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REACTIONS OF STILBENE EPISULPHOXIDES AND EPISULPHIDES WITH ORGANOLITHIUM COMPOUNDS. EVIDENCE FOR ATTACK AT SULPHUR AND AT PROTON.

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The reaction of organolithium compounds with stilbene episulphoxides and episulphides leads to stereospecific desulphurization and to ring opening. The stereochemistry of the latter reaction depends on the structural features.

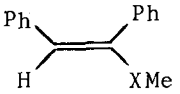
The reactions of organolithium derivatives with episulphones and episulphides have been already investigated.[1-3] Cis-stilbene episulphone suffers[1] thermolysis as well as attack to proton leading to cis-stilbene and to a vinyl sulphinate whose configuration at the stilbene skeleton was found to be inverted.[4] Vilsmaier[2] attributed the stereospecific formation of the olefin from cis-2-butene episulphone to attack by the lithium reagent at sulphur. The exclusive and stereospecific desulphurization of 2-butene episulphides was explained by Trost[3] through the intervention of a hypervalent sulphur. The behaviour of episulphoxides with bases until now was unknown.

We have treated stereomerically pure cis- and trans-stilbene episulphoxides[5] (I, II) and episulphides with two molar equivalents of n-butyllithium at 0°C in ether (or alternatively phenyllithium under the same conditions). After 30 min. the reaction mixture was quenched with excess methyl iodide and the products separated and characterized by GLC and thick layer chromatography. Each reaction was repeated at least three times.

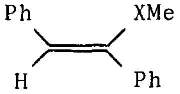
Cis-stilbene episulphoxide (I) gave cis-stilbene (41%), di-n-butyl sulphide (41%) and (E)-1,2-diphenyl-1-methylsulphinyl ethene (IIIb) (31%). Trans-stilbene episulphoxide (II) gave trans-stilbene (97%), di-n-butyl sulphide (95%) and Z/E 1,2-diphenyl-1-methylsulphinyl ethene (IIIb, IVb) (1.5%, Z > E) (see Scheme 1). The isolated products were compared (m.p., NMR, GLC, IR, MS) with authentic samples.

Comparable results were obtained with phenyllithium: in addition to those described above some minor products determined by the nature of the phenyl group were isolated.

The independent synthesis of the two 1,2-diphenyl-1-methylsulphinyl ethenes allowed us to establish their stereochemistry. The mixture of Z/E 1,2-diphenyl-1-methylmercapto ethenes[6] was separated by preparative liquid chromatography on Merck silicagel H60. The two sulphides isolated gave characteristic elemental analysis and mass spectra. Their configuration was established,[7] after oxidation to the corresponding sulphoxides and sulphones, by the LIS effect[8] on the olefinic protons using Eu(dpm)$_3$ for sulphoxides and Yb(dpm)$_3$ for sulphones (see Table).



(III)a X = S
b X = SO
c X = SO_2



(IV)a X = S
b X = SO
c X = SO_2

Table - PMR parameters (ppm) of compounds (IIIa-c), (IVa-c)

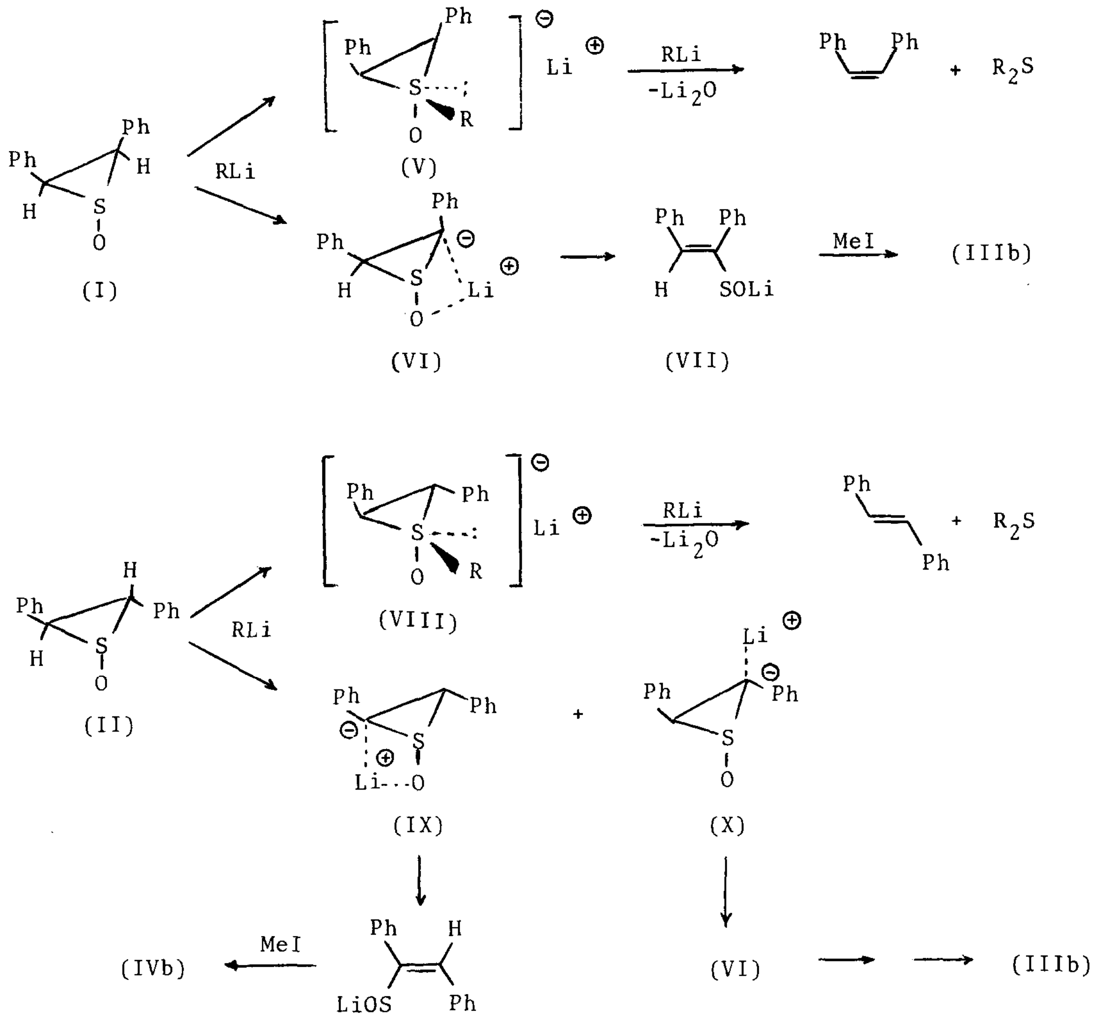
Compound	m.p. °C	CH_3	H	aromatic protons	LIS
IIIa	oil	2.20	6.54	6.9 -7.1 (5H,m); 7.32(5H,s)	-
b	72-73	2.43	7.40	7.18-7.50(10H,m)	5.55
c	121-122	2.80	7.83	7.0 -7.45(5H,m); 7.48(5H,s)	0.93
IVa	oil	1.89	6.74	7.2 -7.9 (10H,m)	-
b	93-94	2.46	7.20	7.30-7.80(10H,m)	1.19
c	119-120	2.70	7.23	7.30-7.80(10H,m)	0.16

The results obtained after reaction of (I) and (II) with n-butyl- or phenyllithium indicate a stereospecific desulphinylation for both stereoisomers, whereas the ring opening process is stereospecific only for (I). In order to account for the experimental results we propose the following reaction scheme (Scheme 1).

The stereospecific formation of stilbenes from both episulphoxides is accounted for by an oxy-sulphurane intermediate[9] (V, VIII); this can further react with the organolithium to give di-n-butyl or diphenyl sulphurane which disaggregates in a concerted and hence stereospecific manner to yield the olefin and the sulphide.

Cis-episulphoxide (I) gave in good yield and stereospecifically the vinyl sulphoxide (IIIb) probably through proton abstraction from the less hindered side of the molecule to give a carbanion (VI) stabilized by chelation[8] of the lithium cation with the syn sulphinyl oxygen; such a carbanion can rearrange to the vinyl sulphenate (VII) which is subsequently methylated to (IIIb). On the other hand

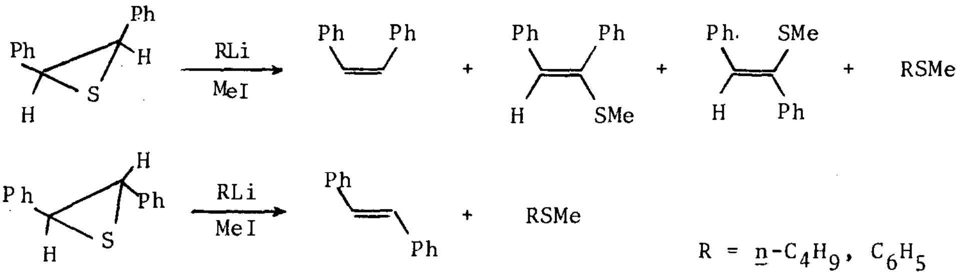
Scheme 1



R = n-C_4H_9, C_6H_5

the trans-episulphoxide (II), having both faces shielded by a phenyl group, gave both the stereoisomeric vinylsulphoxides (IIIb, IVb) in very poor yield. These must arise from two isomeric carbanions (IX, X). The inversion of configuration at the carbon skeleton found in (IIIb) is tentatively explained through the formation of a carbanion (X), anti with respect to the sulphinyl oxygen, which can invert to (VI); the driving force for such an inversion would be the possibility of chelation with the lithium cation. Such considerations are supported by the behaviour of the corresponding episulphides under exactly the same reaction conditions (Scheme 2).

Scheme 2



Cis-stilbene episulphide gave *cis*-stilbene (47%), *n*-butyl methyl sulphide (44%) along with a 38% mixture of Z/E 1,2-diphenyl-1-methylmercapto ethenes (IIIa, IVa) (Z/E ≃ 1/18) (GLC).

Trans-stilbene episulphide gave exclusively *trans*-stilbene (99%) and *n*-butyl methyl sulphide (99%) (GLC). Phenyllithium gave the same results.

The stereospecific formation of both stilbenes[11] can be explained by accepting the sulphurane mechanism proposed by Trost[3] for the desulphurization of the 2-butene episulphides. The formation of a mixture of the two vinyl sulphides (IIIa, IVa) supports the possibility of inversion of the carbanion (formed by attack of the base on the less hindered face of *cis*-stilbene episulphide) when the stabilization brought about by the sulphinyl oxygen is absent. On the other hand the exclusive desulphurization of the *trans*-stilbene episulphide confirms that the attack of the base on the proton is rendered more difficult by the shielding of the *syn*-phenyl.

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