

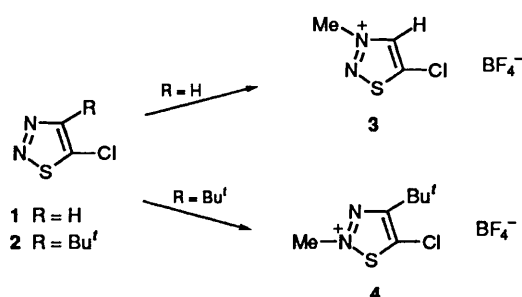
## Reactions of Methylated 5-Chloro-1,2,3-thiadiazolium Salts with Cyclohexane-1,3-diones: X-Ray Crystal Structure Analysis of the Thiapentalenic Products

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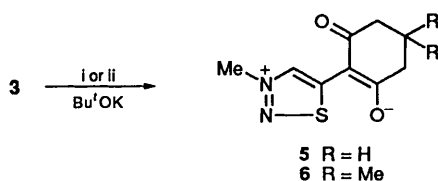
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The N-3 methylated thiadiazolium salt **3** reacts with cyclohexane-1,3-dione and 5,5-dimethylcyclohexane-1,3-dione to give mesoionic 1,2,3-thiadiazoles (**5** and **6**) with short intramolecular S...O contacts, whereas the N-2 methylated thiadiazolium salt **4** furnishes oxathiole derivatives (**7** and **8**) with short intramolecular S...N contacts.

We have recently reported<sup>1</sup> that 5-chloro-1,2,3-thiadiazole **1** is methylated with Meerwein's reagent exclusively at the N-3 position to give the salt **3**. If a bulky substituent is attached to the C-4 atom, such as in **2**, then methylation occurs at the N-2 atom and the salt **4** is obtained. The salts **3** and **4** differ fundamentally in their reactions with cyclohexane-1,3-diones as shown in this paper.



Treatment of 5-chloro-3-methyl-1,2,3-thiadiazolium tetrafluoroborate **3** under basic conditions with cyclohexane-1,3-dione (1 equiv.) yielded product **5** which was characterized on the basis of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectral results and microanalysis. In particular, in the <sup>1</sup>H NMR spectrum two triplets for CH<sub>2</sub>CO were observed ( $\delta$  2.55 and 2.65), and in the <sup>13</sup>C NMR spectrum two different CH<sub>2</sub>CO resonances (CH<sub>2</sub> at  $\delta$  34.3/37.4 and CO at  $\delta$  192.5/192.9; CDCl<sub>3</sub> as solvent) Product **6**, obtained by reaction of **3** with dimedone, (5,5-dimethylcyclohexane-1,3-dione) also exhibited two different CH<sub>2</sub>CO resonances. The magnetic non-equivalence of the CH<sub>2</sub>CO groups in the NMR spectra indicates restricted rotation around the C-5 atom due to the S...O contact. This weak interaction disappeared when trifluoroacetic acid (trace) was added to the NMR sample of **5**, resulting in the observation of only one CH<sub>2</sub>CO resonance with doubled intensity. Also, the triplet resonances in the <sup>1</sup>H NMR spectrum coalesced upon raising the temperature to 70 °C in deuterated dimethyl sulfoxide solution.



Reagents: i, cyclohexane-1,3-dione; ii, dimedone

Further information about the structure of **5** was obtained by a single crystal X-ray analysis, the results of which are shown in Fig. 1. The atoms C(7), C(8) and O(13) are coplanar with the thiadiazole ring, with O(13) lying close to the extended N(2)–S(1) bond axis (172°). The S(1)–N(2) bond length (1.67 Å)

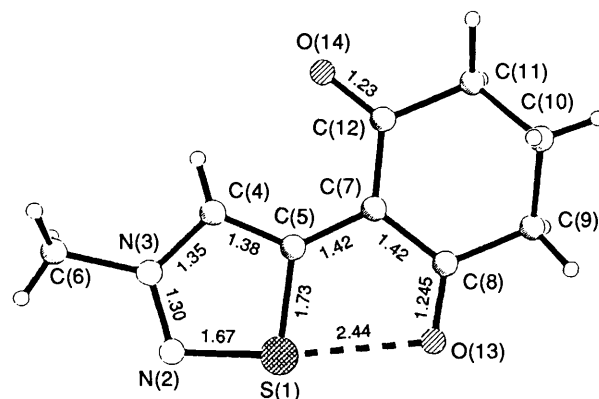


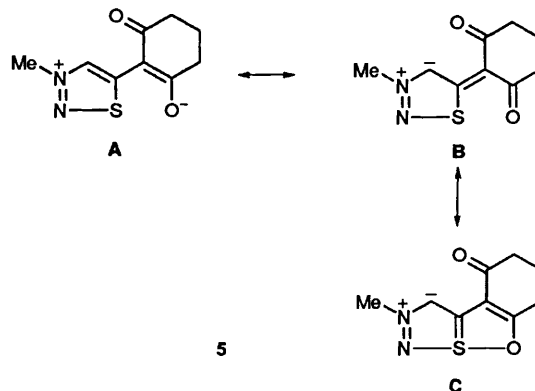
Fig. 1 Molecular structure of **5** with arbitrary numbering scheme and selected bond lengths

is normal for a thiadiazole<sup>2</sup> and the S...O distance (2.44 Å) is significantly shorter than the sum of the corresponding van der Waals radii (3.2 Å) and slightly shorter than the Huggins constant energy distance of 2.58 Å.<sup>3</sup> The covalent bond strength can be estimated by using Huggins' equation [eqn. (1)];

$$D_{AB} = 10^{2(r_A^* + r_B^* - r_{AB})} \quad (1)$$

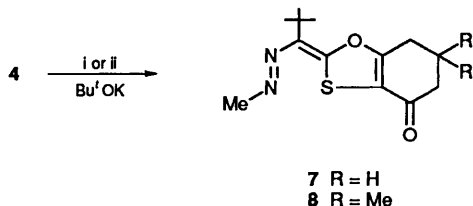
where  $D_{AB}$  is the bond dissociation energy in kcal mol<sup>-1</sup>,  $r_{AB}$  is the observed bond distance, and  $r_A^*$  and  $r_B^*$  are the computed constant energy radii for the atoms A and B. The calculated dissociation energy for S(1)–O(13) is only 2 kcal mol<sup>-1</sup> and we conclude that there is very little covalent bonding between the sulfur and the oxygen. Thus, resonance hybrid **5C**, having a hypervalent sulfur atom,<sup>4</sup> would hardly contribute to the overall structure of the molecule; a conclusion in compliance with the single bond character of the S(1)–C(5) bond (1.73 Å).

The bond lengths C(5)–C(7) and C(7)–C(8) are equal to within experimental limits (1.42 Å) and intermediate between a single (1.535 Å) and a double bond (1.326 Å),<sup>5</sup> whereas C(8)–O(13)



(1.245 Å) is longer than C(12)–O(14) (1.23 Å). This is best represented by canonical structures **5A** and **5B** showing electron delocalisation of the conjugated system. The accumulation of negative charge on C(4) is consolidated by the chemical shift value of this atom in the  $^{13}\text{C}$  NMR spectrum ( $\delta$  133) which is shielded by 5 ppm compared with that of the protonated molecule ( $\delta$  138).

When the enolate anions of both cyclohexane-1,3-dione and dimedone were treated with the thiadiazolium salt **4**, the reactions took a different course and yielded the oxathioles **7** and **8** respectively. Thus, the chlorine atom of **4** is substituted by the enolate oxygen and the resulting enol intermediate has undergone cyclisation at sulfur with concurrent ring-opening of the thiadiazole nucleus. This skeletal rearrangement is accompanied by a shift of the N-methyl resonances in the NMR spectra; namely from  $\delta_{\text{H}}$  4.6 and  $\delta_{\text{C}}$  47.5 ( $^1J$  147) in **4** to  $\delta_{\text{H}}$  3.92 and  $\delta_{\text{C}}$  52.7 ( $^1J$  136) in the products. Also, one of the original carbonyl resonances undergoes a large upfield shift when it becomes part of the oxathiole ring ( $\delta$  164–165).



Reagents: i, cyclohexane-1,3-dione; ii, dimedone

The structure of compound **8** was finally established by an X-ray analysis; selected bond lengths are shown in Fig. 2. The bonds N(2)–N(3) (1.27 Å), C(4)–C(5) (1.35), C(7)–C(8) (1.34) and C(14)–O(18) (1.21) have double-bond character, whereas N(3)–C(4) (1.39) is longer than a normal N(sp<sup>2</sup>)–C(sp<sup>2</sup>) single bond (1.355).<sup>5</sup> Thus, no pronounced electron delocalisation is observed, although the conjugated system is quasi-planar with a mean deviation of 0.073 Å from the best plane through the eight atoms 1–8. The C(4)–C(5)–S(1) angle (128°) is large and causes the atoms N(2)···S(1)–C(8) to deviate from colinearity (internal angle 160.5°). The S(1)···N(2) separation of 2.54 Å is slightly smaller than the Huggins constant energy distance of 2.58 Å,<sup>3</sup> indicating virtually no covalent bonding but rather a close interacting contact. From these results we conclude that compound **8** has no thiapentalenic characteristics and that the canonical form **8** is the best representation of the molecule.

## Experimental

2-(3-Methyl-1,2,3-thiadiazol-5-*io*)-3-oxocyclohex-1-enolate **5**.—Compound **3** (445 mg, 2 mmol) was added to a suspension

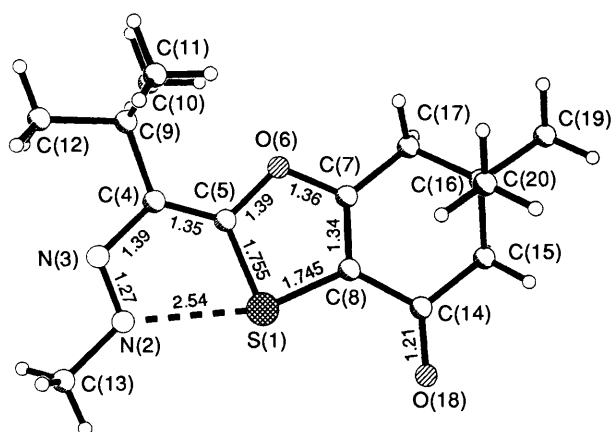


Fig. 2 Molecular structure of **8** with arbitrary numbering scheme and selected bond lengths

of cyclohexane-1,3-dione (246 mg, 2.2 mmol) and potassium *tert*-butoxide (493 mg, 4.4 mmol) in acetonitrile (20 cm<sup>3</sup>) and the mixture was stirred for 15 min. After removal of the solvent, the residue was chromatographed on silica gel with chloroform–methanol (5:1) as the eluent to give the *thiadiazole* **5** (310 mg, 74%), m.p. 265 °C (from EtOH);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 3120s and 1620s;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 2.05 (2 H, quint.,  $J$  6.5), 2.55 (2 H, t,  $J$  6.5), 2.65 (2 H, t,  $J$  6.5), 4.40 (3 H, s, NMe) and 9.80 (1 H, s, aromatic H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 20.8, 34.3 and 37.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 45.5 (NMe,  $^1J_{\text{CH}}$  144,  $^3J_{\text{CH}}$  2), 107.3 (CO–C=O), 133.2 (thiadiazole C-4), 158.8 (thiadiazole C-5,  $^2J_{\text{CH}}$  10), 192.5 and 192.9 (CO);  $m/z$  210 (M<sup>+</sup>, 92%), 182 (M<sup>+</sup> – CO, 29), 169 (13), 140 (M<sup>+</sup> – CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO, 100), 94 (13), 53 (28) and 43 (36) (Found: C, 51.6; H, 4.75. C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 51.41; H, 4.79%).

Note: Compound **6** (m.p. 205 °C) was similarly prepared in 73% yield from the thiadiazolium salt **3** and dimedone.

*Crystal Structure of Compound 5*.—Crystal Data: C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S,  $M$  = 210.3. Monoclinic,  $a$  = 4.539(1),  $b$  = 14.083(4),  $c$  = 14.813(4) Å,  $\beta$  = 95.33(2)°,  $V$  = 942.7(4) Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 20 automatically centred reflections,  $\lambda$  = 1.541 84 Å), space group  $P2_1/c$  (No. 14),  $Z$  = 4,  $D_x$  = 1.481 g cm<sup>-3</sup>. Brown–yellow needles from ethanol. Crystal dimensions 0.45 × 0.15 × 0.10 mm<sup>3</sup>,  $\mu(\text{Cu-K}\alpha)$  = 28.60 cm<sup>-1</sup>.

*Data Collection and Processing*. Siemens P4-PC diffractometer,  $\omega$  –  $2\theta$  mode with  $\omega$  scan width 0.60 deg,  $\omega$  scan speed 2–60 deg min<sup>-1</sup>, graphite-monochromated Cu-K $\alpha$  radiation; 2055 reflections measured ( $2.0 \leq 2\theta \leq 113.5^\circ$ ,  $+h, +k, +l$ ), 1247 unique [merging  $R$  = 0.0227 after absorption correction (max., min. transmission factors = 0.508, 0.432)], giving 1100 with  $F > 4\sigma(F)$ . Three check reflections measured every 100 reflections showed no significant decrease in intensity.

*Structure analysis and refinement*. Heavy atom methods. Full matrix least-squares with all non-hydrogen atoms anisotropic, hydrogen atoms with isotropic U, unit weights. Final  $R$  and  $R_w$  values are 0.0426 and 0.0504. Siemens SHELXTL PLUS (PC version)<sup>6</sup> program used for calculations and drawings.

2-[2,2-Dimethyl-1-(methylazo)propylidene]-6,7-dihydro-6,6-dimethyl-1,3-benzoxathiol-4(5H)-one **8**.—Compound **4** (557 mg, 2 mmol) was added to a suspension of dimedone (308 mg, 2.2 mmol) and potassium *tert*-butoxide (493 mg, 4.4 mmol) in acetonitrile (20 cm<sup>3</sup>), and the mixture was stirred at room temperature for 15 min. After removal of the solvent, the residue was chromatographed on silica gel with diethyl ether–hexane (1:1) as the eluent to give the *oxathiole* **8** (230 mg, 39%), m.p. 130 °C (from Et<sub>2</sub>O–hexane);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1671s;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.17 (6 H, s, 2 Me), 1.44 (9 H, s, Bu'), 2.39 (2 H, s, CH<sub>2</sub>CO), 2.68 (2 H, s, CH<sub>2</sub>C=C) and 3.92 (3 H, s, NMe);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 28.4 and 34.5 (CMe<sub>2</sub>), 29.5 and 36.1 (Bu'), 37.7 and 51.4 (CH<sub>2</sub>), 52.7 (NMe,  $^1J$  136), 112.9 (C-3a,  $^3J$  1.5 and 4), 136.1 (C-Bu,  $^4J$  1.5), 147.3 (C-2,  $^5J$  1.3), 163.8 (C-7a,  $^2J$  9) and 192.2 (CO,  $^2J$  6.5);  $m/z$  294 (M<sup>+</sup>, 11%), 251 (M<sup>+</sup> – MeN<sub>2</sub>, 30), 212 (12), 97 (BuCN<sub>2</sub><sup>+</sup>, 96), 83 (23), 70 (15), 69 (C<sub>5</sub>H<sub>9</sub><sup>+</sup>, 100), 67 (22), 57 (*t*-Bu<sup>+</sup>, 13), 55 (16), 43 (MeN<sub>2</sub><sup>+</sup>, 30) and 41 (93) (Found: C, 61.1; H, 7.5. C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 61.20; H, 7.53%).

Note: Compound **7** (m.p. 159 °C) was similarly prepared in 29% yield from the thiadiazolium salt **4** and cyclohexane-1,3-dione.

*Crystal Structure of Compound 8*.—Crystal data: C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S,  $M$  = 294.4. Orthorhombic,  $a$  = 12.348(2),  $b$  = 14.367(3),  $c$  = 18.360(4) Å,  $V$  = 3257(2) Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 20 automatically centred reflections,  $\lambda$  = 1.541 84 Å), space group  $Pcab$  (alt.  $Pbca$  No. 61),  $Z$  = 8,  $D_x$  = 1.201 g cm<sup>-3</sup>. Orange parallel-

epipeds from diethyl ether-hexane. Crystal dimensions  $0.40 \times 0.08 \times 0.04 \text{ mm}^3$ ,  $\mu(\text{Cu-K}\alpha) = 17.90 \text{ cm}^{-1}$ .

**Data Collection and Processing.** Siemens P4-PC diffractometer,  $\omega - 2\theta$  mode with  $\omega$  scan width 0.60 deg,  $\omega$  scan speed 2-60 deg  $\text{min}^{-1}$ , graphite-monochromated Cu-K $\alpha$  radiation; 2447 reflections measured ( $2.0 \leq 2\theta \leq 105.47^\circ$ ,  $+h, +k, l$ ), 1873 unique [merging  $R = 0.0757$  after absorption correction (max., min. transmission factors = 1.000, 0.626)], giving 1085 with  $F > 4\sigma(F)$ . Three check reflections measured every 100 reflections showed no significant decrease in intensity.

**Structure Analysis and Refinement.** Direct methods. Full matrix least-squares with all non-hydrogen atoms anisotropic, hydrogen atoms in calculated positions with isotropic  $U$ , weighting scheme  $w = 1/[\sigma^2(F_o) + 0.0049F_o^2]$ . Final  $R$  and  $R_w$  values are 0.0778 and 0.1002. Siemens SHELXTL PLUS (PC-version)<sup>6</sup> program used for calculations and drawings.

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