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

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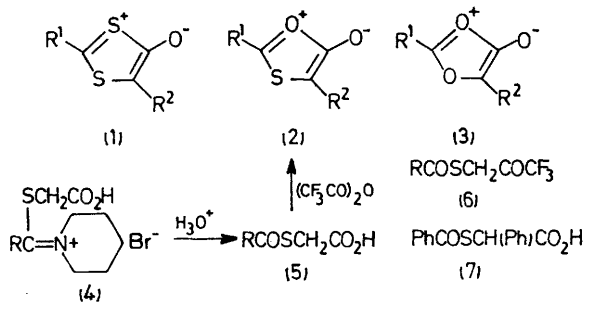
Summary Cyclodehydration of *p*-chlorobenzoylthioglycollic acid and *p*-methoxybenzoylthioglycollic acid with trifluoroacetic anhydride gave *anhydro*-2-*p*-chlorophenyl-5-hydroxy-4-trifluoroacetyl-1,3-oxathiolium hydroxide and the corresponding 2-*p*-methoxyphenyl derivative, respectively; these are 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,[1] the noticeable exception being the *anhydro*-4-hydroxy-1,3-dithiolium hydroxide system[2] (**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[3] (**4**; R = *p*-ClC_6H_4) gave *p*-chlorobenzoylthioglycollic acid (**5**; R = *p*-ClC_6H_4) 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^1 = *p*-ClC_6H_4, R^2 = $COCF_3$) separated as hygroscopic, bright red needles, m.p. 144—147° (decomp.) [n.m.r. ($CDCl_3$) AA'BB' absorption at δ 7·96—7·52, J 9 Hz; i.r. (KBr) ν_{COCF_3} 1815, ν_{CO} 1640 cm^{-1}; M^+ 308 (0·1), *p*-$ClC_6H_4CO^+$ 139 (100)]. Similarly, *p*-methoxybenzoylthioglycollic acid (**5**, R = *p*-$MeOC_6H_4$), 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^1 = *p*-$MeOC_6H_4$; R^2 = $COCF_3$) as hygroscopic, tiny brick-red plates, m.p. 160—165° (decomp.)‡ [n.m.r. ($CDCl_3$) AA'BB' absorption at δ 7·95—6·96, J 8 Hz; 3·90, s, 3H, OMe; i.r. (KBr) ν_{COCF_3} 1800, ν_{CO} 1640 cm^{-1}; M^+ 304 (0·5), *p*-$MeOC_6H_4CO^+$ 135 (100)]. In the mass spectrum of each product, ions at *m/e* 282 (R = *p*-ClC_6H_4) and *m/e* 278 (R = *p*-$MeOC_6H_4$) corresponding to (**6**; R = *p*-ClC_6H_4 and *p*-$MeOC_6H_4$, 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_6H_4) gas evolution occurred almost immediately and (**6**; R = *p*-ClC_6H_4) was obtained [ν_{COCF_3} 1770, ν_{COS} 1670 cm^{-1}; M^+ 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.

[1] 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.

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

[3] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, 1961, **15**, 1087.