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HYDROLYTIC RING-OPENING OF α,β-EPOXYSILANES TO α,β-DIHYDROXYSILANES

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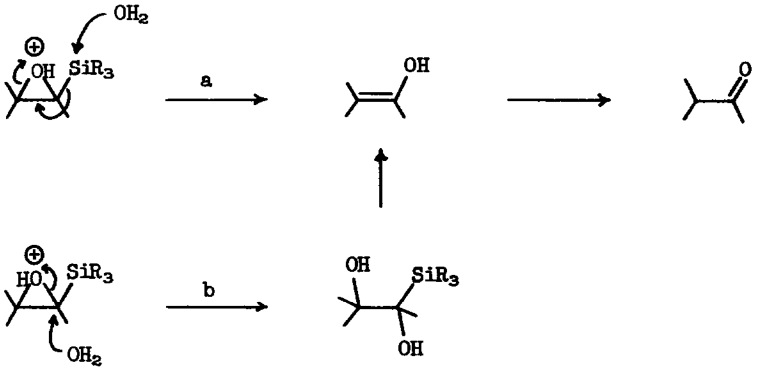
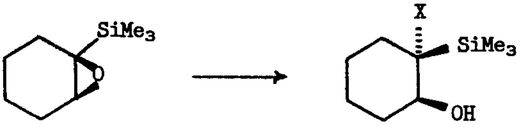
Stork has shown that α,β-epoxysilanes undergo acid-catalyzed hydrolysis to aldehydes and ketones,[1] allowing the epoxysilanes (and the vinylsilane precursors) to serve as latent carbonyl groups in organic synthesis.[1,2] This reaction could occur by at least two distinct pathways, shown below, involving (a) displacement at silicon with β-elimination to generate an enol, or (b) epoxide opening at the α (or β) carbon to give a diol, followed by β-elimination to the enol.



Robbins and Whitham have recently reported that acid-catalyzed hydrolysis of epoxide 1, derived from a cyclic vinylsilane, gave the diol 2a,[3] in which the Me_3Si and OH groups cannot achieve the anti relationship necessary for facile acid-catalyzed β-elimination,[4,5] thus supporting path (b). We wish to report the results of our own experiments in this area, which further support path (b). We have found that epoxides derived from both cyclic and acyclic vinylsilanes can be converted to diols if mild conditions are used. Although the acyclic diol (4a) is readily converted to the ketone on further treatment with acid, the cyclic diol (2a) is resistant to acid.

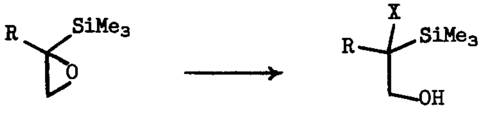


1 2

a, X = OH

b, X = Br

c, X = OMe



3 4

R = n-C_6H_{13}

When epoxide 1[6] was treated with aqueous acid (0.1 M H_2SO_4 in aqueous dioxane, room temp, 2 hr), diol 2a, mp 79.5-80.5°, was isolated in 90% yield. Epoxide 3[7] was similarly converted (dilute acid in aqueous THF, room temp, 30 hr) to diol 4a, mp 48-52°, in 61% yield (not optimized). Diol 4a could be converted to 2-octanone with stronger acid or longer reaction times, while diol 2a was quite stable and reacted only after prolonged treatment at higher temperatures (0.2 M H_2SO_4, aqueous dioxane, 100°, 36 hr) to give an as yet uncharacterized mixture of products.

The hydrolysis reactions almost certainly proceed via ring-opening α to silicon. We have previously demonstrated that α,β-epoxysilanes undergo α ring-opening in a regio- and stereospecific manner[8] by R_2CuLi,[5] $MgBr_2$,[6] HBr,[7] AcOH,[7] MeOH,[7] and CH_3CN.[7] Epoxide 1 is thus readily converted to bromohydrin 2b (HBr, Et_2O, 0°, 30 min; 97% yield) and to methoxy-alcohol 2c, mp 70-72° (MeOH, CF_3CO_2H, room temp, 15 hr; 90% yield); epoxide 3 is readily converted to 4b (HBr, Et_2O, -25°, 30 min; 95% yield) and to 4c (MeOH, CF_3CO_2H, room temp, 3 hr; 92% yield).[11]

The isolation of diols from both epoxides 1 and 3 strongly supports path (b), in agreement with the conclusions of Robbins and Whitham.[3] Furthermore, the stability of diol 2a to acid suggests that the standard hydrolysis conditions can be used for the preparation of carbonyl compounds only from epoxides derived from acyclic vinylsilanes. It is noteworthy that only such epoxides have so far been converted to aldehydes and ketones.[1,2] In principle, conversion of diols 2a and 4a to cyclohexanone and 2-octanone, respectively, should be possible by treatment with base, since base-induced elimination reactions of β-hydroxysilanes have been shown to proceed in a *syn* manner.[4,5,12] We are currently investigating this possibility.[13]

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8. Robbins and Whitham[3] have also reported regio- and stereospecific ring-opening of 1 by HBr and MeOH. The predominant α-opening of α,β-epoxysilanes by $LiAlH_4$[9] was also found to be stereospecific.[3] In contrast, products resulting from both α and β ring-opening were formed in the reactions of triphenylsilylethylene oxide with HCl, with $MgBr_2$, and with amines.[10]
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11. These intermediates are readily converted to heteroatom-substituted olefins.[7] Thus, treatment of **4b** with $BF_3 \cdot Et_2O$ (CH_2Cl_2, 0°, 8 hr) gave 2-bromo-1-octene in 86% yield; treatment of **4c** with KH (THF, 0°, 45 min) gave 2-methoxy-1-octene in 83% yield.

12. See also P. B. Dervan and M. A. Shippey, J. Am. Chem. Soc., 98, 1265 (1976); M. T. Reetz and M. Plachky, Synthesis, 199 (1976).

13. We thank the National Institutes of Health, the Research Council of Rutgers University, and the Exxon Education Foundation (Summer Fellowship to R. N. M.) for their support of this work.