Tetrahedron Letters No. 12, pp. 935-936, 1970. Pergamon Press. Printed in Great Britain.

α,β-EPOXYSULFONES BY EPOXIDATION OF α,β-UNSATURATED SULFONES

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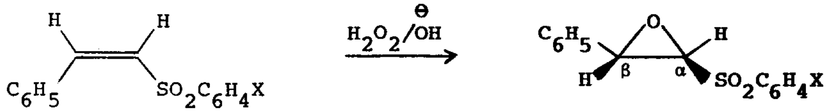
(Received in UK 19 January 1970; accepted for publication 29 January 1970)

We wish to report the synthesis of α,β-epoxysulfones by alkaline epoxidation of α,β-unsaturated sulfones. Treatment of cis-phenyl-β-styryl sulfone (Ia) with hydrogen peroxide under basic conditions produces the trans-epoxysulfone (II) in 85% yield. Similarly, alkaline epoxidation of cis-β-styryl p-tolyl sulfone (III) afforded trans-epoxysulfone IV (94%).



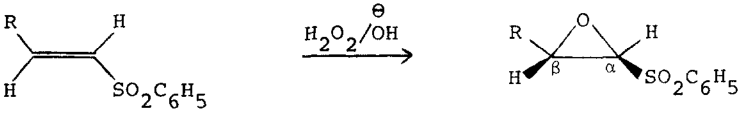
Ia : X = H
III : X = CH_3-p

II : X = H
IV : X = CH_3-p

Compound IV, m.p. 155-158° dec., exhibits in the IR spectrum strong sulfone absorptions at 1310 and 1140 cm^{-1}, and epoxide bands at 1215, 905 and 825 cm^{-1}. The PMR spectrum (in $CDCl_3$) showed, in addition to the protons of the aromatic substituents, two doublets, one proton each, at δ 4.16 (H_α) and δ 4.53 ppm (H_β) with $J_{\alpha\beta}$ 1.5 cps. These data for IV accord fully with those reported recently by Vogt and Tavares[1], and also by Bohlmann and Haffer[2], who synthesized this epoxysulfone by a Darzens condensation of benzaldehyde and chloromethyl p-tolyl sulfone. The value of $J_{\alpha\beta}$ is indicative[1,3] for the trans configuration of the epoxide.

The IR spectrum of II (m.p. 102-104°)[4] was similar to that of IV, as was the PMR spectrum in which the protons H_α and H_β appeared as doublets at δ 4.18 and δ 4.55 ppm, respectively, with $J_{\alpha\beta}$ 1.5 cps. This value of $J_{\alpha\beta}$ points to a trans configuration for II.

Treatment of the geometrical isomer of Ia, e.g. trans-phenyl β-styryl sulfone (Ib), with alkaline hydrogen peroxide gave the trans epoxide II in 83% yield. Alkaline epoxidation of trans-phenyl 1-propenyl sulfone V with hydrogen peroxide produced the trans-epoxysulfone VI (m.p. 51.5-52.5°) in 67% yield[4]. The PMR spectrum (in $CDCl_3$) of VI shows H_α as a doublet at δ 3.91 ($J_{\alpha\beta}$ 1.5 cps), H_β as two superimposed quartets at δ 3.64 and 3.67 ($J_{\alpha\beta}$1.5; $J_{\beta\text{-}CH_3}$ 5.2 cps) and the methyl protons as a doublet at δ 1.41 ppm (J 5.2 cps). Hence, in the latter two cases the stereochemical configuration of the starting material is retained in the epoxide.



Ib : R = C_6H_5
V : R = CH_3

II : R = C_6H_5
VI : R = CH_3

Bohlmann and Haffer[2] have recently reported that their attempts to prepare an epoxysulfone by the above method were unsuccessful.

From the results described above we may conclude that the alkaline epoxidation of α,β-unsaturated sulfones is a stereoselective process, i.e. irrespective of the configuration of the starting material a single stereoisomer of the product is obtained. Thus, the stereochemical course of this epoxidation resembles that of α,β-unsaturated ketones which is also stereoselective[5].

The following procedure is representative: To a solution of 0.77 g (3 mmoles) of III in 10 ml of acetone 1.0 ml of 2.2 N aqueous sodium hydroxide was added, followed by 0.84 ml of 30% aqueous hydrogen peroxide over 10 min. at 40 to 45°. After the addition was completed, stirring was continued for 30 min. at 45-50°. After cooling to room temperature the reaction mixture was poured into 100 ml of water. Subsequent chilling to 0° and filtration, gave the epoxide IV, which was recrystallized from carbon tetrachloride/hexane (1:1); yield 0.77 g (94%), m.p. 155-158° dec.

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