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THE INFLUENCE OF THE OXIDIZING NUCLEOPHILE ON STEREOCHEMISTRY IN THE ALKALINE EPOXIDATION OF α,β-UNSATURED SULFONES

Ruggero Curci* and Fulvio DiFuria

Centro CNR di Studio di Meccanismi di Reazioni Organiche, Istituto di Chimica Organica, University of Padova, 35100 Padova, Italy

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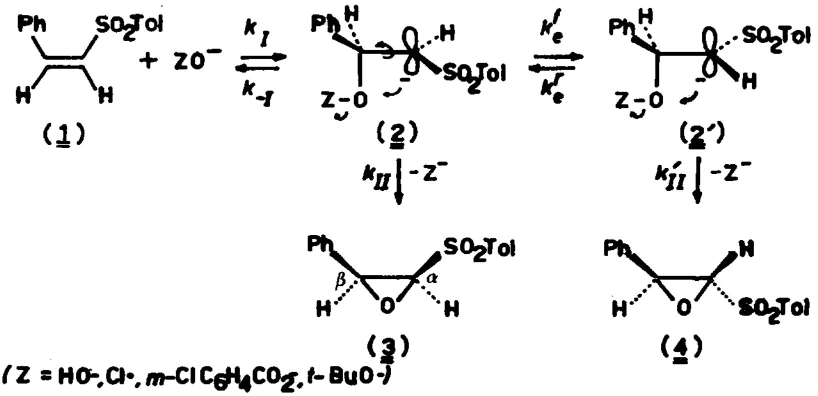
THE epoxidation of α,β-unsatured carbonyl compounds by hydrogen peroxide in alkaline media is known to be non-stereospecific, yielding the same epoxide from either stereoisomeric reactant.[1,2] Alkaline epoxidation of α,β-unsatured sulfones show similar features, as it was reported that treatment of *cis*-1-phenyl-2-(*p*-tolylsulfonyl)ethene 1 or of its *trans*-isomer 1' with alkaline hydrogen peroxide in aqueous acetone at 45° affords *trans*-epoxysulfone 4.[3]

SCHEME



Apparently, under these conditions (in the Scheme, Z = HO-), the initially formed carbanion adduct 2 has sufficient lifetime to undergo $C_\alpha - C_\beta$ rotational equilibration with the intermediate 2', yielding the thermodynamically more stable epoxide 4. Thus, high stereoselectivity is observed.

We now report that the reaction of 1 with ClO^- in aqueous dioxan results in the exclusive formation of *cis*-epoxysulfone 3. The following procedure is representative: to a solution of 0.5 g (1.9 mmol) of 1 dissolved in a mixture of 30 ml dioxan and 8 ml water, 7 ml of 0.62 M KOCl aqueous alkaline solution are added over a period of 3-4 min. (excess oxidant is used due to competing autodecomposition[4]); the reaction solution is kept at 40° for ~ 1 hr., while the apparent[5] pH is kept constant at 13.5 using a pH-stat. The reaction mixture is then poured into water and the precipitate collected giving 0.48 g of product mp 99-104°; pmr spectra show this material to be epoxide 3, accompanied only by some unreacted 1.

Crystallization from CCl_4/*n*-hexane gives 0.40 g (1.53 mmol, yield > 80%) of pure epoxysulfone **3** : mp 109-110°; ir ($CHCl_3$) 1330, 1152 (SO_2 strech), and 908 cm^{-1}(epoxide C-O strech); pmr (acetone-d_6) τ 7.59 (3, s, ArCH_3), 5.48 (2, *H*C=C*H* AB system, J = 3.9 Hz, H_α 5.43, H_β 5.53) , and 2.49-2.73 ppm (9, complex m, Ar*H*). The value of the $H_\alpha H_\beta$ coupling constant leaves no doubt concerning the *cis* configuration [6] of this previously unreported epoxide, $J_{H\alpha H\beta}$ being 1.5 Hz for the corresponding *trans* compound.[3] Thus, epoxidation of **1** by ClO^- appears to be completely stereospecific. When the epoxidation of **1** is carried out with *m*-chloroperoxybenzoic acid (MCPBA) in alkaline ($pH_{app} \approx 14$) dioxan-water 2:1 at 40°, the pmr spectra of the reaction product indicate that the *cis*-epoxide is formed along with small amounts (≤5%) of the *trans* isomer . By way of contrast, the reaction of **1** with hydrogen peroxide or with *t*-butyl hydroperoxide in the same alkaline medium at 40° gives predominantly the *trans*-epoxide, as both **3** and **4** are produced in the ratio of *ca.* 1 : 9 . Independent experiments verified that epimerization of diastereoisomeric epoxides **3** and **4** does not occur in the conditions adopted for epoxidation.

The stereochemistry of epoxidation of **1** seems then to depend upon the nature of the epoxidizing nucleophile. In fact, on going from *t*-$BuOO^-$ and HOO^- to *m*-$ClC_6H_4CO_3^-$ to ClO^-, the reaction proceeds from being highly stereoselective to completely stereospecific. Examining the adopted mechanism (Scheme),these findings might be rationalized : indeed, the leaving group ability is expected to increase in the order *t*-$BuO^- < HO^- <$ *m*-$ClC_6H_4CO_2^- < Cl^-$;[2] clearly, as the efficiency of the leaving group is enhanced, expulsion of Z^- from intermediate **2** can compete favorably with rotation, leading to epoxide **3** .

These findings might have useful synthetic implications. In fact,'electrophilic' epoxidation (which is stereospecific) of alkenes carrying substituents capable of conjugation with the C=C bond by peroxyacids is often difficult .[1] For example,our attempts to epoxidize **1** in $CHCl_3$ with excess MCPBA or with CF_3CO_3H (a powerful oxidant)[2] have failed.

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