Pergamon

Tetrahedron Letters, Vol. 37, No. 31, pp. 5613-5614, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01138-0

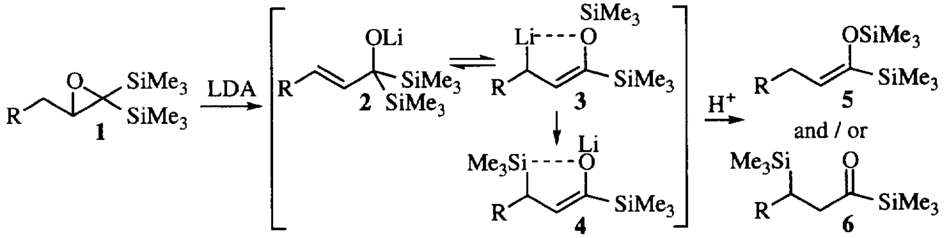
A Remarkable Base-Induced Rearrangement of Epoxydisilanes

David M. Hodgson* and Paul J. Comina

The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, UK

Abstract: The LDA-induced rearrangements of epoxydisilane **1** (R = Ph), to give predominantly β-trimethylsilyl acylsilane **6** (R = Ph), and of epoxydisilanes **1** (R = alkyl) remarkably to give silanols **7**, are described.

We recently reported a method for the preparation of acylsilanes from epoxydisilanes **1** using H_2SO_4 in MeOH.[1] 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.[2] 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 β-trimethylsilyl acylsilane **6** on protic work-up.

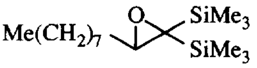
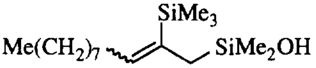
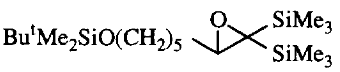
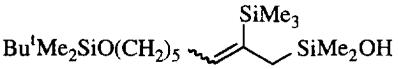
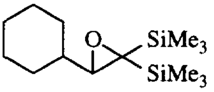
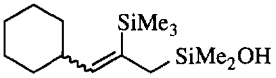


(1)

Trimethylsilyl ethers derived from allylic primary alcohols undergo the reverse Brook (silyl-Wittig) rearrangement on treatment with Bu^{t}Li to give on protic work-up 1-(trimethylsilyl)allylic alcohols.[3] 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; β-trimethylsilyl ketones can form when using stoichiometric quantities of BuLi.[4] These latter reactions were found to be facilitated by steric bulk in the alkyl group and an ability to stabilise an adjacent negative charge;[4] both factors would be present if the alkyl group were replaced by a trialkylsilyl substituent.

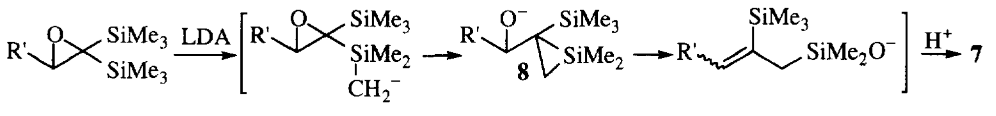
In the event, epoxydisilane **1** (R = Ph)[1] rearranged using LDA (3.5 equivs.) in Et_2O at reflux (0.5 h) to give the *E*-disilyl enol ether **5**[5] (R = Ph, 19%)[6] and the β-trimethylsilyl acylsilane **6**[7] (R = Ph, 71%). However, epoxydisilanes which lacked the activating effect provided by the 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.

Epoxydisilane	Silanol **7**		*E*- : *Z*-	Yield,[6] %
		**7a**	1 : 1	90
			1 : 1	74
			1 : 2.3	96

The structures of the silanols **7** were rigorously established by extensive spectroscopic studies. For example, silanol *Z*-**7a**[8] gave a strong, broad absorbance in the IR (neat) at 3306 cm^{-1}, the ^1H NMR spectrum showed typical vinyl- and allyl-silane signals [δ_H 5.86 (1H, t, *J* 7.5, HC=) and 1.63 (2H, s, $=CCH_2Si$) respectively] and integration in the SiMe region gave $SiMe_3$ and $SiMe_2$ assignments (δ_H 0.14 and 0.12 respectively), the ^{13}C NMR DEPT spectra showed 8 CH_2 signals, and the ^{29}Si NMR spectrum supported the presence of R_3SiOR' and $=CSiR_3$ functionality (δ_{Si} 14.5 and -7.2 respectively).[9] Long-range COSY experiments (^1H–^{13}C and ^1H–^{29}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 $=CC\mathit{H}_2Si$ and $Si(C\mathit{H}_3)_2$ [but not to $Si(C\mathit{H}_3)_3$], and between $=\mathit{C}CH_2Si$ and $Si(C\mathit{H}_3)_3$ [but not to $Si(C\mathit{H}_3)_2$].

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

 (2)

Acknowledgements: We thank the EPSRC for an Earmarked Studentship (to P. J. C.) and a Research Grant (GR/J02445) and the EPSRC Mass Spectrometry Service Centre for mass spectra. We also thank Zeneca (Strategic Research Fund) for a generous unrestricted grant.

REFERENCES AND NOTES

1. Hodgson, D. M.; Comina, P. J. *Chem. Commun.* **1996**, 755-756.
2. Crandall, J. K.; Apparu, M. *Org. React. (N. Y.)* **1983**, *29*, 345-443.
3. Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-M.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393-5396.
4. Kuwajima, I. *J. Organomet. Chem.* **1985**, *285*, 137-148; Kato, M.; Mori, A.; Oshino, H.; Enda, J.; Kobayashi, K.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1773-1778.
5. Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609-5617.
6. Isolated total yields of chromatographically homogeneous, spectroscopically pure products.
7. Dunoguès, J.; Bolourtchian, M.; Calas, R.; Duffaut, N.; Picard, J.-P. *J. Organomet. Chem.* **1972**, *43*, 157-162.
8. *Z*-**7a** was separated from *E*-**7a** [δ_H 5.65 (HC=)] by column chromatography. *E*- / *Z*- Assignments were based on nOe studies.
9. Williams, E. A. NMR Spectroscopy of Organosilicon Compounds. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z. Eds.; Wiley: Chichester; 1989; pp. 511-554.
10. Ager, D. J. *Org. React. (N. Y.)* **1990**, *38*, 1-223.

(*Received in UK* 24 *May* 1996; *accepted* 7 *June* 1996)