

Effect of Substituents on the Stereoselectivity of the Acid-catalysed Hydrolysis of a Series of Aryloxirans. A New Application of the Hammett Equation

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Summary Correlation of the logarithms of the ratios of *cis* to *trans* diols formed in the acid-catalysed hydrolysis of 13 1-arylcyclohexene oxides with the σ^+ constants indicates that there is a higher degree of carbocationic character in the transition state leading to the *cis*-product.

THE epoxide ring in aryloxirans¹ can open in a *syn*- or an *anti*-fashion, the steric course being dependent on the nature of the aryl group, type of reagent, structure and conformation of the substrate, solvent, *etc.* We have investigated^{2,3} the steric course of the ring opening of several derivatives of 1-phenylcyclohexene oxide with different *meta*- and *para*-substituents and found a wide variation in the ratios of *cis* to *trans* adducts.³ In order to obtain a more quantitative correlation between the substituent and the steric course of these reactions, it appeared

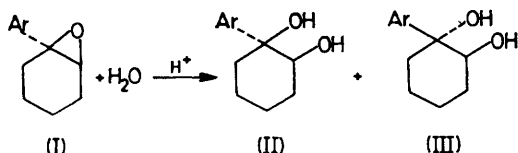
desirable to apply a Hammett-type correlation to the hydrolysis of these epoxides, but direct kinetic measurements were made difficult by insolubility of the epoxides in water, non-availability of a simple spectrophotometric analytical technique, too high rates of hydrolysis of some of the compounds, formation of carbonyl side-products, *etc.*

We therefore devised a new simple approach, which we hoped would give the difference between the Hammett ρ constants for the parallel reactions leading from the epoxides respectively to the *cis*- and *trans*-glycols, simply on the basis of their ratios in the reaction products, these being easily determined by g.l.c. Term by term subtraction of the Hammett equation for the formation of the *trans*-diol from that for the formation of the *cis*-diol gives equation (1), where the subscripts C and T refer to the *cis*- and *trans*-isomers and the superscripts 0 to the unsubstituted compounds. The rate ratios k_C/k_T can be equated with the

$$\log \frac{k_C}{k_T} \times \frac{k_T^\circ}{k_C^\circ} = (\rho_C - \rho_T)\sigma^+ \quad (1)$$

$$\log \frac{[C]}{[T]} \times \frac{[T^\circ]}{[C^\circ]} = (\rho_C - \rho_T)\sigma^+ \quad (2)$$

concentration ratios $[C]/[T]$, leading to equation (2), provided that the two parallel reactions follow the same type of rate equation, a likely assumption in the case of solvolytic reactions.



A series of 13 epoxides of type (I) was used. Suspensions (50 mg) of these were hydrolysed in 0.2N-H₂SO₄ (5 ml) at 25 ± 0.1 °C for 24 h and the products were analysed by g.l.c., giving the ratios of (II) to (III) shown in the Table. These were obtained from two or more runs on each compound. The overall yields of diols were almost quantitative (about 97% for the *p*-methoxy derivative, over 99% in the other cases), the only side-products being identified as rearrangement products (2-arylcyclohexanones, 1-arylcyclopentane-1-carbaldehydes, and 2-arylcyclohex-2-en-1-ols), and it was ascertained that these were not derived from a further transformation of (II) or (III). Some of the epoxides and diols have already been described;³ the others will be discussed elsewhere.

TABLE

Ratios of *cis*- to *trans*-diols formed in the hydrolysis of epoxides of type (I)

Ar	(II) : (III)
<i>p</i> -MeOC ₆ H ₄	95.3 : 4.7
<i>p</i> -MeC ₆ H ₄	82.9 : 17.1
<i>p</i> -Bu ^t C ₆ H ₄	78.2 : 21.8
<i>p</i> -FC ₆ H ₄	70.6 : 29.4
Ph	62.6 : 37.4
<i>m</i> -MeOC ₆ H ₄	60.1 : 39.9
<i>p</i> -ClC ₆ H ₄	60.9 : 39.1
<i>p</i> -BrC ₆ H ₄	54.6 : 45.4
<i>m</i> -FC ₆ H ₄	37.0 : 63.0
<i>m</i> -ClC ₆ H ₄	36.2 : 63.8
<i>m</i> -BrC ₆ H ₄	35.0 : 65.0
<i>m</i> -CF ₃ C ₆ H ₄	26.0 : 74.0
<i>p</i> -NO ₂ C ₆ H ₄	7.5 : 92.5

¹ R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 1959, **59**, 737; J. G. Buchanan and H. Z. Sable, in 'Selective Organic Transformations,' ed. B.S. Thyagarajan, Wiley-Interscience, New York, 1972, vol. I p. 1.

² See, e.g., A. Balsamo, P. Crotti, B. Macchia, and F. Macchia, *Tetrahedron*, 1973, **29**, 199.

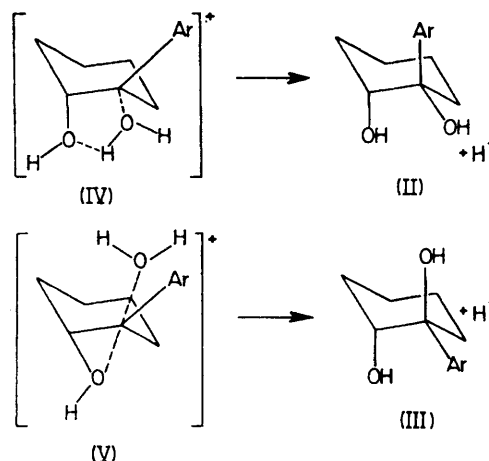
³ See, e.g., G. Bellucci, B. Macchia, and F. Macchia, *Ann. Chim. (Italy)*, 1969, **59**, 1176; G. Bellucci, G. Berti, B. Macchia, and F. Macchia, *Gazzetta*, 1973, **103**, 345; A. Balsamo, P. Crotti, B. Macchia, and F. Macchia, *Tetrahedron*, 1973, **29**, 2183.

⁴ H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

⁵ P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

⁶ D. H. McDaniels and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

Plots of the logarithms of the ratios against the σ^+ constants⁴ were very satisfactory. The correlation coefficient r of 0.991 and standard deviation s of 0.09⁵ proved the soundness of the approach, since even the extreme values for the *p*-methoxy- and *p*-nitro-derivatives fitted reasonably well on the curve. The slope indicated a value of -1.43 for the difference $\rho_C - \rho_T$. The plot obtained when using the σ values of McDaniel and Brown,⁶ is considerably worse ($r = 0.963$, $s = 0.20$), indicating that the transition states leading to the *cis*- and *trans*-diols must both have a pronounced degree of carbocationic character, and that nucleo-



philic attack takes predominantly or exclusively at C-1. The negative value of the difference $\rho_C - \rho_T$ shows that the transition state leading to (II) has a higher carbocationic character, in agreement with previous hypotheses.^{2,3} A likely interpretation is that the intermediate leading to the *cis*-diol (II) is a selectively solvated carbocation such as (IV) which collapses to the *cis*-diol, whereas the transition state leading from the protonated epoxide to the *trans*-diol should have a more borderline A-1 type of structure (V), in which a lower degree of bond-breaking causes preferential approach of the water nucleophile from the *trans*-side. The prevalence of the former mechanism over the latter will increase with increasing electron-donating properties of the aryl group, in good agreement with the more negative value of ρ that we found for the formation of the *cis*-diols.

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