Flash Thermolysis: a Synthesis of Very Reactive Thiocarbonyls. Thioacrolein and Thiobenzaldehyde

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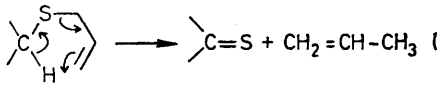
Summary The flash thermolysis (*ca.* 900 K) of four allyl sulphides has been shown to generate the corresponding thiocarbonyl compounds; thioacrolein and thiobenzaldehyde have been characterised spectroscopically at *ca.* 77 K.

ALTHOUGH a number of routes to thiocarbonyl compounds are available, they are generally only suitable for the preparation of modestly reactive substances.[1] We now report a route that allows very reactive members of this series to be trapped for spectroscopic and, in principle, chemical studies.


(1)

In an initial investigation of the suitability of the flash thermolytic degradation of allyl sulphides as a route to thiocarbonyl compounds by process (1),† allyl *exo*-2-bornyl sulphide‡ (**1**) and allyl cyclohexyl sulphide‡ (**2**) were thermolysed under conditions indicated in the Table in an apparatus described elsewhere;[2] contact times were *ca.* 1 ms. The products, thiocamphor and cyclohexanethione, are known.[3,4] The reaction appeared to proceed with high efficiency as shown by the propene yields, but low yields of the thiones were obtained probably because of their decomposition§ and the non-quantitative yields in the reactions employed in their estimation.[5] The products of possible elimination processes in (**1**) and (**2**), 2-bornene and cyclohexene, were not important constituents of the thermolysates under these conditions (<1 and 6%, respectively). In addition, the high yields of propene, rather than hexa-1,5-diene, indicated the absence of any major free-radical process.[6]

Compound	Thermolysis temp. (t/K), ±5°	Composition (%) of isolated material		
		Propene	Thio-carbonyl	Starting material
(**1**)	923	99	28	0
(**2**)	888	54	31[a]	17
(**3**)	923	91	—	None recovered
(**4**)	888	75	75[b]	14

[a] Estimated as trimer.[5,8] [b] Estimated as polymer. This was converted, in up to 80% yield, into *cis*-2,4,6-triphenyl-1,3,5-trithian.[9]

The reaction has been applied to the synthesis of two highly reactive compounds that have not been characterised previously, *viz.*, thioacrolein and thiobenzaldehyde, which were prepared from diallyl sulphide (**3**) and allyl benzyl sulphide (**4**), respectively. Because both thioaldehydes react far below ambient temperatures, the yields could not be measured directly. However, some indication of these may be gathered from the yields obtained of propene and of thiobenzaldehyde polymer.

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† Related transformations of oxygen-containing compounds have been published, R. C. Cookson and S. R. Wallis, *J. Chem. Soc. (B)*, 1966, 1245.

‡ Satisfactory analytical and spectroscopic data were obtained for these compounds.

§ Independent experiments have shown that thiocamphor is labile under these flash thermolysis conditions. For the flash thermolysis of camphor, see T. Sato, *Tetrahedron*, 1965, **21**, 2947.

The low temperature (*ca.* 77 K) spectra of thioacrolein and thiobenzaldehyde were obtained by deposition on a sodium chloride plate in a cryostat.[2] Thioacrolein showed maxima at 275 and 580 nm in the u.v.–visible spectrum, and thiobenzaldehyde had maxima at 228, 320, and 575 nm. These values are in good agreement with values calculated for these molecules.[7] In the low-temperature i.r. spectra, strong bands at 1590, 1420, 1178, 1064, and 959 cm^{-1} were assigned to thioacrolein and those at 1597, 1366, 1290, 1218, 1174, 1041, 1022, 746, 703, and 680 cm^{-1} to thiobenzaldehyde. Monitoring of the i.r. spectra showed that thioacrolein reacts at a detectable rate at *ca.* 77 K while thiobenzaldehyde is unreactive up to 110 K.

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