Journal of

The Chemical Society,

Chemical Communications

NUMBER 13/1979 5 JULY

Participation by Remote Epoxy Oxygen in the Solvolysis of *syn*-6-oxabicyclo[3.1.0]hexan-3-ylmethyl *p*-Bromobenzenesulphonate

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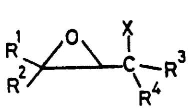
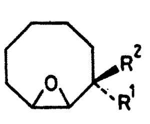
Summary The kinetic data and products obtained from solvolysis of the *syn*- and *anti*-6-oxabicyclo[3.1.0]-hexan-3-ylmethyl *p*-bromobenzenesulphonates (**4a**) and (**5a**) in aqueous ethanol demonstrate that solvolysis of (**4a**) probably involves participation of the epoxy oxygen to form the oxonium ion (**7**) which affords the rearranged products (**6b**) and (**6c**); however, such a participation is stereoelectronically prohibited in the *anti*-analogue (**5a**) and results mainly in the much slower formation of the unrearranged products (**5b**) and (**5c**).

RECENTLY there has been considerable interest in the effects of neighbouring epoxy groups in solvolyses.[1-6] In simple acyclic epoxy systems[1-4] such as (**1**), and in the medium-sized ring derivatives[5,6] (**2**) and (**3**), the rates of solvolysis are usually either slightly faster[1,3,4,6] or much slower[1,2] than the selected model compounds. This is thought to be due to a lack of effective stabilization at the positive charge centre by the carbon–carbon bond of the oxiranyl ring relative to that of the cyclopropyl group. In systems where the solvolysis products were partly or predominantly rearranged and/or the rates of solvolysis were moderately faster than those of the models,[3,4] it was assumed that participation of the neighbouring epoxy group occurred. However, considering the electronic structure of ethylene oxide,[7] one would expect that the epoxy oxygen would be a more efficient internal nucleophile than the carbon–carbon single bond of the ring. Thus, it is doubtful whether anchimeric assistance by the neighbouring epoxy group has really been observed in the past.

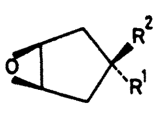


(1)

R^1, R^2, R^3, R^4 = H or Me
X = Cl, p-$BrC_6H_4SO_2 \cdot O$-, or p-$NO_2C_6H_4CO_2^-$

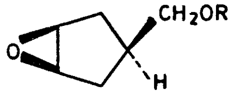


(2)

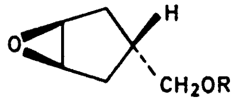


(3)

a; R^1 = H, R^2 = p-$BrC_6H_4SO_2 \cdot O$-
b; R^1 = p-$BrC_6H_4SO_2 \cdot O$-, R^2 = H



(4)

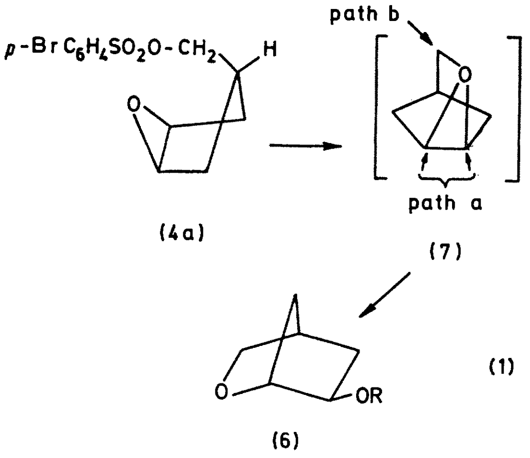


(5)

a; R = p-$BrC_6H_4SO_2$
b; R = H
c; R = Et

We report here the dramatic effect of anchimeric assistance by the epoxy oxygen which is spatially proximate but positionally remote from the reaction centre. The *syn*- and *anti*-3-(hydroxymethyl)-6-oxabicyclo[3.1.0]-hexane (**4b**) and (**5b**) were converted into the brosylates (**4a**) and (**5a**), and solvolysed in 90% aqueous ethanol at 25 °C. Compound (**4a**) (k_{4a} 1·24 × 10^{-4} s^{-1}) was as nearly reactive as *exo*-2-oxabicyclo[2.2.1]heptan-6-yl brosylate (**6a**), (k_{6a} 4·56 × 10^{-4} s^{-1}), and afforded *exo*-2-oxabicyclo-[2.2.1]heptan-6-ol (**6b**) and the ether (**6c**) as the only v.p.c. detectable products. Under the same conditions (**5a**) proved to be kinetically inert. Even though a reasonable rate of solvolysis of (**5a**) could be obtained in 50% aqueous ethanol at 70 °C, a good first order rate constant was not observed.† The products of solvolysis of (**5a**) under the latter conditions were largely the unrearranged alcohol (**5b**) and the ether (**5c**).

Owing to the rate enhancement observed for (**4a**), it is very difficult to find a good model for this system. When either (**5a**) or (**3a**) is used as a model, the rate of solvolysis of (**4a**) is surprisingly faster than that of these compounds by a factor of 10^4.‡ In addition, k_{4a}/k_{5a} is *ca.* 10^4 times larger than k_{3a}/k_{3b}.§ The observed rate enhancement for (**4a**) over the rates for (**5a**) and (**3a**) and the completely rearranged products from the solvolysis of (**4a**) can be accounted for by the fact that the oxonium ion (**7**), arising from participation of the nonbonded electrons of the epoxy-oxygen atom, is involved in the transition state of the ionization of (**4a**). Subsequent selective attack by the solvent on either side of the epoxide ring (path a) gives rise to the products (**6b**) and (**6c**) as shown in equation (1). The absence of formation of the unrearranged products (**5b**) and (**5c**) (path b) is probably best explained in terms of the greater relief of strain achieved by cleavage of the three-membered ring rather than of the five-membered ring.[8]



a; R = p-$BrC_6H_4SO_2$

b; R = H

c; R = Et

Even though a precise estimate of the anchimeric effect of the epoxy oxygen in the solvolysis of (**4a**) cannot be obtained at the moment, the data clearly reflect that the rate acceleration due to participation of the epoxy oxygen is greater than the rate retarding effect of the inductive and polar field effects of the epoxide ring by the largest factor ever reported.[1–6]

Partial support to this work by the National Research Council of Brazil (C.N.Pq.) is gratefully acknowledged.

(*Received, 24th January* 1979; *Com.* 073.)

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† The solvolysis rate drifted upward slightly.

‡ Extrapolated from 70 °C, 50% aqueous ethanol.

§ Rates of solvolysis for (**3a**) and (**3b**) in 50% aqueous ethanol (70 °C) have been studied here and a reverse order of reactivity was observed; k_{3a} $5{\cdot}9 \times 10^{-5}\ s^{-1}$, k_{3b} $1{\cdot}4 \times 10^{-4}\ s^{-1}$. The slightly retarded rate (2·4×) of (**3a**) compared with that of (**3b**) is interpreted as the result of the inductive and polar field effects of the destabilized transition state of (**3a**) (see D. S. Tarbell and J. R. Hazen, *J. Amer. Chem. Soc.*, 1969, **91**, 7657; L. A. Paquette and M. K. Scott, *ibid.*, 1972, **94**, 6760).

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