Condensed 1,3-Benzothiazinones. 2. Synthesis of 2-Substituted 1,2,4-Triazolo[5,1-*b*][1,3]benzothiazin-9-ones [1]

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Heating 3-amino-2-imino-3,4-dihydro-2*H*-1,3-benzothiazin-4-one (**1**) with formic acid neat or with trimethyl orthoformate (**2a**) in xylene gave 1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3a**) in 49 and 81% yields, respectively. An analogous reaction of **1** with triethyl orthoacetate (**2b**) and orthopropionate (**2c**), trifluoroacetic and trichloroacetic anhydride (**2d,e**), trichloroacetonitrile, dichloroacetyl, chloroacetyl, 2-chloropropionyl, 3-chloropropionyl, ethoxyoxalyl chloride (**2f-j**) and benzoyl chloride (**2k**) under suitable conditions afforded a series of 2-substituted 1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-ones (**3b-k**) in 59-98% yields. Facile procedures for the preparation of 2-hydroxy and 2-mercapto derivative **3l,m** were developed by treating **1** with *N,N'*-carbonyl- and thiocarbonyldiimidazole (**2l,m**). The structures of all products were assigned on the bases of spectral and elemental analyses. Compound **3m** was found to exist predominantly in the 2-thioxo form.

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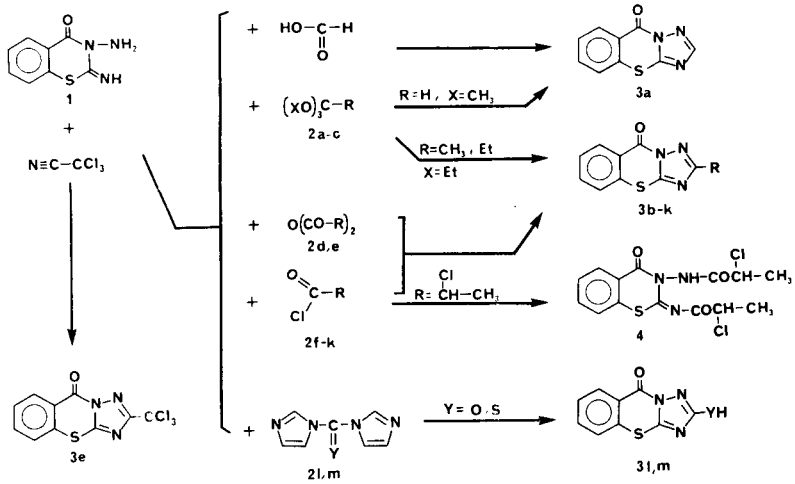
In the previous communication of this series [1], we reported an improved method for the preparation of 3-amino-2-imino-3,4-dihydro-2*H*-1,3-benzothiazin-4-one (**1**), a useful intermediate for the synthesis of condensed 1,3-benzothiazinones reported for the first time by Heindel and co-worker [2] in 1975. Now, we wish to describe the cyclocondensation of compound **1** with appropriate carboxylic acid derivatives. The reaction was first performed by heating **1** with an excess amount of formic acid neat under reflux for 8 hours. It gave 1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3a**) in 49% yield. An improvement of preparing this compound was achieved using trimethyl orthoformate (**2a**) by refluxing in xylene at about 140°. Compound **3a** was then obtained in 81% yield. When triethyl orthoacetate (**2b**) and orthopropionate (**2c**) were used in the above condensation, the corresponding 2-methyl- and 2-ethyl-1,2,4-triazolo[5,1-*b*][1,3]-benzothiazin-9-ones (**3b** and **3c**) were produced in almost the same yields (79 and 80%).

The reaction of compound **1** with carboxylic acid anhydrides was tried with trifluoro- and trichloroacetic anhydride **2d, 2e** by stirring at 0-5° for 12 hours. The products, 2-trifluoromethyl- and 2-trichloromethyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-ones (**3d** and **3e**) were isolated in 81 and 87% yields; respectively. Compound **3e** was further prepared in 62% yield by heating **1** with excess amount of trichloroacetonitrile neat at 85° for 24 hours according to a procedure we applied for construction of allied heterocyclic system [3].

The reaction of **1** with representative carboxylic acid chlorides was accomplished in dimethylformamide either by stirring at 0-5° for 12 hours or by heating under reflux



for 5 hours. The acid chlorides selected are dichloroacetyl, chloroacetyl, 2-chloropropionyl, 3-chloropropionyl chloride (**2f-2i**) and ethyl oxalyl chloride (**2j**). The cyclized products, 2-dichloromethyl-, 2-chloromethyl-, 2-(1-chloroethyl)-, 2-(2-chloroethyl)- and 2-(ethoxycarbonyl)-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-ones **3f-j** were obtained in 67-98% yield. It was a surprise that when **1** was treated with **2h** by stirring at 0-5°, a bi-acylated product, 3-(2-chloropropionamido)-2-(2-chloropropionimido)-3,4-dihydro-2*H*-1,3-benzothiazin-4-one (**4**) was isolated in 81% yield. Similar treatment of **1** with **2g,i,j** at this temperature gave **3g,i,j** in relatively lower yield (30-76%). Attempted ring closure of **4** though heating at ~150° for 2 hours was unsuccessful.

The reaction of **2** with benzoyl chloride (**2k**) was first tried by Heindel and Schaeffer [2] on heating in dioxan, where 2-phenyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3k**) was isolated in very low yield (11%). We carried out this reaction by heating **1** with excess amount of **2k** at 200° for 5 hours and obtained **3k** as white scales after recrystallization from ethanol in 77% yield. Though the melting point of our product was found to be 5-7° lower than that reported by the mentioned authors, the purity and structure of this compound were confirmed by thin-layer chromatography, spectral and elemental analysis.

Heindel and Schaeffer [2] reported further that when compound **1** was treated with phosgene in the presence of triethylamine by stirring at room temperature in tetrahydrofuran, 1,2-dihydro-1,2,4-triazolo[5,1-*b*][1,3]benzothiazine-2,9-dione was produced in 51% yield. However, no spectral data were provided to confirm the assigned structure, and in addition because of the involvement of highly toxic phosgene, this process was apparently very inconvenient for practical application. Wright [4] reported for the first time the use of *N,N'*-carbonyldiimidazole (**2l**) as a means of construction of the 2-oxo function in the 5-membered heterocyclic systems. Accordingly, we performed this reaction by heating **1** and **2l** in toluene [5] under reflux for 2 hours and then isolated a white crystalline product with a mp of 274-275° after recrystallization from a mixture of dimethylformamide and ethanol. The analytical data of this product are consistent with those of 1,2-dihydro-1,2,4-triazolo[5,1-*b*][1,3]benzothiazine-2,9-dione reported by Heindel and co-worker [2]. However, its depressed mp, *i.e.* 35-38° lower than that of this known compound suggested that our product might exist in the enol form. Such a structural feature was evidenced by the presence of an intense hydroxyl absorption band at 3490 cm^{-1} in the ir spectrum. And this function was also seen as a broad singlet at δ 12.50 ppm in the ^1H nmr spectrum.

An analogous reaction of **1** with *N,N'*-thiocarbonyldiimidazole (**2m**) was accomplished by stirring at room temperature in dimethylformamide. It gave the crystalline product also in 85% yield. Spectral analysis demonstrated that this compound existed just contrary to **3l**, in the 2-thioxo-1,2-dihydro form **3m**. The ir spectrum showed the heterocyclic NH absorption band at 3400 and the C=S stretching band at 1190 cm^{-1}. No signal of SH could be observed anywhere while an NH singlet was found immersed in the aromatic cluster at δ 7.01-7.96 ppm in the ^1H nmr spectrum.

Finally, it might be understood that starting from 3-amino-2-imino-3,4-dihydro-2*H*-1,3-benzothiazin-4-one a number of 2-substituted 1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-ones could be conveniently prepared in satisfactory yields by treating with different carboxylic acid derivatives under suitable conditions. The biological activities of these products are still under investigation and the results will be discussed elsewhere.

EXPERIMENTAL

All melting points were determined with Fisher Johns 5193-LK 328 apparatus and are uncorrected. The thin-layer chromatography was done on silica gel G, Merk, using ethyl acetate/*n*-hexane (4:3) as the developing system. The ultraviolet and infrared spectra were measured with Shimadzu 210A and Perkin Elmer 938 G spectrophotometers, respectively. The ^1H nuclear magnetic resonance and mass spectra were recorded on JEOL FX 100 or Bruker AM-300 WB and JEOL JMS-D 300 spectrometers, respectively. The elemental analyses were performed in the Instrument Center at National Taiwan University, Taipei and National Chengkung University, Tainan, Republic of China.

1,2,4-Triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3a**).

Procedure A.

A mixture of 3.9 g (0.02 mole) of **1** and 40 ml (0.7 mole) of formic acid was refluxed under stirring for 8 hours and then filtered while hot. The filtrate was diluted with 380 ml of 50% ethanol and allowed to stand at 4° overnight. The precipitate was collected and recrystallized from ethanol to give 2.0 g (49%) of pale yellow crystals, mp 213-214°, Rf 0.48; uv (ethanol): λ max (log ϵ) 223 (4.22), 236 (4.15), 316 (3.48) nm; λ min (log ϵ) 233 (4.12), 280 (2.79) nm; ir (potassium bromide): 3093, 3066 (=C-H), 1722 (C=O), 1594, 1495 (C=N/C=C), 1332 (C-N) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 7.56-8.04 (m, 3H, ArH), 8.06-8.57 (m, 1H, H-8), 8.59 (s, 1H, H-2); ms: (70 eV) m/z 203 (M^+, 100), 175 (M-CO, 27), 136 (C_6H_4COS, 10), 120 (C_6H_4CS, 36), 104 (C_6H_4CO, 16), 76 (C_6H_4, 18).

Anal. Calcd. for $C_9H_5N_3OS$: C, 53.19; H, 2.48; N, 20.68. Found: C, 53.15; H, 2.54; N, 20.66.

Procedure B.

A solution of 1.95 g (0.01 mole) of **1** and 2.2 g (0.02 mole) of trimethyl orthoformate (**2a**) in 100 ml of xylene was refluxed under stirring for 8 hours and then filtered while hot. The filtrate was concentrated under reduced pressure to about 30 ml and then allowed to stand at 4° overnight. The precipitate was collected and recrystallized from benzene to give 1.6 g (81%) of light yellow crystals, mp 213-214°.

2-Methyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3b**).

A solution of 3.9 g (0.02 mole) of **1** and 6.6 g (0.04 mole) of

triethyl orthoacetate (**2b**) in 200 ml of xylene was heated under reflux for 24 hours and then filtered while hot. The filtrate was concentrated under reduced pressure to about 50 ml and allowed to stand at 4° for 4 hours. The precipitate was collected and recrystallized from ethanol to yield 2.6 g (59%) of white crystals, mp 257-258°, Rf 0.42; uv (ethanol): λ max (log ε) 224 (4.23), 238 (4.09), 314 (3.50) nm; λ min (log ε) 233 (4.06), 280 (2.92) nm; ir (potassium bromide): 3086, 3006 (=C-H), 1710 (C=O), 1585, 1525 (C=N/C=C), 1306 (C-N) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 2.45 (s, 3H, CH_3), 7.65-8.00 (m, 3H, ArH), 8.47-8.49 (m, 1H, H-8); ms: (70 eV) m/z 217 (M^+, 100), 189 (M-CO, 13), 136 (C_6H_4COS, 37), 120 (C_6H_4CS, 22), 104 (C_6H_4CO, 12).

Anal. Calcd. for $C_{10}H_7N_3OS$: C, 55.29; H, 3.25; N, 19.34. Found: C, 55.30; H, 3.18; N, 19.58.

2-Ethyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3c**).

A solution of 1.95 g (0.01 mole) of **1** and 3.4 g (0.02 mole) of triethyl orthopropionate (**2c**) in 100 ml of xylene was heated under reflux for 8 hours and then worked out as described above to produce 1.9 g (80%) of white crystals, mp 184-185°, Rf 0.55; uv (ethanol): λ max (log ε) 224 (4.22), 238 (4.14), 314 (3.52) nm; λ min (log ε) 232 (4.09), 280 (2.90) nm; ir (potassium bromide): 3097, 3058 (=C-H), 1700 (C=O), 1591, 1512 (C=N/C=C), 1312 (C-N) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 1.30 (t, 3H, CH_3, J = 7.5 Hz), 2.81 (q, 2H, CH_2, J = 7.5 Hz), 7.65-7.99 (m, 3H, ArH), 8.46-8.49 (m, 1H, H-8); ms: (70 eV) m/z 231 (M^+, 100), 203 (M-CO, 8), 136 (C_6H_4COS, 75), 120 (C_6H_4CS, 11), 104 (C_6H_4CO, 10).

Anal. Calcd. for $C_{11}H_9N_3OS$: C, 57.13; H, 3.92; N, 18.17. Found: C, 57.11; H, 3.94; N, 18.28.

2-Trifluoromethyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3d**).

A solution of 1.95 g (0.01 mole) of **1** in 25 ml of dimethylformamide was kept at 0° and then treated by dropping 4.3 g (0.02 mole) of trifluoroacetic anhydride (**2d**). After stirring at 0-5° for 12 hours, the reaction mixture was poured into 380 ml of ice-water and the precipitate was collected on a filter, washed with water and recrystallized from ethanol to afford 2.2 g (81%) of fine crystals, mp 218-219°, Rf 0.75; uv (ethanol): λ max (log ε) 237 (4.36), 258 (4.07), 324 (3.61) nm; λ min (log ε) 249 (4.04), 283 (2.90) nm; ir (potassium bromide): 3057, 3018 (=C-H), 1715 (C=O), 1599, 1459 (C=N/C=C), 1307 (C-N), 766 (C-F), 745 (C-S) cm^{-1}; ms: (70 eV) m/z 271 (M^+, 100), 243 (M-CO, 23), 174 ($C_8H_4N_3S$, 20), 120 (C_6H_4CS, 52), 104 (10).

Anal. Calcd. for $C_{10}H_4F_3N_3OS$: C, 44.28; H, 1.49; N, 15.49. Found: C, 44.15; H, 1.44; N, 15.52.

2-Trichloromethyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3e**).

Procedure A.

A solution of 1.95 g (0.01 mole) of **1** in 25 ml of dimethylformamide was treated with 6.2 g (0.02 mole) of trichloroacetic anhydride (**2e**) at 0-5° and worked out as described above to give 2.7 g (81%) of brown scale crystals, mp 193-194°, Rf 0.75; uv (ethanol): λ max (log ε) 238 (4.52), 330 (3.63) nm; λ min (log ε) 284 (2.80) nm; ir (potassium bromide): 3085, 3025 (=C-H), 1719 (C=O), 1589, 1492 (C=N/C=C), 1347 (C-N), 824 (C-Cl), 742 (C-S) cm^{-1}; ms: (70 eV) m/z 320 (M^+, 20), 284 (M-Cl, 100), 256 (284-CO, 16), 136 (C_6H_4COS, 15), 120 (10).

Anal. Calcd. for $C_{10}H_4Cl_3N_3OS$: C, 37.47; H, 1.26; N, 13.11. Found: C, 37.46; H, 1.22; N, 13.11.

Procedure B.

A mixture of 1.95 g (0.01 mole) of **1** and 20 ml (0.2 mole) of trichloroacetonitrile was heated under reflux for 24 hours. After cooling, the solid product was collected on a filter, washed with a small amount of ethanol and recrystallized from ethanol to afford 1.0 g (62%) of brown scales, mp 193-194°.

2-Dichloromethyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3f**).

A solution of 1.95 g (0.01 mole) of **1** in 20 ml of dimethylformamide was kept at 0° and then added dropwise with 3.1 g (0.02 mole) of dichloroacetyl chloride (**2f**) and stirred 0-5° for 12 hours. The reaction mixture was poured into 400 ml of ice water and the precipitate was collected on a filter, washed with water and recrystallized from ethanol to afford 2.7 g (96%) of crystals, mp 205-206°, Rf 0.70; uv (ethanol): λ max (log ε) 217 (4.22), 237 (4.54), 326 (3.64) nm; λ min (log ε) 232 (4.20), 284 (2.76) nm; ir (potassium bromide): 3062, 3040 (=C-H), 1721 (C=O), 1590, 1511 (C=N/C=C), 1353 (C-N), 820 (C-Cl) 743 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6: δ (ppm) 7.62-8.07 (m, 3H, ArH), 7.79 (s, 1H, $CHCl_2$), 8.45-8.54 (m, 1H, H-8); ms: (70 eV) m/z 286 (M^+, 51), 250 (M-Cl, 100), 222 (250-CO, 35), 159 (C_9H_5NS, 20), 136 (34), 120 (10).

Anal. Calcd. for $C_{10}H_5Cl_2N_3OS$: C, 41.98; H, 1.76; N, 14.69. Found: C, 41.99; H, 1.78; N, 14.74.

2-Chloromethyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3g**).

To a solution of 1.95 g (0.01 mole) of **1** in 30 ml of dimethylformamide was added 2.3 g (0.02 mole) of chloroacetyl chloride (**2g**) dropwise under stirring. The reaction mixture was then heated on a steam bath for 2 hours and after cooling, poured into 400 ml of ice water. The precipitate was collected on a filter, washed with water and recrystallized from ethanol to yield 2.2 g (87%) of crystals, mp 218-219°, Rf 0.68; uv (ethanol): λ max (log ε) 238 (4.36), 317 (3.55) nm; λ min (log ε) 283 (2.86) nm; ir (potassium bromide): 3053, 3020 (=C-H), 1713 (C=O), 1586, 1512 (C=N/C=C), 1356 (C-N), 803 (C-Cl) 746 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 4.94 (s, 2H, CH_2Cl), 7.56-8.05 (m, 3H, ArH), 8.42-8.52 (m, 1H, H-8); ms: (70 eV) m/z 251 (M^+, 100), 216 (M-Cl, 39), 188 ($C_9H_6N_3S$, 65), 136 (15), 120 (10).

Anal. Calcd. for $C_{10}H_6ClN_3OS$: C, 47.72; H, 2.40; N, 16.70. Found: C, 47.71; H, 2.34; N, 16.88.

2-(1-Chloroethyl)-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3h**).

Compound **3h** was prepared from 1.95 (0.01 mole) of **1** and 2.6 g (0.02 mole) of 2-chloropropionyl chloride (**2h**) according to the procedure described for **3g**. It provided 2.6 g (98%) of fine crystals, mp 179-180°, Rf 0.67; uv (ethanol): λ max (log ε) 237 (4.50), 322 (3.60) nm; λ min (log ε) 282 (3.09) nm; ir (potassium bromide): 3058, 3010 (=C-H), 1726 (C=O), 1592, 1517 (C=N/C=C), 1317 (C-N), 763 (C-Cl), 723 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 1.90 (d, 3H, CH_3, J = 6.6 Hz), 5.53 (q, 1H, CHCl, J = 6.6 Hz), 7.56-8.04 (m, 3H, ArH), 8.45-8.53 (m, 1H, H-8); ms: (70 eV) m/z 265 (M^+, 91), 230 (M-Cl, 100), 202 ($C_{10}H_8N_3S$, 46), 188 (42), 177 (20), 136 (48), 120 (18).

Anal. Calcd. for $C_{11}H_8ClN_3OS$: C, 49.72; H, 3.03; N, 15.81. Found: C, 49.87; H, 2.95; N, 15.92.

3-(2-Chloropropionamido)-2-(2-chloropropionimido)-3,4-dihydro-2*H*-1,3-benzothiazin-4-one (**4**).

A solution of 1.95 g (0.01 mole) of **1** and 2.6 g (0.02 mole) of **2h** in 20 ml of dimethylformamide was stirred at 0-5° for 12 hours and then poured into 400 ml of ice water. The precipitate was col-

lected on a filter, washed with water and recrystallized from ethanol to give 3.0 g (81%) of white needles, mp 199-200°, Rf 0.01; uv (ethanol): λ max (log ε) 220 (4.52), 293 (4.00) nm; λ min (log ε) 276 (4.12) nm; ir (potassium bromide): 3200 (N-H), 3031, 3011 (=C-H), 1711, 1681 (C=O), 1589, 1534 (C=N/C=C), 1343, 1274 (C-N), 741 (C-Cl) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 1.64 (m, 6H, $2CH_3$), 4.76 (m, 2H, 2CHCl), 7.55-7.85 (m, 3H, ArH), 8.15-8.23 (m, 1H, H-5), 11.4 (s, 1H, NH); ms: (70 eV) m/z 373 (M^+, 40), 310 (M-C_2H_4Cl, 22), 220 (15), 136 (100).

Anal. Calcd. for $C_{14}H_{13}Cl_2N_3O_3S$: C, 44.93; H, 3.50; N, 11.23. Found: C, 44.93; H, 3.50; N, 11.24.

2-(2-Chloroethyl)-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3i**).

Compound **3i** was prepared from 1.95 g (0.01 mole) of **1** and 2.6 g (0.02 mole) of 3-chloropropionyl chloride (**2i**) according to the procedure described for **3g**. It afforded 1.6 g (59%) of yellow crystals, mp 206-207°, Rf 0.54; uv (ethanol): λ max (log ε) 239 (4.50), 322 (3.60) nm; λ min (log ε) 284 (2.88) nm; ir (potassium bromide): 3058, 3040 (=C-H), 1709 (C=O), 1596, 1522 (C=N/C=C), 1322 (C-N), 790 (C-Cl), 747 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 1.06 (t, 2H, CH_2, J = 6.5 Hz), 4.06 (t, 2H, CH_2, J = 6.5 Hz), 7.56-7.97 (m, 3H, ArH), 8.47-8.50 (1H, H-8); ms: (70 eV) m/z 256 (M^+, 42), 230 (M-Cl, 100), 202 ($C_{10}H_8N_3S$, 75), 188 (42), 175 (35), 136 (40), 120 (58),

Anal. Calcd. for $C_{11}H_8ClN_3OS$: C, 49.72; H, 3.03; N, 15.81. Found: C, 49.72; H, 3.01; N, 15.81.

2-(Ethoxycarbonyl)-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3j**).

Compound **3j** was prepared from 1.95 g (0.01 mole) of **1** and 2.8 g (0.02 mole) of ethyloxalyl chloride (**2j**) according to the procedure described under **3g**. It gave 1.8 g (67%) of crystals, mp 192-193°, Rf 0.62; uv (ethanol): λ max (log ε) 220 (4.43), 238 (4.47), 324 (3.67) nm; λ min (log ε) 226 (4.41), 290 (3.28) nm; ir (potassium bromide): 3063, 3023 (=C-H), 1721 (C=O), 1594, 1544 (C=N/C=C), 1311 (C-N), 1190 (C-O), 743 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 1.37 (t, 3H, CH_3, J = 7.1 Hz), 4.43 (q, 2H, CH_2, J = 7.1 Hz), 7.58-8.04 (m, 3H, ArH), 8.42-8.50 (m, 1H, H-8); ms: (70 eV) m/z 275 (M^+), 95), 230 (M-C_2H_5O, 42), 202 (M-$CO_2C_2H_5$, 100), 174 ($C_8H_4N_3S$, 12), 146 (C_8H_4NS, 80), 136 (90).

Anal. Calcd. for $C_{12}H_9N_3O_3S$: C, 52.36; H, 3.29; N, 15.26. Found: C, 52.37; H, 3.29; N, 15.24.

2-Phenyl-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3k**).

A mixture of 1.94 g (0.01 mole) of **1** and 12 ml (0.1 mole) of benzoyl chloride (**2k**) was heated at 200° for 5 hours. After cooling, the precipitate was collected on a filter, washed with ethanol and recrystallized from ethanol to give 2.1 g (77%) of white scales, mp 275-276°, lit yield 11%, mp 281-282° [2], Rf 0.72; uv (ethanol): λ max (log ε) 224 (4.28), 259 (4.45) nm; λ min (log ε) 212 (3.96), 229 (4.26) nm; ir (potassium bromide): 3061, 3026 (=C-H), 1703 (C=O), 1590, 1518 (C=N/C=C), 1343 (C-N) 739 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 7.56-7.93 (m, 5H, ArH), 8.02-8.20 (m, 3H, ArH), 8.52-8.55 (m, 1H, H-8); ms: (70 eV) m/z 279 (M^+, 100), 251 (M-CO, 38), 120 (24), 104 (15).

Anal. Calcd. for $C_{15}H_9N_3OS$: C, 64.50; H, 3.25; N, 15.04. Found: C, 64.41; H, 3.16; N, 14.96.

2-Hydroxy-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3l**).

A solution of 1.95 g (0.01 mole) of **1** and 3.3 g (0.02 mole) of *N,N'*-carbonyldiimidazole (**2l**) in 200 ml of toluene was heated under reflux for 2 hours. After cooling, the precipitate was collected on a filter, washed with petroleum ether and then suspended in 200 ml of ice water and acidified with acetic acid. The reaction mixture was allowed to stand at room temperature for 1 hour and then filtered. The solid product was washed with water and recrystallized from a mixture of dimethylformamide and ethanol to yield 1.9 g (85%) of white crystals, mp 274-275°, lit yield 51%, mp 310-312° [2], Rf 0.23; uv (ethanol): λ max (log ε) 237 (4.31), 249 (4.35), 329 (3.75) nm; λ min (log ε) 235 (4.77), 285 (3.38) nm; ir (potassium bromide): 3490 (O-H), 3040 (=C-H), 1705 (C=O), 1580, 1560 (C=N/C=C), 1320 (C-N), 1180 (C-O), 730 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 7.52-7.97 (m, 3H, ArH), 8.38-8.47 (m, 1H, H-8), 12.50 (s, br, 1H, OH); ms: (70 eV) m/z 219 (M^+, 100), 190 (M-COH, 13), 162 (M-CHN_2O, 38), 136 (C_6H_4COS, 50), 104 (30).

Anal. Calcd. for $C_9H_5N_3O_2S$: C, 49.30; H, 2.30; N, 19.16. Found: C, 49.33; H, 2.28; N, 19.20.

2-Thioxo-1,2-dihydro-1,2,4-triazolo[5,1-*b*][1,3]benzothiazin-9-one (**3m**).

A solution of 1.95 g (0.01 mole) of **1** in 20 ml of dimethylformamide was kept at 4° and treated with 3.6 g (0.02 mole) of *N,N'*-thiocarbonyldiimidazole (**2m**) in small portions. The reaction mixture was then stirred at room temperature overnight and poured into 400 ml of ice-water and acidified with acetic acid. The precipitate was collected, washed with water and recrystallized from a mixture of dimethylformamide and ethanol to give 2.0 g (85%) of dark brown crystals, mp >300°; ir (potassium bromide): 3400 (N-H), 3030 (=C-H), 1775 (C=O), 1596, 1555 (C=N/C=C), 1320 (C-N), 1190 (C=S), 740 (C-S) cm^{-1}; ^1H nmr (DMSO-d_6): δ (ppm) 7.01-7.96 (m, 4H, ArH, NH), 8.15-8.65 (m, 1H, ArH); ms: (70 eV) m/z 235 (M^+, 100), 202 (M-SH, 20), 162 (M-CHN_2S, 18), 136 (C_6H_4COS, 68), 108 (C_6H_4S, 23).

Anal. Calcd. for $C_9H_5N_3OS_2$: C, 45.94; H, 2.14; N, 17.86. Found: C, 45.86; H, 1.78; N, 17.58.

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