

## Preparation of the Parent Heterocycles, 1,4,2-Dithiazole-5-thione, 1,4,2-Dithiazol-5-one, and the 1,4,2-Dithiazolium Cation

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The first syntheses of the title parent heterocycles are described, using a sequence of steps involving common reagents; some spectroscopic data are given, together with evidence for charge delocalization in the 1,4,2-dithiazolium cation.

Parent ring systems have always been of interest, since their structural parameters, spectroscopic data, and chemical properties may be measured without the perturbing influence of substituents, and may subsequently be compared with theoretical data. We now report the first preparation of the three title compounds, using a simple starting material, and common reagents, and also include some preliminary spectroscopic data.

We have recently prepared examples of both 5-aryl-1,4,2-dithiazolium salts unsubstituted at C-3,<sup>1</sup> using a development of Shibuya's strategy,<sup>2</sup> and 3-aryl-1,4,2-dithiazolium salts unsubstituted at C-5,<sup>3</sup> using an approach similar to that tried unsuccessfully in an earlier report.<sup>4</sup> The syntheses described here combine the two strategies.

Sodium piperidinedithiocarboxylate (1) was converted into the sulphenamide (2) (79%) using hydroxylamine *O*-sulphonic acid in the presence of sodium hydroxide,<sup>2</sup> and *N*-formylated with formic-acetic anhydride in chloroform at 50 °C,<sup>1</sup> to give the formamide (3) (82%) as a mixture of rotational isomers [ $\delta_{\text{H}}(\text{CDCl}_3)$  7.25 and 7.95 (2 d, *J* 11 Hz), and 7.79 and 8.72 (2s)]. Cyclization to the dithiazolium salt (4) (60%) [ $\delta_{\text{H}}(\text{CF}_3\text{CO}_2\text{D}-\text{CD}_3\text{NO}_2)$  9.08 (3-H);  $\delta_{\text{C}}$  158.05 (C-3) and 193.91 (C-5)] was achieved with 60% perchloric acid in acetic anhydride,<sup>2</sup> at 0 °C. Treatment of (4) with hydrogen sulphide in methanol at 25 °C gave 5*H*-1,4,2-dithiazole-5-thione (5) as a liquid (74%) which was purified by column chromatography (SiO<sub>2</sub>; eluant CH<sub>2</sub>Cl<sub>2</sub>-light petroleum) [ $\delta_{\text{H}}(\text{CDCl}_3)$  8.91 (3-H);  $\delta_{\text{C}}$  160.2 (C-3) and 217.1 (C-5);  $\nu_{\text{max}}(\text{film})$  3 024, 2 943, 1 480, and 1 075 cm<sup>-1</sup>;  $\lambda_{\text{max}}(\log \epsilon)$  229 (3.86), 268 (3.37), and 339 nm (4.14)]; it was converted into the volatile oxo analogue (6) with mercury(II) acetate<sup>6</sup> in acetic acid-chloroform at 70 °C, and was purified as for (5) (24%) [ $\delta_{\text{H}}(\text{CDCl}_3)$  8.85 (3-H);  $\delta_{\text{C}}$  153.4 (C-3) and 196.9 (C-5);  $\nu_{\text{max}}(\text{film})$  3 046, 2 950, 1 706, 1 657, 1 630, and 1 489 cm<sup>-1</sup>;  $\lambda_{\text{max}}(\log \epsilon)$  237 (3.70) and 339 nm (2.62)]. Methylation<sup>5</sup> of the thione (5) with dimethyl sulphate, followed by addition of 52% fluoroboric acid yielded the metho salt (7) (81%) [ $\delta_{\text{H}}(\text{CF}_3\text{CO}_2\text{D}-\text{CD}_3\text{NO}_2)$  9.99 (3-H);  $\delta_{\text{C}}$  169.9 (C-3) and 221.4 (C-5)], which with sodium borohydride in diethyl ether-water<sup>4</sup> below 5 °C was reduced to the 5*H*-1,4,2-dithiazole (8), a liquid, purified as for (5) and (6) (78%) [ $\delta_{\text{H}}(\text{CDCl}_3)$  6.45 (5-H) and 7.78 (3-H);  $\delta_{\text{C}}$  62.9 (C-5) and 145.9 (C-3)]. Solvolysis of (8) was achieved with 60% perchloric acid in acetic anhydride below 5 °C, and the parent 1,4,2-dithiazolium salt (9) was precipitated with dry diethyl ether in moderate yield as an extremely hygroscopic solid [ $\delta_{\text{H}}(\text{CF}_3\text{CO}_2\text{D}-\text{CD}_3\text{NO}_2)$  10.80 (3-H) and 12.51 (5-H),  $^4J_{\text{HH}}$  0.55 Hz;  $\delta_{\text{C}}$  168.7 (C-3) and 195.7 (C-5);  $\nu_{\text{max}}(\text{Nujol})$  1 691, 1 108, and 1 089 cm<sup>-1</sup>].

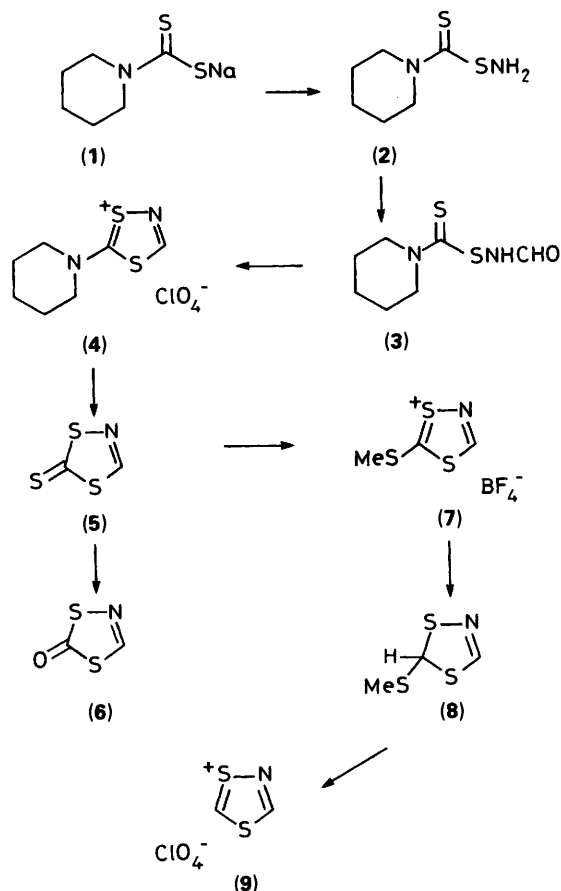
The salt (9) is highly electrophilic, and unstable in those polar solvents in which it is soluble, decomposing for example in CF<sub>3</sub>CO<sub>2</sub>D in *ca.* 1 h. A comparison of <sup>1</sup>H and <sup>13</sup>C data for 3-H and C-3 respectively in the series of salts (4), (7), and (9) suggests increasing positive charge and/or ring current effects at these sites and is consistent with increasing delocalization of the  $\pi$  electrons in these potentially heteroaromatic cations.

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