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CONVERSION OF α,β-EPOXYSILANES TO SILYL ENOL ETHERS; AN UNPRECEDENTED STEREOCHEMICAL RESULT

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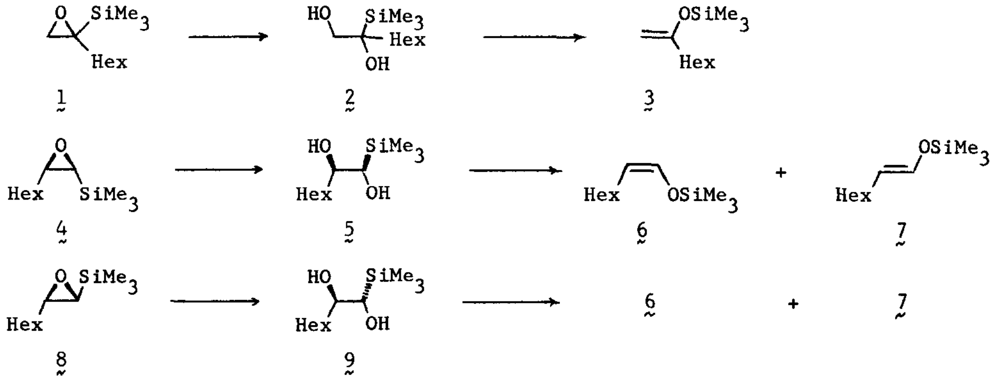
Abstract: Acyclic α,β-dihydroxysilanes (prepared from α,β-epoxysilanes) react with KH to give silyl enol ethers; the predominant stereochemistry is consistent with anti elimination via α-oxidosilanes.

We have recently shown that α,β-epoxysilanes can serve as stereospecific vinyl cation equivalents in the synthesis of olefins[2] and heteroatom-substituted olefins.[3] This synthesis is based on the finding that α,β-epoxysilanes undergo regio- and stereospecific α-opening by a variety of nucleophiles to produce diastereomerically pure β-hydroxysilanes,[2-5] and that these β-hydroxysilanes undergo stereospecific syn or anti β-elimination reactions under basic or acidic conditions, respectively.[2,3,6] We have also previously demonstrated that an acyclic α,β-epoxysilane can undergo acid-catalyzed ring opening with water under mild conditions to produce an α,β-dihydroxysilane.[4] (Such α,β-dihydroxysilanes are believed to be intermediates[4,5] in the hydrolysis[7] of acyclic α,β-epoxysilanes to carbonyl compounds.) With a view toward extending the synthesis of heteroatom-substituted olefins to the generation of stereoisomerically pure enolate anions, we decided to study the base-induced elimination reactions of such α,β-dihydroxysilanes.

Treatment of α,β-epoxysilane **1**[3,4,8] with aqueous H_2SO_4 in THF[9] afforded α,β-dihydroxysilane **2**[4,10] (mp 53-54°) in 76% yield. Similar treatment[11] of the cis α,β-epoxysilane **4**[3] produced α,β-dihydroxysilane **5**[10] in 83% yield. Treatment of these α,β-dihydroxysilanes with KH (ether, 0°, 1 hr) (to effect syn β-elimination), followed by Me_3SiCl (to trap enolate anions), produced trimethylsilyl enol ethers **3**[10,12] (from **2**, 52-89% yield) and a mixture of **6**[10a,b,13] and **7**[10a,b,13] in a 1:5 ratio (from **5**, 98% yield). When the trans α,β-epoxysilane **8**[3] was treated with aqueous



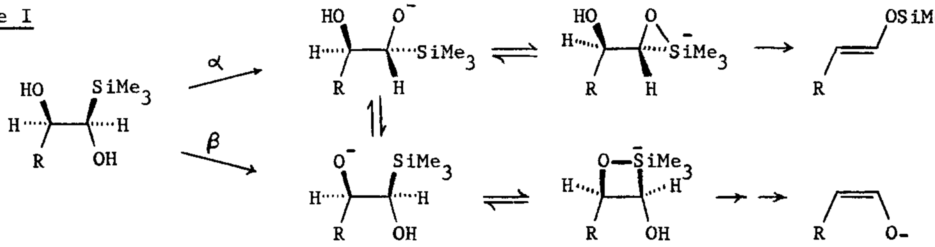
H_2SO_4 in THF, a slower reaction took place in which hydrolysis to octanal appeared to compete with formation of the α,β-dihydroxysilane. The α,β-dihydroxysilane (9)[10a] could be isolated in low (30%) yield, and preliminary experiments indicated that treatment with KH (in ether) followed by Me_3SiCl similarly resulted in a mixture of silyl enol ethers 6 and 7 (2:1 ratio).

Assuming stereospecific epoxide ring opening (as shown), syn β-elimination would have resulted in the cis silyl enol ether 6 from epoxide 4, and the trans silyl enol ether 7 from epoxide 8. In these reactions, not only were cis-trans mixtures formed, but the *unexpected isomers predominated* in each case.

Surprisingly, when the reactions of the α,β-dihydroxysilanes (2 and 5[14]) with KH in ether were quenched with aqueous $NaHCO_3$ rather than Me_3SiCl, the silyl enol ethers were again formed as the major products (along with smaller amounts of the corresponding carbonyl compounds, 2-octanone from 2 and octanal from 5). Moreover, the silyl enol ether product from 5 (isolated in 63% yield) consisted *almost exclusively of the trans isomer 7* with only 1-4% of the cis isomer 6 present.

When α,β-dihydroxysilanes are treated with base, interaction of silicon with the α- as well as the β-alkoxide may be involved (see Scheme I). A considerable amount of experimental work indicates that α-oxidosilanes undergo rearrangements to α-siloxycarbanions, with the equilibria favoring the α-oxidosilanes in the absence of carbanion-stabilizing groups.[15] The rearrangement can be driven by protonation of the carbanion (the Brook rearrangement)[15a] or by the loss of a leaving group β to the carbanion.[16] The latter pathway would provide a mechanism for the formation of the silyl enol ethers. This pathway has little precedent[16] and nothing is known of its stereochemistry.

Scheme I



The work presented here suggests that the base-induced elimination reactions of α,β-dihydroxysilanes take place by the α-oxidosilane pathway (to give silyl enol ethers) in competition with the β-oxidosilane pathway (to give initially enols or enolates),[17] and that elimination via the α-oxidosilane pathway proceeds with predominant *anti* stereochemistry. The following communication describes the results of experiments in a cyclic system, which substantiate this idea.[18]

References and Notes

1. (a) Howard University; (b) Rutgers University.
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7. G. Stork and E. Colvin, *J. Am. Chem. Soc.*, **93**, 2080 (1971); see also refs cited in ref 4.
8. P. F. Hudrlik, R. H. Schwartz, and J. C. Hogan, *J. Org. Chem.*, **44**, 155 (1979).
9. 535 mg (2.67 mmol) **1**, 9 ml THF, 5 ml H_2O, 2.4 ml 1 *M* H_2SO_4, 0° for 3 hr followed by RT for 9 hr.
10. (a) Satisfactory IR and NMR spectra were obtained. (b) A satisfactory mass spectrum was obtained. (c) A satisfactory elemental analysis was obtained.
11. 140 mg (0.70 mmol) **4**, 2.2 ml THF, 1.1 ml H_2O, 0.6 ml 1 *M* H_2SO_4, 0° for 3 hr followed by RT for 2 hr. After aqueous ($NaHCO_3$) workup, the crude product was purified by chromatography on Florisil.
12. In some of the reactions, considerable amounts (~30%) of the regioisomeric silyl enol ethers were obtained, presumably due to partial equilibration. A comparison sample of the mixture of silyl enol ethers was prepared by treatment of 2-octanone with $Me_3SiCl/Et_3N/DMF$ using the procedure of H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).
13. The ratio of **6** and **7** varied from 1:4 to 1:6 in a number of different runs. Silyl enol ethers **6** and **7** were purified by preparative VPC. Compound **6** (cis) had the following spectra: IR (film) 1654, 1256, 1094, 852 cm^{-1}; NMR (CCl_4) δ 6.05 (d, *J* = 6 Hz, of m), 4.38 (appears as q, *J* = 7 Hz). Compound **7** (trans) had the following spectra: IR (film) 1664, 1256, 1170, 852 cm^{-1}; NMR (CCl_4) δ 6.12 (d, *J* = 12 Hz, of m), 4.86 (d, *J* = 12 Hz, of t, *J* = 7 Hz). A comparison mixture of **6** and **7** was prepared by treatment of octanal with $Me_3SiCl/Et_3N/DMF$ using the procedure of House, *et al.*, (see footnote 12). The mass spectra of **6** and **7** were very similar: *m/e* 200, 185, 157, 129, 75, 73.
14. For these experiments, α,β-dihydroxysilane **5** was obtained from a mixture of epoxides **4** and **8** (86:14 ratio) prepared from the reaction of heptanal with α-chloro-α-trimethylsilylmethyllithium (see C. Burford, F. Cooke, E. Ehlinger, and P. Magnus, *J. Am. Chem. Soc.*, **99**, 4536 (1977)). As mentioned above, reaction of the cis epoxide **4** with aqueous H_2SO_4 in THF was faster than the corresponding reaction of the trans epoxide **8**. We found that treatment of this mixture of epoxides under conditions used for the conversion of **4** → **5** (see footnote 10) yielded a mixture consisting primarily of **5** together with unreacted **8**. Purification by chromatography on Florisil yielded 61-77% of **5**.
15. For leading references, see (a) A. G. Brook, *Acc. Chem. Res.*, **7**, 77-84 (1974); (b) R. West, *Adv. Organometal. Chem.*, **16**, 1-31 (1977), especially pp 18-24.
16. α-Oxidosilanes having a leaving group β to silicon are thought to be intermediates in the

reactions of acylsilanes with CH_2N_2 (A. G. Brook, W. W. Limburg, D. M. MacRae, and S. A. Fieldhouse, *J. Am. Chem. Soc.*, **89**, 704 (1967)) and with Wittig reagents (A. G. Brook and S. A. Fieldhouse, *J. Organometal. Chem.*, **10**, 235 (1967)). Some of these reactions give silyl enol ethers (see also ref 15a). (In the reactions of acylsilanes with CH_2N_2, β-ketosilanes were also observed, suggesting α-oxidosilanes with a β-leaving group can undergo migration of the R_3Si group to the β carbon with loss of the leaving group. This pathway has also been observed in the reactions of α-chloroacylsilanes with Grignard reagents--see T. Sato, T. Abe, and I. Kuwajima, *Tetrahedron Lett.*, 259 (1978).) Reich has recently developed an efficient regiospecific synthesis of silyl enol ethers (as mixtures of cis and trans isomers) using reactions in which α-oxidosilanes with a β-leaving group are presumably involved (H. J. Reich and J. J. Rusek, 12th Organosilicon Award Symposium, Ames, Iowa, March 11, 1978). We thank Professor Reich for sending us a preprint of his work.

17. When the elimination reactions of **2** and **5** were carried out in THF rather than ether, and quenched with aqueous $NaHCO_3$, only the carbonyl compounds (2-octanone from **2** and octanal from **5**) were formed. (When the reactions were quenched with Me_3SiCl, the silyl enol ethers were formed, although in somewhat lower yields than in ether.)

18. We thank the National Science Foundation (CHE77-10523) and the National Institutes of Health (CA-18897 and CA-23037) for their support of this work, and we thank Dr. Anne M. Hudrlik for useful discussions and for assistance in the preparation of the manuscript.

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