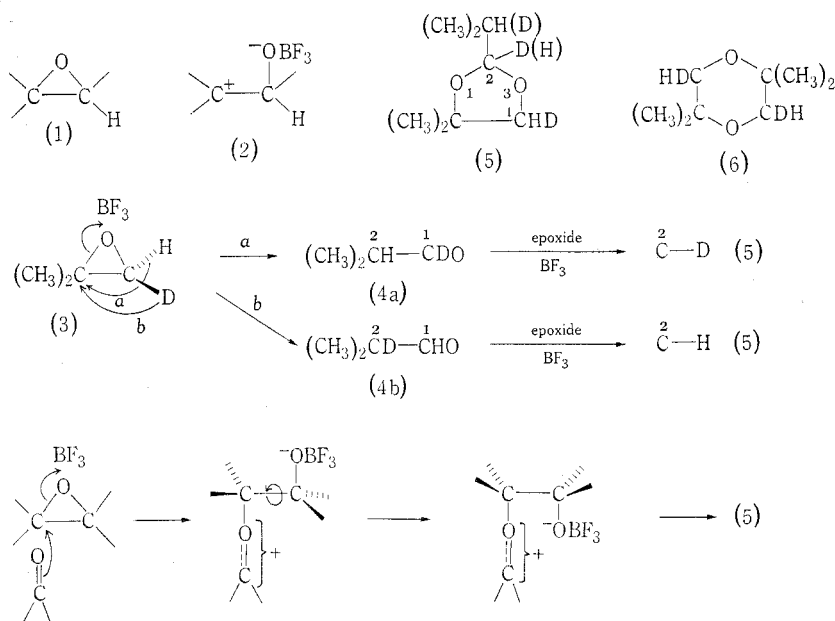


THE DEUTERIUM ISOTOPE EFFECT FOR THE BORON TRIFLUORIDE CATALYSED REARRANGEMENT OF 2-METHYL-1,2-EPOXYPROPANE

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For the boron trifluoride catalysed rearrangement of epoxides with the structural feature (1), stereochemical data have been obtained¹ which are readily interpreted only in terms of the intermediacy of the discrete carbonium ion (2). As part of a study with the objective of investigating the characteristics of the subsequent rearrangement processes of these carbonium ions (2) we examined the BF_3 -catalysed rearrangement of the deuterated epoxide (3) (Scheme 1). Comparison of the relative



Scheme 1

yields of isobutyraldehyde, deuterated at C1 when formed by hydride shift (4a), and at C2 by deuteride shift (4b), would allow an estimate to be made of the primary deuterium isotope effect (k_H/k_D) for the hydride (deuteride) shift. It is necessary to study an internal H/D-competitive reaction since the required information is related to the *fast* reaction in the two-step rearrangement process.

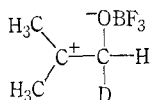
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¹ Coxon, J. M., Hartshorn, M. P., and Sutherland, B. L. S., *Tetrahedron Lett.*, 1969, 4029; Blackett, B. N., Coxon, J. M., Hartshorn, M. P., and Richards, K. E., *Tetrahedron*, 1969, **25**, 4999; Coxon, J. M., Hartshorn, M. P., and Muir, C. N., *Tetrahedron*, 1969, **25**, 3925; Blackett, B. N., Coxon, J. M., Hartshorn, M. P., Jackson, B. L. J., and Muir, C. N., *Tetrahedron*, 1969, **25**, 459; and references cited therein.

Reaction of the epoxide (3) with boron trifluoride or boron trifluoride etherate in a variety of solvents gave crude products whose volatile components were isobutyraldehyde (4), the dioxolan (5), and the dioxan (6). The dioxolan (5) is formed² by boron trifluoride catalysed reaction (cf. Scheme 1) of the epoxide (3) with isobutyraldehyde (4). It was recognized at the outset that this subsequent reaction might later complicate (by introducing an additional secondary isotope effect) the interpretation of the results for the deuterated epoxide (3). However, the relative n.m.r. integrals of protons at C2 and C4 of the dioxolan (5) in the volatile product mixture provide the most satisfactory method of determining the percentage of deuterium labelling at C1 in the initially formed isobutyraldehyde.

Reaction of the epoxide (3) with boron trifluoride in carbon tetrachloride at 0° for 15 min, followed by quenching with anhydrous potassium carbonate, gave a crude product [isobutyraldehyde (17%), dioxolan (5) (79%), and dioxan (6) (4%)] from which a dioxolan fraction was separated by distillation. Integration of the n.m.r. signals* due to the C2-H (4.60 p.p.m.; $W_{\frac{1}{2}}$ 1.8 Hz) and C4-H (3.46 p.p.m.) functions in dioxolan (5), compensating for the presence of 5.6% undeuterated epoxide (3), allowed the competitive migrating aptitude for the epoxide (3) $\rightarrow$ aldehyde (4a+4b) reaction, $M_H/M_D = 1.92$ (standard deviation 0.04), to be evaluated. Since the aldehyde (4) is not completely converted into dioxolan (5) this value for the ratio must be regarded as the lower limit, requiring to be increased slightly by some function of the secondary isotope effect arising in the epoxide+aldehyde $\rightarrow$ dioxolan reaction.

The primary deuterium isotope effect (k_H/k_D) for the hydride (deuteride) shift in the epoxide $\rightarrow$ aldehyde reaction could be derived from the ratio $M_H/M_D = 1.92$ if, in addition to the above correction, the secondary isotope effect implicit in all internal H/D-competitive studies were allowed for. The effect of this correction would be again to introduce a further minor amendment (increase) in the value (1.92) determined here.



A value of *c.* 2 for the primary deuterium isotope effect for the hydride shift in the rearrangement of the discrete carbonium ion (7) appears consistent with the location of the transition state close to the carbonium ion (7) in the carbonium ion $\rightarrow$ aldehyde reaction coordinate. This conclusion is in accord with the prediction based on Hammond's principle,³ since the carbonium

ion $\rightarrow$ aldehyde reaction would be expected to be strongly exothermic.

Acknowledgment

We acknowledge grants from the Research Committee of the New Zealand Universities Grants Committee.

* Determined at 60 MHz for carbon tetrachloride solutions with chloroform and tetramethylsilane as internal standards.

² Blackett, B. N., Coxon, J. M., Hartshorn, M. P., Lewis, A. J., Little, G. R., and Wright, G. J., *Tetrahedron*, 1969, in press.

³ Hammond, G. S., *J. Am. chem. Soc.*, 1955, **77**, 334.