1,2-Oxathiolan[1]

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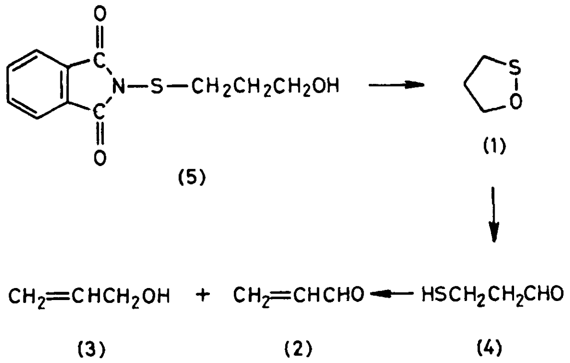
Summary 1,2-Oxathiolan has been isolated in the gas phase and characterized by its electron-impact and thermally induced decompositions.

IN a recent paper we suggested the intermediacy of 1,2-oxathiolan (**1**), the first unsubstituted cyclic sulphenate (sultene),† in the gas-phase thermolyses of thietan 1-oxide and 1,2-oxathiolan 2-oxide,[2] the identity of (**1**) being established by characterizing the consecutively formed decomposition products acrolein (**2**) and a C_3H_6O isomer (**3**), generated *via* 3-mercaptopropanal (**4**) by H_2S and S extrusions, respectively.

Whitham and Davis investigated the possible formation of (**1**) by thermal decomposition of 3-(phthalimidothio)-propan-1-ol (**5**) *in vacuo*.[3] On the basis of ^1H and ^{13}C n.m.r. spectroscopy and 70 eV electron-impact mass spectrometry, they suggested that (**1**) was in fact formed. We report here the isolation of the cyclic sulphenate (**1**) in the gas phase and the decomposition of (**1**) under electron-impact and gas-phase thermolytic conditions.



Following smooth heating of compound (**5**) *in vacuo* to around 380 K we collected the volatile reaction products in the gas inlet of a Varian MAT CH5 D double focussing mass spectrometer equipped with a combined electron impact–field ionization–field desorption (e.i.–f.i.–f.d.) ion source.

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† A heavily substituted sultene has previously been reported by G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, 1975, **97**, 6909.

The resulting f.i. mass spectrum revealed only a single peak at m/z 90, strongly indicative of the formation of a compound (hereafter called '90') with molecular weight 90 a.m.u. as the only volatile product. Phthalimide was detected as the remaining substance in the reaction chamber. Electron impact (70 eV) induced decomposition of the product '90' gave rise to the following fragments: m/z 90 ($M^{\cdot+}$, 74), 73 (17), 63 (7), 62 (11), 59 (17), 45 (25), 43 (10), 42 (24), 41 (100), and 39 (15%). The actual composition of the molecular ion (m/z 90) was, by high resolution, established to be C_3H_6OS (found: 90·0139, calc.: 90·0139).

The similarities between the 70 eV e.i. mass spectrum and that previously reported for thietan 1-oxide[4] are striking; however, minor but significant differences are observed, especially in the cluster of peaks around m/z 60. Thus, thietan 1-oxide must be considered as a likely candidate for the reaction product '90,' in spite of the ^1H n.m.r. spectrum recorded by Whitham and Davis,[3] which does not unambiguously define (**1**).

In addition to 1,2-oxathiolan (**1**) and thietan 1-oxide a variety of cyclic and non-cyclic compounds have *a priori* to be considered as possible candidates for '90.' However, a common feature of these compounds is the presence of an XH group (X = O, S) as a structural unit. The possible candidature of these compounds was ruled out by isolating the reaction product following cracking of the OD-analogue of (**5**).‡ No deuterium incorporation in the reaction product was observed, *i.e.* the mass spectra remained unchanged, establishing the absence of a possible XH group in the compound '90.'§

To distinguish between the cyclic sulphenate (**1**) and thietan 1-oxide the gas-phase thermolytic decomposition of compound '90' appeared to be advantageous, since thietan 1-oxide in addition to the common products (**2**) and (**3**) gives rise to the formation of considerable amounts of thietan and C_3H_6 by O and SO extrusions, respectively.[2] Application of flash-vacuum pyrolysis–field-ionization mass spectrometry[6] (f.v.t.–f.i.m.s.) revealed a f.i.m.s. spectrum exhibiting molecular ions corresponding to thermally generated product. Scrutiny of the f.i.m.s. spectrum following thermolysis at 1043 K revealed intense peaks at m/z 56 and 58, whereas a total absence of peaks at m/z 74 and 42, corresponding to thietan and C_3H_6, respectively, was also noted, on which basis we unambiguously assigned 1,2-oxathiolan as compound '90.'

Field-ionization–collision-activation (f.i.–c.a.) mass spectra of the consecutively formed products, exhibiting molecular ions m/z 56 and 58, were found to be identical to those of authentic acrolein and allyl alcohol,¶ respectively.

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‡ In order to avoid D–H exchange the gas inlet was first saturated with D_2O vapour.

§ The applicability of this technique has unequivocally been demonstrated by studying 3-mercaptopropanal (**4**) as a representative of the XH-bearing C_3H_6OS isomers (ref. 5).

¶ Since only quantitative differences in the f.i.–c.a. spectra of allyl alcohol, propanal, and oxetan are observed, we are not able to elucidate whether minor amounts of one of the latter two compounds are present in addition to allyl alcohol.

[1] For part 5 of the series 'Gas-Phase Thermolyses' see L. Carlsen, H. Egsgaard, and P. Pagsberg, *J. Chem. Soc., Perkin Trans.* 2, in the press; for part 4 see ref. 2; for part 3 see L. Carlsen, H. Egsgaard, E. Schaumann, H. Mrotzek, and W.-R. Klein, *J. Chem. Soc. Perkin Trans.* 2, 1980, 1557.

[2] L. Carlsen, H. Egsgaard, and D. N. Harpp, *J. Chem. Soc., Perkin Trans.* 2, in the press.

[3] G. H. Whitham and A. P. Davis, preceding communication.

[4] S. R. Heller and G. W. A. Milne, 'EPA/NIH Mass Spectra Data Base,' NSRDS-NBS 63, vol. 1, 1978.

[5] H. Egsgaard and L. Carlsen, to be published.

[6] L. Carlsen and H. Egsgaard, *Thermochim. Acta*, 1980, **38**, 47.