

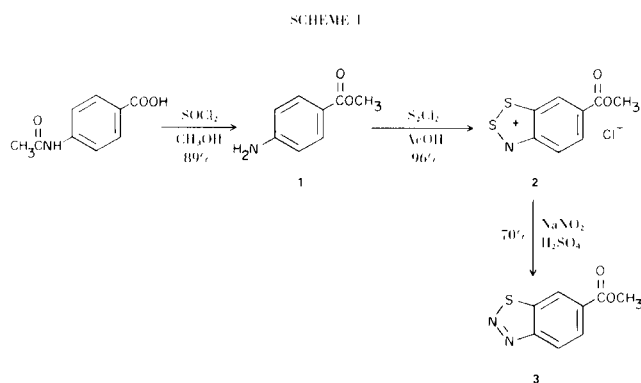
## Methyl 1,2,3-Benzothiadiazole-6-carboxylate

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The only previous reports of the title compound (**3**) (1,2) involved a tedious seven-step synthesis from *O*-ethyl phenylthiocarbamate. The facile three-step synthesis of **3** from 4-acetamidobenzoic acid in an overall 60% yield is reported herein (Scheme I). 4-Acetamidobenzoic acid was converted to methyl 4-aminobenzoate (**1**) by the



combined esterification and deacylation with thionyl chloride in anhydrous methanol according to the esterification procedure of Kirsch and Katchalski (3). The Herz reaction on **1** at 65-75° afforded 6-methoxycarbonyl-1,3,2-benzothiazathiolium chloride (**2**) (4). No evidence was found for displacement of the methoxycarbonyl group of **1** by chlorine as has been reported for the nitro group of *p*-nitroaniline under Herz reaction conditions (5). Diazotization of **2** with nitrosyl-sulfuric acid according to the procedure of Kirby and co-workers (6) gave methyl 1,2,3-benzothiadiazole-6-carboxylate (**3**). As suggested by these workers (6) the conversion of **2** to **3** probably proceeds through the acid catalyzed hydrolysis of **2** to the corresponding *o*-aminothioliol. Under diazotization conditions *o*-aminothioliols are known to afford 1,2,3-benzothiadiazoles (7). This reaction sequence affords a simple route to **3** from which additional 6-substituted-1,2,3-benzothiadiazoles can be prepared by conventional synthetic techniques.

## EXPERIMENTAL

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The author wishes to express his gratitude to Mr. P. M. Saliman and co-workers for the elemental analyses.

Methyl 4-Aminobenzoate (**1**).

To a stirred suspension of 60 g. (0.034 mole) 4-acetamidobenzoic acid in 200 ml. anhydrous methanol at 5° was added dropwise 79 ml. (130 g., 1.1 moles) of thionyl chloride. The reaction temperature was maintained at 0-5° during the addition and then allowed to come to room temperature. The reaction mixture was stirred at ambient temperature for 16 hours, and stripped, and the residue was dissolved in water. Sodium carbonate was added to basicity and the resulting solids were filtered, washed with water and dried to give 40.8 g. (89%) white, crystalline **1**, m.p. 108-110° (lit., (8) 112-113°).

Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>: N, 9.3; alkoxy, 151. Found: N, 9.3; alkoxy, 154.

6-Methoxycarbonyl-1,3,2-benzothiazathiolium Chloride (**2**).

A slurry of 15.1 g. (0.10 mole) **1** in 50 ml. of acetic acid was added slowly to 56 ml. (94.5 g., 0.7 mole) of ice-cooled, stirred sulfur monochloride. After stirring at ambient temperature for one hour, the reaction mixture was heated to 70-80° for three hours. After cooling, 60 ml. of benzene was added and the solids were filtered, washed extensively with benzene and air dried to give 23.7 g. (96%) of orange solid **2**. This solid darkened with charring above 150° and then melted from 178-182° with decomposition. The majority of **2** was used in the next reaction without further purification or analysis.

A small sample of **2** was converted via the corresponding oxide to the known perchlorate salt, (4), m.p. 241° (explodes) (acetic acid) (lit., (4) 249-251°).

Anal. Calcd. for C<sub>8</sub>H<sub>6</sub>ClNO<sub>6</sub>S<sub>2</sub>: C, 30.8; H, 1.9; N, 4.5. Found: C, 30.5; H, 1.9; N, 4.6.

Methyl 1,2,3-Benzothiadiazole-6-carboxylate (**3**).

To a stirred solution of 12.1 g. (0.049 mole) **2** in 100 ml. of concentrated sulfuric acid at 0-5° was added dropwise a solution of 6.9 g. (0.1 mole) sodium nitrite in 75 ml. of sulfuric acid so that the reaction temperature was maintained at less than 5°. The reaction mixture was stirred at 0-5° for one hour, poured over ice and allowed to stand for one hour with occasional stirring to allow the oxides of nitrogen to be removed. This mixture was extracted with dichloromethane and the combined extracts were washed with water, dried (magnesium sulfate) and stripped to give 8.6 g. of crude **3**. Chromatography through silica gel-G (Grace, grade

950, 20-200 mesh) with dichloromethane as the eluent gave, after evaporation of the solvent, 6.6 g. (70%) of white crystalline **3**, m.p. 144-145° (dichloromethane, ethanol) (lit., (1) 150-151° (alc)); ir (dichloromethane): 2960 (OCH<sub>3</sub>), 1725 (C=O), 1434, 1217, 1127 and 1117; nmr (deuteriochloroform, TMS): 4.0 Hz (singlet) (CH<sub>3</sub>); 8.20 Hz (quartet) (aromatic H<sub>5</sub>) 8.65 Hz (broad doublet) (aromatic H<sub>4</sub>); 8.77 Hz (broad singlet) (aromatic H<sub>7</sub>); J<sub>4,5</sub> = 8.5 cps; J<sub>5,6</sub> = 1.5 cps.

Anal. Calcd. for C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S: C, 49.5; H, 3.1; N, 14.4. Found: C, 49.4; H, 3.1; N, 14.5.

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