**Journal of**

**The Chemical Society,**

**Chemical Communications**

NUMBER 8/1973 18 APRIL

---

# Acid-catalysed Rearrangements of *trans*- and *cis*-1-Acetoxy-3,4-epoxypentane and 1-Acetoxy-4,5-epoxyhexane

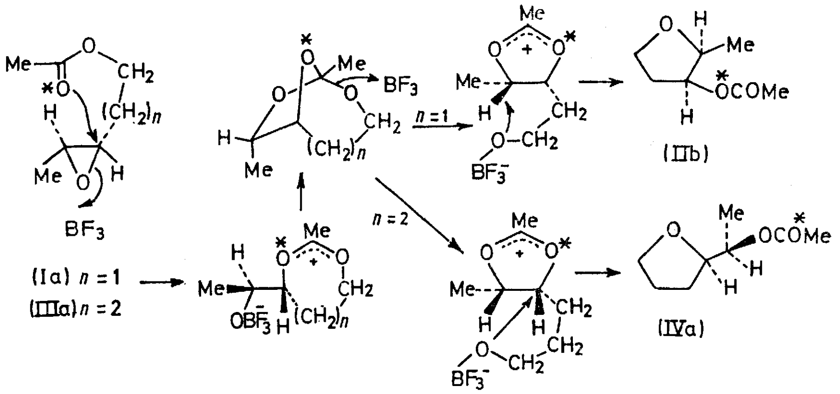
By J. M. Coxon,* M. P. Hartshorn, and W. H. Swallow

(*Department of Chemistry, University of Canterbury, Christchurch, New Zealand*)

*Summary* Acid-catalysed rearrangement of *trans*- and *cis*-1-acetoxy-3,4-epoxypentanes and 1-acetoxy-4,5-epoxyhexanes give *cis*- and *trans*-2-methyl-3-acetoxytetrahydrofuran and *threo*- and *erythro*-2-(1-acetoxyethyl)tetrahydrofuran respectively with retention of configuration at the epoxide carbon atoms; the mechanism is consistent with the intermediary of orthoesters.

As part of a study of the acid-catalysed rearrangements of epoxides, having neighbouring groups capable of nucleophilic participation, we have examined the acid-catalysed reactions of the *trans*- and *cis*-1-acetoxy-3,4-epoxypentanes and the 1-acetoxy-4,5-epoxyhexanes.† We now report evidence in support of the intermediary of ortho-esters in these rearrangements which proceed with overall retention of configuration at the epoxide ring carbon atoms.

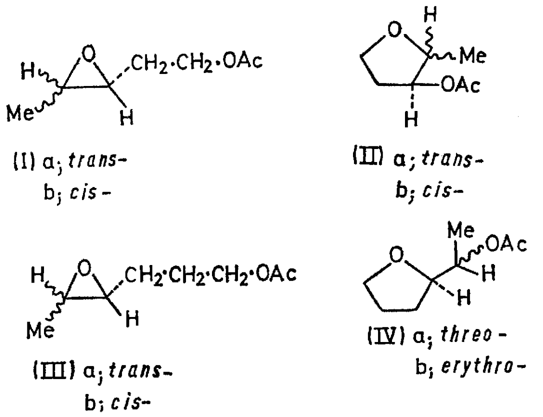
Reaction of a solution of *trans*-1-acetoxy-3,4-epoxypentane (Ia) in ether with a three molar excess of boron trifluoride–diethyl etherate for 2½ h gave *cis*-3-acetoxy-2-methyltetrahydrofuran (IIb) (68%). Under the same reaction conditions *cis*-acetoxy-3,4-epoxypentane (Ib) gave *trans*-3-acetoxy-2-methyltetrahydrofuran (IIa) (40%). In each reaction only a single acetoxyfuran could be detected by g.l.c. The same reactions occurred when the Lewis acid was replaced by an equivalent amount of trifluoroacetic acid, but under these conditions a trace of the isomeric acetoxyfuran could be detected in each reaction. The product furans (II) were also obtained by reduction of 2-methyldihydrofuran-3(2*H*)-one with lithium aluminium hydride or sodium in moist ether to give mixtures (52:48 and 88:12) of *trans*- and *cis*-3-hydroxy-2-methylfuran, the thermodynamically more stable *trans*-isomer predominating



---

† Prepared by reaction of the corresponding acetoxy-olefins with monoperoxyphthalic acid.

under the latter conditions. The methyl group for the *cis*-isomer was deshielded in the n.m.r. spectra ($\delta$ 1·25) relative to the *trans*-isomer ($\delta$ 1·18), consistent with the proximity of the methyl and hydroxy-groups in the former compound.[2] Acetylation of these alcohols gave the corresponding 3-acetoxy-2-methyltetrahydrofurans (II).



Scheme

Rearrangement of *trans*-1-acetoxy-3,4-epoxypentane (Ia), $^{18}O$-enriched at the acetate carbonyl, gave *cis*-3-acetoxy-2-methyltetrahydrofuran (IIb) (21·5% $^{18}O$) which on hydrolysis to the alcohol showed no significant loss of oxygen label (20% $^{18}O$). The carbonyl oxygen of the starting acetate must therefore be present as the ether or hydroxy oxygen in the product.

Reaction of the *cis*- and *trans*-1-acetoxy-4,5-epoxyhexanes (III) under the same reaction conditions gave, in addition to ketones and fluoroalcohols, (IVb) (30% from *cis*-) and (IVa) (62% from *trans*-). The *erythro*- and *threo*-isomers were differentiated by comparison of the i.r. spectra[3] of the corresponding alcohols. Intramolecular hydrogen bonding is less favoured for the *erythro*-isomer compared to the *threo*-isomer. Reaction of (IIIa) labelled at the carbonyl oxygen with $^{18}O$ afforded labelled (IVa) (21% $^{18}O$) which on hydrolysis gave *threo*-2-(1-hydroxyethyl)tetrahydrofuran with complete loss of the oxygen label.

The known stereochemistry of products, coupled with the labelling experiments reported in this present study, distinguish between several possible reaction pathways (Scheme). The intermediate orthoesters are formed by initial attack of acetate on the epoxide with inversion of configuration and subsequently rearrange by two alternate routes. For the 1-acetoxy-3,4-epoxypentanes (I), where $n = 1$, rearrangement occurs to give the 3-acetoxy-2-methyltetrahydrofurans (II), while for the 1-acetoxy-4,5-epoxyhexanes (III), where $n = 2$, rearrangement occurs to give the 2-(1-acetoxyethyl)tetrahydrofurans (IV). For both systems, $n = 1$ and $n = 2$, the reaction path involves cleavage of the orthoester to give the more stable five-membered ring acetonium ion which undergoes intramolecular rearrangement to form the furan ring. A full report of this work will be presented elsewhere.

We thank the Research Committee of the New Zealand Grants Committee for grants.

(*Received*, 29*th January* 1973; *Com.* 121.)

---

[1] L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1950, 873; M. Julia, S. Julia, and S. Y. Tchen, *Bull. Soc. chim. France*, 1961.

[2] N. S. Bhacca and D. H. Williams, 'Applications of NMR Spectroscopy in Organic Chemistry,' Holden-Day, Inc., San Francisco, London, Amsterdam, 1964.

[3] D. Gagnaire and M. Leclercq, *Bull. Soc. chim. France*, 1963, 721.