsulfonyl)cyclopropanecarboxylate (**7**) in 50% yield. Reaction of **7** with ammonia, however, gave 6-phenyl-4,4,8-trioxo-4-thia-7-azaspiro[2.5]octane (**9**) in 41% yield instead of the expected **8** (R = H). Cyclization to 1,4-thiazines **10** and **11** occurred similarly on treatment with hydrazine and hydroxylamine, respectively.

Previously, we reported dimethylaminomethylation of β-ketosulfones and their cyclization to pyrimidines [16] and pyrazoles [17]. Application of this method was undertaken to prepare pyrimido[5,4-*b*][1,4] thiazines and pyrazolo[4,3-*b*][1,4]thiazines. A mixture of **2** and *N,N*-dimethylformamide dimethylacetal in methanol was heated under reflux to give 2-(dimethylamino)methylene-1,4-thiazine (**12**) in 87% yield (Scheme 3). Cyclization of

Scheme 3



12 to pyrazolo[4,3-*b*][1,4]thiazine on treatment with hydrazine hydrate gave the intermediary hydrazino derivative **13** (91%). Attempted condensation of **12** with *S*-methylisothiourea yielded 2-(methylsulfuranyl)methylene derivative **14** (56%) instead of the expected condensed product **16**. Reaction with acetamidine similarly yielded 2-aminomethylene derivative **15** (50%), failing to form **17**. Finally, synthesis of the expected pyrimido[5,4-*b*][1,4]thiazine **18** was achieved in a low yield (16%) when benzamidine was used as the nucleophile. To date, there have been only limited reports about the cyclization of 1,4-thiazines to pyrimido[5,4-*b*][1,4]thiazines [18]. Some of these derivatives are regarded as 5-thiapterines, and were evaluated as a cofactor for phenylalanine hydroxylase [19].

EXPERIMENTAL

All melting points were determined with a MRK MEL-TEMP II and are uncorrected. The ir, mass, and ^{1}H-nmr spectra were recorded on a JASCO A-102, JEOL JMS-DX 300, and JEOL GSX-400, respectively. Microanalyses were performed with a YANAKO CHN Coder MT-5.

5-Phenyl-2,3,5,6-tetrahydro-4*H*-1,4-thiazin-3-one 1,1-Dioxide (**2**).

Method A.

A mixture of **1** [5] (7.20 g, 30 mmoles) and concentrated ammonia (20 ml) in methanol (100 ml) was stirred at room temperature overnight. The residue obtained after evaporation of the solvent was recrystallized from methanol to give **2** (4.38 g, 65%), mp 176-177°; ir (potassium bromide): 3470, 3180, 1655, 1400, 1310, 1120 cm^{-1}; ms: m/z 225 (M$^+$, 1), 160 (100), 120 (58); ^{1}H nmr (DMSO-d_6): δ 3.60 (dd, J = 12 and 14 Hz, 1H, C_6-H), 3.68 (ddd, J = 4, 4, and 14 Hz, 1H, C_6-H), 4.02 (dd, J = 4 and 17 Hz, 1H, C_2-H), 4.42 (d, J = 17 Hz, 1H, C_2-H), 4.79 (dd, J = 4 and 12 Hz, 1H, C_5-H), 7.33-7.77 (m, 5H, Ph), 8.58 (s, 1H, deuterium oxide-exchangeable, NH).

Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.31; H, 4.93; N, 6.22. Found: C, 53.48; H, 5.00; N, 5.91.

Method B.

Gaseous ammonia was bubbled into a mixture of **1** (480 mg, 2.0 mmoles) in methanol (8 ml) with stirring for 3 hours. After evaporation of the solvent the residue was recrystallized from methanol to give **2** (315 mg, 70%).

4-Amino-5-phenyl-2,3,5,6-tetrahydro-4*H*-1,4-thiazin-3-one 1,1-Dioxide (**3**).

To a stirred and ice-cooled mixture of **1** (480 mg, 2.0 mmoles) in ethanol (10 ml) was added hydrazine hydrate (150 mg, 3.0 mmoles), and the stirring was continued for one day. The precipitates formed were collected by filtration and were recrystallized from methanol to give **3** (241 mg, 51%), mp 215-217°; ir (potassium bromide): 3300, 2970, 1630, 1580, 1440, 1320, 1115 cm^{-1}; ms: m/z 240 (M$^+$, 17), 176 (12), 160 (14), 104 (100); ^{1}H nmr (DMSO-d_6): δ 3.82 (dd, J = 11 and 13 Hz, 1H, C_6-H), 3.90 (ddd, J = 5, 5, and 13 Hz, 1H, C_6-H), 4.19 (dd, J = 5 and 17 Hz, 1H, C_2-H), 4.65 (br s, 2H, NH_2), 4.80 (d, J = 17 Hz, 1H, C_2-H), 4.86 (dd, J = 5 and 11 Hz, 1H, C_5-H), 7.31-7.40 (m, 5H, Ph).

Anal. Calcd. for $C_{10}H_{12}N_2O_3S$: C, 49.98; H, 5.04; N, 11.66. Found: C, 49.81; H, 5.01; N, 11.83.

4-Hydroxy-5-phenyl-2,3,5,6-tetrahydro-4*H*-1,4-thiazin-3-one 1,1-Dioxide (**4**).

A mixture of **1** (240 mg, 1.0 mmole), hydroxylamine hydrochloride (109 mg, 1.6 mmoles), and sodium carbonate (165 mg, 1.6 mmoles) in a mixed solvent of methanol (3 ml) and water (3 ml) was stirred at room temperature for one day. The mixture was neutralized with dilute hydrochloric acid and extracted with ethyl acetate. After drying over magnesium sulfate, removal of the solvent left a solid, which was recrystallized from methanol to give **4** (105 mg, 44%), mp 126-127°; ir: 3500, 3150, 2910, 1630, 1300, 1130 cm^{-1}; ms: m/z 241 (M$^+$, 30), 160 (44), 104 (100); ^{1}H nmr (DMSO-d_6): δ 3.87 (dd, J = 10 and 14 Hz, 1H, C_6-H), 3.93 (ddd, J = 4, 5, and 14 Hz, 1H, C_6-H), 4.17 (dd, J = 4 and 16 Hz, 1H, C_2-H), 4.86-4.92 (m, 2H, C_2-H and C_5-H), 7.30-7.44 (m, 5H, Ph), 9.69 (s, 1H, OH).

Anal. Calcd. for $C_{10}H_{11}NO_4S$: C, 49.77; H, 4.60; N, 5.81. Found: C, 49.39; H, 4.65; N, 5.57.

Methyl 2-Benzoyl-2-(styrylsulfonyl)acetate (**5**).

Sodium hydride in oil (50%) (256 mg, 6.4 mmoles) was washed with hexane and suspended in tetrahydrofuran (5 ml) under nitrogen atmosphere. The mixture was refluxed, and was added with a solution of **1** (488 mg, 2.0 mmoles) in tetrahydrofuran (4 ml) dropwise during 5 minutes. A solution of benzoyl chloride (321 mg, 2.3 mmoles) in tetrahydrofuran (1 ml) was then added, and the mixture was refluxed for 3 hours. After cooling, water, ether, and dilute hydrochloric acid were added successively to the mixture, which was extracted with dichloromethane. Usual workup of the extract gave a resinous residue, which was recrystallized from ethanol to give **5** (582 mg, 83%), mp 110-112°; ir (potassium bromide): 1750, 1680, 1610, 1335, 1320, 1260, 1185, 1155, 1105 cm^{-1}; ms: m/z 281 (M^+, 9), 161 (8), 134 (36), 105 (100); ^1H nmr (deuteriochloroform): δ 3.80 (s, 3H, OCH_3), 5.86 (s, 1H, SO_2CH), 7.11 (d, J = 13 Hz, 1H, PhCH=), 7.29 (d, J = 13 Hz, 1H, SO_2CH=), 7.35-7.96 (m, 10H, 2Ph).

Anal. Calcd. for $C_{18}H_{16}O_5S$: C, 62.77; H, 4.69. Found: C, 62.95; H, 4.72.

Methyl 1-(Styrylsulfonyl)cyclopropanecarboxylate (**7**).

A mixture of **1** (240 mg, 1.0 mmole), potassium carbonate (334 mg, 2.4 mmoles), and 1,2-dibromoethane (282 mg, 1.5 mmoles) in freshly distilled *N,N*-dimethylformamide (2 ml) was stirred under nitrogen atmosphere for 2 days. The mixture was diluted with water and extracted with dichloromethane. The usual workup of the extract gave an oily residue, which was purified by column-chromatography on silica gel with an eluent of hexane-ethyl acetate (3:2) to give **7** (133 mg, 50%), oil; ir (neat): 3030, 1715, 1600, 1430, 1290, 1110 cm^{-1}; ms: m/z 266 (M^+, 6), 245 (6), 202 (9), 143 (100); ^1H nmr (acetone-d_6): δ 2.43 (s, 4H, CH_2CH_2), 4.11 (s, 3H, OCH_3), 7.39 (d, J = 12 Hz, 1H, PhCH=), 7.64 (d, J = 12 Hz, 1H, SO_2CH=), 7.78-8.10 (m, 5H, Ph).

Anal. Calcd. for $C_{13}H_{14}O_4S$: C, 58.62; H, 5.31. Found: C, 58.39; H, 5.35.

6-Phenyl-4,4,8-trioxo-4-thia-7-azaspiro[2.5]octane (**9**).

A mixture of the crude **7** prepared from **1** (240 mg, 1.0 mmole) as described above in methanol (4 ml) was added with concentrated aqueous ammonia (2 ml) and was stirred at room temperature for one day. Evaporation of the solvent left a solid, which was recrystallized from methanol to give **9** (102 mg, 41% from **1**), mp 203-205°; ir (potassium bromide): 3200, 3060, 1680, 1410, 1300, 1120 cm^{-1}; ms: m/z 251 (M^+, 1), 186 (100), 103 (26); ^1H nmr (DMSO-d_6): δ 1.47-1.71 (m, 4H, CH_2CH_2), 3.71 (dd, J = 12 and 15 Hz, 1H, C_6-H), 3.84 (dd, J = 4 and 15 Hz, 1H, C_6-H), 4.92 (dd, J = 4 and 12 Hz, 1H, C_5-H), 7.33-7.48 (m, 5H, Ph), 8.67 (s, 1H, NH).

Anal. Calcd. for $C_{12}H_{13}NO_3S$: C, 57.34; H, 5.22; N, 5.57. Found: C, 57.07; H, 5.13; N, 5.44.

7-Amino-6-phenyl-4,4,8-trioxo-4-thia-7-azaspiro[2.5]octane (**10**).

A mixture of crude **7** prepared from **1** (480 mg, 2.0 mmoles) as described above and hydrazine hydrate (240 mg, 4.0 mmoles) in ethanol (7 ml) was stirred at room temperature for 3 days. The precipitate was collected by filtration, and recrystallized from methanol to give **10** (222 mg, 42% from **1**), mp 184-186°; ir (potassium bromide): 3300, 1590, 1400, 1295, 1110 cm^{-1}; ms: m/z 266 (M^+, 59), 186 (49), 131 (59), 104 (100); ^1H nmr (DMSO-d_6): δ 1.51-1.77 (m, 4H, CH_2CH_2), 3.86 (dd, J = 10 and 14 Hz, 1H, C_6-H), 4.04 (dd, J = 5 and 14 Hz, 1H, C_6-H), 4.69 (s, 2H, NH_2), 5.04 (dd, J = 5 and 10 Hz, 1H, C_5-H), 7.29-7.41 (m, 5H, Ph).

Anal. Calcd. for $C_{12}H_{14}N_2O_3S$: C, 54.11; H, 5.31; N, 10.52. Found: C, 54.08; H, 5.39; N, 10.25.

7-Hydroxy-6-phenyl-4,4,8-trioxo-4-thia-7-azaspiro[2,5]octane (**11**).

To a solution of crude **7** prepared from **1** (480 mg, 2.0 mmoles) as described above in methanol (6 ml) was added a solution of hydroxylamine hydrochloride (208 mg, 3.0 mmoles) and sodium carbonate (318 mg, 3.0 mmoles) in water (6 ml). The mixture was stirred at room temperature overnight, concentrated, water added, and then extracted with ethyl acetate. The usual workup of the extract gave a solid residue, which was recrystallized from methanol to give **11** (150 mg, 28% from **1**), mp 210-211°; ir (potassium bromide): 3100, 2850, 1640, 1425, 1300, 1135 cm^{-1}; ms: m/z 267 (M^+, 60), 235 (17), 202 (32), 186 (49), 135 (52), 104 (100); ^1H nmr (DMSO-d_6): δ 1.50-1.78 (m, 4H, CH_2CH_2), 3.96 (dd, J = 8 and 12 Hz, 1H, C_6-H), 4.09 (dd, J = 4 and 12 Hz, 1H, C_6-H), 5.10 (dd, J = 4 and 8 Hz, 1H, C_5-H), 7.32-7.43 (m, 5H, Ph), 9.86 (d, 1H, deuterium oxide-exchangeable, OH).

Anal. Calcd. for $C_{12}H_{13}NO_4S$: C, 53.91; H, 4.91; N, 5.24. Found: C, 53.89; H, 4.97; N, 5.15.

2-(*N,N*-Dimethylamino)methylene-5-phenyl-2,3,5,6-tetrahydro-4*H*-1,4-thiazin-3-one 1,1-Dioxide (**12**).

A mixture of **2** (1.35 g, 6.0 mmoles) and *N,N*-dimethylformamide dimethylacetal (2.47 g, 21 mmoles) in methanol (15 ml) was refluxed for 2 hours. The precipitate began to separate out immediately after heating. After cooling the mixture was concentrated *in vacuo*, and the precipitate was collected by filtration to give the crude **12** (1.47 g, 87%), which was recrystallized from methanol to give pure **12**, mp 207-208°; ir (potassium bromide): 3140, 3000, 1590, 1360, 1310, 1270, 1105 cm^{-1}; ms: m/z 280 (M^+, 18), 174 (12), 98 (100); ^1H nmr (DMSO-d_6): δ 3.28 (s, 6H, $N(CH_3)_2$), 3.38 (dd, J = 3 and 14 Hz, 1H, C_6-H), 3.51 (dd, J = 12 and 14 Hz, 1H, C_6-H), 4.79 (dd, J = 3 and 12 Hz, 1H, C_5-H), 7.29-7.43 (m, 5H, Ph), 7.72 (s, 1H, NCH=), 7.82 (s, 1H, deuterium oxide-exchangeable, NH).

Anal. Calcd. for $C_{13}H_{16}N_2O_3S$: C, 55.69; H, 5.76; N, 9.99. Found: C, 55.75; H, 5.83; N, 9.74.

2-Hydrazinomethylene-5-phenyl-2,3,5,6-4*H*-tetrahydro-1,4-thiazin-3-one 1,1-Dioxide (**13**).

A mixture of **12** (280 mg, 1.0 mmole) and hydrazine hydrate (110 mg, 1.8 mmoles) in methanol (2 ml) was refluxed for 2 hours under a nitrogen atmosphere. Addition of a large amount of ethanol to this mixture resulted in the formation of a precipitate, which was collected by filtration and recrystallized from methanol to give **13** (243 mg, 91%), mp 193° dec; ir (potassium bromide): 3320, 3170, 1680, 1430, 1320, 1260, 1150 cm^{-1}; ms: m/z 267 (M^+, 95), 188 (12), 160 (13), 119 (38), 104 (100); ^1H nmr (DMSO-d_6): δ 3.30 (t, J = 11 and 14 Hz, 1H, C_6-H), 3.41 (dd, J = 4 and 14 Hz, 1H, C_6-H), 4.78 (dd, J = 4 and 11 Hz, 1H, C_5-H), 5.36 (s, 2H, deuterium oxide-exchangeable, N-NH_2), 7.32-7.43 (m, 5H, Ph), 7.56 (d, J = 10 Hz, 1H, deuterium oxide-exchangeable to singlet, =CH-N), 7.79 (s, 1H, deuterium oxide-exchageable,

CO-NH), 10.01 (d, J = 10 Hz, 1H, deuterium oxide-exchangeable, C-NH-N).

Anal. Calcd. for $C_{11}H_{13}N_3O_3S$: C, 49.42; H, 4.91; N, 15.72. Found: C, 49.19; H, 4.90; N, 15.78.

2-(Methylthio)methylene-5-phenyl-2,3,5,6-4*H*-tetrahydro-1,4-thiazin-3-one 1,1-Dioxide (**14**).

A mixture of **12** (840 mg, 3.0 mmoles), methylisothiourea sulfate (1.25 g, 9.0 mmoles), and sodium carbonate (477 mg, 9.0 mmoles) in a mixed solvent of methanol (9 ml) and water (6 ml) was stirred at room temperature for 2 days. A large amount of water was added to the mixture to precipitate the product, which was collected by filtration and was recrystallized from methanol to give **14** (481 mg, 56%), mp 253-255°; ir (potassium bromide): 3330, 1640, 1550, 1440, 1390, 1290, 1120 cm^{-1}; ms: m/z 283 (M^+, 83), 268 (33), 218 (32), 204 (45), 167 (29), 104 (100); ^1H nmr (DMSO-d_6): δ 2.47 (s, 3H, SCH_3), 3.63 (dd, J = 11 and 12 Hz, 1H, C_6-H), 3.68 (dd, J = 4 and 12 Hz, 1H, C_6-H), 4.79 (dd, J = 4 and 11 Hz, 1H, C_5-H), 7.28-7.43 (m, 5H, Ph), 8.27 (s, 1H, S-CH=), 8.47 (s, 1H, deuterium oxide-exchangeable, NH).

Anal. Calcd. for $C_{12}H_{13}NO_3S_2$: C, 50.85; H, 4.63; N, 4.94. Found: C, 50.89; H, 4.59; N, 4.90.

2-Aminomethylene-5-phenyl-2,3,5,6-4*H*-tetrahydro-1,4-thiazin-3-one 1,1-Dioxide (**15**).

A mixture of **12** (280 mg, 1.0 mmole), acetamidine hydrochloride (189 mg, 2.0 mmoles), and sodium carbonate (212 mg, 2.0 mmoles) in a mixed solvent of methanol (3 ml) and water (2 ml) was stirred at room temperature overnight and then at about 40° for one day. A large amount of water was added to the mixture to precipitate the product, which was collected by filtration and recrystallized from methanol to give **15** (125 mg, 50%), mp 216° dec; ir (potassium bromide): 3350, 3200, 1640, 1430, 1270, 1110 cm^{-1}; ms: m/z 252 (M^+, 17), 234 (18), 187 (100), 119 (68); nmr (DMSO-d_6): δ 3.34 (dd, J = 12 and 13 Hz, 1H, C_6-H), 3.41 (dd, J = 3 and 14 Hz, 1H, C_6-H), 4.78 (dd, J = 3 and 12 Hz, 1H, C_5-H), 7.08 (s, 1H, deuterium oxide-exchangeable, CONH), 7.30-7.44 (m, 5H, Ph), 7.57 (dd, J = 8 and 15 Hz, deuterium oxide-exchangeable to a singlet, N-CH=), 8.08 (br t, J = 5 and 8 Hz, 1H, deuterium oxide-exchangeable, C-NH), 8.69 (dd, J = 5 and 15 Hz, 1H, deuterium oxide-exchangeable, C-NH).

Anal. Calcd. for $C_{11}H_{12}N_2O_3S$: C, 52.36; H, 4.80; N, 11.10. Found: C, 52.10; H, 4.83; N, 11.02.

Compound **15** (66%) was also obtained from formamidine acetate in the same manner.

2,7-Diphenyl-6,7-dihydro-8*H*-pyrimido[5,4-*b*][1,4]thiazine 5,5-Dioxide (**18**).

A mixture of benzamidine sulfate (110 mg, 0.70 mmole) and sodium carbonate (74 mg, 0.70 mmole) in a mixed solvent of methanol (2 ml) and water (2 ml) was stirred at room temperature for 30 minutes. To the mixture was added **12** (141 mg, 0.50 mmole) , and the mixture was refluxed for 2 hours. After cooling, it was neutralized with dilute hydrochloric acid and extracted with ethyl acetate. After the usual workup of the extract, the solid residue was recrystallized from methanol to give **18** (27 mg, 16%), mp 243-244°; ir (potassium bromide): 3360, 1560, 1410, 1305, 1155 cm^{-1}; ms: m/z 337 (M^+, 70), 320 (100), 319 (96), 272 (19), 170 (16), 104 (100); ^1H nmr (DMSO-d_6): δ 3.75 (dd, J = 3 and 14 Hz, 1H, C_2-H), 3.95 (dd, J = 12 and 14 Hz, 1H, C_2-H), 5.09 (dd, J = 3 and 12 Hz, 1H, C_3-H), 7.37-8.35 (m, 10H, 2Ph), 8.80 (s, 1H, C_8-H), 9.03 (s, 1H, deuterium oxide-exchangeable, NH).

Anal. Calcd. for $C_{18}H_{15}N_3O_2S$: C, 64.07; H, 4.49; N, 12.46. Found: C, 64.05; H, 4.48; N, 12.34.

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