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## A Remarkable Base-Induced Rearrangement of Epoxydisilanes

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**Abstract:** The LDA-induced rearrangements of epoxydisilane 1 (R = Ph), to give predominantly  $\beta$ -trimethylsilyl acylsilane 6 (R = Ph), and of epoxydisilanes 1 (R = alkyl) remarkably to give silanols 7, are described. Copyright © 1996 Elsevier Science Ltd

We recently reported a method for the preparation of acylsilanes from epoxydisilanes 1 using H<sub>2</sub>SO<sub>4</sub> in MeOH.<sup>1</sup> As an extension of this work we communicate here our preliminary results concerning base-induced rearrangements of epoxydisilanes 1. The reaction of bases such as LDA with simple epoxides generally produces allylic alkoxides which give allylic alcohols on protic work-up.<sup>2</sup> Should an epoxydisilane 1 rearrange analogously there exists the possibility of a subsequent Brook rearrangement from the allylic alkoxide 2 to generate a lithium homoenolate 3 (Eq. 1). Direct protonation of the homoenolate 3 could lead to the disilyl enol ether 5. Alternatively, the homoenolate 3 could rearrange to the enolate 4, which would give a  $\beta$ -trimethylsilyl acylsilane 6 on protic work-up.



Trimethylsilyl ethers derived from allylic primary alcohols undergo the reverse Brook (silyl-Wittig) rearrangement on treatment with Bu<sup>4</sup>Li to give on protic work-up 1-(trimethylsilyl)allylic alcohols.<sup>3</sup> However, 1-(trimethylsilyl)allylic alcohols which are further substituted by an alkyl group in the 1-position generally give silyl enol ethers on treatment with catalytic BuLi;  $\beta$ -trimethylsilyl ketones can form when using stoichiometric quantities of BuLi.<sup>4</sup> These latter reactions were found to be facilitated by steric bulk in the alkyl group and an ability to stabilise an adjacent negative charge;<sup>4</sup> both factors would be present if the alkyl group were replaced by a trialkylsilyl substituent.

In the event, epoxydisilane 1 (R = Ph)<sup>1</sup> rearranged using LDA (3.5 equivs.) in Et<sub>2</sub>O at reflux (0.5 h) to give the *E*-disilyl enol ether 5<sup>5</sup> (R = Ph, 19%)<sup>6</sup> and the  $\beta$ -trimethylsilyl acylsilane 6<sup>7</sup> (R = Ph, 71%). However, epoxydisilanes which lacked the activating effect provided by the aryl group underwent a remarkable and profoundly different transformation on treatment with LDA to give silanols 7 (Table 1); disiloxanes were not observed.



Table 1. LDA-mediated rearrangement of epoxydisilanes.

The structures of the silanols 7 were rigorously established by extensive spectroscopic studies. For example, silanol Z-**7a**<sup>8</sup> gave a strong, broad absorbance in the IR (neat) at 3306 cm<sup>-1</sup>, the <sup>1</sup>H NMR spectrum showed typical vinyl- and allyl-silane signals [ $\delta_H$  5.86 (1H, t, J 7.5, HC=) and 1.63 (2H, s, =CCH<sub>2</sub>Si) respectively] and integration in the SiMe region gave SiMe<sub>3</sub> and SiMe<sub>2</sub> assignments ( $\delta_H$  0.14 and 0.12 respectively), the <sup>13</sup>C NMR DEPT spectra showed 8 CH<sub>2</sub> signals, and the <sup>29</sup>Si NMR spectrum supported the presence of R<sub>3</sub>SiOR' and =CSiR<sub>3</sub> functionality ( $\delta_{Si}$  14.5 and -7.2 respectively).<sup>9</sup> Long-range COSY experiments (<sup>1</sup>H-<sup>13</sup>C and <sup>1</sup>H-<sup>29</sup>Si HMBC) were used to establish that the allylic silicon, rather than the vinylic silicon, bears the OH group. For example, correlations were observed between =CCH<sub>2</sub>Si and Si(CH<sub>3</sub>)<sub>2</sub> [but not to Si(CH<sub>3</sub>)<sub>3</sub>], and between =CCH<sub>2</sub>Si and Si(CH<sub>3</sub>)<sub>3</sub> [but not to Si(CH<sub>3</sub>)<sub>2</sub>].

In order to explain this unusual rearrangement to give a silanol 7, we tentatively suggest a mechanism which involves (reversible) deprotonation  $\alpha$  to silicon followed by irreversible intramolecular epoxide opening at the proximal epoxide carbon<sup>1</sup> to generate a silirane 8 which collapses by a Peterson-type reaction (Eq. 2).<sup>10</sup>



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