

EPISULPHOXIDE FORMATION FROM SULPHINES¹

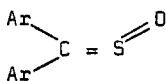
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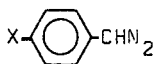
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We wish to describe here an unusual², non oxidative preparation of episulphoxides so far normally obtained by oxidation of the corresponding episulphides³.

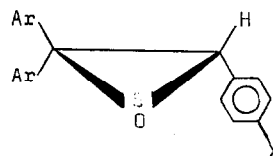
When the aromatic sulphines (I) dissolved in pentane or ether are allowed to react with aryldiazomethane (II) at 0-10°C, a mixture of diastereoisomeric episulphoxides (III) is obtained as a crystalline precipitate. The same sulphines react with diazomethane or alkyl substituted diazomethane yielding the Δ^3 -1,3,4-thiadiazoline-1-oxide system^{4,5}.



(I)



(II)



(III)

a : Ar = C₆H₅

a : X = H

a:Ar = C₆H₅, X = H (yield 55%)

b : X = CH₃

b:Ar = C₆H₅, X = CH₃ (" 40%)

b : Ar/Ar = = Fl

c:Ar/Ar = Fl, X = H (" 92%)

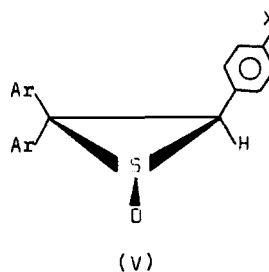
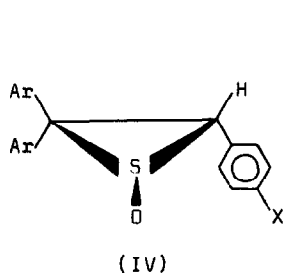
d:Ar/Ar = Fl, X = CH₃ (" 80%)

The structure of the episulphoxides (III) is supported by ir and nmr spectral

data (vide infra) and correct elemental analyses. The structure (III) was finally confirmed by comparison of (IIIa) with an independently synthesized sample obtained by oxidation of 1,1,2-triphenylethylsulfide⁶ with an equimolar amount of monoperphthalic acid in 60% yield.

The episulphoxides easily lose sulphur monoxide to give the olefinic derivatives. In fact, chromatography of (III) on silica, using benzene/petroleum ether as eluant, gave almost quantitatively triphenylethylene⁷, 1,1-diphenyl-2-p-tolylolethylene⁸: 9-benzylidenfluorene⁹, and 9-(p-methyl)-benzylidenfluorene¹⁰ respectively. This experiment also supports the structures of (III).

All the episulphoxides (III) having two asymmetric centres may assume two configurations, i.e. cis or trans (IV) and (V) respectively.



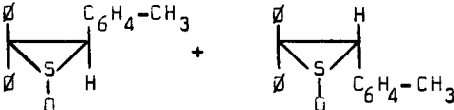
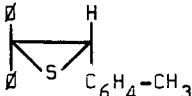
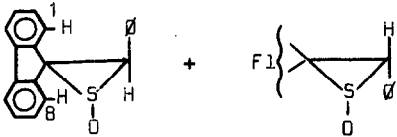
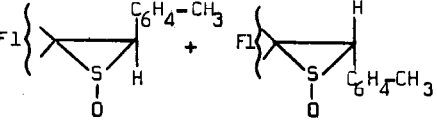


Actually all the nmr spectra of (III) are typical of a mixture of two diastereoisomers (see Table).

Any attempt to separate the two components by the usual chromatographic methods failed owing to the instability of the compounds.

In the Table the chemical shifts of the C₂-hydrogens in the mixtures of diastereoisomeric episulphoxides are compared with those of the parent episulphides, when available. According to the asymmetry of the SO group, it is believed^{3, 11} that protons located in the close proximity of the S=O bond should be deshielded, while protons on the opposite side should be shielded with respect to the same protons of the parent sulphide. This assumption has been used to assign the configuration of a number of 1,4-oxathian-5-oxides¹¹ and of simple episulphoxides³. On this basis, the isomer formed in higher quantity in our three membered cyclic systems is always that with the S=O bond and the aryl group in position-2 having the trans configuration. In the episulphoxides (IIIc) and (IIIId), both isomers

TABLE - Nmr and ir data for the episulphoxides (III).^a

Products	% Isomers	C ₂ -Protons	Fluorenic Protons (H ₁ or H ₈)	p-Methyl	ν_{SO} cm ⁻¹
 <p>trans</p> <p>cis</p>	<p>trans 72</p> <p>cis 28</p>	<p>4.83 (s)</p> <p>4.42 (s)</p>			1085
		4.67 (s)			
 <p>trans</p> <p>cis</p>	<p>trans 83</p> <p>cis 17</p>	<p>4.52 (s)</p> <p>4.18 (s)</p>		<p>2.25 (s)</p> <p>2.31 (s)</p>	1080, 1090
		4.43 (s)		2.16 (s)	
 <p>trans</p> <p>cis</p>	<p>trans 63</p> <p>cis 37</p>	<p>5.20 (s)</p> <p>4.56 (s)</p>	<p>5.80 (d)</p> <p>6.44 (d)</p>		1080
 <p>trans</p> <p>cis</p>	<p>trans 65</p> <p>cis 35</p>	<p>5.16 (s)</p> <p>4.63 (s)</p>	<p>5.93 (d)</p> <p>6.58 (d)</p>	<p>2.31 (s)</p> <p>2.40 (s)</p>	1085

^a Nmr spectra were obtained at 60 MHz with a Jeol, C 60 HL spectrometer for solutions in CDCl₃ with Me₄Si as internal reference. Chemical shifts are given in p.p.m.

showed one fluorenic hydrogen shifted upfield with respect to the remaining aromatic protons¹². At present we cannot distinguish between H₁ or H₈ but further studies are in progress in order to reach an unambiguous assignment as well as to demonstrate the mechanism of formation with different diazoalkanes either of the thiadiazoline⁴ or of the episulphoxide system.

References

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- 12) For a similar case see ref. 3.