

# 1,2-Benzisothiazole 1,1-Dioxide: a Convenient Synthesis. The Question of the Possible Aromaticity of 1,2-Benzothiazepine 1,1-Dioxides

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A convenient synthesis of 1,2-benzisothiazole 1,1-dioxide from toluene-*o*-sulphonamide is reported, and this allows the preparation of a number of 1,2-benzothiazepine 1,1-dioxides bearing hydrogen atoms in the seven-membered ring; <sup>1</sup>H n.m.r. spectroscopy suggests that the latter is not aromatic.

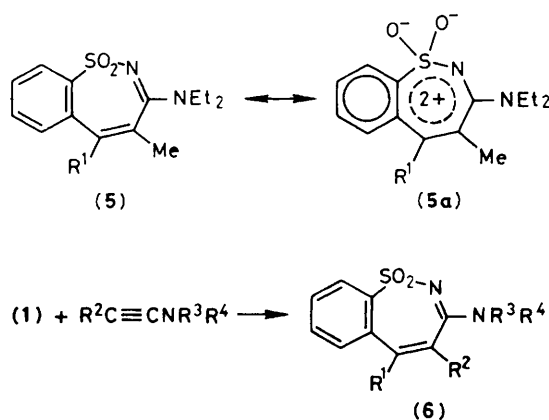
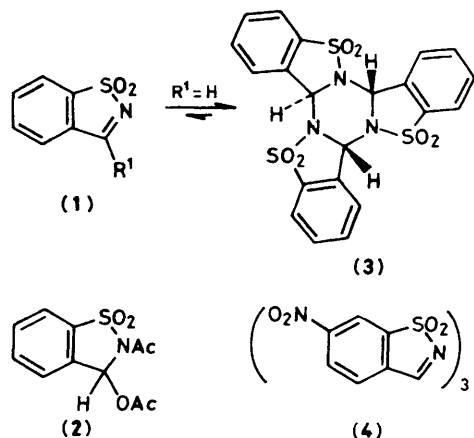
3-Alkyl- and 3-aryl-1,2-benzisothiazole 1,1-dioxides (**1**) are now readily available.<sup>1</sup> There is, however, only one reported<sup>2</sup> synthesis of the parent compound (**1**; R<sup>1</sup> = H) (in extremely poor yield) from *o*-chloramine T by a two-step process, each step leading to complex mixtures. The product so formed was thought to be either the monomer or the dimer. We now report a convenient synthesis of (**1**; R<sup>1</sup> = H) and discuss the possible aromaticity of its ring expansion products, the 1,2-benzothiazepine 1,1-dioxides.

Numerous attempts to reduce saccharin *pseudochloride* (**1**; R<sup>1</sup> = Cl) or to dehydrogenate 2,3-dihydro-1,2-benzisothiazoline 1,1-dioxide to (**1**; R<sup>1</sup> = H) failed. For example, oxidation of the dihydro-compound with (PhSeO)<sub>2</sub>O gave *N*-phenylselenylsaccharin. Similarly, treatment of benzenesulphonamide with Bu<sup>n</sup>Li and then trimethylorthoformate did not give the desired dimethylformamide (DMF) [which could have been cyclized to (**1**) in acid]. On the other hand, oxidation of toluene-*o*-sulphonamide with chromium trioxide in acetic anhydride gave the *N,O*-diacetyl derivative (**2**) (50%, m.p. 152–154 °C.† When (**2**) was dissolved in conc. H<sub>2</sub>SO<sub>4</sub> at room temp., and the solution was stirred for 3 h and then poured onto crushed ice, (**1**; R<sup>1</sup> = H) was formed (30%), m.p. 230–232 °C. The compound initially formed was the monomer (soluble in chloroform). Following one recrystallization (EtOH or DMF) it was totally insoluble in chloroform. An ebullioscopic molecular weight determination in DMF gave a value of 531 (calc. for trimer 501). On the other hand, a freezing point depression study (camphor) gave a value of 166.5 (calc. for monomer 167). The mass spectrum of the trimer had no peak at *m/z* 501, but peaks at 437 (trimer – SO<sub>2</sub>), 334 (dimer), 270 (dimer – SO<sub>2</sub>), 269 (100%), and 167 (monomer) were present. The <sup>1</sup>H n.m.r. spectrum of the trimer in dimethyl sulphoxide (DMSO) exhibited three singlets at δ 7.2, 6.5, and 6.0, suggesting that it existed in a *cis-cis-trans* arrangement (**3**) of the triazine.<sup>3</sup> The product was identical to that obtained by the earlier procedure.<sup>2</sup>

A variable-temperature n.m.r. study<sup>4</sup> of (**1**) ⇌ (**3**) in [<sup>2</sup>H<sub>6</sub>]DMSO, showed the appearance of a band at δ 9.3, attributed to the monomer (**1**; R<sup>1</sup> = H), as the temperature was raised, with a concurrent decrease in the intensities of the bands at δ 7.2, 6.5, and 6.0. Even after the solution had been heated to 190 °C and then cooled to 30 °C some monomer (*ca.* 30%) still persisted in solution. Such a procedure allowed us to carry out cycloadditions on the monomer at room temperature.

6-Nitro-1,2-benzisothiazole 1,1-dioxide (**4**), m.p. 256–258 °C, was prepared similarly (30% yield) from 4-nitrotoluene-2-sulphonamide and also existed as the trimer (δ 7.5, 6.7, and 6.3).

It was shown earlier that (**1**) could be ring-expanded to give 1,2-benzothiazepine 1,1-dioxides (**5**) on treatment with ynamines.<sup>5</sup> These benzothiazepines exhibited remarkable chemical stability and the possibility was raised that the seven-membered ring in (**5**) might have aromatic character, as implied by structure (**5a**). The availability of (**1**; R<sup>1</sup> = H) allowed an examination of this possibility. A number of 3-dialkylamino-1,2-benzothiazepine 1,1-dioxides (**6**) (particularly with R<sup>1</sup> and/or R<sup>2</sup> = H) were synthesized and their <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were studied. The <sup>1</sup>H n.m.r. spectra of compounds in (**6a–c**) were particularly informative. C-5–H in (**6a**) and (**6c**) resonated at δ 6.2 and 6.3, respectively. C-4–H in (**6b**) and (**6c**) resonated at δ 7.1 and 7.2, respectively. These values may be compared with those for the vinyl protons of cinnamic acid, for instance: δ 6.3 and 7.7.<sup>6</sup> A structure such as (**5a**; R<sup>1</sup> = H) would have been expected to deshield strongly protons bonded to the positively charged aromatic seven-membered ring. Also *J*<sub>4,5</sub> in (**6c**) was found to be 12.7 Hz, much larger than expected for an aromatic system; vicinal proton couplings in aromatic rings are generally in the range 6–9.5 Hz, but in the range of 2–12.5 Hz for *cis*-olefins.<sup>7</sup> These results suggest that the seven-membered ring in (**6**) is not aromatic and that its relative chemical inertness requires another explanation.



† All new compounds gave appropriate microanalytical and spectral (i.r., n.m.r., and mass) data.

a; R<sup>1</sup> = H, R<sup>2</sup> = Me  
b; R<sup>1</sup> = Me, R<sup>2</sup> = H  
c; R<sup>1</sup> = R<sup>2</sup> = H

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