The Kinetic Effect of Ring Strain in an Elimination Reaction

By Robert J. Palmer and Charles J. M. Stirling*
(*School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd* LL57 2UW)

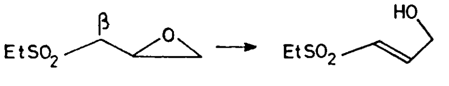
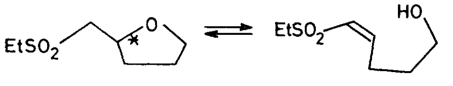
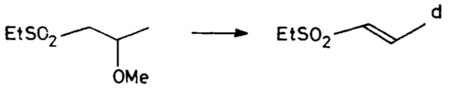
Summary Incorporation of an oxygen leaving group in a 3-membered ring increases reactivity in an activated elimination at least two million fold.

Displacement of poor leaving groups such as alkoxide from *sp*^{3} carbon is a very slow and seldom observed process. It is greatly accelerated, though by how much is not known, when the leaving group is incorporated in a strained, particularly 3-membered, ring. The energy of activation for the displacement process is then reduced by a contribution from the strain energy released and epoxides readily undergo C–O bond fission in reactions with nucleophiles. We now have the first quantitative information with which to assess the contribution of ring strain to the acceleration of an elimination reaction.

The sulphone (**1**), obtained by epoxidation (*m*-chloroperoxybenzoic acid in 1,2-dichloroethane at 75 °C) of allyl ethyl sulphone, gave the alcohol (**4**) on treatment with ethanolic sodium ethoxide. The reaction was followed by stopped-flow spectrometry at 236 nm, and the primary deuterium isotope effect ($k_H/k_D = 2{\cdot}5$) suggests the operation of the $(E_1cB)_I$ mechanism in which deprotonation is rate-determining.[1] A similar result has been obtained by Barton and Houminer[2] in oxo-activated eliminative ring fission of steroid epoxides.

The sulphone (**2**) was obtained from reaction of ethanethiolate ion in ethanol with the tosylate of (+)-tetrahydrofurfuryl alcohol[3] and subsequent oxidation [H_2O_2, $(NH_4)_6Mo_7O_{24}$, MeOH] of the resulting sulphide. The sulphone, but not the sulphide or (+)-tetrahydrofurfuryl alcohol, racemised in ethanolic sodium ethoxide but was recovered intact showing that recyclisation of the alcohol (**5**) is rapid. Racemisation of the sulphone (**2**) occurs with a primary deuterium isotope effect of 0·98, indicating the $(E_1cB)_R$ mechanism for elimination, with ring opening rate determining. The $(E_1cB)_R$ mechanism for elimination in acyclic β-alkoxy-sulphones (**3**; Et=Ph) has already been established.[4]

TABLE

	$k^a_{\mathrm{rel.}}$
 (1) (4)	$2{\cdot}46 \times 10^6$ [b]
 (2) (5)	18·5 [c]
 (3)	1 [b]

[a] For reactions in NaOEt–EtOH at 25 °C. [b] For elimination. [c] For racemisation equated with elimination. [d] Isolated as ethoxy-adduct.

The ring-strain of the epoxy-group, therefore, accelerates eliminative ring fission in the sulphone (**1**) to such an extent that β-deprotonation becomes rate determining. This occurs $2{\cdot}46 \times 10^6$ times faster than elimination in the acyclic sulphone (**3**) and the minimum acceleration of elimination due to ring strain is thus defined.

Ring strain in an epoxide[5] is about 27 kcal mol^{-1} so that about one third of the strain energy is expressed in a reduced energy of activation notwithstanding the evidence that extension of the bond to the leaving group in activated eliminations is probably small.[6] The 5-membered ring sulphone (**2**) shows modest acceleration over the acyclic model consistent with the relief of a small degree of strain (5·6 kcal mol^{-1}).[5]

The absolute leaving ability of carbon groups is very much lower than that of oxygen groups in activated eliminations.[7] We plan to compare eliminative ring cleavage of cyclopropanes with that of larger alicyclic systems. In these cases, rates of deprotonation are unlikely to be rate determining and hence actual rather than minimum rate enhancements should be derivable.

We thank the S.R.C. for equipment and a maintenance grant (to R.J.P.) and Dr. D. R. Marshall for valuable discussions.

(*Received*, 17*th January* 1978; *Com.* 043.)

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