Thermolysis of Unsaturated Sulphonyl Species: the "Sulpho-Cope" Rearrangement

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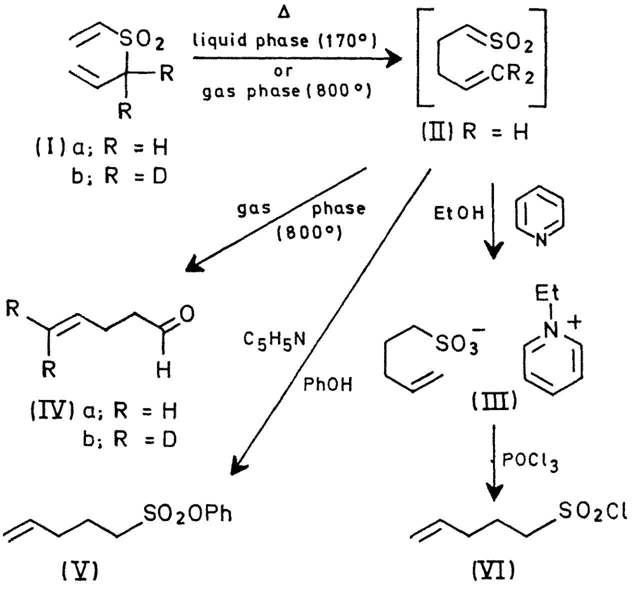
Summary Evidence is presented that a sulphene may be generated by (a) Cope rearrangement of allyl vinyl sulphone in either the gas or liquid phase, and (b) flash thermolysis of ethylenesulphonyl chloride.

PREVIOUS reports[1] have described experiments directed toward generation of sulphenes by thermolysis of sulphonyl derivatives. We report two new thermal reactions of unsaturated sulphonyl species which take place *via* sulphenes.

As part of the classic study of the rearrangement of hexa-1,5-dienes Cope *et al.*[2] attempted to rearrange allyl vinyl sulphone (Ia); they apparently expected to form (II), but obtained only intractable material. We find that by using appropriate sulphene trapping reagents and conditions designed to suppress side reactions (such as polymerisation or addition to the vinylsulphone group), we obtain products derived from the sulphene (II). When heated in a mixture of pyridine and ethanol at 165—170° (Carius tube) for 2 h, (Ia) gave a 70% yield of *N*-ethyl-pyridinium pent-4-enesulphonate (III), identified by (a) conversion into the sulphonyl chloride (VI) and (b) comparison with an authentic specimen prepared (in 93% yield) by reaction of ethyl pent-4-enesulphonate with pyridine in ethanol at 165—170°. Similar heating of (Ia) in a mixture of pyridine and phenol gave the phenyl ester (V) though in only 14% yield. The simplest interpretation of these facts is that (Ia) undergoes Cope rearrangement to the sulphene (II) as shown in Scheme 1.

In the vapour phase under the conditions of flash thermolysis,[1c] (Ia) at 800° gave pent-4-enal[3] in low (8%) yield along with the characteristic indications[1c] of sulphur monoxide. The loss of SO[1c] and the formation of a carbonyl compound has been found in various systems[1] to be a characteristic reaction of sulphenes on flash thermolysis above *ca.* 700°.

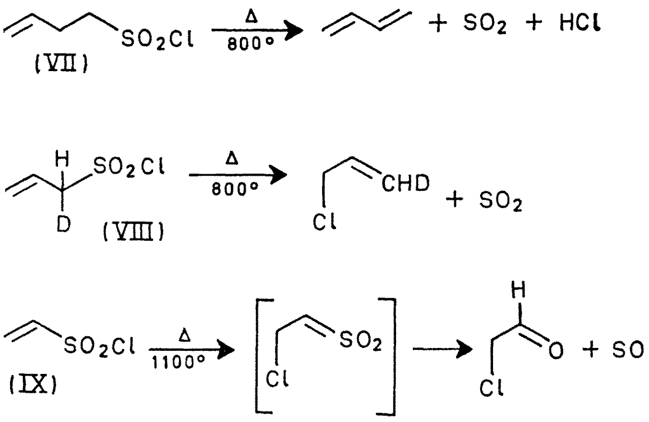


SCHEME 1

Proof that the rearrangement (Ia) → (II) is of order [3,3] was obtained from the reaction of (Ib), which gave

(IVb) with no sign of the [3-$^2H_2$]- aldehyde. With EtOD and pyridine (followed by reaction with $POCl_3$), (Ib) gave [1-$^2H_1$, 5-$^2H_2$]-pent-4-enesulphonyl chloride, as expected.

Though flash thermolysis of methanesulphonyl[4] and ethanesulphonyl chlorides has given formaldehyde and acetaldehyde, respectively, in fairly good yields, similar treatment of (VI) yielded no (IVa). Thermolysis of the lower homologues of (VI), however, gave the results summarized in Scheme 2. At 800° good yields of butadiene, hydrogen chloride and sulphur dioxide, and allyl chloride and sulphur dioxide, were obtained from (VII) and (VIII),[5] respectively. The latter reaction was shown to be intramolecular (as would be expected of a reaction in a flow system with short contact times) by deuterium labelling (Scheme 2); the n.m.r. spectrum of the allyl chloride from [1-$^2H_1$]-prop-2-enesulphonyl chloride indicated the presence of [3-$^2H_1$]-allyl chloride with no detectable proportion of the [1-$^2H_1$]-allyl isomer. Ethylenesulphonyl chloride[6] (IX) at 1100° gave α-chloroacetaldehyde; the reaction is readily rationalizable as an intramolecular rearrangement to chloromethylsulphene followed, as with other sulphenes at this temperature, by the loss of SO.



SCHEME 2

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