

1,2-Oxathiolan, a Simple Sultene

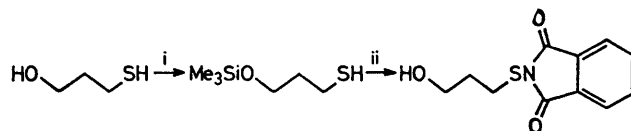
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Summary Evidence is presented which indicates that pyrolysis of *N*-(3-hydroxypropylthio)phthalimide gives 1,2-oxathiolan as a volatile product *via* an intermediate tentatively identified as a cyclic oligomer.

In recent years a number of examples of cyclic sulphenic acid esters (sultenes) in which the heteroatoms are part of a five-membered ring have been described.¹ In all instances however the sultene system is heavily disguised by the presence of bulky substituents and/or neighbouring functional groups. We now describe the preparation of a compound which on the basis of ¹H and ¹³C n.m.r., u.v., and m.s. data is suggested to be the parent heterocycle 1,2-oxathiolan (1).

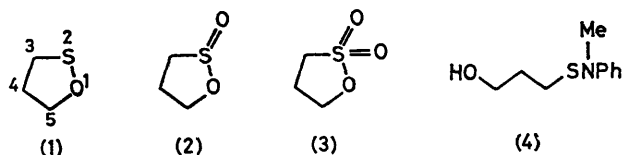
N-(3-Hydroxypropylthio)phthalimide, prepared as shown in the Scheme, was pyrolysed at 100 °C and 0.07 mmHg and the products were collected in a cold trap (liq. N₂) to give a waxy solid which was purified by trituration with ether. Immediately after dissolving in CDCl₃ the ¹H n.m.r.



SCHEME. *Reagents*: i, Me₃SiCl-Et₃N;
ii, phthalimide-Br₂-pyridine, then H₃O⁺.

spectrum of the product showed δ 3.82 (2H, t, *J* 6.5 Hz, CH₂O), 3.06 (2H, t, *J* 6.5 Hz, CH₂S), and 1.97 (2H, quintet, *J* 6.5 Hz); the solid is considered to be a cyclic oligomer (OCH₂CH₂CH₂S)_{*n*}. After allowing the solution to stand for 20 h at 20 °C a new set of peaks had appeared in the n.m.r. spectrum and the product responsible could be purified by co-distillation with CDCl₃ at 20 °C and 0.1 mmHg. The distillate had δ 3.96 (2H, t, *J* 6.5 Hz, CH₂O), 3.61 (2H, t, *J* 6.5 Hz, CH₂S), and 2.20 (2H, quintet, *J* 6.5 Hz, H-4); ¹³C n.m.r. δ 75.1 (CH₂O), 36.5 (CH₂S), and 29.8 (C-4) p.p.m.;

λ_{\max} 317 nm (ϵ 53);† g.l.c.-m.s. showed a single component with m/z 90 (M^+ , 100), 73 (22), 59 (20), and 45 (25%).



Chemical evidence which supports the identification of the volatile product as 1,2-oxathiolan includes: (i) reaction with 1 equiv. of *m*-chloroperbenzoic acid which gave 1,2-oxathiolan 2-oxide (2),² δ (CDCl_3) 4.2—5.0 (2H, m, CH_2O), 3.05 (2H, m, CH_2S), and 2.04—2.84 (2H, m, H-4) and, with 2 equiv., 1,2-oxathiolan 2,2-dioxide (3),³ δ (CDCl_3) 4.45 (2H,

t, CH_2O), 3.23 (2H, m, CH_2S), and 2.67 (2H, m, H-4), and (ii) reaction with *N*-methylaniline to give the sulphenamide (4), δ (CDCl_3) 6.5—7.4 (m, aromatic), 3.66 (t, J 6 Hz, CH_2O), 3.32 (s, Me), 2.80 (t, J 7 Hz, CH_2S), 1.99 (br. s, OH), and 1.78 (quintet, J 7 Hz, CH_2). The compound (1) underwent rapid reaction on shaking a CDCl_3 solution with water to give a mixture of bis-(3-hydroxypropyl) disulphide and the sultine (2), whereas the acyclic analogue *n*-propyl propane-sulphenate was less sensitive to water. It is known that sulphenates can react with water to give a mixture of disulphide and sulphinic acid.⁴

The accompanying communication⁵ provides corroborative evidence that 1,2-oxathiolan is obtained on thermolysis of neat *N*-(3-hydroxypropylthio)phthalimide *in vacuo*.

(Received, 8th April 1981; Com. 415.)

† For comparison *n*-propyl propane-sulphenate has λ_{\max} (CDCl_3) 273 nm (ϵ 104).

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