Vinyldisilanes as masked acylsilanes

David M. Hodgson* and Paul J. Comina

The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QY,† and Department of Chemistry, The University of Reading, Whiteknights, Reading, UK RG6 2AD

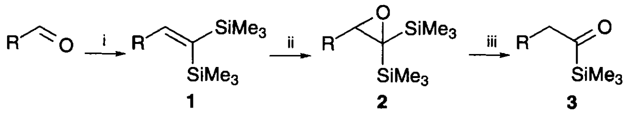
The synthesis of acylsilanes 3 from vinyldisilanes 1 by epoxidation and treatment of the resulting epoxydisilanes 2 with H_2SO_4 in MeOH is described.

We recently reported a one step method for the preparation of vinyldisilanes **1** from aldehydes (Scheme 1).[1] The potential of vinyldisilanes **1** in organic synthesis is largely unexplored, unlike vinylsilanes which have established utility.[2] One important transformation of vinylsilanes is epoxidation and hydrolysis of the resultant epoxysilanes with acid to reveal a carbonyl group, in which the carbonyl carbon originally bore the silyl group.[3] Since vinylsilanes can be prepared in one step by one-carbon homologation of aldehydes[4] and epoxysilanes can be prepared directly from aldehydes or ketones by a version of the Darzens reaction,[3b] then significant methodology for achieving overall carbonyl chain extension is also available. As part of an investigation into the synthetic utility of vinyldisilanes **1**, we communicate here our preliminary results concerning the reaction of acids with the easily derived epoxydisilanes **2**, which provide new routes to synthetically valuable acylsilanes **3**[5] (Scheme 1) and 1-halo-1-trimethylsilylalkenes **6** (X = Cl, Br or I).[6]

A number of experimental conditions known to hydrolyse epoxides[3] were examined for their ability to convert epoxydisilane **2** [R = cyclohexyl (cy)] into the corresponding acylsilane **3** (R = cy). H_2SO_4 in MeOH[3c] was found to be the most effective combination to achieve this transformation to give the acylsilane **3** (R = cy)[7] directly (77%)‡ (Scheme 1). These conditions were then applied to a range of epoxydisilanes **2** (Table 1).§

When following the formation of the acylsilane **3** (R = cy) by ^1H NMR, the enol ether **4** (R = cy), but not the dimethyl acetal **5** (R = cy), could be detected (Scheme 2). The acylsilane **3** (R = cy) could also be obtained under the reaction conditions when starting from either the enol ether **4** (R = cy, *E*:*Z*, 50:50) [75%, prepared (68%) from acylsilane **3** (R = cy), $(MeO)_3CH$, cat. PTSA, MeOH], or the dimethyl acetal **5** (R = cy) [54%, prepared[8] (57%) from acylsilane **3** (R = cy), $MeOSiMe_3$, cat. Me_3SiOTf, CH_2Cl_2], the latter reaction proceeding *via* rapid formation (by ^1H NMR) of the enol ether **4** (R = cy).

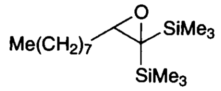
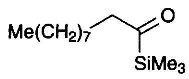
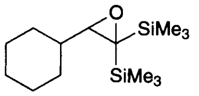
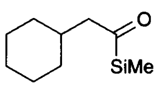
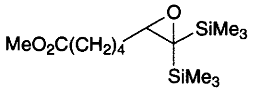
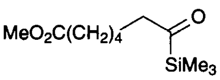
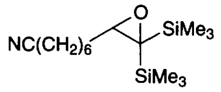
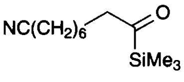
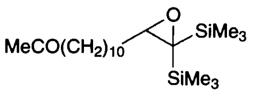
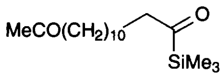
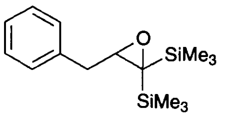
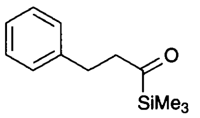
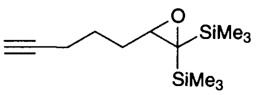
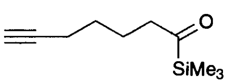
The above observations, when taken in isolation, do not rule out other potentially competing acid-catalysed pathways. These could start with regioisomeric addition of MeOH to the epoxydisilane **2** (R = cy), initial addition by the small amount of water (or HSO_4^-) present, or direct protodesilylation [to first give the enol of the acylsilane **3** (R = cy)]. However, we have additional results which support MeOH addition to the epoxydisilanes **2** as the predominant reaction and that this is highly regioselective for the disilyl-substituted carbon. X-Ray crystallographic analysis of an epoxydisilane **2** (R = 3,5-dinitrobenzoyloxymethyl), prepared from 3,3-bis(trimethylsilyl)prop-2-enol,[9] indicates a significantly longer, and therefore presumably weaker, epoxide O–C$(SiMe_3)_2$ bond (1.53 Å) compared with the epoxide O–CH(alkyl) bond (1.43 Å).[10] Also, treatment of epoxydisilanes **2** (R = cy or octyl) with hydrogen halides results in the direct formation of (*Z*)-1-halo-trimethylsilylalkenes **6**[6] (R = cy or octyl, Scheme 3), which are useful for the synthesis of geometrically defined trisubstituted alkenes.[11]

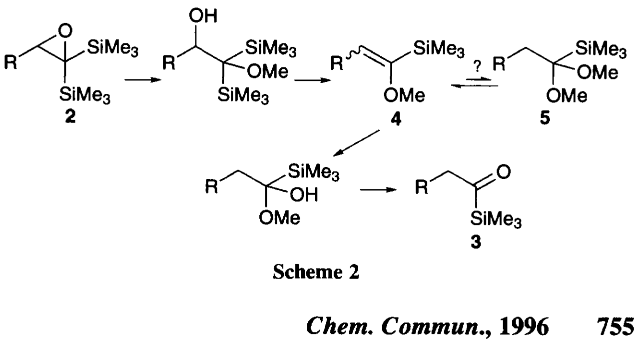


Scheme 1 *Reagents and conditions*: i, $Br_2C(SiMe_3)_2$, $CrCl_2$, DMF, 25 °C, 24 h; ii, MCPBA (1.1 equiv.), CH_2Cl_2, 25 °C, 2–24 h; iii, c. H_2SO_4 (1.1 equiv.), MeOH, 25 °C, 0.7–3 h

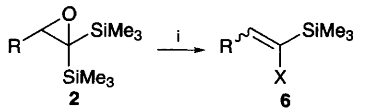
Acylsilanes **3** (R = cy or octyl), which would be the expected products arising from the alternative regiochemistry of epoxide opening with hydrogen halides, were not observed in the crude ^1H NMR spectra of these reactions.

Table 1 Synthesis of acylsilanes **3**

Epoxydisilane **2**	Yield (%)	Acylsilane **3**	Yield (%)
	84		97
	87		77
	79		78
	89		79
	85		65
	81		93
	79		85



Scheme 2



99%, *E*:*Z*, 1:99 (R = cy, X = Cl)
99%, *E*:*Z*, 1:99 (R = octyl, X = Cl)
99%, *E*:*Z*, <1:>99 (R = cy, X = Br)
99%, *E*:*Z*, 1:99 (R = octyl, X = Br)
91%, *E*:*Z*, <1:>99 (R = cy, X = I)
90%, *E*:*Z*, 2:98 (R = octyl, X = I)

Scheme 3 *Reagents and conditions*: i, HX, THF, reflux, 4.5–15 h

In summary, we have developed a method for the conversion of epoxydisilanes **2** to synthetically valuable[5] acylsilanes **3**. This means that vinyldisilanes **1** can be regarded as masked acylsilanes **3**. Because of the high chemoselectivity available in our preparation of vinyldisilanes **1** from aldehydes[1] and the subsequent chemistry outlined herein, then overall our methodology allows for one-carbon homologation of aldehydes to functionalised acylsilanes **3**.

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.

Footnotes

† Address for correspondence.

‡ Isolated total yields of chromatographically homogeneous, spectroscopically pure products are reported. All new compounds were characterised by a full range of spectroscopic data, including ^{1}H and ^{13}C NMR and microanalysis and/or high resolution mass spectrometry.

§ *Representative Procedure*. Concentrated H_2SO_4 (18 mol dm^{-3}; 34 mm^3, 0.38 mmol) was added dropwise to a stirred solution of epoxydisilane **2** (R = Bn) (94 mg, 0.34 mmol) in MeOH (1 cm^3) at 25 °C. After 2 h at 25 °C, saturated aqueous $NaHCO_3$ (5 cm^3) was added to the reaction mixture and the MeOH was removed by evaporation under reduced pressure. The aqueous phase was extracted with Et_2O (3 × 5 cm^3) and the combined organic extracts were washed with water (10 cm^3), brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography [SiO_2, 5% Et_2O in light petroleum (boiling range 40–60 °C)] gave a colourless oil, the acylsilane **3** (R = Bn)[7] (65 mg, 93%).‡

References

1 D. M. Hodgson and P. J. Comina, *Tetrahedron Lett.*, 1994, **35**, 9469.
2 I. Fleming, J. Dunoguès and R. Smithers, *Org. React. (N.Y.)*, 1989, **39**, 57.
3 (*a*) P. F. Hudrlik and A. M. Hudrlik, α,β-Epoxysilanes, in *Advances in Silicon Chemistry*, ed. G. L. Larson, JAI, Greenwich, 1993, vol. 2, p. 1; (*b*) G. Burford, F. Cooke, G. Roy and P. Magnus, *Tetrahedron*, 1983, **39**, 867; (*c*) G. Stork and E. Colvin, *J. Am. Chem. Soc.*, 1971, **93**, 2080.
4 K. Takai, Y. Kataoka, T. Okazoe and K. Utimoto, *Tetrahedron Lett.*, 1987, **28**, 1443.
5 Recent reviews: C. Nàjera and M. Yus, *Org. Prep. Proced. Int.*, 1995, **27**, 385; P. F. Cirillo and J. S. Panek, *Org. Prep. Proced. Int.*, 1992, **24**, 555; P. C. Bulman Page, S. S. Klair and S. Rosenthal, *Chem. Soc. Rev.*, 1990, **19**, 195; A. Ricci and A. Degl'Innocenti, *Synthesis*, 1989, 647.
6 G. Zweifel, R. E. Murray and H. P. On, *J. Org. Chem.*, 1981, **46**, 1292; G. Zweifel and W. Lewis, *J. Org. Chem.*, 1978, **43**, 2739.
7 J. Yoshida, S. Matsunaga, Y. Ishichi, T. Maekawa and S. Isoe, *J. Org. Chem.*, 1991, **56**, 1307.
8 T. Mandai, S. Matsumoto, M. Kohama, M. Kawada, J. Tsuji, S. Sato and T. Moriwake, *J. Org. Chem.*, 1990, **55**, 5671.
9 K. D. Kim and P. A. Magriotis, *Tetrahedron Lett.*, 1990, **31**, 6137.
10 D. M. Hodgson, P. J. Comina, M. G. B. Drew and A. Jahans, unpublished work.
11 R. B. Miller and G. McGarvey, *J. Org. Chem.*, 1979, **44**, 4623.

Received, 24th January 1996; Com. 6/00547K