Orientation Control in Ring Opening of an αβ-Epoxysilane

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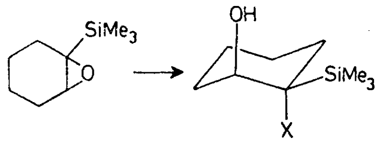
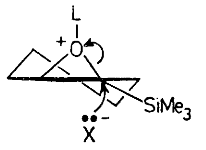
Summary 1,2-Epoxy-1-trimethylsilylcyclohexane (**1**) undergoes ring-opening by nucleophilic attack at C-1 with inversion of configuration; in this way the glycol (**2**, X = OH), the glycol monoether (**2**, X = OMe), the bromohydrin (**2**, X = Br), and the alcohol (**2**, X = H) have been prepared in high yield.

Recent developments in the applications of organosilicon compounds to organic synthesis[1] have emphasised the need for regio- and stereo-specific reactions in this area. We report that the ring opening of 1,2-epoxy-1-trimethylsilylcyclohexane (**1**), under conditions of probable electrophilic catalysis, occurs with a number of reagents by nucleophilic displacement at the carbon atom bearing silicon (C-1) with inversion of configuration.

Thus treatment of (**1**) with 5% sulphuric acid–acetone/water (10:1) gave the glycol (**2**, X = OH) in 83% yield. Similarly 5% sulphuric acid–methanol gave the methyl ether (**2**, X = OMe), 78%, together with a small amount of the glycol, and aqueous hydrobromic acid (48%) led to the bromohydrin (**2**, X = Br), 90%. The three reactions proceed rapidly at 20 °C. An analogous ring opening occurred on treatment with lithium aluminium hydride in ether, the product being *cis*-2-trimethylsilylcyclohexanol[2] after work up. In each case only one stereoisomer was isolated. Configurations were established in the case of (**2**, X = OMe) by its ready Peterson-elimination[3] (NaH, dimethylformamide at 20 °C) to 1-methoxycyclohexene, and in the case of (**2**, X = H) from spectroscopic and literature[2] data, and comparison with its *trans*-isomer. In the other two cases configurations were assigned by chemical and spectroscopic analogy.



(1) (2)



(3)

We believe that the reactions are S_N2 'borderline' type[4] displacements on the epoxide [*cf.* (**3**)], which is either protonated (acid catalysis) or co-ordinated to $Li^+(LiAlH_4)$.[5] Clearly the α-trimethylsilyl group provides electronic facilitation, overriding expected steric effects, along the lines suggested for nucleophilic displacement on α-silyl halides.[6] The possibility that the lithium aluminium hydride reaction involves initial rearrangement to 2-trimethylsilylcyclohexanone, followed by subsequent reduction, is excluded by our finding that reduction of the ketone under the same conditions gave a mixture of *cis*- and *trans*-2-trimethylsilylcyclohexanol in the ratio 1:0·2. A preference for α-opening of αβ-epoxysilanes has also been observed by Hudrlik and his co-workers in reactions with organocuprates[3b] and rearrangements with magnesium bromide.[7]

In the light of our results it seems likely that the conversion of αβ-epoxysilanes into ketones developed by Stork[8] proceeds by initial solvolysis as in (**1**) → (**2**) followed by acid-catalysed elimination. For the system (**2**, X = OH), elimination is geometrically disfavoured since the Me_3Si and OH groups cannot achieve the preferred *anti*-relationship.

(*Received*, 27*th May* 1976; *Com.* 605.)

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