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*N*-Amination of 2-aminonaphtho[1,2-*d*]thiazole (**1**) with *O*-mesitylenesulfonylhydroxylamine (**2**) afforded the corresponding 2,3-diaminonaphthothiazolium salt **3a**. Cyclocondensation of **3a** or its free base **3b** with appropriate carboxylic acid derivatives **4a-f** gave the title compounds **5a-f** in satisfactory yields (54-95%). Structures of the products were assigned on the bases of spectral and elemental analyses.

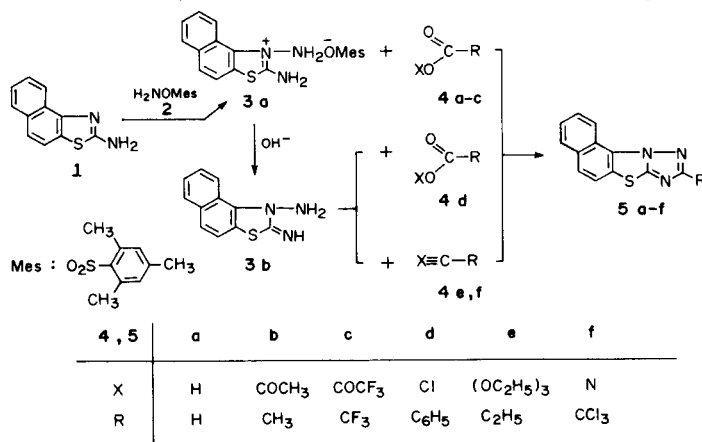
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In some recent publications [2-5], we reported the synthesis and biological activities of a number of fused naphtho[1,2-*d*]thiazole derivatives. As an extension of our studies in this series, we wish now to describe the process of fusing this heterocyclic system onto an 1,2,4-triazole component. The starting material, 2-aminonaphtho[1,2-*d*]thiazole (**1**) was obtained from 1-naphthylthiourea by oxidation with bromine [3], which was then *N*-aminated with *O*-mesitylenesulfonylhydroxylamine (**2**) [6] to the corresponding 2,3-diaminonaphthothiazolium salt **3a** in 85% yield. Treating **3a** in dioxane with aqueous sodium hydroxide converted it into the free base, 3-amino-2-iminonaphtho[1,2-*d*]thiazole (**3b**). It has been reported that the deprotonated heterocyclic *N*-aminoazonium salts occurred mostly in the unstable *N*-imine or inner salt form [7]. But our product was stabilized in the free base form virtually because of the presence of a vicinal amino group, which provided a proton for the *N*-imine and caused the shift of C=N bond from endo to exo state. The absorption characteristics of the amino and imino groups of **3b** were observed at 3320 and 3150 cm<sup>-1</sup> in the ir region and recognized as two singlets at  $\delta$  5.64 and 9.66 ppm like two wings of the aromatic proton clusters in the nmr spectrum.

Reaction of **3a** or **3b** with appropriate carboxylic acid derivatives, namely, formic acid (**4a**), acetic anhydride (**4b**), trifluoroacetic anhydride (**4c**), benzoyl chloride (**4d**),

triethyl orthopropionate (**4e**) or even with a carboxylic acid precursor, trichloroacetonitrile (**4f**) occurred preferentially on the *N*-amino group [8] and the intermediates cyclized readily on heating neatly or in a suitable medium to give the title compounds **5a-f** in 54-95% yields.

The uv spectra of these products displayed one intensive absorption maximum at  $\lambda$  241-244 and two medium or weak maxima at  $\lambda$  293-301 and 329-332 nm, reflecting the consistent electronic properties of this fused ring system. The ir spectra were all characterized by the presence of prominent C=N / C=C ring skeletal stretching bands at 1620-1600 and 1590-1505 cm<sup>-1</sup> and disappearance of N-H bands from 3320 and 3150 cm<sup>-1</sup>. The nmr spectra showed the aromatic clusters as two overlapped multiplets at  $\delta$  7.48-8.22 and 7.85-8.34 ppm accompanied by a doublet at  $\delta$  9.24-9.38 ppm with the integrated intensity ratio of 4:1:1 corresponding to the protons at C-6-9, C-5 and C-10, respectively. The ms fragmentation of **5a-f** proceeded by the occurrence of parent molecular ion peaks with expected masses followed by a general pattern of successive cleavage of the triazole and thiazole components and showed the homologous fragments of C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>S, C<sub>10</sub>H<sub>6</sub>NS, C<sub>10</sub>H<sub>6</sub>S and C<sub>10</sub>H<sub>6</sub>N at *m/e* 198, 172, 154 and 140, respectively. These spectral findings as well as the satisfactory elemental analytical data are thus evidence for the assigned structures of our synthetic products.



The cyclocondensations of **3** with some dielectrophiles, for example, ethyl pyruvate, diethyl oxalate and others are also investigated. The results will be described subsequently elsewhere.

## EXPERIMENTAL

### *O*-Mesitylenesulfonylhydroxylamine (**2**).

Compound **2** was prepared from 41.3 g (0.4 mole) of ethyl acetohydroxamate according to a known procedure [6], yield, 67.2 g (78%), mp 93-94°.

### 2,3-Diaminonaphtho[1,2-*d*]thiazolium Mesitylenesulfonate (**3a**).

To an ice-cooled solution of 40.1 g (0.2 mole) of **1** in 200 ml of dichloromethane was added dropwise a solution of 53.3 g (0.25 mole) of **2** in 250 ml of dichloromethane. The reaction mixture was stirred at room temperature for 1 hour, then diluted with 300 ml of ether, the precipitate was collected, washed with ether and recrystallized from ethanol to yield 71.2 g (85%) of white platelet crystals, mp 234-235°. It was used directly in the next reaction.

### 3-Amino-2-iminonaphtho[1,2-*d*]thiazole (**3b**).

A solution of 20.8 g (0.05 mole) of **3a** in 50 ml of dioxane was added with stirring to 50 ml of 20% sodium hydroxide. The solution was stirred at room temperature for 2 hours, then poured into 400 ml of ice-water and the precipitate was collected, washed with water and recrystallized from ethanol to yield 10.7 g (95%) of white needle crystals, mp 190-191°; uv (methanol):  $\lambda$  max (log  $\epsilon$ ) 237 (4.53), 252 (4.54), 313 (3.76), 327 (3.75) nm;  $\lambda$  min (log  $\epsilon$ ) 244 (4.46), 282 (3.59), 324 (3.71); ir (potassium bromide): 3320, 3150 (N-H), 3020 (=C-H), 1600 (C=C), 1165 (C-N), 600 (C-S)  $\text{cm}^{-1}$ ; nmr (DMSO- $d_6$ ):  $\delta$  (ppm) 5.64 (s,  $\text{NH}_2$ ), 7.44-7.62 (m, 4H, ArH), 7.92 (m, H-4), 8.14 (d, H-9,  $J = 8.0$  Hz), 9.66 (s, NH).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_9\text{N}_3\text{S}$ : C, 61.37; H, 4.21; N, 19.52; S, 14.89. Found: C, 61.27; H, 4.53; N, 19.21; S, 15.29.

### Naphtho[1',2':4,5]thiazolo[3,2-*b*]-1,2,4-triazole (**5a**).

A solution of 4.2 g (0.01 mole) of **3a** in 6.0 ml of pyridine was added with 8.0 ml (0.2 mole) of **4a** and the reaction mixture was refluxed for 8 hours. After cooling, it was poured into 100 ml of ice-water and the precipitate was collected and recrystallized from ethanol and then from benzene to yield 2.0 g (89%) of dark brown needle crystals, mp 205-206°; uv (methanol):  $\lambda$  max (log  $\epsilon$ ) 243 (4.64), 293 (3.97), 329 (3.13) nm;  $\lambda$  min (log  $\epsilon$ ) 268 (3.70), 326 (2.83); ir (potassium bromide): 3100 (=C-H), 1640, 1590 (C=N / C=C), 1450, 1165 (C-N), 750, 650 (C-S)  $\text{cm}^{-1}$ ; nmr (DMSO- $d_6$ ):  $\delta$  (ppm) 7.74-8.06 (m, 4H, ArH), 8.28 (m, H-5), 8.64 (s, H-2), 9.24 (d, H-10,  $J = 7.0$  Hz); ms (70 eV),  $m/e$ : 225 ( $M^+$ , 100), 198 (M-27, 55), 172 (18), 154 (32), 140 (16).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_7\text{N}_3\text{S}$ : C, 63.98; H, 3.13; N, 18.65; S, 14.23. Found: C, 63.67; H, 3.30; N, 18.65; S, 14.19.

### 2-Methylnaphtho[1',2':4,5]thiazolo[3,2-*b*]-1,2,4-triazole (**5b**).

A solution of 4.2 g (0.01 mole) of **3a** in 10.0 ml (0.1 mole) of **4b** was heated under reflux for 2 hours. After cooling, the precipitated crystals were collected, then suspended in 40 ml of 10% sodium hydroxide solution and filtered. The product was washed with water and recrystallized from benzene-*n*-hexane to give 2.0 g (84%) of white crystals, mp 146-147°; uv (methanol):  $\lambda$  max (log  $\epsilon$ ) 244 (4.62), 295 (3.96), 330 (3.08);  $\lambda$  min (log  $\epsilon$ ) 269 (3.68), 326 (2.68); ir (potassium bromide): 3080 (=C-H), 1617, 1575 (C=N / C=C), 1440, 1310 (C-N), 710, 650 (C-S)  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  (ppm) 2.65 (s,  $\text{CH}_3$ ), 7.50-7.80 (m, 4H, ArH), 7.90 (m, H-5), 9.25 (d, H-10,  $J = 7.0$  Hz); ms (70 eV),  $m/e$ : 239 ( $M^+$ , 100), 198 (M-41, 52), 172 (12), 154 (25), 140 (14).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_8\text{N}_3\text{S}$ : C, 65.25; H, 3.79; N, 17.55; S, 13.39. Found: C, 65.51; H, 4.07; N, 17.32; S, 13.30.

### 2-Trifluoromethylnaphtho[1',2':4,5]thiazolo[3,2-*b*]-1,2,4-triazole (**5c**).

A solution of 4.2 g (0.01 mole) of **3a** in 10 ml of pyridine was added to 2.4 ml (0.02 mole) of **4c** and heated under reflux for 5 hours. The reaction

mixture was filtered while hot and the filtrate was diluted with 160 ml of ethanol and allowed to stand at 4° overnight. The precipitate formed was collected, washed with ethanol and recrystallized from ethanol to give 2.8 g (95%) of light yellow needle crystals, mp 184-185°; uv (methanol):  $\lambda$  max (log  $\epsilon$ ) 241 (4.67), 293 (4.00), 329 (3.31);  $\lambda$  min (log  $\epsilon$ ) 266 (3.67), 325 (2.90); ir (potassium bromide): 3080 (=C-H), 1600, 1505 (C=N / C=C), 1475, 1180 (C-N), 700, 670 (C-S)  $\text{cm}^{-1}$ ; ms (70 eV),  $m/e = 293$  ( $M^+$ , 100), 224 (M-69, 20), 198 (50), 172 (18), 154 (30), 140 (10).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_6\text{N}_3\text{F}_3\text{S}$ : C, 53.24; H, 2.06; N, 14.33; F, 19.43; S, 10.93. Found: C, 53.44; H, 2.01; N, 14.05; F, 19.28; S, 11.28.

### 2-Phenylnaphtho[1',2':4,5]thiazolo[3,2-*b*]-1,2,4-triazole (**5d**).

A mixture of 2.2 g (0.01 mole) of **3b** and 10 ml (0.08 mole) of **4d** was heated under reflux for 5 hours. After cooling, the crystalline precipitate was collected, washed with ethanol and recrystallized from dimethylformamide-ethanol to yield 1.7 g (56%) of white needle crystals, mp 195-196°; uv (methanol):  $\lambda$  max (log  $\epsilon$ ) 234 (4.67), 305 (4.34), 332 (3.76);  $\lambda$  min (log  $\epsilon$ ) 278 (3.98), 329 (3.56); ir (potassium bromide): 3080 (=C-H), 1600, 1560 (C=N / C=C), 1475, 1320 (C-N), 700, 650 (C-S)  $\text{cm}^{-1}$ ; nmr (DMSO- $d_6$ ):  $\delta$  (ppm) 7.56-7.86 (m, 5H, ArH), 7.86-8.22 (m, 4H, ArH), 8.34 (m, H-5), 9.38 (d, H-10,  $J = 7.0$  Hz).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{S}$ : C, 71.73; H, 3.67; N, 13.94; S, 10.78. Found: C, 71.35; H, 3.63; N, 13.82; S, 11.05.

### 2-Ethyl-naphtho[1',2':4,5]thiazolo[3,2-*b*]-1,2,4-triazole (**5e**).

A mixture of 2.2 g (0.01 mole) of **3b** and 4.0 ml (0.02 mole) of **4e** was heated under reflux for 12 hours. The excess of **4e** was distilled under reduced pressure and the residue was recrystallized from ethanol to give 1.4 g (54%) of colorless crystals, mp 68-70°; uv (methanol):  $\lambda$  max (log  $\epsilon$ ) 242 (4.42), 295 (3.96), 330 (3.10);  $\lambda$  min (log  $\epsilon$ ) 268 (3.66), 326 (2.86); ir (potassium bromide): 3100 (=C-H), 1610, 1545 (C=N / C=C), 1470, 1310 (C-N), 700, 640 (C-S)  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  (ppm) 1.51 (t,  $\text{CH}_3$ ,  $J = 6.0$  Hz), 3.03 (q,  $\text{CH}_2$ ,  $J = 6.0$  Hz), 7.48-7.82 (m, 4H, ArH), 7.85 (m, H-5), 9.24 (d, H-10,  $J = 7.0$  Hz); ms (70 eV),  $m/e$ : 253 ( $M^+$ , 100), 225 (M-28, 20), 198 (31), 172 (8), 154 (16), 140 (10).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{11}\text{N}_3\text{S}$ : C, 66.38; H, 4.37; N, 16.58; S, 12.65. Found: C, 66.26; H, 4.51; N, 16.40; S, 12.34.

### 2-Trichloromethylnaphtho[1',2':4,5]thiazolo[3,2-*b*]-1,2,4-triazole (**5f**).

A mixture of 2.2 g (0.01 mole) of **3b** and 10 ml (0.1 mole) of **4f** was heated under reflux for 24 hours. After cooling, the crystalline product was collected, washed with ethanol and recrystallized from dimethylformamide-ethanol to yield 3.0 g (88%) of white needle crystals, mp 229-230°; uv (methanol):  $\lambda$  max (log  $\epsilon$ ) 243 (4.62), 301 (4.09), 330 (3.53);  $\lambda$  min (log  $\epsilon$ ) 270 (3.74), 327 (3.14); ir (potassium bromide): 3060 (=C-H), 1620, 1580 (C=N / C=C), 1475, 1310 (C-N), 710, 650 (C-S)  $\text{cm}^{-1}$ ; ms (70 eV)  $m/e$ , 342 ( $M^+$ , 20), 307 (M-35, 100), 182 (26), 154 (25), 140 (40).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_6\text{N}_3\text{Cl}_3\text{S}$ : C, 45.57; H, 1.76; N, 12.26; Cl, 31.04; S, 9.36. Found: C, 45.27; H, 1.74; N, 12.17; Cl, 30.98; S, 9.47.

## REFERENCES AND NOTES

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- [4] K. C. Liu, L. C. Lee, B. J. Shih, C. F. Chen and T. M. Tao, *ibid.*, **315**, 872 (1982).
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- [6] Y. Tamura, J. Minamikawa, K. Sumamoto, S. Fujii and M. Ikeda, *J. Org. Chem.*, **38**, 1239 (1973).
- [7] Y. Tamura and M. Ikeda in "Advances in Heterocyclic Chemistry", Vol 29, Academic Press, Inc., New York, 1981, p 76.
- [8] Reaction of **3b** with  $\alpha$ - or  $\beta$ -chloropropionylchloride led to the formation of the corresponding *N*-acylamino intermediates (mp 228-230° and 199-201°) whose structure was elucidated by ir, nmr and ms analyses in a separate experiment.