1,2-Oxathiolan, a Simple Sultene

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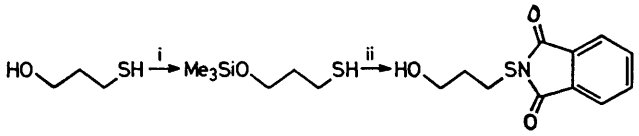
Summary Evidence is presented which indicates that pyrolysis of *N*-(3-hydroxypropylthio)phthalimide gives 1,2-oxathiolan as a volatile product *via* an intermediate tentatively identified as a cyclic oligomer.

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 ^{13}C n.m.r., u.v., and m.s. data is suggested to be the parent heterocycle 1,2-oxathiolan (**1**).

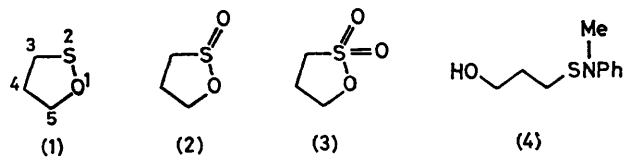
N-(3-Hydroxypropylthio)phthalimide, prepared as shown in the Scheme, was pyrolysed at 100 °C and 0·07 mmHg and the products were collected in a cold trap (liq. N_2) to give a waxy solid which was purified by trituration with ether. Immediately after dissolving in $CDCl_3$ the ^1H n.m.r.



SCHEME. *Reagents:* i, Me_3SiCl–Et_3N; ii, phthalimide–Br_2–pyridine, then H_3O^+.

spectrum of the product showed δ 3·82 (2H, t, *J* 6·5 Hz, CH_2O), 3·06 (2H, t, *J* 6·5 Hz, CH_2S), and 1·97 (2H, quintet, *J* 6·5 Hz); the solid is considered to be a cyclic oligomer $(OCH_2CH_2CH_2S)_n$. 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 $CDCl_3$ at 20 °C and 0·1 mmHg. The distillate had δ 3·96 (2H, t, *J* 6·5 Hz, CH_2O), 3·61 (2H, t, *J* 6·5 Hz, CH_2S), and 2·20 (2H, quintet, *J* 6·5 Hz, H-4); ^{13}C n.m.r. δ 75·1 (CH_2O), 36·5 (CH_2S), 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%).



(1) (2) (3) (4)

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 propanesulphenate was less sensitive to water. It is known that sulphenates can react with water to give a mixture of disulphide and sulphinate.[4]

The accompanying communication[5] provides corroborative evidence that 1,2-oxathiolan is obtained on thermolysis of neat *N*-(3-hydroxypropylthio)phthalimide *in vacuo*.

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† For comparison n-propyl propanesulphenate has λ_{max} ($CDCl_3$) 273 nm (ϵ 104).

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