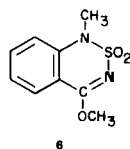
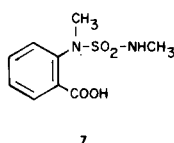


both had aromatic signals and two *N*-methyl signals in the ratio of 4:3:3. The mass spectra of the mixture and of each pure component appear to be almost identical. The major component was assigned structure **1b** and the minor component the structure 1-methyl-4-methoxy-2,1,3-benzothiadiazin 2,2-dioxide (**6**) based on infra-red evidence.



The absence of strong bands above 3000 cm^{-1} in the infra-red due to NH or OH stretching argues against the presence of non-ring-closed structures such as *N,N'*-dimethyl-*N*-sulfamoylanthranilic acid (**7**). The SO_2 group



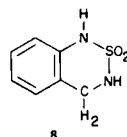
should absorb in the regions $1320\text{--}1360$ and $1150\text{--}1180\text{ cm}^{-1}$ and strong bands can be seen. The minor component shows an additional strong absorption in the region $1100\text{--}1200\text{ cm}^{-1}$, which suggests the C-O stretching vibration of the ether linkage. In addition the minor component shows a band at 1610 cm^{-1} and the major component a band at 1685 cm^{-1} , which are reasonably assigned the C=N and C=O stretchings, respectively.

The following 3-substituted compounds have been prepared by reaction of **1a** with a suitable alkyl halide or alkyl sulfate: 3-trideuteromethyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1e**); 1,3-diethyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1g**); 3-phenacyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1i**); and 1,3-ethoxycarbonylmethyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1j**).

Since a nitro benzothiadiazine could not be prepared by ring closure of the nitroanthranilates, 1,3-dimethyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1b**) was nitrated with concentrated nitric acid/sulfuric acid in acetic acid solution. That 6-nitration has occurred is deduced from the fact that the 6- and 8-positions of 1,3-dimethyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide should be positions of highest electron density being *para* and *ortho* to the *N*-methyl group. Mono-nitration should thus give the 6- or 8-nitro isomer. The aromatic proton adjacent to the strongly electron withdrawing carbonyl group (position 5-) in the parent compound is assigned to the signal at lowest field in the benzene- d_6 nmr spectrum at τ 1.9. This doublet of a doublet has splitting of 7.5 and 1.8 Hz. On mononitration this signal moves to lower field (τ 1.23) and becomes a doublet with a splitting of 2.75 Hz. If nitration had occurred at the 7- or 8-positions, the 5-

proton signal would appear with large (*ca.* 7 Hz) *ortho* coupling.

Lithium aluminum hydride reduction of **1a** yielded 3,4-dihydro-2,1,3-benzothiadiazine 2,2-dioxide (**8**).



EXPERIMENTAL

N-Carbonylsulfamoyl chloride was prepared by the method of Graf (2). Sulfamoyl chloride (3) was freshly prepared for each experiment. Tlc was carried out on plates with Merck silica gel GF .254 or PF .254 (preparative). Nmr spectra were recorded with a Varian (100 MHz) spectrometer for solutions with tetramethylsilane as internal standard. Ir spectra were measured (potassium bromide) with a Perkin-Elmer 337. Uv spectra were recorded with a Unicam SP 800 instrument, and mass spectra were measured with an A.E.I. MS 9 instrument (4). The following compounds were synthesized by the method of Cohen and Klarberg (1): 1*H*-2,1,3-Benzothiadiazin-4(3*H*)one 2,2-dioxide (**1a**) (4); 1-methyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1c**); 3-methyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1d**) (4); and 6-methyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)one 2,2-dioxide (**1f**). 1,3-Dimethyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-Dioxide (**1b**) (4) and 1-Methyl-4-methoxy-2,1,3-benzothiadiazine 2,2-Dioxide (**6**).

Dimethylsulfate (10 ml., 0.04 mole) and **1a** (5 g., 0.025 mole) were dissolved in 10% sodium bicarbonate (100 ml.) and stirred for 12 hours. The crude solid was filtered and crystallized from aqueous ethanol to give 4.3 g., m.p. $96\text{--}100^\circ$ (lit. (1) for **1b**, m.p. $98\text{--}100^\circ$). The nmr spectrum indicated the presence of two compounds, which were separated by preparative tlc using chloroform as eluent. The major component (*ca.* 90%) had Rf 0.27 and the minor component Rf 0.17.

Major Component.

This compound was assigned structure **1b**; uv (ethanol): λ max (ϵ mole $^{-1}\text{dm}^{-2}$) 219 (202×10^3), 237 (673×10^2) and 305 (148×10^2) nm; nmr (benzene- d_6): τ 1.85 (multiplet, 5-H), 3.1 (multiplet, 7-H), 3.3 (multiplet, 6-H), 3.6 (multiplet, 8-H), 6.85 (singlet, 1-Me) and 7.35 (singlet, 3-Me); ir: ν max 1155 (SO_2), 1360 (SO_2) and 1685 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_2\text{SO}_3$: C, 47.8; H, 4.45; N, 12.38. Found: C, 47.6; H, 4.67; N, 12.21.

Minor Component.

This compound was assigned structure **6**; uv (ethanol): λ max (ϵ mole $^{-1}\text{dm}^{-2}$) 222 (275×10^3), 258 (533×10^2), 265 (476×10^2) and 333 (287×10^2) nm; nmr (benzene- d_6): τ 2.45 (multiplet, 5-H), 3.02 (multiplet, 7-H), 3.45 (multiplet, 6-H), 3.75 (multiplet, 8-H), 6.7 (singlet, Me) and 7.1 (singlet, Me); ir: ν max 1135 (C-O), 1170 (SO_2), 1360 (SO_2) and 1610 cm^{-1} (C=N).

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_2\text{SO}_3$: C, 47.8; H, 4.51; N, 12.50. Found: C, 47.8; H, 4.51; N, 12.50.

3-Trideuteromethyl-2,1,3-benzothiadiazin-4(3*H*)one 2,2-Dioxide (**1e**) (4).

Potassium carbonate (0.97 g., 7 mmoles) and **1a** (1.4 g., 7 mmoles) were dissolved in water (3 ml.), methanol (3 ml.) and trideuteromethyl iodide (0.97 g., 7 mmoles) and the solution

refluxed for 3 hours. The solvent was removed under reduced pressure and the crude product acidified with concentrated hydrochloric acid was filtered to yield 1.2 g. (80%) of **1e**, m.p. and mixed m.p. with undeuterated sample **1a** 209-210° (lit. (1) gives m.p. 201-203°).

Anal. Calcd. for $C_8H_5D_3N_2SO_3$: C, 44.6; H, 3.72; N, 13.02. Found: C, 44.9; H, 3.87; N, 13.15.

1,3-Diethyl-2,1,3-benzothiadiazin-4(3H)one 2,2-Dioxide (**1g**) (4).

Diethyl sulfate (16.4 g., 0.1 mole) and **1a** (10 g., 0.05 mole) were dissolved in 10% sodium hydroxide (200 ml.) and the solution stirred for 15 hours. The crude solid (9.5 g.), m.p. 190-200°, was purified by glc (7' x 3/8" 20% APL at 264°); molecular weight 254 (mass spectrum).

Anal. Calcd. for $C_{11}H_{14}N_2SO_3$: C, 51.9; H, 5.55; N, 11.02. Found: C, 52.1; H, 5.32; N, 11.13.

6-Nitro-1,3-dimethyl-2,1,3-benzothiadiazin-4(3H)one 2,2-Dioxide (**1h**).

Crude compound **1b** was nitrated by the method of Vogel (5). Crystallization of the product yielded pale yellow needles, m.p. 89-90°; nmr (benzene- d_6): τ 1.23 (doublet, 5-H), 2.35 (multiplet, 7-H), 4.05 (doublet, 8-H), 6.96 (singlet, methyl) and 7.41 (singlet, methyl).

Anal. Calcd. for $C_9H_9N_3O_5S$: C, 39.85; H, 3.34; N, 15.49. Found: C, 39.83; H, 3.5; N, 15.11.

3-Phenacyl-2,1,3-benzothiadiazin-4(3H)one 2,2-Dioxide (**1i**) (4).

A saturated solution of **1a** (6 g., 0.03 mole) in 10% sodium carbonate and a solution of phenacyl bromide (6 g., 0.03 mole) in ethanol were refluxed for 6 hours. The ethanol was removed and the acidified product extracted with ether. From the ethereal layer was obtained a thick oily material which was washed with petroleum ether (b.p. 40-60°) and crystallized first from chloroform and then ethanol (7.5 g., 80%), m.p. 188-190°.

Anal. Calcd. for $C_{15}H_{12}N_2O_4S$: C, 57.0; H, 3.8; N, 8.9; S, 10.0. Found: C, 57.01; H, 3.80; N, 8.75; S, 10.08.

1,3-Ethoxycarbonylmethyl-2,1,3-benzothiadiazin-4(3H)one 2,2-Dioxide (**1j**).

To a solution of **1a** (3 g., 0.015 mole) in ethanol and aqueous

sodium hydroxide (0.6 g., 0.015 mole) was refluxed for 20 hours. Ethanol was removed from the mixture which was acidified with hydrochloric acid, and ether extracted. The oil obtained from the ether extract was purified by glc (7' x 3/8" 5% SE30 at 270°). Insufficient was purified for analysis but the ir spectrum showed the presence of a new carbonyl carbon and the loss of the N-H bond; molecular weight 370 (mass spectrum).

Naphtho[2,3-d][1,2,6]thiadiazin-4-one 2,2-Dioxide (**2**) (4).

The method of Cohen and Klarberg (1) was used except that the reaction mixture was refluxed for 7 hours before the addition of sodium hydroxide. The white crystalline product had m.p. 238-240°.

Anal. Calcd. for $C_{11}H_8N_2O_3S$: C, 53.22; H, 3.25; N, 11.28. Found: C, 53.3; H, 3.4; N, 11.15.

3,4-Dihydro-2,1,3-benzothiadiazine 2,2-Dioxide (**8**) (4).

Compound **1a** was refluxed in dry ether with excess lithium aluminum hydride for 15 hours. The crude compound crystallized from methanol had m.p. 186-189°. It showed loss of a carbonyl; molecular weight 184 (mass spectrum).

Anal. Calcd. for $C_7H_8N_2O_2S$: C, 45.64; H, 4.38; N, 15.21. Found: C, 45.71; H, 4.5; N, 15.06.

Acknowledgement.

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