

## The *anhydro*-5-Hydroxy-1,3-oxathiolium Hydroxide System, a New Mesoionic Ring System

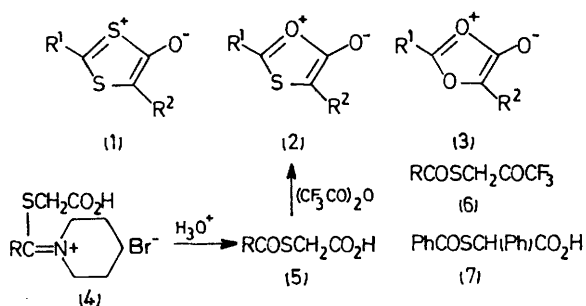
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**Summary** Cyclodehydration of *p*-chlorobenzoylthioglycollic acid and *p*-methoxybenzoylthioglycollic acid with trifluoroacetic anhydride gave *anhydro*-2-*p*-chlorophenyl-5-hydroxy-4-trifluoroacetyl-1,3-oxathiolium hydroxide and the corresponding 2-*p*-methoxyphenyl derivative, respectively; these are the first examples of a 5-membered mesoionic ring system containing only oxygen and sulphur as nuclear heteroatoms.

THE majority of the 5-membered mesoionic ring systems prepared contain at least one nitrogen atom,<sup>1</sup> the noticeable exception being the *anhydro*-4-hydroxy-1,3-dithiolium hydroxide system<sup>2</sup> (**1**). This is a very reactive ring system and it was of interest to study the effect of replacing the sulphur atoms in (**1**) to yield, respectively, the *anhydro*-5-hydroxy-1,3-oxathiolium hydroxide system (**2**) and the *anhydro*-4-hydroxy-1,3-dioxolium hydroxide system (**3**). We now

report the preparation of system (2) which also indicates that the synthesis of (3) is probably unattainable.



Hot, dilute acid (2N-HCl) hydrolysis of the S-carboxymethylpiperidinium bromide<sup>3</sup> (4; R = *p*-ClC<sub>6</sub>H<sub>4</sub>) gave *p*-chlorobenzoylthioglycollic acid (5; R = *p*-ClC<sub>6</sub>H<sub>4</sub>) as cream plates, m.p. 135—136°.† Treatment of this acid with a minimum volume of trifluoroacetic anhydride at room temperature in a drybox resulted in a progressive colour change of the reaction mixture from colourless through orange to red. After 2 h, anhydrous ether (*ca.* 1 ml) was added and a quantitative yield of (2; R<sup>1</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = COCF<sub>3</sub>) separated as hygroscopic, bright red needles, m.p. 144—147° (decomp.) [n.m.r. (CDCl<sub>3</sub>) AA'BB' absorption at  $\delta$  7.96—7.52, *J* 9 Hz; i.r. (KBr)  $\nu_{COCF_3}$  1815,  $\nu_{CO}$  1640 cm<sup>-1</sup>; *M*<sup>+</sup> 308 (0.1), *p*-ClC<sub>6</sub>H<sub>4</sub>CO<sup>+</sup> 139 (100)]. Similarly, *p*-methoxybenzoylthioglycollic acid (5, R = *p*-MeOC<sub>6</sub>H<sub>4</sub>), colourless needles, m.p. 132—133°, in dry

benzene (2 ml) and trifluoroacetic anhydride (2 ml) gave after 10 min the corresponding *anhydro*-5-hydroxy-2-*p*-methoxyphenyl-4-trifluoroacetyl-1,3-oxathiolium hydroxide (2; R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>; R<sup>2</sup> = COCF<sub>3</sub>) as hygroscopic, tiny brick-red plates, m.p. 160—165° (decomp.)‡ [n.m.r. (CDCl<sub>3</sub>) AA'BB' absorption at  $\delta$  7.95—6.96, *J* 8 Hz; 3.90, s, 3H, OMe; i.r. (KBr)  $\nu_{COCF_3}$  1800,  $\nu_{CO}$  1640 cm<sup>-1</sup>; *M*<sup>+</sup> 304 (0.5), *p*-MeOC<sub>6</sub>H<sub>4</sub>CO<sup>+</sup> 135 (100)]. In the mass spectrum of each product, ions at *m/e* 282 (R = *p*-ClC<sub>6</sub>H<sub>4</sub>) and *m/e* 278 (R = *p*-MeOC<sub>6</sub>H<sub>4</sub>) corresponding to (6; R = *p*-ClC<sub>6</sub>H<sub>4</sub> and *p*-MeOC<sub>6</sub>H<sub>4</sub>, respectively) were observed. These presumably arise by hydrolysis of (2) and subsequent decarboxylation and illustrate the sensitivity of this ring system to traces of moisture. On addition of water to (2; R = *p*-ClC<sub>6</sub>H<sub>4</sub>) gas evolution occurred almost immediately and (6; R = *p*-ClC<sub>6</sub>H<sub>4</sub>) was obtained [ $\nu_{COCF_3}$  1770,  $\nu_{CO}$  1670 cm<sup>-1</sup>; *M*<sup>+</sup> 282 (0.5)].

The trifluoroacetyl group in (2) appears to be essential for the stability of the ring system, other customary cyclodehydration agents being unsuccessful. All attempts to effect ring closure of benzoylphenylthioglycollic acid (7) colourless needles, m.p. 97—98°, with trifluoroacetic anhydride under a variety of conditions were unsuccessful. The extreme sensitivity of (2) to moisture suggests that present efforts to obtain (3) will be unsuccessful.

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† Satisfactory analytical and spectral data were obtained for the products described.

‡ M.p. determined in a sealed capillary tube.

<sup>1</sup> For reviews see: M. Ohta and H. Kato in 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, 4; W. Baker and W. D. Ollis, *Quart. Rev. Chem. Soc.*, 1957, 11, 15. For other recent references see: K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *J. Org. Chem.*, 1974, 39, 3619; K. T. Potts, E. Houghton, and U. P. Singh, *ibid.*, p. 3627; K. T. Potts, J. Baum, and E. Houghton, *ibid.*, p. 3631.

<sup>2</sup> K. T. Potts and U. P. Singh, *Chem. Comm.*, 1969, 570; H. Gotthardt and B. Christl, *Tetrahedron Letters*, 1968, 4743.

<sup>3</sup> K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, 1961, 15, 1087.