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MAGNESIUM BROMIDE INDUCED REARRANGEMENTS OF α,β-EPOXYSILANES[1]

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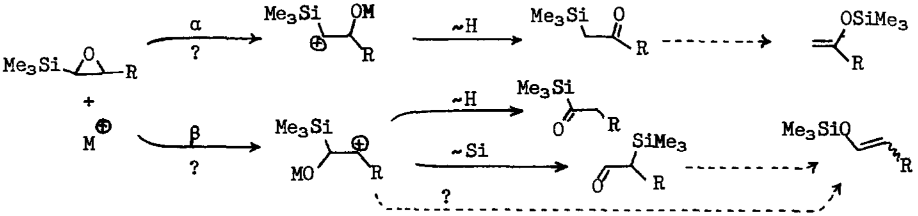
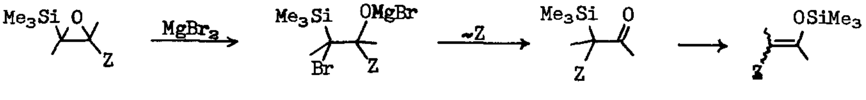
α,β-Epoxysilanes have been found to undergo rearrangements to isomeric silyl enol ethers, independently by us[2] (gas phase, 600°) and by Brook and co-workers[3] (160-320°, longer times). Because of the many synthetic uses of silyl enol ethers,[4] we are seeking ways of accomplishing such rearrangements under non-pyrolytic conditions. We report here our initial investigations of the use of Lewis acids for this purpose.

Lewis acid-catalyzed rearrangements of epoxides to carbonyl compounds are well known.[5] With α,β-epoxysilanes, such rearrangements might lead to acylsilanes or to β-ketosilanes, via one of the pathways shown below.[6] Formation of β-ketosilanes (or the corresponding aldehydes) would be particularly useful; the synthetic potential of these compounds is just beginning to be realized,[9] and facile isomerizations to silyl enol ethers have been reported.[9d,10]

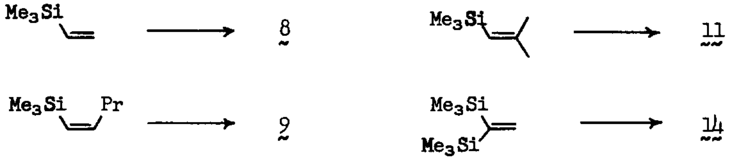


With simple epoxides, acid-catalyzed rearrangements yield products derived from cleavage of the C-O bond in the direction expected to produce the more stable cation.[5] Although a fully developed cation might not be formed in such rearrangements, one might expect β-cleavage to predominate with α,β-epoxysilanes in view of the well known stability of cations β to silicon[11] (and the evidence that cations α to silicon are destabilized[12]). Our results using magnesium bromide etherate (Table 1) show that this is not the case. All of the products formed in these reactions are consistent with α-cleavage of the α,β-epoxysilanes, and can be accounted for by the mechanism shown below.



Only bromohydrins were obtained from epoxides **1** and **3**. Bromohydrins were isolated after short reaction times with epoxides **2c** (as well as the trans isomer) and **6**, although further rearrangement to β-ketosilanes (or aldehydes) took place after longer times. Epoxides **4** and **5** yielded silyl enol ethers; intermediate aldehydes could be detected in the NMR after short reaction times.

In every case, the bromohydrins were the α-bromo-β-hydroxysilanes, as could be readily shown (for **8**, **9**, and **14**) by the downfield shift of the β-protons in the NMR spectra of the derived acetates.[13] For comparison, bromohydrins were prepared directly from the vinylsilanes by treatment with N-bromoacetamide in aqueous dioxane, since this method generally yields bromohydrins of opposite regiochemistry to those obtained from epoxide openings. However, the bromohydrins obtained (**8**, **9**, **11**, and **14**) were identical with those obtained from the epoxides. (The NBA reactions were not clean, and we have not yet optimized the conditions.)



The exclusive α-opening of these epoxides by magnesium bromide is particularly striking in the case of epoxide **3**, where β-cleavage would result in a developing tertiary cation β to silicon. In retrospect, the lack of β-opening, although remarkable, is perhaps less surprising in view of the relative orientation of the C-Si bond and the β C-O bond, which greatly deviate from the parallel alignment favorable for stabilization of a developing positive charge by the silicon.[9b,11,12d,14] Moreover, there is no doubt considerable nucleophilic assistance by bromide in the ring-opening reactions. The preference for α-opening in these reactions suggests that the trimethylsilyl group may facilitate nucleophilic displacements α to silicon.[15]

The fact that β-ketosilanes or the corresponding silyl enol ethers can be isolated in good yields from the rearrangements of a variety of α,β-epoxysilanes with magnesium bromide indicates the potential utility of these rearrangements. The rearrangement of **4** is remarkable in that mostly (93%) the cis silyl enol ether is obtained; the rearrangement of **5** is particularly interesting in that a clean ring contraction is achieved under mild conditions. We are beginning to investigate the use of other Lewis acids in these rearrangements and have found that the conversions of **4** to **12** and of **7** to **15** can be effected with a number of reagents (e.g. $ZnCl_2$, MgI_2), although none so far with more efficiency than magnesium bromide etherate.

Preparation of α,β-Epoxysilanes. Epoxides **1**-**3** were prepared as previously described.[2,16] Epoxide **4**[17] (bp 83-85° (50 mm); NMR (CCl_4) δ 2.47 (s, 2 H)) was prepared in 84% yield from 2-trimethylsilyl-1-pentene[18] by treatment with m-chloroperbenzoic acid (CH_2Cl_2, room temp, 6 hr). Epoxide **5**[17] (bp 106-107° (57 mm); NMR (CCl_4) δ 2.68 (m, 1 H)) was prepared in 86% yield from 1-trimethylsilylcyclohexene[20] by treatment with MCPBA (CH_2Cl_2, 0°, 3 hr). Similarly, epoxide **6**[3,17] (bp 69-70° (18 mm); NMR (CCl_4) δ 2.70 (s, 2 H)) was prepared from 1,1-bis(trimethylsilyl)ethylene[21] (MCPBA, CH_2Cl_2, room temp, 20 hr, 70%), and epoxide **7**[3,17] (bp 61-62° (13 mm); NMR (CCl_4) δ 1.89 (s, 2 H)) was prepared from trans-1,2-bis(trimethylsilyl)ethylene[22,23] (MCPBA, CH_2Cl_2, room temp, 20 hr, 84%).

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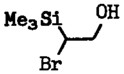
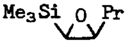
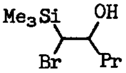
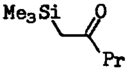
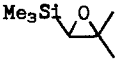
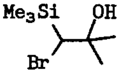
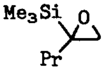
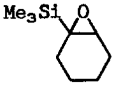
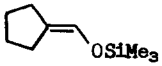
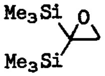
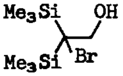
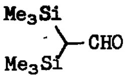
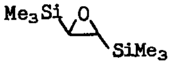
Table 1. Treatment of α,β-Epoxysilanes with $MgBr_2$ in Ether.[a]

Epoxide		Conditions[a]	Products		Isolated Yields
1		room temp 3 hr	8[b,c,d]		72%
2c		0° 1 hr	9[b,c,e]		86%
		5 equiv $MgBr_2$ room temp 6 hr	10[b,f,g]		93%
3		room temp 12 hr	11[b,f]		98%
4		room temp 2 hr	12[b,h]		82%
5		room temp 7 hr	13[b,f,i]		84%
6		reflux THF[j] 4 hr	14[b,c]		72%
		room temp 4 hr	15[b,f,k]		88%
7		0° 1.5 hr	15		90%

(a) Unless otherwise indicated, 1-3 equiv of $MgBr_2$ in ether were used. (b) Satisfactory IR and NMR spectra were obtained. (c) Satisfactory mass spectra were obtained for this compound and for the derived acetate. (d) Reported in ref 24. (e) Obtained as a white, low-melting solid. Compound 9 was obtained in higher yield and purity from the reaction of 2c with PrMgBr (2 equiv, Et_2O, 0°, 1.5 hr, 89%). (f) A satisfactory mass spectrum was obtained for this compound. (g) Obtained in about 90% purity. Identified by comparison with samples prepared independently by D. Peterson (from Me_3SiCH_2MgCl + PrCOCl and from Me_3SiCH_2COCl + Pr_2CuLi). (h) NMR (CCl_4) δ 4.36 (m, 1 H), 6.05 (dt, $J = 6$, 2 Hz, 1 H); 93% cis by VPC; identified by comparison with an authentic sample (see ref 2) and by conversion to the 2,4-DNP of valeraldehyde, mp 106.5-108°. (i) NMR (CCl_4) δ 6.06 (crude pentet, $J = 2.1$ Hz, 1 H); treatment with 2,4-DNP reagent gave the 2,4-DNP of cyclopentanecarboxaldehyde, mp 159.5-161° (lit.[25] mp 160.5-161.5°). (j) Treatment of epoxide 6 with $MgBr_2$ in Et_2O (room temp, 1 hr) gave a mixture of 6, 14, and 15. (k) IR (film) 5.95 μ; NMR (CCl_4) δ 0.13 (s, 18 H), 2.09 (d, $J = 6$ Hz, 1 H), 9.62 (d, $J = 6$ Hz, 1 H); treatment with 2,4-DNP reagent gave the 2,4-DNP of acetaldehyde, mp 146-147°.

References and Notes

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6. The only such rearrangement reported previously is the magnesium bromide catalyzed rearrange-

ment of triphenylsilylethylene oxide to triphenylsilylacetaldehyde.[7,10b] An attempt[7b] to extend this reaction to phenyldimethylsilylethylene oxide gave diphenyltetramethylsiloxane resulting from hydrolytic cleavage of the C-Si bond. In the reactions of Grignard reagents with the epoxides **1** and **2c**, we obtained alcohols which were presumably derived from rearranged carbonyl compounds.[8]

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13. The acetates were prepared from the bromohydrins **8**, **9**, and **14** by treatment with acetic anhydride in pyridine (100°, 2-5 hr). Bromohydrin **11** (with a tertiary OH) was not acetylated under these conditions; the structure of **11** was confirmed by conversion to isobutenyl bromide by treatment with $BF_3 \cdot Et_2O$ in CCl_4 (0°, 1 hr)[9b] (92% yield by NMR).
14. In contrast, β,γ-epoxysilanes have no such geometric constraint and are much more labile: P. F. Hudrlik and G. P. Withers, Tetrahedron Lett., 29 (1976).
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17. Satisfactory IR, NMR, and mass spectra were obtained.
18. Prepared from 2-bromo-1-pentene[19] by treatment with chlorotrimethylsilane and excess sodium in ether (32% overall from 1-trimethylsilyl-1-pentyne).
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