

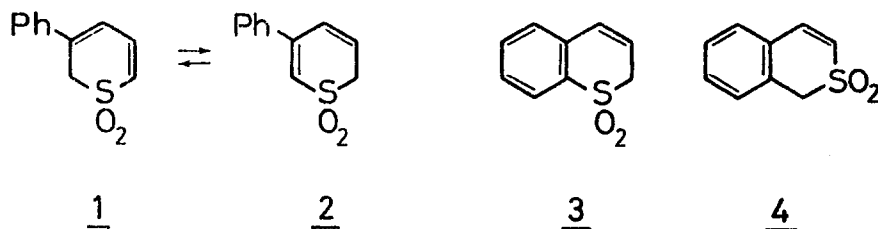
FLASH VACUUM THERMOLYSES OF THIOPYRAN 1,1-DIOXIDES

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Conjugated sulphene intermediates have been generated from thermolysis<sup>1</sup> and photolysis<sup>2</sup> of thiete sulphones. In studies designed to extend this work to 4π electron systems we inferred that sulphenes could be intermediates in the photolysis of benzothiopyran 1,1-dioxides but no such intermediates were trapped.<sup>3</sup> Our interest in flash vacuum thermolysis<sup>4</sup> prompted us to study the thermolysis of these and related systems in the hope of trapping possible sulphene intermediates. We chose 3-phenyl-2H-thiopyran 1,1-dioxide (1)<sup>5</sup> as our initial compound to study. However (1) undergoes a [1,5] hydride shift on gentle warming to give a mixture of (1) and (2). Consequently thermolysis gave a complex mixture. In view of this difficulty we turned our attention to systems where such rearrangements are not possible, namely (3) and (4).

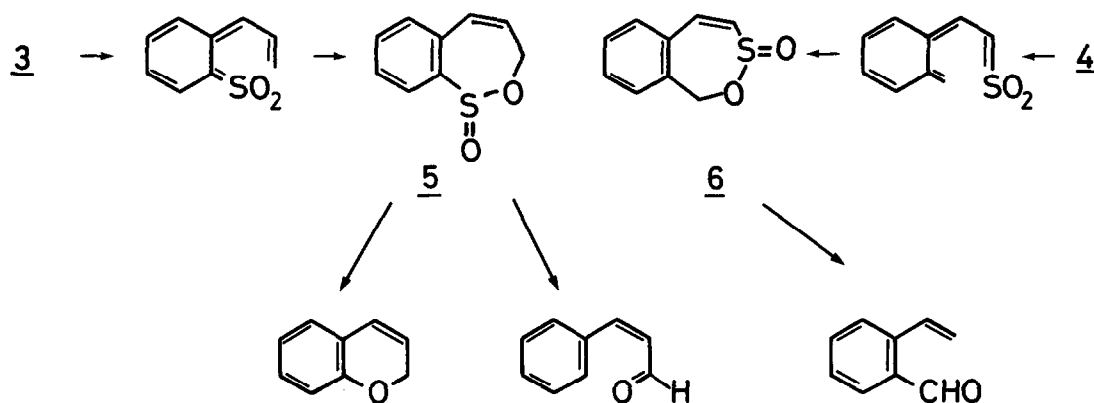


The thiopyran 1,1-dioxides were sublimed through a heated silica tube (10 cm, 1 cm I.D.) at 0.001 mm Hg, the products collected at a cold-finger cooled in acetone/dry ice, and analysed by <sup>1</sup>H n.m.r. and by g.l.c. (Table). Trapping experiments with phenol or methanol on the cold-finger failed to alter the product ratios. Red sulphur monoxide was also obtained on the cold-finger, but no sulphur containing organic products were obtained. The amount of indene produced rises sharply with temperature from both (3) and (4), but the ratio of cinnamaldehyde to 2H-1-benzopyran from (3) remains constant. Contrary to precedent<sup>6</sup> no ring expanded products, e.g. (5), were obtained although the products except indene are probably obtained from such species. The most likely course of these reactions is via conjugated sulphenes to (5) and (6), as shown. Cleavage of the S-O-alkyl bond will give diradical species which can ring-close or transfer a hydrogen atom. Compound (6) can undergo a [1,5] hydride shift and then lose SO. Only o-vinylbenzaldehyde<sup>7</sup> was isolated when (6)<sup>3</sup> was subjected to our

thermolysis conditions. Indene probably arises, at least in bulk, from direct extrusion of  $\text{SO}_2$  from (3) and (4). In these reactions and in the corresponding photolytic experiments the conjugated sulphenes are not trapped probably because of a rapid cyclisation back to aromaticity.

Table

<u>Thermolysis of (3)</u>				<u>Thermolysis of (4)</u>		
<u>Product</u>	<u>Furnace Temperature</u>			<u>Product</u>	<u>Furnace Temperature</u>	
	<u>650°C</u>	<u>675°C</u>	<u>775°C</u>		<u>700°C</u>	<u>775°C</u>
(3)	100%	75%	15%	(4)	50%	12%
indene		5%	20%	indene	23%	42%
cinnamaldehyde		10%	30%	<i>o</i> -vinylbenzaldehyde	23%	36%
2H-1-benzopyran		6%	18%			



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