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THERMAL DETHIONYLATION OF STILBENE EPISULFOXIDES EVIDENCE FOR A TWO-STEP MECHANISM[1]

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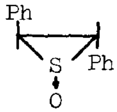
Recent report on the thermal fragmentation of 2-butene episulfoxides[2] have prompted us to communicate our own findings on the related problem. In previous publications,[3] we reported a facile method of the synthesis of episulfoxides and could isolate two pairs of stereoisomers, *i.e.*, *cis*- and *trans*-2-butene episulfoxides and *cis*- and *trans*-stilbene episulfoxides. Of these substances, *trans*-2-butene episulfoxide was found too unstable to handle at room temperature. Thus, we focused our attention on the thermal behavior of the latter pairs.

The stereoisomeric stilbene episulfoxide (I) were each pyrolyzed in toluene at 0, 25, and 50°, as well as in the heated inlet of a glpc system at 150, 240, and 290°. In all cases examined, the extrusion of sulfur monoxide proceeded smoothly and stilbenes were obtained in more than 70% yield. The isomeric ratios of the olefins were determined from glpc peak areas (Table I).

The observed data demonstrate that the extrusion of sulfur monoxide from *trans*-episulfoxide proceeds almost stereospecifically, while that from *cis*-isomer occurs with complete loss of stereospecificity and especially in the latter case, the ratios of *cis* *vs*. *trans*-olefin were dependent on the decomposition temperature. This means that the thermal decomposition of I must proceed in a stepwise mechanism and not in the manner of a symmetry allowed nonlinear cheletropic reaction.[4,5]



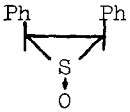


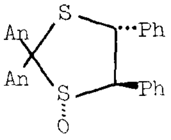
Table I. Stilbenes from Stilbene Episulfoxides^a

Decomp. temp.	from *trans*-I		from *cis*-I	
	cis(%)	*trans*(%)	*cis*(%)	*trans*(%)
0	0	100	61	39
25	0	100	60	40
50	0	100	45	55
150	0	100	7	93
240	1	99	11	89
290	2	98	13	87

^{a}Errors are estimated to be 2%.

A remaining question to be answered is the nature of the reaction intermediate. Dipolar ion and diradical species are the feasible ones. However, the former seemed to us less attractive, because all our attempts to prove the one by trapping with 1,3-dipolarophiles were resulted in vain. On the other hand, the intervention of diradical intermediate was ascertained as follows by trapping experiment with thiocarbonyl compounds, a well known scavenger for carbon radicals.[6]

When di-*p*-anisyl thioketone was added to the thermolysis system in toluene, a 1:1 adduct was obtained in good yield. The structural assignment based on spectra and analyses indicated that the product is a mixture of stereoisomeric 2,2-bis(*p*-methoxyphenyl)-4,5-diphenyl-1,3-dithiolane-1-oxides (II ∼ V). The 100MHz nmr spectra revealed that the product derived from *trans*-I is a mixture of II and III (81% total yield) in the ratio of 3:1 at 25^o, while that from *cis*-I is a mixture of all four isomers (69% total yield)[7]. In the case of *cis*-isomer, temperature dependence of the relative ratios of dithiolane-1-oxides was again observed (Table II).



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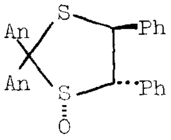

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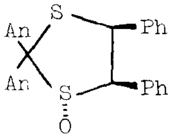
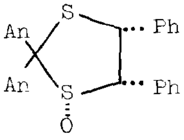


IV



V

Table II. The Reaction of cis-Stilbene Episulfoxide with Di-p-anisyl Thioketone

Reaction temp. (°C)	Total Y.	Dithiolane-1-oxides II	III	IV	V
0	66	25	1	54	20
25	69	36	7	29	28
50	57	35	12	24	29

For more quantitative analysis, the reaction rates of I with di-p-anisyl thioketone were measured. The observed addition rate was first-order in the episulfoxides and independent of the concentration of the thioketone. This means that the addition of episulfoxides to thioketone depends only on the rate of self-decomposition of episulfoxide. The calculated rates of the decomposition of I in several solvents are collected in Table III. It is evident from the Table that the ionizing power of the medium has little effect on the decomposition rates, suggesting the intermediacy of a homopolar species.

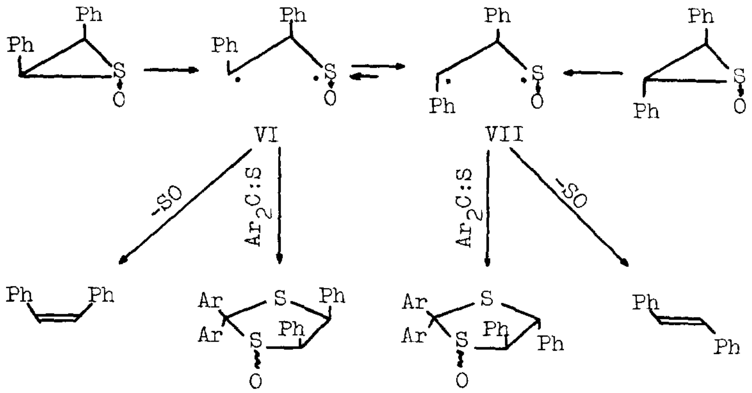
The observed kinetics clearly demonstrate that the thermal fragmentation of I is a unimolecular reaction and proceeds through a diradical intermediate. The diradical intermediates, VI and VII (Scheme I), are capable of internal rotation about the carbon-carbon bond. The rotation, however, would be restricted owing to the steric repulsion of the two phenyl groups. The temperature dependence in the cis-I cases indicates that the intermediate VII is the thermally favorable conformer. As a result, the decomposition of trans-I apparently proceeded with high degree of stereospecificity, while that of cis-I non-stereospecificity.

Table III. The Decomposition Rates of Stilbene Episulfoxides in Several Solvents.[a]

Solvent	trans-I $k \times 10^5$ (sec^{-1})	cis-I $k \times 10^6$ (sec^{-1})
THF	2.1	8.9
CH_2Cl_2	1.1	5.7
DMSO	1.1	1.8

[a] All rates were measured at 26.0°.

Scheme I.



Other episulfoxides also reacted with various thioketones to afford the corresponding dithiolane-1-oxides in excellent yields. Thus, it may be concluded that the thermal fragmentation of episulfoxides to afford olefins and sulfur monoxide is a general process, and proceeds stepwise through the diradical intermediate and, hence, essentially in non-stereospecific sense.

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(7) Two ring protons in VI were observed as an AB quartet at τ 5.92 and 5.24 (J=4.5 Hz), VII at 5.85 and 4.95 (J=4.5 Hz), VIII at 6.01 and 5.49 (J=6.0 Hz), and IX at 5.68 and 5.29 (J=5.4 Hz).