

# 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,<sup>†</sup> 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<sub>2</sub>SO<sub>4</sub> in MeOH is described.

We recently reported a one step method for the preparation of vinyldisilanes **1** from aldehydes (Scheme 1).<sup>1</sup> The potential of vinyldisilanes **1** in organic synthesis is largely unexplored, unlike vinylsilanes which have established utility.<sup>2</sup> 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.<sup>3</sup> Since vinylsilanes can be prepared in one step by one-carbon homologation of aldehydes<sup>4</sup> and epoxysilanes can be prepared directly from aldehydes or ketones by a version of the Darzens reaction,<sup>3b</sup> 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**<sup>5</sup> (Scheme 1) and 1-halo-1-trimethylsilylalkenes **6** (X = Cl, Br or I).<sup>6</sup>

A number of experimental conditions known to hydrolyse epoxides<sup>3</sup> were examined for their ability to convert epoxydisilane **2** [R = cyclohexyl (cy)] into the corresponding acylsilane **3** (R = cy). H<sub>2</sub>SO<sub>4</sub> in MeOH<sup>3c</sup> was found to be the most effective combination to achieve this transformation to give the acylsilane **3** (R = cy)<sup>7</sup> directly (77%)<sup>‡</sup> (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 <sup>1</sup>H 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)<sub>3</sub>CH, cat. PTSA, MeOH], or the dimethyl acetal **5** (R = cy) [54%, prepared<sup>8</sup> (57%) from acylsilane **3** (R = cy), MeOSiMe<sub>3</sub>, cat. Me<sub>3</sub>SiOTf, CH<sub>2</sub>Cl<sub>2</sub>], the latter reaction proceeding *via* rapid formation (by <sup>1</sup>H NMR) of the enol ether **4** (R = cy).

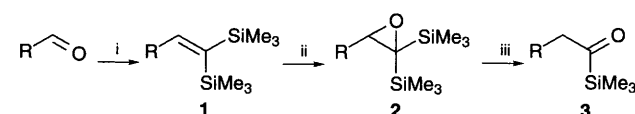
The above observations, when taken in isolation, do not rule out other potentially competing acid-catalysed pathways. These could start with regioisomeric addition of MeOH to the epoxydisilane **2** (R = cy), initial addition by the small amount of water (or HSO<sub>4</sub><sup>−</sup>) present, or direct 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,<sup>9</sup> indicates a significantly longer, and therefore presumably weaker, epoxide O–C(SiMe<sub>3</sub>)<sub>2</sub> bond (1.53 Å) compared with the epoxide O–CH(alkyl) bond (1.43 Å).<sup>10</sup> Also, treatment of epoxydisilanes **2** (R = cy or octyl) with hydrogen halides results in the direct formation of (*Z*)-1-halo-trimethylsilylalkenes **6**<sup>6</sup> (R = cy or octyl, Scheme 3), which are useful for the synthesis of geometrically defined trisubstituted alkenes.<sup>11</sup>

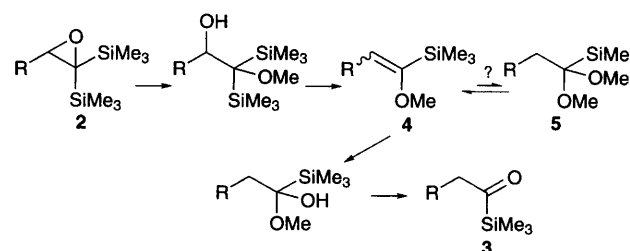
Acylsilanes **3** (R = cy or octyl), which would be the expected products arising from the alternative regiochemistry of epoxide opening with hydrogen halides, were not observed in the crude <sup>1</sup>H NMR spectra of these reactions.

Table 1 Synthesis of acylsilanes **3**

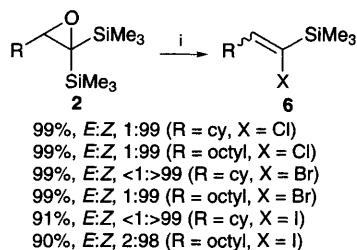
Epoxydisilane <b>2</b>	Yield (%)	Acylsilane <b>3</b>	Yield (%)
	84		97
	87		77
	79		78
	89		79
	85		65
	81		93
	79		85



Scheme 1 Reagents and conditions: i, Br<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>, CrCl<sub>2</sub>, DMF, 25 °C, 24 h; ii, MCPBA (1.1 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, 25 °C, 2–24 h; iii, c. H<sub>2</sub>SO<sub>4</sub> (1.1 equiv.), MeOH, 25 °C, 0.7–3 h



Scheme 2



**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<sup>5</sup> acylsilanes **3**. This means that vinylsilanes **1** can be regarded as masked acylsilanes **3**. Because of the high chemoselectivity available in our preparation of vinylsilanes **1** from aldehydes<sup>1</sup> 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 <sup>1</sup>H and <sup>13</sup>C NMR and microanalysis and/or high resolution mass spectrometry.

§ *Representative Procedure.* Concentrated H<sub>2</sub>SO<sub>4</sub> (18 mol dm<sup>-3</sup>; 34 mm<sup>3</sup>, 0.38 mmol) was added dropwise to a stirred solution of epoxydisilane **2** (R = Bn) (94 mg, 0.34 mmol) in MeOH (1 cm<sup>3</sup>) at 25 °C. After 2 h at 25 °C,

saturated aqueous NaHCO<sub>3</sub> (5 cm<sup>3</sup>) was added to the reaction mixture and the MeOH was removed by evaporation under reduced pressure. The aqueous phase was extracted with Et<sub>2</sub>O (3 × 5 cm<sup>3</sup>) and the combined organic extracts were washed with water (10 cm<sup>3</sup>), brine (10 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. Purification of the residue by column chromatography [SiO<sub>2</sub>, 5% Et<sub>2</sub>O in light petroleum (boiling range 40–60 °C)] gave a colourless oil, the acylsilane **3** (R = Bn)<sup>7</sup> (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-Epoxydisilanes, 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. Nájera 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