

Chromium(II)-mediated synthesis of vinylbis(silanes) from aldehydes and a study of acid- and base-induced reactions of the derived epoxybis(silanes): a synthesis of acylsilanes

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The synthesis of vinylbis(silanes) **1** from aldehydes and dibromomethylenebis(trimethylsilane) using chromium(II) chloride in DMF is described. Epoxidation of vinylbis(silanes) **1** and treatment of the resulting epoxybis(silanes) **2** with sulfuric acid in methanol gives acylsilanes **3**. Mechanistic studies of acylsilane formation, together with a crystal structure of epoxybis(silane) **2** (R = 3,5-dinitrobenzoyloxymethyl) and the finding that 1-halovinylsilanes **7** (X = Cl, Br, I) can be prepared from epoxybis(silanes) **2** using hydrogen halides, all indicate that the preferred site of nucleophilic attack in epoxybis(silanes) **2** is at the disilyl-substituted carbon. Reaction of alkyl-substituted epoxybis(silanes) such as **2b,c** with LDA proceeds by an unusual rearrangement process to give silanols **14**.

Three principal aspects of vinylsilane chemistry have contributed to the now well-established utility of vinylsilanes in organic synthesis.¹ Firstly, a variety of methods are available for preparing the vinylsilane group with high regio- and stereo-control. Secondly, the vinylsilane group is stable to many commonly used reagents, thus allowing the group to be carried through many synthetic sequences unchanged. Thirdly, replacement of the silyl substituent on the alkene is possible with a range of electrophiles (intramolecular C–C bond formation is particularly useful) and generally occurs with high and predictable control in the translation of stereochemistry from the vinylsilane into the product alkene. Vinylbis(silanes) **1** might be anticipated to possess broadly similar attributes to vinylsilanes for use in synthesis. In contrast to vinylsilanes however, vinylbis(silanes) **1** are a relatively unexplored class of materials. A deterrent to investigating their chemistry is the lack of concise methods available for their preparation, particularly under mild conditions. The development of a method for direct homologation of aldehydes to vinylbis(silanes) **1**, which would not be restricted to non-enolisable aldehydes and which proceeded with high chemoselectivity, would be desirable, since it would provide simple access to highly functionalised vinylbis(silanes) **1** and better allow their potential in synthesis to be realised. In this paper we detail our studies on the development and scope of such a method.² In addition, we report in full our studies of the derived epoxybis(silanes) **2** to provide access to acylsilanes **3** and 1-halovinylsilanes **7** (X = Cl, Br, I),³ as well as the unusual base-induced rearrangements of alkyl-substituted epoxybis(silanes) such as **2b,c** to silanols **14**.⁴

Although a potentially attractive method to make vinylbis(silanes) **1** would be by olefination of carbonyl compounds, Peterson reaction using LiC(SiMe₃)₃ is essentially restricted to non-enolisable aldehydes and ketones,⁵ as is reaction with Li₂C(SiMe₃)₂⁶ or (MgBr)₂C(SiMe₃)₂.⁷ Reaction of esters with phenyldimethylsilyllithium (2.4 equiv.), followed by dehydration of the resultant 1,1-bis(silyl) alcohols using thionyl chloride in pyridine, provides an alternative route to vinylbis(silanes) **1**.⁸ Vinylbis(silanes) **1** can be prepared in three steps from 1-alkynes by initial conversion to 1-alkynylsilanes followed by hydroalumination–halogenolysis to give 1-halovinyl-

silanes **7** (X = Cl, Br, I) then replacement of the halide substituent by a silyl group *via* halogen–lithium exchange using an alkyllithium.^{9,10} Subsequent transformations of vinylbis(silanes) **1** prepared by the above routes have only been briefly examined. Seebach *et al.* studied the carbolithiation of vinylbis(silanes) **1** and reaction of the intermediate bis(silyl) anions with non-enolisable aldehydes to provide a route to vinylsilanes *via* a Peterson reaction.¹¹ Gröbel and Seebach reported the monobromodesilylation of ethenylbis(trimethylsilane).¹² Negishi *et al.* found that cyclisation of a bromovinylbis(silane) using diisobutylaluminium chloride gave a cyclobut-1-enylsilane.⁹ Overman and co-workers reported a single example of an iminium ion initiated vinylbis(silane) terminated cyclisation reaction to generate a 3-(trimethylsilyl)-1,2,5,6-tetrahydropyridine.¹⁰ These last three examples indicate the potential for selective electrophilic substitution in vinylbis(silanes) **1**.

gem-Dichromium reagents, derived from *gem*-dihalides, have recently been developed to homologate aldehydes to 1,2-disubstituted alkenes [including (*E*)-vinylsilanes]¹³ under very mild conditions.¹⁴ However, no trisubstituted alkenes have been satisfactorily prepared from aldehydes by this method.¹⁵ In order to examine this chemistry in the context of an approach to vinylbis(silanes) **1** we first required an efficient synthesis of a suitable bis(silyl)-substituted dihalide. Consideration of the stability, handling and storage problems of bis(silyl)-substituted diiodides,¹⁶ as well as the greater reactivity of *gem*-dibromides over *gem*-dichlorides in chromium-mediated alkene synthesis,¹⁷ led us to study Br₂C(SiMe₃)₂. This dibromide was prepared on a multigram scale in one step by a slight modification of a procedure reported by Bickelhaupt *et al.*^{7a} Thus, addition of CH₂Br₂ to lithium diisopropylamide (LDA) (2 equiv.) in the presence of Me₃SiCl (3 equiv., rather than the originally reported 2 equiv.) at –110 °C gave almost quantitative formation of Br₂C(SiMe₃)₂. Excess Me₃SiCl may prevent decomposition of the presumed intermediate carbenoids [LiCHBr₂ and BrLiC(SiMe₃)₂] before silylation and/or prevent C–C bond formation between BrLiC(SiMe₃)₂ and Br₂C(SiMe₃)₂. Initial experiments with aldehydes indicated that Br₂C(SiMe₃)₂ was not reduced effectively by CrCl₂ in neat THF, even in the presence of LiI,¹⁴ and addition of DMF as a co-solvent was required before successful reaction was observed. The use of neat DMF as solvent led to rapid reduction of

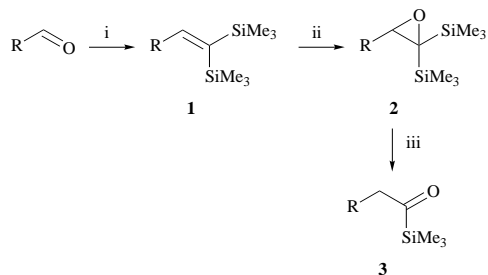
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Table 1 Synthesis of vinylbis(silanes) **1**, epoxybis(silanes) **2** and acylsilanes **3**

Aldehyde	Vinylbis(silane) 1	Yield (%)	Epoxybis(silane) 2	Yield (%)	Acylsilane 3	Yield (%)
		84		78		
	1a (ref. 5a)		2a	(ref. 18)		
$\text{CH}_3(\text{CH}_2)_7\text{CHO}$		78		84		97
	1b		2b		3b	
		79		94		77
	1c		2c		3c (ref. 33)	
Bu^tCHO		28				
	1d (ref. 5a)					
$\text{MeO}_2\text{C}(\text{CH}_2)_4\text{CHO}$ (ref. 19)		64		97		78
	1e		2e		3e	
$\text{NC}(\text{CH}_2)_6\text{CHO}$ (ref. 20)		70		89		79
	1f		2f		3f	
$\text{MeCO}(\text{CH}_2)_{10}\text{CHO}$ (ref. 21)		58		85		65
	1g		2g		3g	
		84				
	1h (ref. 5a)					
		73				
	1i					
		39 ^a		81		93
	1j		2j		3j (ref. 33)	
		38		79		85
	1k		2k		3k	

^a 29% using $\text{Br}_2\text{C}(\text{SiMe}_3)_2$ and CrCl_2 as limiting reagents [**1j**: $\text{Br}_2\text{C}(\text{SiMe}_3)_2$: CrCl_2 = 4:1:4].

$\text{Br}_2\text{C}(\text{SiMe}_3)_2$ and gave improved yields of the desired vinylbis(silanes) **1** (Scheme 1). The reaction was found to be applicable



Scheme 1 Reagents and conditions: i, $\text{Br}_2\text{C}(\text{SiMe}_3)_2$, CrCl_2 , DMF, 25 °C, 24 h; ii, MCPBA (1.1 equiv.), CH_2Cl_2 , 25 °C, 2–24 h; iii, conc. H_2SO_4 (1.1 equiv.), MeOH, 25 °C, 0.7–3 h

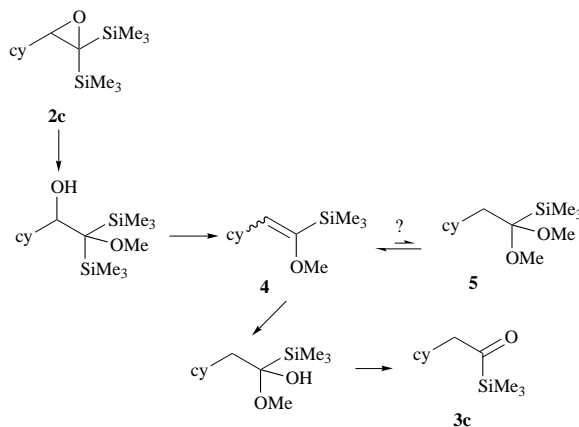
to a range of aldehydes (Table 1). It is evident that the reaction shows the usual high chemoselectivity which is characteristic of chromium(II)-mediated transformations.¹⁴

Aside from electrophilic substitution, one of the synthetically most useful transformations 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 substituent.²³ Given the utility of acylsilanes **3** in synthesis²⁴ and the now ready availability of vinylbis(silanes) **1** (*vide supra*), then the development of a method to convert vinylbis(silanes) **1** into acylsilanes **3** *via* epoxybis(silanes) **2** would be of value (Scheme 1). Epoxybis(silanes) **2** also have other potential applications. Hudrlík *et al.* prepared the first epoxybis(silane), by MCPBA-mediated epoxidation of ethenylbis(trimethylsilyl), and found that it underwent a variety of transformations: pyrolysis in the gas phase at 600 °C resulted in isomerisation into a geometric mixture of silyl enol ethers;²⁵ reaction at room temperature using MgBr_2 in Et_2O gave 2,2-bis(trimethylsilyl)ethanal, whereas reaction in THF at reflux gave 2,2-bis(trimethylsilyl)-2-bromoethanol;²⁶ reaction with acetic acid containing 10–20% acetic anhydride and 0.2% $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at room temperature led to the enol acetate of

ethanoyltrimethylsilane.²⁷ Epoxybis(silanes) have also been prepared by α -lithiation-silylation of epoxysilanes^{28,29} and by a version of the Darzens reaction using $\text{LiBrC}(\text{SiMe}_3)_2$ with non-enolisable ketones [aldehydes gave 1-bromovinylsilanes **7** ($\text{X} = \text{Br}$), except for ethanal which also gave the epoxybis(silane) **2** ($\text{R} = \text{Me}$) as a minor by-product].³⁰

A number of experimental conditions known to hydrolyse epoxides¹⁸ were examined for their ability to convert epoxybis(silane) **2c** into the corresponding acylsilane **3c**. No reaction was observed using acetic acid in aq. THF at room temperature (14 d) or subsequently at 60 °C (7 d); toluene-*p*-sulfonic acid (PTSA) in aq. THF at room temperature gave the crude acylsilane (85%), but required 13 d; HClO_4 ²⁹ in aq. THF at 60 °C for 4 h gave the acylsilane **3c** (81%), but this method could not be successfully extended to the preparation of other acylsilanes **3**.³¹ H_2SO_4 in MeOH³² was found to be the most generally effective combination to achieve the transformation of epoxybis(silanes) **2** directly into acylsilanes **3** (Scheme 1, Table 1). Overall, we have developed a three-step procedure which provides access to functionalised acylsilanes **3** by one-carbon homologation of aldehydes. The method can be compared with the two-step synthesis performed by Yoshida *et al.* of acylsilanes **3** from aldehydes *via* reaction with lithiated methoxymethylenebis(trimethylsilane) and hydrolysis of the resulting methyl enol ethers, although the synthesis of functionalised acylsilanes **3** by this route was not reported.³³

When following the formation of the acylsilane **3c** by ¹H NMR spectroscopy, the enol ether **4**, but not the dimethyl acetal **5**, could be detected (Scheme 2, *cy* = cyclohexyl). The



acylsilane **3c** could also be obtained under the reaction conditions when starting from either the enol ether **4** (*E:Z* = 50:50) [75%, prepared (68%) from acylsilane **3c**, $(\text{MeO})_3\text{CH}$, cat. PTSA, MeOH], or the dimethyl acetal **5** [54%, prepared³⁴ (57%) from acylsilane **3c**, MeOSiMe_3 , cat. Me_3SiOTf , CH_2Cl_2], the latter reaction proceeding *via* rapid formation (by ¹H NMR spectroscopy) of the enol ether **4**.

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 epoxybis(silane) **2c**, initial addition by the small amount of water (or HSO_4^-) present, or direct protodesilylation (to first give the enol of the acylsilane **3c**). However, Whitham *et al.* isolated 2-methoxy-2-(trimethylsilyl)cyclohexanol from treatment of 1-trimethylsilylcyclohexene oxide with H_2SO_4 in MeOH; subsequent treatment with NaH gave 1-methoxycyclohexene.³⁵ We also have additional results which support MeOH addition to epoxybis(silanes) **2** as the predominant reaction and that this process is highly regioselective for the bis(silyl)-substituted carbon. Firstly, the reaction of epoxybis(silanes) **2** with hydrogen halides gives 1-halovinylsilanes **7** ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (*vide infra*). Secondly, X-ray crystallographic analysis of an epoxybis-

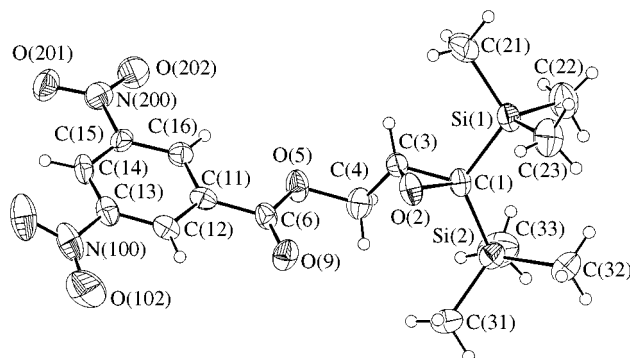
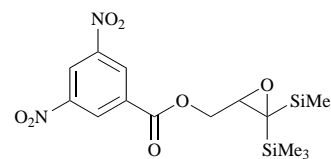


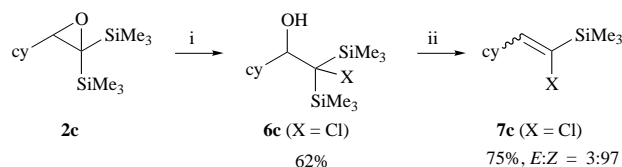
Fig. 1 ORTEP view of [3,3-bis(trimethylsilyl)oxiran-2-yl]methyl 3,5-dinitrobenzoate **2** ($\text{R} = 3,5$ -dinitrobenzoyloxymethyl)



Epoxybis(silane) **2** ($\text{R} = 3,5$ -dinitrobenzoyloxymethyl)

(silane) **2** ($\text{R} = 3,5$ -dinitrobenzoyloxymethyl), prepared from 3,3-bis(trimethylsilyl)prop-2-enol,³⁶ indicates a significantly longer, and therefore presumably weaker, epoxide $\text{O}-\text{C}(\text{SiMe}_3)_2$ bond (1.53 Å) compared with the epoxide $\text{O}-\text{CH}(\text{alkyl})$ bond (1.43 Å). Although this is the first X-ray structure of an epoxybis(silane), it shows similarities to C–O bond lengths (ranging from 1.485–1.499 and 1.411–1.448 Å respectively) found in reported X-ray structures of epoxysilanes.³⁷ The HOMO of a silyl or alkyl substituted epoxide can be derived from a linear combination of an oxygen 2p orbital and a contribution from the C–Si or (exocyclic) C–C σ -orbitals. The wavefunction of the HOMO is C–O antibonding and the stronger antibonding interaction between the 2p lone pair and the C–Si σ -orbital (compared with the C–C σ -orbital) has been suggested as the cause of the weakening of the $\text{O}-\text{CSiMe}_3$ bond in epoxy-silanes.³⁸

1-Halovinylsilanes **7** ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are useful for the synthesis of geometrically defined trisubstituted alkenes,³⁹ and as synthetic equivalents of carbonyl anions and cations.⁴⁰ We had previously attempted to prepare 1-bromovinylsilanes **7** ($\text{X} = \text{Br}$) by a chromium(II)-mediated alkene synthesis from aldehydes and $\text{Me}_3\text{SiCBr}_3$, which instead resulted in homologation to the corresponding methyl ketones.⁴¹ An alternative method for 1-halovinylsilane synthesis could be *via* reaction of epoxybis(silanes) **1** with hydrogen halides. Reaction of epoxybis(silane) **2c** with HCl in aq. THF at room temperature gave chlorohydrin **6c** ($\text{X} = \text{Cl}$, 62%), which upon treatment with NaH in THF gave 1-chlorovinylsilane **7c** ($\text{X} = \text{Cl}$,⁴² 75%, Scheme 3) with excellent



Scheme 3 Reagents and conditions: i, HCl, THF, 25 °C, 28 h; ii, NaH, THF, 25 °C, 4 h

stereocontrol (*E:Z* = 3:97). Formation of the *E*-alkene is most likely greatly favoured due to pronounced differences in eclipsing interactions between the two possible conformations for *syn* elimination.⁴³

Heating hydrogen halides with epoxybis(silanes) **2b,c** gave 1-halovinylsilanes **7b,c** ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) directly and with excellent control over alkene geometry (Scheme 4). In these cases loss of

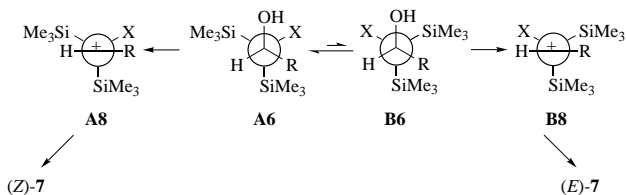
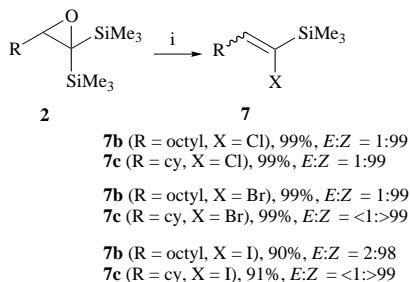


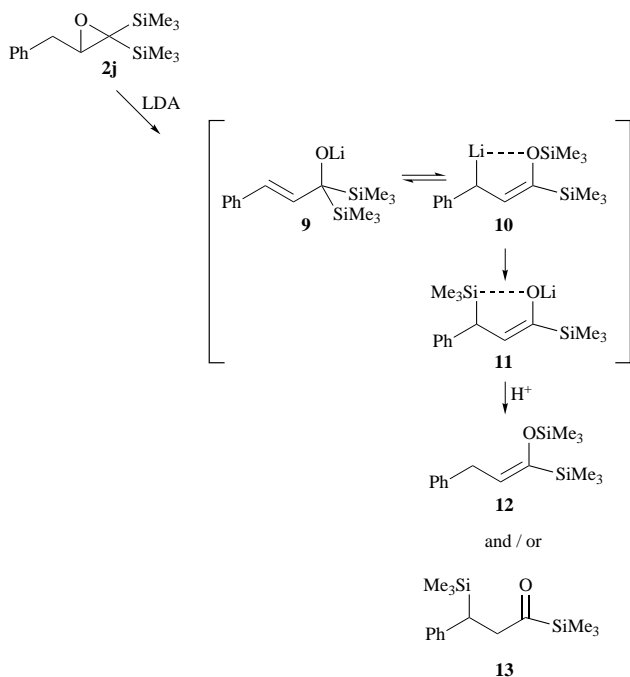
Fig. 2



Scheme 4 Reagents and conditions: i, HX, THF, reflux, 4.5–15 h

water following protonation of the intermediate halohydrins **6** would proceed much more easily from the major staggered conformer **A6** than from the minor conformer **B6**, as steric effects become magnified *en route* to the intermediate carbocations **A8** and **B8**, which are stabilised by the original *anti*-Me₃Si substituents (Fig. 2). Acylsilanes **3b,c**, 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. It has been suggested that the alignment of the C–Si bond in an epoxysilane is such that it is unable to aid stabilisation of any developing positive charge on the β-carbon.²³

In order to compare the reactions of acids and bases with epoxybis(silanes) **2** we examined the reactions of epoxybis(silanes) **2** with LDA. The reaction of bases such as LDA with simple epoxides generally produces allylic alkoxides which give allylic alcohols on protic work-up.⁴⁴ Should an epoxybis(silane) such as **2j** rearrange analogously there exists the possibility of a subsequent Brook rearrangement from the allylic alkoxide **9** to generate a lithium homoenolate **10** (Scheme 5). Direct proton-



Scheme 5

ation of the homoenolate **10** could lead to the bis(silyl) enol ether **12**. Alternatively, the homoenolate **10** could rearrange to

Table 2 LDA-mediated rearrangement of epoxybis(silanes) **2**

Epoxybis(silane) 2	Silanol 14
 2b	 14b , 90%, <i>E:Z</i> = 50:50
 2c	 14c , 96%, <i>E:Z</i> = 30:70
 2 [R = (CH ₂) ₅ OSiMe ₂ Bu']	 14 [R = (CH ₂) ₅ OSiMe ₂ Bu'], 74%, <i>E:Z</i> = 50:50

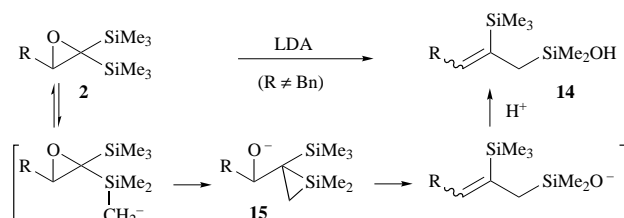
the enolate **11**, which would give a β-trimethylsilyl acylsilane **13** on protic work-up.

Trimethylsilyl ethers derived from allylic primary alcohols undergo the reverse Brook (silyl-Wittig) rearrangement on treatment with Bu^tLi to give on protic work-up 1-(trimethylsilyl)allylic alcohols.⁴⁵ However, 1-(trimethylsilyl)allylic alcohols which are further substituted by an alkyl group at the 1-position generally give silyl enol ethers on treatment with catalytic BuLi; β-trimethylsilyl ketones can form when using stoichiometric quantities of BuLi.⁴⁶ These latter reactions were found to be facilitated by steric bulk in the alkyl group and an ability to stabilise an adjacent negative charge;⁴⁶ both factors would be present if the alkyl group were replaced by a trialkylsilyl substituent.

In the event, epoxybis(silane) **2j** rearranged using LDA (3.5 equiv.) in Et₂O at reflux (0.5 h) to give the *E*-bis(silyl) enol ether **12**⁴² (19%) and the β-trimethylsilyl acylsilane **13**⁴⁷ (71%). However, epoxybis(silanes) **2** which lacked the activating effect provided by the aryl group present in epoxybis(silane) **2j** underwent a remarkable and profoundly different transformation on treatment with LDA to give silanols **14** (Table 2); disiloxanes were not observed.

The structures of the silanols **14** were rigorously established by extensive spectroscopic studies. For example, silanol *Z*-**14b** gave a strong, broad absorbance in the IR spectrum (neat) at 3306 cm⁻¹, the ¹H NMR spectrum showed typical vinyl- and allyl-silane signals [δ_{H} 5.86 (1 H, t, *J* 7.5, HC=) and 1.63 (2 H, s, =CCH₂Si) respectively] and integration in the SiMe region gave the SiMe₃ and SiMe₂ assignments (δ_{H} 0.14 and 0.12 respectively), the ¹³C NMR DEPT spectra showed eight CH₂ signals, and the ²⁹Si NMR spectrum supported the presence of R₃SiOR' and =CSiR₃ functionality (δ_{Si} 14.5 and -7.2 respectively).⁴⁹ Long-range COSY experiments (¹H-¹³C and ¹H-²⁹Si HMBC) were used to establish that the allylic silicon, rather than the vinylic silicon, bears the OH group. For example, correlations were observed between =CCH₂Si and Si(CH₃)₂ [but not to Si(CH₃)₃], and between =CCH₂Si and Si(CH₃)₃ [but not to Si(CH₃)₂]. In order to explain this unusual rearrangement to give a silanol **14**, we tentatively suggest a mechanism which involves (reversible) deprotonation α to silicon, followed by irreversible intramolecular epoxide opening at the proximal epoxide carbon to generate a silirane **15** which collapses by a Peterson-type reaction (Scheme 6).⁴³

In conclusion, this paper reports methods which broaden access to several classes of organosilicon compounds of demonstrated or potential use in organic synthesis. Vinylbis(silanes) **1** are now readily available in one step from aldehydes by a highly chemoselective process. On treatment with acids, the derived epoxybis(silanes) **2** provide routes to acylsilanes **3** and to (*Z*)-1-halovinylsilanes **7** (X = Cl, Br, I); in these reactions all the evidence, including a crystal structure of the epoxybis(silane) **2** (R = 3,5-dinitrobenzoyloxymethyl), is consistent



Scheme 6

with the bis(silyl)-substituted carbon being the site of nucleophilic attack. Finally, an unusual LDA-induced rearrangement of alkyl-substituted epoxybis(silanes) **2** gives a novel class of silanols **14**.

Experimental

General details

All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of argon. Syringes and needles for the transfer of reagents were dried at 140 °C for 12 h and allowed to cool in a desiccator over P₂O₅ before use. Ethers were distilled from sodium benzophenone ketyl, (chlorinated) hydrocarbons and amines from CaH₂. DMF was distilled from CaH₂ under reduced pressure. Internal reaction temperatures are reported unless stated otherwise. All reactions were monitored by TLC using commercially available glass-backed plates, pre-coated with a 0.25 mm layer of silica containing a fluorescent indicator (Merck). Column chromatography was carried out on Kieselgel 60 (40–63 μm). Light petroleum refers to the fraction with bp 40–60 °C. IR spectra were recorded as thin films unless stated otherwise, using Perkin-Elmer 881 or 983 spectrophotometers. ¹H and ¹³C NMR spectra were recorded in CDCl₃ unless stated otherwise with Varian Gemini 200, Bruker AC200, Bruker WM250, Bruker WH300, JEOL EX400 or Bruker AC500 spectrometers. Chemical shifts are reported relative to CHCl₃ [δ_{H} 7.26, δ_{C} (central line of t) 77.0]. Coupling constants (*J*) are given in Hz.

(Dibromomethylene)bis(trimethylsilane)

Butyllithium (2.5 mol dm⁻³ in hexanes; 42.0 cm³, 105 mmol) was added dropwise to a stirred solution of diisopropylamine (15.4 cm³, 110 mmol) in pentane (150 cm³)-THF (150 cm³) at -20 °C. The solution was then cooled to -110 °C and treated dropwise with Me₃SiCl (19.1 cm³, 150 mmol). After stirring for 10 min a solution of CH₂Br₂ (3.5 cm³, 50 mmol) in THF (25 cm³) was added slowly dropwise. The reaction was then allowed to warm to room temperature over 12 h. Saturated aq. NH₄Cl (50 cm³) was added dropwise and the mixture was evaporated under reduced pressure. The residue was extracted with Et₂O (3 × 50 cm³) and the combined organic layers were washed successively with water (50 cm³) and brine (50 cm³), dried (MgSO₄) and evaporated under reduced pressure. The residue was purified by sublimation (50–70 °C/1 mmHg) to give a white solid, the *dibromide* (15.9 g, 99%); *R*_f 0.8 (20% Et₂O in light petroleum); mp 68–69 °C (lit.^{7a} 68–73 °C; lit.⁵⁰ 68–69 °C); δ_{H} (400 MHz) 0.29 (18 H, s, *J*_{H-Si} 6.5, 2 × SiMe₃); δ_{C} (63 MHz) 58.0 (CBr₂) and -1.0 (2 × SiMe₃).

Typical procedure for the preparation of vinylbis(silanes) **1**

(*E*)-4-Phenylbuta-1,3-diene-1,1-diylbis(trimethylsilane) **1h**.^{5a} A solution of cinnamaldehyde (133 mg, 1 mmol) and (Me₃Si)₂CBr₂ (640 mg, 2.01 mmol) in dry, deoxygenated DMF (5.0 cm³) was added dropwise to a well-stirred solution of CrCl₂ (Aldrich, 95% w/w pure; 1030 mg, 7.96 mmol) in dry, deoxygenated DMF (9.0 cm³) under argon at 25 °C. After 24 h at 25 °C, water (40 cm³) was added and the mixture was extracted with Et₂O (3 × 40 cm³). The combined organic extracts were washed successively with aq. CuSO₄ (1 mol dm⁻³; 40 cm³), water (40 cm³) and brine (40 cm³), dried (MgSO₄) and

evaporated under reduced pressure. Purification of the residue by column chromatography (pentane) gave a colourless oil, the *vinylbis(silane)* **1h** (233 mg, 84%); *R*_f 0.7 (pentane).

Analytical data for previously undescribed vinylbis(silanes) **1** in Table 1

Dec-1-ene-1,1-diylbis(trimethylsilane) 1b. A colourless oil; *R*_f 0.8 (2.5% Et₂O in pentane); ν_{max} /cm⁻¹ 2956, 2925, 2855, 1567, 1466, 1248, 900, 862, 838 and 762; δ_{H} (400 MHz) 6.59 (1 H, t, *J* 7, HC=), 2.20 (2 H, dt, *J* 7 and 7.5, CH₂CH=C), 1.41–1.23 (12 H, m, 6 × CH₂), 0.88 (3 H, t, *J* 6.5, Me), 0.15 (9 H, s, *J*_{H-Si} 6.5, SiMe₃) and 0.07 (9 H, s, *J*_{H-Si} 6, SiMe₃); δ_{C} (100 MHz) 158.2 (HC=), 139.8 (*J*_{C-Si} 53.5, =C, quat.), 35.8 (CH₂), 32.0 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 22.7 (CH₂), 14.2 (Me), 1.9 (*J*_{C-Si} 51.5, SiMe₃) and 0.41 (*J*_{C-Si} 51.5, SiMe₃); *m/z* (EI) 284 (M⁺, 1%), 269 (M - Me⁺, 8), 195 (25), 98 (48) and 73 (100) (Found: M⁺, 284.2356. C₁₆H₃₆Si₂ requires *M*, 284.2356).

2-Cyclohexylethene-1,1-diylbis(trimethylsilane) 1c. A colourless oil; *R*_f 0.95 (pentane); ν_{max} /cm⁻¹ 2927, 2851, 1567, 1449, 1247, 923, 877, 863, 838 and 762; δ_{H} (400 MHz) 6.34 (1 H, d, *J* 10, HC=), 2.27 (1 H, dtt, *J* 10, 10 and 4, CH), 1.75–1.45 (5 H, m, 5 × CHH), 1.31–1.07 (5 H, m, 5 × CHH), 0.14 (9 H, s, *J*_{H-Si} 6, SiMe₃) and 0.06 (9 H, s, *J*_{H-Si} 6, SiMe₃); δ_{C} (100 MHz) 163.3 (HC=), 136.9 (*J*_{C-Si} 53.5, =C, quat.), 44.3 (CH), 32.5 (2 × CH₂), 26.0 (CH₂), 25.7 (2 × CH₂), 2.0 (*J*_{C-Si} 51.5, SiMe₃) and 0.4 (*J*_{C-Si} 51.5, SiMe₃); *m/z* (EI) 254 (M⁺, 5%), 239 (10), 165 (15) and 73 (100) (Found: M⁺, 254.1886. C₁₄H₃₀Si₂ requires *M*, 254.1886).

Methyl 7,7-bis(trimethylsilyl)hept-6-enoate 1e. A colourless oil; *R*_f 0.75 (50% Et₂O in light petroleum); ν_{max} /cm⁻¹ 2952, 1743, 1566, 1436, 1248, 894, 864, 838 and 763; δ_{H} (400 MHz) 6.54 (1 H, t, *J* 8, HC=), 3.65 (3 H, s, MeO), 2.31 (2 H, t, *J* 7.5, MeO₂CCH₂), 2.20 (2 H, dt, *J* 7 and 7, CH₂CH=C), 1.63 (2 H, app. quintet, *J* 7.5, CH₂), 1.41 (2 H, app. quintet, *J* 7.5, CH₂), 0.13 (9 H, s, *J*_{H-Si} 6.5, SiMe₃) and 0.05 (9 H, s, *J*_{H-Si} 6.5, SiMe₃); δ_{C} (100 MHz) 176.0 (MeO₂C), 159.1 (HC=), 142.6 (=C, quat.), 53.4 (MeO), 37.3 (CH₂), 36.0 (CH₂), 31.0 (CH₂), 26.7 (CH₂), 3.8 (*J*_{C-Si} 53.5, SiMe₃) and 2.3 (*J*_{C-Si} 51.5, SiMe₃); *m/z* (thermospray, NH₃) 304 (M + NH₄⁺, 90%), 288 (100) and 143 (44) (Found: M + NH₄⁺, 304.2128. C₁₄H₃₄NO₂Si₂ requires *M*, 304.2128).

9,9-Bis(trimethylsilyl)non-8-enenitrile 1f. A colourless oil; *R*_f 0.4 (15% Et₂O in pentane); ν_{max} /cm⁻¹ 2951, 2856, 2247, 1566, 1248, 904, 889, 864, 839, 816, 763 and 735; δ_{H} (400 MHz) 6.56 (1 H, t, *J* 7, HC=), 2.34 (2 H, t, *J* 7, NCCH₂), 2.21 (2 H, dt, *J* 7 and 6.5, CH₂CH=C), 1.67 (2 H, app. quintet, *J* 7, CH₂), 1.50–1.30 (6 H, m, 3 × CH₂), 0.15 (9 H, s, *J*_{H-Si} 6, SiMe₃) and 0.07 (9 H, s, *J*_{H-Si} 6.5, SiMe₃); δ_{C} (100 MHz) 157.3 (HC=), 140.4 (*J*_{C-Si} 53.0, =C, quat.), 119.7 (CN), 35.4 (CH₂), 29.1 (CH₂), 28.6 (CH₂), 28.5 (CH₂), 25.3 (CH₂), 17.1 (CH₂), 1.78 (*J*_{C-Si} 51.5, SiMe₃) and 0.30 (*J*_{C-Si} 51.5, SiMe₃); *m/z* (thermospray, NH₃) 299 (M + NH₄⁺, 62%), 282 (M + H⁺, 100) and 132 (8) (Found: M + H⁺, 282.2073. C₁₅H₃₂NSi₂ requires *M*, 282.2073).

14,14-Bis(trimethylsilyl)tetradec-13-en-2-one 1g. A colourless oil; *R*_f 0.6 (20% Et₂O in pentane); ν_{max} /cm⁻¹ 2932, 2852, 1717, 1568, 1463, 1360, 1262, 1245, 1165, 908, 863, 844, 816, 763, 736, 686, 647 and 619; δ_{H} (400 MHz) 6.56 (1 H, t, *J* 7, HC=), 2.38 (2 H, t, *J* 7.5, MeCOCH₂), 2.18–2.12 (2 H, m, CH₂CH=C), 2.10 (3 H, s, Me), 1.56–1.51 (2 H, m, MeCOCH₂CH₂), 1.34–1.17 (14 H, m, 7 × CH₂), 0.12 (9 H, s, *J*_{H-Si} 6.5, SiMe₃) and 0.04 (9 H, s, *J*_{H-Si} 6.5, SiMe₃); δ_{C} (100 MHz) 209.0 (C=O), 158.1 (HC=), 139.7 (*J*_{C-Si} 55, =C, quat.), 43.7 (CH₂), 35.7 (CH₂), 29.7 (Me), 29.5 (CH₂), 29.4 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 23.8 (CH₂), 1.8 (*J*_{C-Si} 51.5, SiMe₃) and 0.3 (*J*_{C-Si} 51.5, SiMe₃); *m/z* (EI) 354 (M⁺, 1%), 339 (2), 147 (30) and 73 (100); *m/z* (CI, NH₃) 355 (M + H⁺, 4%), 202 (8) and 90 (100) (Found: M + H⁺, 355.2852. C₂₀H₄₃OSi₂ requires *M*, 355.2852).

4-Methylpenta-1,3-diene-1,1-diylbis(trimethylsilane) 1i. A colourless oil; *R*_f 0.6 (pentane); ν_{max} /cm⁻¹ 2954, 2903, 1632, 1528, 1249, 907, 862, 839, 740, 651 and 618; δ_{H} (400 MHz) 7.37 [1 H, d, *J* 11.5, CH=C(SiMe₃)₂], 6.21 (1 H, m, Me₂C=CH), 1.85 (3 H, s, Me), 1.84 (3 H, s, Me), 0.21 (9 H, s, *J*_{H-Si} 6, SiMe₃) and 0.13 (9

H, s, $J_{\text{H-Si}}$ 6, SiMe₃); δ_{C} (63 MHz) 149.0 [CH=C(SiMe₃)₂], 140.4 and 139.1 [Me₂C=CHCH=C(SiMe₃)₂], 126.7 (Me₂C=CH), 26.7 (Me), 17.9 (Me), 1.9 ($J_{\text{C-Si}}$ 50.5, SiMe₃) and 0.5 ($J_{\text{C-Si}}$ 50.5, SiMe₃); m/z (EI) 226 (M⁺, 5%) and 73 (100) (Found: M⁺, 226.1573. C₁₂H₂₆Si₂ requires M , 226.1573).

3-Phenylprop-1-ene-1,1-diylbis(trimethylsilane) 1j. A colourless oil; R_f 0.8 (5% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 3084, 3063, 3027, 2953, 2897, 1561, 1496, 1454, 1249, 905, 838 and 698; δ_{H} (400 MHz) 7.36–7.22 (5 H, m, 5 × ArH), 6.77 (1 H, t, J 7, HC=), 3.65 (2 H, d, J 7, CH₂), 0.29 (9 H, s, $J_{\text{H-Si}}$ 6, SiMe₃) and 0.15 (9 H, s, $J_{\text{H-Si}}$ 6, SiMe₃); δ_{C} (100 MHz) 155.1 (HC=), 141.8 (quat.), 140.4 (quat.), 128.5 (Ar), 126.0 (Ar), 41.6 (CH₂), 1.9 ($J_{\text{C-Si}}$ 51.5, SiMe₃) and 0.3 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (EI) 262 (M⁺, 6%), 247 (12), 171 (30) and 73 (100) (Found: M⁺, 262.1573. C₁₅H₂₆Si₂ requires M , 262.1573).

Hept-1-en-6-yne-1,1-diylbis(trimethylsilane) 1k. A colourless oil; R_f 0.5 (pentane); $\nu_{\text{max}}/\text{cm}^{-1}$ 3310, 2954, 1568, 1249, 909, 862, 839, 736 and 620; δ_{H} (400 MHz) 6.56 (1 H, t, J 7, HC=), 2.33 (2 H, dt, J 8 and 8, CH₂CH=C), 2.21 (2 H, td, J 7 and 2.5, HC=CCCH₂), 1.95 (1 H, t, J 2.5, HC=), 1.64 (2 H, app. quintet, J 7.5, CH₂CH₂CH₂), 0.16 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃) and 0.01 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 156.3 (HC=), 141.6 (=C, quat.), 84.3 (=C, quat.), 68.6 (HC=), 34.7 (CH₂), 28.4 (CH₂), 18.2 (CH₂), 1.8 ($J_{\text{C-Si}}$ 51.5, SiMe₃) and 0.4 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (EI) 237 (M + H⁺, 3%) and 73 (100) (Found: M + H⁺, 237.1495. C₁₃H₂₆Si₂ requires M , 237.1495).

Typical procedure for the preparation of epoxybis(silanes) 2

1,2-Epoxydecane-1,1-diylbis(trimethylsilane) 2b. A mixture of vinylbis(silane) **1b** (386 mg, 1.36 mmol), MCPBA (50% w/w pure; 515 mg, 1.49 mmol) and CH₂Cl₂ (15 cm³) was stirred at room temperature for 18 h. CH₂Cl₂ (15 cm³) was then added and the reaction was washed with aq. NaHCO₃ (5 × 30 cm³), water (30 cm³) and brine (30 cm³), dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by column chromatography (2% Et₂O in light petroleum) to give a colourless oil, epoxybis(silane) **2b** (343 mg, 84%); R_f 0.8 (5% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 2955, 2923, 2854, 1467, 1407, 1261, 1250, 999, 843, 812, 763, 736, 688, 637 and 618; δ_{H} (400 MHz) 2.93 (1 H, dd, J 7, 4.5, epoxide CH), 1.67–1.55 (1 H, m, CHHCHO), 1.54–1.39 (3 H, m, MeCH₂ and CHHCHO), 1.26 (10 H, br s, 5 × CH₂), 0.87 (3 H, t, J 7, Me), 0.11 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃) and 0.02 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (CDCl₃, 100 MHz) 61.9 (CH), 51.4 (quat.), 31.8 (CH₂), 31.5 (CH₂), 29.6 (2 × CH₂), 29.2 (CH₂), 27.5 (CH₂), 22.6 (CH₂), 14.1 (Me), 0.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃) and -2.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (EI) 299 (M - H⁺, 6%), 227 (20), 201 (11), 147 (75) and 73 (100) (Found: M - H⁺, 299.2239. C₁₆H₃₅OSi₂ requires M , 299.2226).

Analytical data for previously undescribed epoxybis(silanes) 2 in Table 1

2-Cyclohexyloxirane-1,1-diylbis(trimethylsilane) 2c. A colourless oil; R_f 0.40 (20% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 2929, 2852, 1452, 1417, 1262, 1251, 937, 913, 880, 843, 814 and 689; δ_{H} (400 MHz) 2.64 (1 H, d, J 9, epoxide CH), 1.92–1.89 (1 H, m, CH), 1.75–1.62 (5 H, m, 5 × CHH), 1.31–1.02 (5 H, m, 5 × CHH), 0.11 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃) and 0.02 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 66.7 (epoxide CH), 52.1 (quat.), 39.1 (CH), 30.8 (CH₂), 30.0 (CH₂), 26.4 (CH₂), 25.6 (CH₂), 25.5 (CH₂), 0.2 ($J_{\text{C-Si}}$ 53.5, SiMe₃) and 0.01 ($J_{\text{C-Si}}$ 53.5, SiMe₃); m/z (CI, NH₃) 271 (M + H⁺, 2%), 198 (9), 181 (9), 164 (15), 116 (100) and 90 (72) (Found: M + H⁺, 271.1913. C₁₄H₃₁OSi₂ requires M , 271.1913).

Methyl 5-[3,3-bis(trimethylsilyl)oxiran-2-yl]pentanoate 2e. A colourless oil; R_f 0.45 (30% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 2956, 1736, 1437, 1262, 1251, 1097, 1021, 909, 843, 812, 732, 689, 649, 636 and 616; δ_{H} (400 MHz) 3.66 (3 H, s, MeO), 2.94 (1 H, dd, J 7 and 4, epoxide CH), 2.33 (2 H, t, J 7, MeO₂CCH₂), 1.73–1.47 (6 H, m, 3 × CH₂), 0.12 (9 H, s, $J_{\text{H-Si}}$ 6, SiMe₃) and 0.03 (9 H, s, $J_{\text{H-Si}}$ 6, SiMe₃); δ_{C} (63 MHz) 173.7 (MeO₂C), 61.5

(CH), 53.3 (quat.), 51.3 (MeO), 33.9 (CH₂), 31.1 (CH₂), 27.0 (CH₂), 24.7 (CH₂), 0.1 ($J_{\text{C-Si}}$ 52.3, SiMe₃) and -2.3 ($J_{\text{C-Si}}$ 52.3, SiMe₃); m/z (EI) 147 (38%) and 73 (100); m/z (CI, NH₃) 303 (M + H⁺, 5%), 133 (18), 90 (100) and 73 (15) (Found: M + H⁺, 303.1812. C₁₄H₃₁O₃Si₂ requires M , 303.1812).

7-[3,3-Bis(trimethylsilyl)oxiran-2-yl]heptanenitrile 2f. A colourless oil; R_f 0.6 (50% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 2954, 2858, 2246, 1462, 1427, 1262, 1251, 901, 886, 843, 814, 637 and 617; δ_{H} (400 MHz) 2.93 (1 H, dd, J 7 and 4.5, epoxide CH), 2.34 (2 H, t, J 7, NCCH₂), 1.73–1.63 (4 H, m, 2 × CH₂), 1.56–1.36 (6 H, m, 3 × CH₂), 0.12 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃) and 0.04 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 119.7 (NC), 61.7 (CH), 51.4 (quat.), 31.3 (CH₂), 28.6 (2 × CH₂), 27.3 (CH₂), 25.2 (CH₂), 17.1 (CH₂), 0.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃) and -2.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (EI) 208 (37%), 147 (45) and 73 (100); m/z (CI, NH₃) 298 (M + H⁺, 20%), 208 (65), 90 (100) and 73 (25) (Found: M + H⁺, 298.2022. C₁₅H₃₂NOSi₂ requires M , 298.2022).

12-[3,3-Bis(trimethylsilyl)oxiran-2-yl]dodecan-2-one 2g. A colourless oil; R_f 0.25 (10% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 2926, 2854, 1742, 1468, 1388, 1250, 1039, 844, 813, 764, 724, 689, 637 and 617; δ_{H} (400 MHz) 2.93 (1 H, dd, J 7 and 4.5, epoxide CH), 2.40 (2 H, t, J 7.5, MeCOCH₂), 2.12 (3 H, s, MeCO), 1.67–1.25 (18 H, m, 9 × CH₂), 0.11 (9 H, s, $J_{\text{H-Si}}$ 6, SiMe₃) and 0.02 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 209.2 (C=O), 61.8 (CH), 51.3 (quat.), 43.7 (CH₂), 31.4 (CH₂), 29.8 (Me), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 27.4 (CH₂), 23.8 (CH₂), 0.15 ($J_{\text{C-Si}}$ 51.5, SiMe₃) and -2.21 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (CI, NH₃) 371 (M + H⁺, 4%), 297 (9), 255 (7), 191 (7), 164 (13), 134 (9) and 90 (100) (Found: M + H⁺, 371.2802. C₂₀H₄₃O₂Si₂ requires M , 371.2802).

3-Benzoyloxirane-2,2-diylbis(trimethylsilane) 2j. A colourless oil; R_f 0.6 (5% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 2956, 2901, 1498, 1455, 1405, 1264, 1252, 910, 844, 825, 736, 700, 649, 637 and 619; δ_{H} (400 MHz) 7.35–7.24 (5 H, m, 5 × ArH), 3.22 (1 H, dd, J 8 and 4, epoxide CH), 3.02 (1 H, dd, J 15 and 4, PhCHH), 2.83 (1 H, dd, J 15 and 8, PhCHH), 0.22 (9 H, s, $J_{\text{H-Si}}$ 6, SiMe₃) and 0.06 (9 H, s, $J_{\text{H-Si}}$ 6, SiMe₃); δ_{C} (100 MHz) 139.2 (Ar, quat.), 128.7 (2 × Ar), 128.5 (2 × Ar), 126.4 (Ar), 62.1 (CH), 51.9 (quat.), 37.9 (CH₂), 0.3 ($J_{\text{C-Si}}$ 51.5, SiMe₃) and -2.1 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (EI) 279.2 (M + H⁺, 11%), 205 (41), 167 (5), 147 (38), 116 (7), 91 (11) and 73 (100) (Found: M + H⁺, 279.1609. C₁₅H₂₇OSi₂ requires M , 279.1600).

5-[3,3-Bis(trimethylsilyl)oxiran-2-yl]pentyne 2k. A colourless oil; R_f 0.6 (10% Et₂O in light petroleum); $\nu_{\text{max}}/\text{cm}^{-1}$ 3313, 2955, 2119, 1456, 1435, 1410, 1252, 908, 842, 811, 763, 689 and 636; δ_{H} (400 MHz) 2.95 (1 H, dd, J 8 and 4, epoxide CH), 2.34–2.19 (2 H, m, CH₂), 1.95 (1 H, t, J 2.5, HC=), 1.86–1.56 (4 H, m, 2 × CH₂), 0.13 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃) and 0.03 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 84.0 (=C, quat.), 68.7 (HC=), 61.2 (CH), 51.4 (quat.), 30.5 (CH₂), 26.4 (CH₂), 18.3 (CH₂), 0.1 ($J_{\text{C-Si}}$ 53.5, SiMe₃) and -2.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (CI, NH₃) 255 (M + H⁺, 3%), 165 (31), 90 (100) and 73 (65) (Found: M + H⁺, 255.1600. C₁₃H₂₇OSi₂ requires M , 255.1600).

Typical procedure for the preparation of acylsilanes 3

Trimethyl(3-phenylpropanoyl)silane 3j.³³ Concentrated H₂SO₄ (18 mol dm⁻³; 34 mm³, 0.61 mmol) was added dropwise to a stirred solution of epoxybis(silane) **2** (94 mg, 0.34 mmol) in MeOH (1 cm³) at 25 °C. After 2 h at 25 °C, saturated aq. NaHCO₃ (5 cm³) was added to the reaction mixture and the MeOH was removed by evaporation under reduced pressure. The residue was extracted with Et₂O (3 × 5 cm³) and the combined organic layers were washed successively with water (10 cm³) and brine (10 cm³), dried (MgSO₄) and evaporated under reduced pressure. Purification of the residue by column chromatography (5% Et₂O in light petroleum) gave a colourless oil, the acylsilane **3j** (65 mg, 93%); R_f 0.4 (5% Et₂O in light petroleum).

Analytical data for previously undescribed acylsilanes 3 in Table 1

Trimethyl(decanoyl)silane 3b. A colourless oil; R_f 0.45 (5% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2956, 2925, 2854, 1644, 1467, 1250, 845, 753 and 623; δ_{H} (400 MHz) 2.56 (2 H, t, J 7, CH₂COSiMe₃), 1.50–1.41 (2 H, m, CH₂CH₂COSiMe₃), 1.23 (12 H, br s, 6 × CH₂), 0.87–0.83 (3 H, m, Me) and 0.17 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 248.6 (COSiMe₃), 48.5 (CH₂), 31.8 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 22.6 (CH₂), 22.2 (CH₂), 14.1 (Me) and –3.2 ($J_{\text{C-Si}}$ 49.5, SiMe₃); m/z (CI, NH₃) 246 (M + NH₄⁺, 53%), 229 (M + H⁺, 100), 90 (93) and 46 (20) (Found: M + H⁺, 229.1988. C₁₃H₂₉O₂Si requires M , 229.1988).

Methyl 7-oxo-7-trimethylsilylheptanoate 3e. A colourless oil; R_f 0.45 (30% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2950, 2864, 1643, 1438, 1251, 1201, 1174 and 847; δ_{H} (400 MHz) 3.63 (3 H, s, MeO₂C), 2.58 (2 H, t, J 7, CH₂COSiMe₃), 2.27 (2 H, t, J 7.5, MeO₂CCH₂), 1.59 (2 H, app. quintet, J 7.5, CH₂), 1.51 (2 H, app. quintet, J 7.5, CH₂), 1.30–1.24 (2 H, m, CH₂) and 0.17 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 248.2 (COSiMe₃), 174.1 (MeO₂C), 51.4 (MeO₂C), 48.1 (CH₂), 33.8 (CH₂), 28.7 (CH₂), 24.7 (CH₂), 21.6 (CH₂) and –3.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (CI, NH₃) 248 (M + NH₄⁺, 20%), 231 (M + H⁺, 18), 192 (100), 175 (18) and 90 (8) (Found: M + H⁺, 231.1416. C₁₁H₂₃O₃Si requires M , 231.1416).

9-Oxo-9-trimethylsilylnonanenitrile 3f. A colourless oil; R_f 0.20 (20% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2934, 2858, 2245, 1643, 1466, 1428, 1403, 1355, 1251, 847 and 754; δ_{H} (400 MHz) 2.57 (2 H, t, J 7, CH₂COSiMe₃), 2.30 (2 H, t, J 7, NCCH₂), 1.62 (2 H, app. quintet, J 7, CH₂), 1.49 (2 H, app. quintet, J 7, CH₂), 1.43–1.31 (2 H, m, CH₂), 1.29–1.23 (4 H, m, 2 × CH₂) and 0.17 (9 H, s, $J_{\text{H-Si}}$ 6.5, SiMe₃); δ_{C} (100 MHz) 248.3 (COSiMe₃), 119.7 (CN), 48.2 (CH₂), 28.9 (CH₂), 28.6 (CH₂), 28.4 (CH₂), 25.2 (CH₂), 21.8 (CH₂), 17.0 (CH₂) and –3.3 (SiMe₃); m/z (CI, NH₃) 243 (M + NH₄⁺, 100), 226 (M + H⁺, 47) and 90 (17) (Found: M + H⁺, 226.1627. C₁₂H₂₄NOSi requires M , 226.1627).

14-Trimethylsilyltetradecan-2,14-dione 3g. A white solid; R_f 0.33 (20% Et₂O in light petroleum); mp 57–58 °C; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 2928, 2854, 1646, 1467, 1408, 1360, 1251, 1167 and 847; δ_{H} (400 MHz) 2.55 (2 H, t, J 7, CH₂COSiMe₃), 2.38 (2 H, t, J 7, MeCOCH₂), 2.09 (3 H, s, MeCO), 1.52–1.39 (4 H, m, 2 × CH₂), 1.21 (14 H, br s, 7 × CH₂) and 0.16 (9 H, s, $J_{\text{H-Si}}$ 7, SiMe₃); δ_{C} (100 MHz) 248.6 (COSiMe₃), 209.3 (MeCO), 48.5 (CH₂), 43.7 (CH₂), 29.8 (Me), 29.4 (CH₂), 29.4 (CH₂), 29.3 (2 × CH₂), 29.3 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 23.8 (CH₂), 22.1 (CH₂) and –3.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (CI, NH₃) 316 (M + NH₄⁺, 70%), 299 (M + H⁺, 100) and 90 (62) (Found: M + H⁺, 299.2406. C₁₇H₃₅O₂Si requires M , 299.2406).

Trimethyl(hept-6-ynoyl)silane 3k. A yellow oil; R_f 0.3 (10% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 3306, 2949, 2117, 1643, 1251 and 845; δ_{H} (400 MHz) 2.60 (2 H, t, J 7.5, CH₂COSiMe₃), 2.16 (2 H, td, J 7 and 3, HC≡CCH₂), 1.92 (1 H, t, J 3, HC≡), 1.62 (2 H, app. quintet, J 7.5, CH₂CH₂COSiMe₃), 1.47 (2 H, app. quintet, J 7, ≡CCH₂CH₂) and 0.18 (9 H, s, $J_{\text{H-Si}}$ 7, SiMe₃); δ_{C} (100 MHz) 247.9 (COSiMe₃), 84.1 (≡C, quat.), 68.4 (HC≡), 47.7 (CH₂), 28.0 (CH₂), 21.2 (CH₂), 18.3 (CH₂) and –3.2 ($J_{\text{C-Si}}$ 51.5, SiMe₃); m/z (CI, NH₃) 183 (M + H⁺, 41%), 90 (95) and 73 (47) (Found: M + H⁺, 183.1205. C₁₀H₁₉O₂Si requires M , 183.1205).

(2-Cyclohexyl-1-methoxyethenyl)trimethylsilane 4 and conversion to acylsilane 3c

A mixture of bis(silane) **2c** (78 mg, 0.38 mmol), (MeO)₃CH (0.318 cm³, 2.91 mmol) and cat. PTSA (*ca.* 2 mg) in MeOH (1 cm³) was heated to reflux for 10 h. After cooling to room temperature, Et₂O (10 cm³) was added and the mixture was washed successively with a mixture of brine (5 cm³) and 5% w/v aq. NaOH (5 cm³), water (10 cm³) and brine (10 cm³). The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by column chrom-

atography (2.5% EtOAc in light petroleum containing *ca.* 1% Et₃N) to give a colourless oil, the *enol ether 4* (57 mg, 68%, $E:Z = 50:50$, by ¹H NMR analysis of the isomeric HC= protons in the δ 4.99–4.90 region); m/z (EI) 212 (M⁺, 2%), 197 (8), 171 (5), 129 (5), 89 (3) and 73 (100) (Found: M⁺, 212.1596. C₁₂H₂₄O₂Si requires M , 212.1596). Further column chromatography gave samples of the individual geometric isomers: (*Z*)-**4**: R_f 0.67 (5% Et₂O in light petroleum containing *ca.* 1% Et₃N); $\nu_{\max}/\text{cm}^{-1}$ 2927, 2850, 1608, 1464, 1449, 1249, 1196, 1161, 1115, 968, 890, 840, 759 and 627; δ_{H} (200 MHz) 4.99 (1 H, d, J 10.5, HC=), 3.43 (3 H, s, OMe), 2.16–2.03 (1 H, m, CH), 1.74–1.59 (5 H, m, 5 × CHH), 1.34–1.01 (5 H, m, 5 × CHH) and 0.17 (9 H, s, SiMe₃); δ_{C} (50 MHz) 159.9 (≡C, quat.), 119.5 (HC=), 54.3 (OMe), 36.8 (CH), 35.0 (2 × CH₂), 26.1 (2 × CH₂), 25.9 (CH₂) and –0.8 (SiMe₃); (*E*)-**4**: R_f 0.55 (5% Et₂O in light petroleum containing *ca.* 1% Et₃N); $\nu_{\max}/\text{cm}^{-1}$ 2926, 2850, 1615, 1449, 1313, 1249, 1199, 1112, 982, 892, 839, 758, 692 and 628; δ_{H} (200 MHz) 4.90 (1 H, d, J 9, HC=), 3.56 (3 H, s, OMe), 2.64–2.52 (1 H, m, CH), 1.71–1.60 (5 H, m, 5 × CHH), 1.37–0.99 (5 H, m, 5 × CHH) and 0.15 (9 H, s, $J_{\text{H-Si}}$ 6.4, SiMe₃); δ_{C} (50 MHz) 159.9 (≡C, quat.), 133.0 (HC=), 59.3 (OMe), 34.2 (CH), 33.4 (2 × CH₂), 26.1 (CH₂), 26.0 (2 × CH₂) and –0.5 (SiMe₃).

A mixture of enol ether **4** (57 mg, 0.27 mmol) and concentrated H₂SO₄ (18 mol dm⁻³; 25 mm³, 0.45 mmol) in MeOH (1 cm³) was stirred at room temperature for 5 d. Standard work-up as described earlier for preparation of acylsilane **3j** gave a residue which was purified by column chromatography (3% Et₂O in light petroleum) to give a colourless oil, the acylsilane **3c** (40 mg, 75%).

(2-Cyclohexyl-1,1-dimethoxyethyl)trimethylsilane 5 and preparation of acylsilane 3c

MeOSiMe₃ (143 mm³, 1.01 mmol) and then acylsilane **3c** (100 mg, 0.50 mmol) were added dropwise to a stirred solution of Me₃SiOTf (1 mm³, 0.005 mmol) in CH₂Cl₂ (50 cm³) at –78 °C. The reaction mixture was stirred at –78 °C for 6 h before addition of pyridine (5 drops) and aq. NaHCO₃ (10 cm³). The solution was allowed to warm to room temperature and extracted with Et₂O (3 × 10 cm³). The combined organic layers were dried (NaHCO₃–Na₂SO₄, 50:50) and evaporated under reduced pressure. Purification of the residue by column chromatography (3% Et₂O in light petroleum containing *ca.* 1% Et₃N) gave a colourless oil, the *dimethyl acetal 5* (70 mg, 57%); R_f 0.50 (5% Et₂O in light petroleum containing *ca.* 1% Et₃N); $\nu_{\max}/\text{cm}^{-1}$ 2923, 2851, 2825, 1450, 1249, 1112, 1035, 841 and 755; δ_{H} (300 MHz) 3.20 (6 H, s, 2 × OMe), 1.82 [2 H, br d, J 12.5, CH₂C(OMe)₂], 1.69–1.60 (3 H, m, 3 × CHH), 1.53–1.51 (2 H, m, 2 × CHH), 1.50–1.41 (1 H, m, CH), 1.25–1.04 (3 H, m, 3 × CHH), 0.94–0.82 (2 H, m, 2 × CHH) and 0.14 (9 H, s, SiMe₃); δ_{C} (50 MHz) 104.1 (quat.), 48.9 (2 × OMe), 43.4 [CH₂C(OMe)₂], 34.5 (2 × CH₂), 34.1 (CH), 26.4 (2 × CH₂), 26.3 (CH₂) and –1.2 (SiMe₃); m/z (CI, NH₃) 229 (M – Me⁺, 1%), 213 (100), 171 (20), 90 (5) and 73 (2) (Found: M – Me⁺, 229.1624. C₁₂H₂₅O₂Si requires M , 229.1624).

A mixture of dimethyl acetal **5** (70 mg, 0.29 mmol) and concentrated H₂SO₄ (4 drops) in MeOH (720 mm³) and CDCl₃ (720 mm³) was stirred at room temperature. Complete conversion of dimethyl acetal **5** to acylsilane **3c** (*via* enol ether **4**) was observed by ¹H NMR spectroscopy after 1 h. Standard work-up as described earlier for preparation of acylsilane **3j** gave a residue which was purified by column chromatography (3% Et₂O in light petroleum) to give a colourless oil, the acylsilane **3c** (30 mg, 54%).

Preparation of crystalline epoxybis(silane) 2 (R = 3,5-dinitrobenzoyloxymethyl)

Et₃N (118 mm³, 0.85 mmol) and Me₃SiCl (86 mm³, 0.85 mmol) were added to a stirred solution of 3-iodo-3-trimethylsilylprop-2-enol⁵¹ (145 mg, 0.57 mmol) in CH₂Cl₂ (2 cm³) at room tem-

perature. After 30 min, SiO₂ was added and the mixture was evaporated under reduced pressure. The residue was purified by column chromatography (5% Et₂O in light petroleum) to give a pale yellow oil, the *silyl ether* (116 mg, 62%); *R*_f 0.85 (20% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2959, 1685, 1448, 1407, 1251, 1031, 909, 883, 839, 751, 735, 697 and 622; δ_{H} (400 MHz) 6.41 (1 H, t, *J* 4.5, HC=), 4.23 (2 H, d, *J* 4.5, CH₂), 0.18 (9 H, s, *J*_{H-Si} 8.5, SiMe₃) and 0.15 (9 H, s, *J*_{H-Si} 6.5, SiMe₃); δ_{C} (100 MHz) 146.4 (HC=), 113.0 (=C, quat.), 69.5 (CH₂) and -1.7 (2 × SiMe₃).

tert-Butyllithium (1.7 mol dm⁻³ in pentane; 340 mm³, 0.58 mmol) was added dropwise to a stirred solution of the above silyl ether (95 mg, 0.29 mmol) in THF (2 cm³) at -78 °C. After 30 min the mixture was allowed to warm to room temperature. After 2.5 h at room temperature the mixture was poured onto saturated aq. NH₄Cl (10 cm³) and extracted with Et₂O (3 × 10 cm³). The combined organic layers were washed with brine (30 cm³), dried (MgSO₄) and concentrated under reduced pressure to give a colourless oil, 3,3-bis(trimethylsilyl)prop-2-enol (28 mg, 48%); *R*_f 0.25 (20% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 3308, 2955, 2899, 1570, 1404, 1354, 1302, 1250, 1035, 893, 839, 814, 764, 687, 649 and 619; δ_{H} (400 MHz) 6.70 (1 H, t, *J* 6, HC=), 4.28 (2 H, d, *J* 6, CH₂), 1.62 (1 H, br s, OH), 0.16 (9 H, s, *J*_{H-Si} 6.4, SiMe₃) and 0.10 (9 H, s, *J*_{H-Si} 6.2, SiMe₃); δ_{C} (50 MHz) 155.6 (HC=), 143.5 (=C, quat.), 64.5 (CH₂), 1.4 (SiMe₃) and -0.1 (SiMe₃); *m/z* (CI, NH₃) 220 (M + NH₄⁺, 5%), 202 (M⁺, 18), 147 (31), 90 (80) and 73 (100) (Found: M + NH₄⁺, 220.1553. C₉H₂₆NOSi₂ requires *M*, 220.1553).

A mixture of 3,3-bis(trimethylsilyl)prop-2-enol (28 mg, 0.14 mmol), 3,5-dinitrobenzoyl chloride (64 mg, 0.28 mmol) and Et₃N (39 mm³, 0.28 mmol) in CH₂Cl₂ (1.5 cm³) was stirred at room temperature. After 21 h CH₂Cl₂ (10 cm³) was added and the mixture was washed with saturated aq. NaHCO₃ (3 × 15 cm³) and brine (20 cm³), dried (MgSO₄) and concentrated under reduced pressure to give a yellow solid, the *dinitrobenzoate* (59 mg, 100%); *R*_f 0.75 (20% Et₂O in light petroleum); mp 83–85 °C; $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 3102, 3055, 2986, 2900, 1734, 1550, 1346, 1280, 1165, 844 and 731; δ_{H} (400 MHz) 9.23 (1 H, t, *J* 2, ArH), 9.19 (2 H, d, *J* 2, 2 × ArH), 6.68 (1 H, t, *J* 6, HC=), 5.08 (2 H, d, *J* 6, CO₂CH₂), 0.25 (9 H, s, *J*_{H-Si} 6.5, SiMe₃) and 0.15 (9 H, s, *J*_{H-Si} 6.5, SiMe₃); δ_{C} (63 MHz) [CO and C(SiMe₃)₃ not observed] 148.7 (2 × Ar, quat.), 147.3 (HC=), 133.9 (Ar, quat.), 129.5 (2 × Ar), 122.4 (Ar), 67.8 (CO₂CH₂), 1.5 (SiMe₃) and 0.0 (SiMe₃); *m/z* (EI) 269 (11%), 195 (31), 149 (28) and 73 (100); *m/z* (CI, NH₃) 391 (M⁺, 20%), 337 (33), 187 (22), 90 (100) and 73 (96) (Found: M⁺, 396.1173. C₁₆H₂₄N₂O₆Si₂ requires *M*, 396.1173).

MCPBA (50% w/w pure; 112 mg, 0.32 mmol) was added to a stirred solution of the above dinitrobenzoate (59 mg, 0.15 mmol) in CH₂Cl₂ (2 cm³) at room temperature. After 42 h the mixture was washed with saturated aq. NaHCO₃ solution (5 × 5 cm³) and brine (5 cm³), dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by column chromatography (20% Et₂O in light petroleum) to give the epoxybis(silane) **2** (R = 3,5-dinitrobenzoyloxymethyl) (43 mg, 75%); *R*_f 0.45 (20% Et₂O in light petroleum); mp 126 °C (from MeOH) (Found: C, 46.85; H, 6.0; N, 6.75. C₁₆H₂₄N₂O₇Si₂ requires C, 46.6; H, 5.85; N, 6.8%); $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$ 3055, 2987, 1736, 1549, 1346, 1273, 1166, 896 and 738; δ_{H} (400 MHz) 9.25 (1 H, t, *J* 2, ArH), 9.22 (2 H, d, *J* 2 and 2 × ArH), 4.85–4.82 (1 H, dd, *J* 12 and 2, CO₂CHH), 4.44–4.39 (1 H, dd, *J* 12 and 8, CO₂CHH), 3.43–3.40 (1 H, dd, *J* 8 and 2, epoxide CH), 0.22 (9 H, s, *J*_{H-Si} 6.4, SiMe₃) and 0.11 (9 H, s, *J*_{H-Si} 6.4, SiMe₃); δ_{C} (50 MHz) 162.7 (ArCO₂), 148.9 (2 × Ar, quat.), 133.7 (Ar, quat.), 129.8 (2 × Ar), 122.8 (Ar), 68.0 (CO₂CH₂), 58.4 (CH), 50.9 (quat.), 0.0 (SiMe₃) and -2.4 (SiMe₃); *m/z* (CI, NH₃) 430 (M + NH₄⁺, 5%), 413 (M + H⁺, 27), 201 (23), 90 (100) and 73 (90) (Found: M + H⁺, 413.1200. C₁₆H₂₅N₂O₇Si₂ requires *M*, 413.1200).

X-Ray structure determination of **2** (R = 3,5-dinitrobenzoyloxymethyl) ‡

C₁₆H₂₄N₂O₇Si₂, *M* = 412.55. Orthorhombic, *a* = 9.141(12), *b* = 12.567(12), *c* = 39.49(3) Å, *V* = 4537(8) Å³, space group *Pcab* (no. 61), *Z* = 8, *D*_c = 1.208 g cm⁻³. Colourless plates. Crystal dimensions: 0.2 × 0.25 × 0.35 mm, $\mu(\text{Mo-K}\alpha) = 0.191 \text{ mm}^{-1}$. 11 410 Independent reflections were measured on a MAR research Image Plate using 95 frames at 2° intervals each measured for 2 min. Data analysis was carried out using the XDS program⁵² to give 3803 independent reflections [*R*(int) = 0.0884] which were used in subsequent calculations. The relatively high *R*(int) value is a consequence of the poor peak shapes. The structure was solved by direct methods using SHELXS-86.⁵³ All non-hydrogen atoms were given anisotropic thermal parameters and hydrogen atoms included in calculated positions given isotropic thermal parameters. The structure was refined on *F*² using SHELXL-93⁵⁴ to give a final conventional *R* factor of 0.0857 (*wR*₂ = 0.2991). The largest peak and hole in the final difference Fourier map were 0.660 and -0.419 e Å⁻³.

Two-step conversion of epoxybis(silane) **2c** to (1-chloro-2-cyclohexylethenyl)trimethylsilane **7c** (X = Cl)⁴²

A mixture of epoxybis(silane) **2c** (103 mg, 0.38 mmol), HCl (2 mol dm⁻³; 0.1 cm³) and water (0.1 cm³) in THF (0.5 cm³) was stirred at room temperature. After 28 h the mixture was evaporated under reduced pressure and CH₂Cl₂ (10 cm³), Na₂CO₃ (50 mg) and then MgSO₄ were added and the resultant slurry was filtered. The filtrate was evaporated under reduced pressure and the residue was purified twice by column chromatography (light petroleum) to give a colourless oil, 2,2-bis(trimethylsilyl)-2-chloro-1-cyclohexylethanol **6c** (X = Cl, 72 mg, 62%); *R*_f 0.45 (5% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 3531, 2925, 2852, 1726, 1450, 1252, 1006 and 843; δ_{H} (400 MHz) 3.76 (1 H, dd, *J* 7.5 and 2.5, CHOH), 1.97 (1 H, d, *J* 12.5, OH), 1.90 (1 H, d, *J* 8, cyclohexyl CH), 1.79–1.60 (5 H, m, 5 × CHH), 1.47–1.09 (5 H, m, 5 × CHH), 0.21 (9 H, s, SiMe₃) and 0.20 (9 H, s, SiMe₃).

The halohydrin **6c** was added dropwise as a solution in THF (1 cm³) to a stirred pre-washed (3 × 4 cm³ pentane) suspension of NaH (30 mg, 1.0 mmol) in THF (4 cm³) at room temperature. After 4 h, saturated aq. NH₄Cl (5 cm³) was added, and the mixture was evaporated under reduced pressure. The residue was extracted with CH₂Cl₂ (3 × 10 cm³) and the combined organic layers were washed with water (15 cm³), dried (MgSO₄) and evaporated under reduced pressure. Purification of the residue by column chromatography (light petroleum) gave a colourless oil, the 1-halovinylsilane **7c** (X = Cl, 38 mg, 75%, *E*:*Z* = 3:97, by ¹H NMR analysis of the isomeric HC=s in the δ 6.2–5.7 region); *R*_f 0.7 (light petroleum).

Typical direct preparation of 1-halovinylsilanes **7** from epoxybis(silanes) **2**

(1-Chloro-2-cyclohexylethenyl)trimethylsilane **7c**.⁴² A mixture of epoxybis(silane) **2c** (59 mg, 0.22 mmol), HCl (2 mol dm⁻³; 500 mm³, 0.99 mmol) and THF (2 cm³) was stirred at 70 °C. After 13 h the reaction mixture was cooled, Et₂O (10 cm³) was then added and the mixture was washed with saturated aq. Na₂CO₃ (2 × 10 cm³), aq. Na₂S₂O₃ (1 mol dm⁻³; 10 cm³), water (10 cm³) and brine (10 cm³). The organic layer was dried (MgSO₄) and evaporated under reduced pressure to give a residue which was purified by column chromatography (5% Et₂O in light petroleum) to give a colourless oil, the 1-halovinylsilane **7c** (X = Cl, 47 mg, 99%, *E*:*Z* = 1:99).

‡ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposit scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for the material should quote the full literature citation and the reference number 207/121.

Analytical data for previously undescribed 1-halovinylsilanes **7** in Scheme 4

(1-Chlorodec-1-enyl)trimethylsilane **7b** (R = octyl, X = Cl).

A colourless oil (*E:Z* = 1:99); R_f 0.85 (5% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2927, 2856, 1615, 1466, 1407, 1379, 1250, 906, 843, 754, 722, 697 and 627; m/z (EI) 246 (M⁺, 3%), 137 (6), 119 (6), 93 (95), 81 (25), 73 (100) and 67 (23) (Found: M⁺, 246.1571. C₁₃H₂₇³⁵ClSi requires *M*, 246.1571); discernible data for major isomer: δ_{H} (300 MHz) 5.97 (1 H, t, *J* 7, HC=), 2.28 (2 H, dt, *J* 7 and 7, CH₂CH=C), 1.43–1.36 (2 H, m, CH₂), 1.28 (10 H, br s, 5 × CH₂), 0.89 (3 H, t, *J* 6.5, Me) and 0.17 (9 H, s, SiMe₃); δ_{C} (50 MHz) 139.7 (HC=), 127.6 (quat.), 31.6 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 28.8 (CH₂), 28.2 (CH₂), 22.4 (CH₂), 13.9 (Me) and –2.6 (SiMe₃); discernible data for minor isomer: δ_{H} (300 MHz) 6.42 (1 H, t, *J* 7, HC=), 2.13–2.06 (2 H, m, CH₂CH=C) and 0.11 (9 H, s, SiMe₃).

(1-Bromodec-1-enyl)trimethylsilane **7b** (R = octyl, X = Br).

A colourless oil (*E:Z* = 1:99); R_f 0.85 (5% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2958, 2926, 2856, 1612, 1466, 1407, 1378, 1249, 1125, 954, 890, 842, 754, 722, 696 and 624; m/z (EI) 290 (M⁺, 3%), 137 (71) and 73 (100) (Found: M⁺, 290.1065. C₁₃H₂₇⁷⁹BrSi requires *M*, 290.1065); discernible data for major isomer: δ_{H} (300 MHz) 6.22 (1 H, t, *J* 6.5, HC=), 2.26 (2 H, dt, *J* 7 and 7, CH₂CH=C), 1.45–1.38 (2 H, m, CH₂), 1.29 (10 H, br s, 5 × CH₂), 0.89 (3 H, t, *J* 6.5, Me) and 0.18 (9 H, s, SiMe₃); δ_{C} (50 MHz) 142.3 (HC=), 131.3 (quat.), 32.2 (CH₂), 31.7 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 28.0 (CH₂), 22.5 (CH₂), 13.9 (Me) and –2.2 (SiMe₃); discernible data for minor isomer: δ_{H} (300 MHz) 6.76 (1 H, t, *J* 6.5, HC=), 2.12–2.07 (2 H, m, CH₂CH=C) and 0.14 (9 H, s, SiMe₃).

(1-Iododec-1-enyl)trimethylsilane **7b** (R = octyl, X = I). A colourless oil (*E:Z* = 2:98); R_f 0.85 (5% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2957, 2926, 2855, 1602, 1466, 1406, 1378, 1248, 1124, 883, 840, 752, 695 and 623; m/z (EI) 338 (M⁺, 7%), 185 (30) and 73 (100) (Found: M⁺, 338.0927. C₁₃H₂₇I Si requires *M*, 338.0927); discernible data for major isomer: δ_{H} (300 MHz) 6.11 (1 H, t, *J* 6.5, HC=), 2.21 (2 H, dt, *J* 7 and 7, CH₂CH=C), 1.46–1.39 (2 H, m, CH₂), 1.30–1.28 (10 H, br m, 5 × CH₂), 0.89 (3 H, t, *J* 7, Me) and 0.18 (9 H, s, SiMe₃); δ_{C} (50 MHz) 148.0 (HC=), 113.3 (quat.), 38.8 (CH₂), 31.7 (CH₂), 29.2 (CH₂), 29.1 (2 × CH₂), 27.7 (CH₂), 22.5 (CH₂), 13.9 (CH₃) and –1.7 (SiMe₃); discernible data for minor isomer: δ_{H} (300 MHz) 7.17 (1 H, t, *J* 7, HC=).

(*E*)-Trimethyl(3-phenyl-1-trimethylsilyloxyprop-1-enyl)silane **12**⁴⁷ and (1-oxo-3-phenylpropane-1,3-diyl)bis(trimethylsilane) **13**⁴⁸

A solution of epoxybis(silane) **2k** (150 mg, 0.54 mmol) in THF (2 cm³) was added dropwise to a solution of LDA [prepared from butyllithium (2.24 mol dm⁻³ in hexanes; 840 mm³, 1.88 mmol) and diisopropylamine (302 mm³, 2.15 mmol)] in THF (2 cm³) at room temperature. After heating to reflux for 30 min the mixture was cooled and water (5 cm³) was added. The mixture was extracted with Et₂O (3 × 10 cm³) and the combined organic layers were washed with water (30 cm³), brine (30 cm³), dried (MgSO₄) and evaporated under reduced pressure to give a residue which was purified by column chromatography (3–10% Et₂O in light petroleum, gradient elution). The first to elute was a colourless oil, the (*E*)-silyl enol ether **12** (28 mg, 19%); R_f 0.80 (20% Et₂O in light petroleum). Second to elute was a pale yellow oil, the β-trimethylsilyl acylsilane **13** (106 mg, 71%); R_f 0.60 (10% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 3083, 3062, 3026, 2957, 2899, 1713, 1646, 1601, 1495, 1451, 1250, 1078, 913, 841, 738 and 701; δ_{H} (300 MHz) 7.20 (2 H, app. dd, *J* 7.5 and 7.5, 2 × ArH), 7.04 (1 H, app. dd, *J* 7.5 and 7.5, ArH), 6.99 (2 H, m, 2 × ArH), 3.25–3.15 (1 H, m, CH), 2.88–2.78 (2 H, m, CH₂), 0.13 (9 H, 2, COSiMe₃) and –0.08 (9 H, s, CHSiMe₃).

Typical procedure for the preparation of silanols **14**

Dimethyl(2-trimethylsilylundec-2-enyl)silanol **14b**. Epoxybis-

(silane) **2c** (101 mg, 0.33 mmol) in THF (3 cm³) was added to a stirred solution of LDA [prepared from butyllithium (2.15 mol dm⁻³ in hexanes; 560 mm³, 1.20 mmol) and diisopropylamine (170 mm³, 1.20 mmol)] in THF (2 cm³) at room temperature. The mixture was heated to reflux for 1.5 h before cooling to room temperature and addition of water (5 cm³). The mixture was extracted with Et₂O (3 × 10 cm³) and the combined organic layers were washed with water (30 cm³) and brine (30 cm³), dried (MgSO₄) and evaporated under reduced pressure. Purification of the residue by column chromatography (7% Et₂O in light petroleum) gave a colourless oil, the silanol **14b** (91 mg, 90%, *E:Z* = 50:50, by ¹H NMR analysis of the isomeric HC= protons in the δ 5.8–5.6 region); m/z (EI) 285 (M – Me⁺, 25%), 223 (22), 149 (100), 133 (40) and 75 (73) (Found: M – Me⁺, 285.2070. C₁₅H₃₃OSi₂ requires *M*, 285.2070). Further column chromatography gave samples of the individual geometric isomers: (*E*)-**14b**: R_f 0.25 (5% Et₂O in light petroleum, triple elution); $\nu_{\max}/\text{cm}^{-1}$ 3307, 2957, 2925, 2855, 1603, 1466, 1409, 1248, 835 and 753; δ_{H} (300 MHz) 5.65 (1 H, t, *J* 6.5, HC=), 2.05–1.98 (2 H, dt, *J* 7 and 7, CH₂CH=C), 1.74 (2 H, s, CH₂SiMe₂OH), 1.67 (1 H, s, OH), 1.36–1.18 (12 H, br s, 6 × CH₂), 0.90–0.83 (3 H, m, Me), 0.15 (6 H, s, SiMe₂OH) and 0.06 (9 H, s, SiMe₃); δ_{C} (100 MHz) 138.6 (HC=), 136.6 (=C, quat.), 31.9 (MeCH₂CH₂), 29.5 (CH₂), 29.5 (2 × CH₂), 29.4 (CH₂), 29.3 (CH₂), 22.7 (MeCH₂), 21.6 (CH₂SiMe₂OH), 14.1 (Me), 0.9 (SiMe₂OH) and –1.1 (SiMe₃); δ_{Si} (47 MHz; CHCl₃; SiMe₄) 14.5 (SiMe₂OH) and –4.7 (SiMe₃). (*Z*)-**14b**: R_f 0.21 (5% Et₂O in light petroleum, triple elution); $\nu_{\max}/\text{cm}^{-1}$ 3306, 2957, 2925, 2855, 1602, 1467, 1408, 1249, 1157, 1057, 835 and 757; δ_{H} (300 MHz) 5.86 (1 H, t, *J* 7.5, HC=), 2.12–2.06 (2 H, dt, *J* 7 and 7, CH₂CH=C), 1.74 (1 H, s, OH), 1.63 (2 H, s, CH₂SiMe₂OH), 1.26 (12 H, br s, 6 × CH₂), 0.89–0.85 (3 H, m, Me), 0.14 (9 H, s, SiMe₃) and 0.12 (6 H, s, SiMe₂OH); δ_{C} (100 MHz) 141.9 (HC=), 134.5 (=C, quat.), 32.4 (CH₂CH=C), 31.9 (MeCH₂CH₂), 30.4 (CH₂CH₂CH=C), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 27.6 (CH₂SiMe₂OH), 22.7 (MeCH₂), 14.1 (Me), 0.5 (SiMe₃) and 0.0 (SiMe₂OH); δ_{Si} (47 MHz; CHCl₃; SiMe₄) 14.5 (SiMe₂OH) and –7.2 (SiMe₃).

(3-Cyclohexyl-2-trimethylsilylprop-2-enyl)dimethylsilanol **14c**.

Prepared following the typical procedure for the preparation of silanols **14** above. A colourless oil (*E:Z* = 30:70); m/z (CI, NH₃) 271 (M + H⁺, 3%), 198 (8), 164 (100) and 90 (40) (Found: M + H⁺, 271.1913. C₁₄H₃₁OSi₂ requires *M*, 271.1913). Further column chromatography gave samples of the individual geometric isomers: (*E*)-**14c**: R_f 0.18 (5% Et₂O in light petroleum, triple elution); $\nu_{\max}/\text{cm}^{-1}$ 3306, 2954, 2926, 2851, 1603, 1449, 1413, 1157, 1009, 834, 754 and 688; δ_{H} (300 MHz) 5.46 (1 H, d, *J* 9, HC=), 2.27–2.14 (1 H, m, cyclohexyl CH), 1.73–1.55 (8 H, m, CH₂SiMe₂OH and 5 × CHH), 1.33–1.01 (5 H, m, 5 × CHH), 0.16 (6 H, s, *J*_{H-Si} 6.5, SiMe₂OH) and 0.05 (9 H, s, *J*_{H-Si} 6.5, SiMe₃); δ_{C} (100 MHz) 144.2 (HC=), 133.8 (=C, quat.), 37.9 (cyclohexyl CH), 32.7 (2 × cyclohexyl CH₂), 26.1 (cyclohexyl CH₂), 26.0 (2 × cyclohexyl CH₂), 21.1 (CH₂SiMe₂OH), 0.9 (SiMe₂OH) and –1.1 (SiMe₃). (*Z*)-**14c**: R_f 0.16 (5% Et₂O in light petroleum, triple elution); $\nu_{\max}/\text{cm}^{-1}$ 3306, 2926, 2850, 1620, 1449, 1407, 1250, 1155, 1059, 1036, 969, 923, 903, 834, 758, 719, 688 and 651; δ_{H} (300 MHz) 5.67 (1 H, d, *J* 10, HC=), 2.21–2.08 (1 H, m, cyclohexyl CH), 1.73–1.56 (8 H, m, CH₂SiMe₂OH and 5 × CHH), 1.43–1.03 (5 H, m, 5 × CHH), 0.14 (9 H, s, SiMe₃) and 0.11 (6 H, s, SiMe₂OH); δ_{C} (100 MHz) 147.9 (HC=), 132.5 (quat.), 41.4 (cyclohexyl CH), 33.5 (2 × cyclohexyl CH₂), 27.4 (CH₂SiMe₂OH), 25.9 (cyclohexyl CH), 25.9 (2 × cyclohexyl CH₂), 0.6 (SiMe₂OH) and –0.1 (SiMe₃).

§ Copies of ¹H-¹³C and ¹H-²⁹Si HMBC spectra for (*E*)- and (*Z*)-**14b** have been deposited at the British Library Document Supply Centre (BLDSC). For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the BLDSC for the material should quote the full literature citation and the reference number 57263, 7pp.

(8-tert-Butyldimethylsilyloxy-2-trimethylsilyloct-2-enyl)-

dimethylsilanol 14. A solution of vinylbis(silane) **1e** (750 mg, 2.6 mmol) in THF (8 cm³) was added dropwise to a stirred suspension of LiAlH₄ (210 mg, 5.5 mmol) in THF (26 cm³) at room temperature. After 1.5 h the reaction was quenched by slow addition of water (5.5 cm³), 10% w/v aq. NaOH (16 cm³) and water (5.5 cm³). Et₂O (100 cm³) was added to the mixture followed by MgSO₄. The resulting mixture was filtered and the filtrate evaporated under reduced pressure. Purification of the residue by column chromatography (50% Et₂O in light petroleum) gave a colourless oil, 7,7-bis(trimethylsilyl)hept-6-enol (639 mg, 99%); *R*_f 0.15 (20% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 3328, 2952, 2858, 1569, 1405, 1354, 1249, 1055, 838, 762, 686, 646 and 619; δ_{H} (400 MHz) 6.59 (1 H, t, *J* 7, HC=), 3.66 (2 H, t, *J* 6.5, HOCH₂), 2.22 (2 H, app. q, *J* 7, CH₂CH=C), 1.59 (2 H, app. quintet, *J* 7, HOCH₂CH₂), 1.46–1.36 (4 H, m, 2 × CH₂), 0.15 (9 H, s, *J*_{H-Si} 6.5, SiMe₃) and 0.07 (9 H, s, *J*_{H-Si} 6.5, SiMe₃); δ_{C} (100 MHz) 157.6 (HC=), 140.2 (=C, quat.), 62.9 (HOCH₂), 35.6 (CH₂), 32.7 (CH₂), 29.3 (CH₂), 25.6 (CH₂), 1.8 (*J*_{C-Si} 51.5, SiMe₃) and 0.3 (*J*_{C-Si} 51.5, SiMe₃); *m/z* (CI, NH₃) 259 (M + H⁺, 100%), 171 (26), 164 (22) and 90 (85) (Found: M + H⁺, 259.1913. C₁₃H₃₁OSi₂ requires *M*, 259.1913).

A mixture of the above alcohol (82 mg, 0.33 mmol), tert-butyldimethylsilyl chloride (60 mg, 0.40 mmol) and imidazole (59 mg, 0.82 mmol) in DMF (0.2 cm³) was stirred at room temperature for 22 h followed by heating at 80 °C for 18 h. CH₂Cl₂ (10 cm³) was then added to the cooled reaction mixture which was washed with water (10 cm³) and brine (19 cm³), dried (MgSO₄) and concentrated under reduced pressure. Purification of the residue by column chromatography (35% Et₂O in light petroleum) gave, as a colourless oil, the silyl ether (78 mg, 63%); *R*_f 0.90 (50% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2955, 2930, 2858, 1736, 1568, 1473, 1463, 1249, 1104, 898, 837, 815, 763 and 619; δ_{H} (250 MHz) 6.59 (1 H, t, *J* 7, HC=), 3.61 (2 H, t, *J* 6.5, OCH₂), 2.21 (2 H, app. q, *J* 7, CH₂CH=C), 1.53–1.37 (6 H, m, 3 × CH₂), 0.90 (9 H, s, *J*_{H-Si} 5.5, Bu^t), 0.15 (9 H, s, *J*_{H-Si} 6.5, SiMe₃), 0.07 (9 H, s, *J*_{H-Si} 6.5, SiMe₃) and 0.05 (6 H, s, *J*_{H-Si} 6.5, Bu^tMe₂Si); δ_{C} (63 MHz) 157.9 (HC=), 140.0 (=C, quat.), 63.2 (OCH₂), 35.7 (CH₂), 32.9 (CH₂), 29.4 (CH₂), 26.0 (Me₃CSi), 25.7 (CH₂), 18.4 (Me₃CSi), 1.9 (SiMe₃), 0.4 (SiMe₃) and –5.2 (Bu^tMe₂Si).

Epoxybis(silane) **2** [R = (CH₂)₅OSiMe₂Bu^t] was prepared (93%) from the above silyl ether following the typical procedure for epoxidation of vinylbis(silanes) **2**; *R*_f 0.65 (5% Et₂O in light petroleum); $\nu_{\max}/\text{cm}^{-1}$ 2956, 2935, 2855, 1472, 1464, 1250, 1102, 840, 775 and 617; δ_{H} (250 MHz) 3.60 (2 H, t, *J* 6.5, OCH₂), 2.97–2.92 (1 H, m, epoxide CH), 1.69–1.39 (6 H, m, 4 × CH₂), 0.88 (9 H, s, *J*_{H-Si} 5.8, Bu^t), 0.16 (9 H, s, *J*_{H-Si} 6.3, SiMe₃), 0.04 (9 H, s, SiMe₃) and 0.03 (6 H, s, *J*_{H-Si} 6.5, Bu^tMe₂Si); δ_{C} (100 MHz) 63.1 (OCH₂), 61.8 (CH), 51.5 (quat.), 38.2 (CH₂), 31.5 (CH₂), 27.3 (CH₂), 26.0 (Me₃CSi), 25.8 (CH₂), 18.3 (Me₃CSi), 0.2 (*J*_{C-Si} 51.5, SiMe₃), –2.2 (*J*_{C-Si} 51.5, SiMe₃) and –5.2 (*J*_{C-Si} 57.0, Bu^tMe₂Si).

Silanol **14** [R = (CH₂)₅OSiMe₂Bu^t] was prepared from the above epoxybis(silane) **2** [R = (CH₂)₅OSiMe₂Bu^t] following the typical procedure for the preparation of silanols **14**. A colourless oil (*E*:*Z* = 50:50); *R*_f 0.40 (20% Et₂O in light petroleum); δ_{H} (300 MHz) 5.86 [0.5 H, t, *J* 7.5, (*Z*)-HC=], 5.65 [0.5 H, t, *J* 6.5, (*E*)-HC=], 3.60 (2 H, t, *J* 6.5, SiOCH₂), 2.12–2.00 (2 H, m, CH₂CH=C), 1.74 [1 H, s, (*E*)-CH₂SiMe₂OH], 1.66 (1 H, s, OH), 1.63 [1 H, s, (*Z*)-CH₂SiMe₂OH], 1.56–1.47 (2 H, app. quintet, *J* 7, SiOCH₂CH₂), 1.36–1.33 (4 H, br m, 2 × CH₂), 0.89 (9 H, s, Bu^t), 0.15 [3 H, s, (*E*)-SiMe₂OH], 0.14 [4.5 H, s, (*Z*)-SiMe₃], 0.12 [3 H, s, (*Z*)-SiMe₂OH], 0.06 [4.5 H, s, (*E*)-SiMe₃] and 0.04 [6 H, s, Bu^tMe₂Si]; δ_{C} (100 MHz) 141.6 [(*Z*)-HC=], 138.3 [(*E*)-HC=], 136.8 [(*E*)-quat.], 134.7 [(*Z*)-quat.], 63.2 (SiOCH₂), 32.8 (CH₂), 32.4 [(*Z*)-CH₂CH=C], 30.2 [(*E*)- or (*Z*)-CH₂CH₂CH=C], 29.4 [(*E*)-CH₂CH=C], 29.2 [(*Z*)- or (*E*)-CH₂CH₂CH=C], 27.6 [(*Z*)-CH₂SiMe₂OH], 26.0 (Me₃CSi), 25.6 (CH₂), 21.7 [(*E*)-CH₂SiMe₂OH], 18.4 (Me₃CSi), 0.9 [(*E*)-SiMe₂OH], 0.5 [(*Z*)-SiMe₃],

0.1 [(*Z*)-SiMe₂OH], –1.1 [(*E*)-SiMe₃] and –5.3 (Bu^tMe₂Si); *m/z* CI (NH₃) 389 (M + H⁺, 5%), 244 (26), 227 (22), 164 (61) and 90 (100) (Found: M + H⁺, 389.2727. C₁₉H₄₅O₂Si₂ requires *M*, 389.2727).

Acknowledgements

We thank the EPSRC for an earmarked studentship (to P. J. C.) and a research grant (GR/J02445), Zeneca (Strategic Research Fund) and Pfizer for additional support, and the EPSRC mass spectrometry service centre for mass spectra. We also thank Mr A. W. Jahans for assistance with the crystallographic investigations and the University of Reading and the EPSRC for funds for an Image Plate System.

References

- 1 E. W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, 1988, pp. 7–19; I. Fleming, J. Dunogués and R. Smithers, *Org. React. (N. Y.)*, 1989, **39**, 57.
- 2 Preliminary communication: D. M. Hodgson and P. J. Comina, *Tetrahedron Lett.*, 1994, **35**, 9469.
- 3 Preliminary communication: D. M. Hodgson and P. J. Comina, *Chem. Commun.*, 1996, 755.
- 4 Preliminary communication: D. M. Hodgson and P. J. Comina, *Tetrahedron Lett.*, 1996, **37**, 5613.
- 5 (a) B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 1977, **110**, 852; (b) I. Fleming and C. D. Floyd, *J. Chem. Soc., Perkin Trans. 1*, 1981, 969.
- 6 N. J. R. van Eikema Hommes, F. Bickelhaupt and G. W. Klumpp, *Tetrahedron Lett.*, 1988, **29**, 5237.
- 7 (a) M. Hogenbirk, N. J. R. van Eikema Hommes, G. Schat, O. S. Akkerman, F. Bickelhaupt and G. W. Klumpp, *Tetrahedron Lett.*, 1989, **30**, 6195; (b) F. Bickelhaupt, *J. Organomet. Chem.*, 1994, **475**, 1.
- 8 I. Fleming and U. Gosh, *J. Chem. Soc., Perkin Trans. 1*, 1994, 257.
- 9 E. Negishi, L. D. Boardman, H. Sawada, V. Bagheri, A. T. Stoll, J. M. Tour and C. L. Rand, *J. Am. Chem. Soc.*, 1988, **110**, 5383.
- 10 T. A. Blumenkopf and L. E. Overman, *Chem. Rev.*, 1986, **86**, 857; C. Flann, T. C. Malone and L. E. Overman, *J. Am. Chem. Soc.*, 1987, **109**, 6097.
- 11 D. Seebach, R. Bürstinghaus, B.-T. Gröbel and M. Kolb, *Liebigs Ann. Chem.*, 1977, 830.
- 12 B.-T. Gröbel and D. Seebach, *Chem. Ber.*, 1977, **110**, 867.
- 13 K. Takai, Y. Kataoka, T. Okazoe and K. Utimoto, *Tetrahedron Lett.*, 1987, **28**, 1443.
- 14 N. A. Saccomano, *Organochromium Reagents*, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 2, pp. 173–209; P. Cintas, *Synthesis*, 1992, 248; D. M. Hodgson, *J. Organomet. Chem.*, 1994, **476**, 1; A. S. K. Hashmi, *J. Prakt. Chem.*, 1996, **338**, 491.
- 15 K. Takai, K. Kimura, T. Kuroda, T. Hiyama and H. Nozaki, *Tetrahedron Lett.*, 1983, **24**, 5281; T. Okazoe, K. Takai and K. Utimoto, *J. Am. Chem. Soc.*, 1987, **109**, 951; M. Knecht and W. Boland, *Synlett*, 1993, 837.
- 16 D. Seyferth and R. L. Lambert, Jr., *J. Organomet. Chem.*, 1973, **54**, 123.
- 17 K. Takai, K. Nitta and K. Utimoto, *J. Am. Chem. Soc.*, 1986, **108**, 7408.
- 18 P. F. Hudrlik, E. L. O. Agwarangbo and A. M. Hudrlik, *J. Org. Chem.*, 1989, **54**, 5613.
- 19 E. Bosone, P. Farina, G. Guazzi, S. Innocenti and V. Marotta, *Synthesis*, 1983, 942.
- 20 M. Ohno, N. Naruse and I. Teresawa, *Org. Synth.*, 1973, **Coll. Vol. V**, 266.
- 21 G. Büchi and H. Wüest, *Helv. Chim. Acta*, 1979, **62**, 2661.
- 22 D. Ma and X. Lu, *Tetrahedron*, 1990, **46**, 6319.
- 23 P. F. Hudrlik and A. M. Hudrlik, *α,β -Epoxyasilanes*, in *Advances in Silicon Chemistry*, ed. G. L. Larson, JAI, Greenwich, 1993, vol. 2, pp. 1–89.
- 24 C. Najera 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.
- 25 P. F. Hudrlik, C.-N. Wan and G. P. Withers, *Tetrahedron Lett.*, 1976, 1449.
- 26 P. F. Hudrlik, R. J. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona and J. P. Arcoleo, *Tetrahedron Lett.*, 1976, 1453.

- 27 P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. J. Misra and G. P. Withers, *J. Am. Chem. Soc.*, 1977, **99**, 1993; See also ref. 23, p. 49.
- 28 J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, 1976, **98**, 4646; J. J. Eisch and J. E. Galle, *J. Organomet. Chem.*, 1988, **341**, 293.
- 29 G. Burford, F. Cooke, G. Roy and P. Magnus, *Tetrahedron*, 1983, **39**, 867.
- 30 D. Seyferth, J. L. Lefferts and R. L. Lambert, Jr., *J. Organomet. Chem.*, 1977, **144**, 39; corrigendum 1979, **168**, C32.
- 31 P. J. Comina, D.Phil Thesis, University of Oxford, 1996.
- 32 G. Stork and E. Colvin, *J. Am. Chem. Soc.*, 1971, **93**, 2080.
- 33 J. Yoshida, S. Matsunaga, Y. Ishichi, T. Maekawa and S. Isoe, *J. Org. Chem.*, 1991, **56**, 1307.
- 34 T. Mandai, S. Matsumoto, M. Kohama, M. Kawada, J. Tsuji, S. Sato and T. Moriwake, *J. Org. Chem.*, 1990, **55**, 5671.
- 35 A. P. Davis, G. J. Hughes, P. R. Lowndes, C. M. Robbins, E. J. Thomas and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1934.
- 36 K. D. Kim and P. A. Magriotis, *Tetrahedron Lett.*, 1990, **31**, 6137.
- 37 U. Siriwardane, S. S. C. Chu and J. D. Buynak, *Acta Crystallogr., Sect. C*, 1989, **45**, 591; G. A. Molander and K. Mautner, *J. Org. Chem.*, 1989, **54**, 4042; K. Yamamoto, Y. Kawanami and M. Miyazawa, *J. Chem. Soc., Chem. Commun.*, 1993, 436; T. Kawai, M. Isobe and S. C. Peters, *Aust. J. Chem.*, 1995, **48**, 115; M. M. Kabat, *J. Org. Chem.*, 1995, **60**, 1823.
- 38 W. E. Fristad, T. R. Bailey, L. A. Paquette, R. Gleiter and M. C. Böhm, *J. Am. Chem. Soc.*, 1979, **101**, 4420.
- 39 R. B. Miller and G. McGarvey, *J. Org. Chem.*, 1979, **44**, 4623; R. A. Angell, P. J. Parsons and A. Naylor, *Synlett*, 1993, 189.
- 40 R. B. Miller, M. I. Al-Hassan and G. McGarvey, *Synth. Commun.*, 1983, **13**, 969.
- 41 D. M. Hodgson and P. J. Comina, *Synlett*, 1994, 663.
- 42 G. Zweifel and W. Lewis, *J. Org. Chem.*, 1978, **43**, 2739; G. Zweifel, R. E. Murray and H. P. On, *J. Org. Chem.*, 1981, **46**, 1292.
- 43 D. J. Ager, *Org. React. (N.Y.)*, 1990, **38**, 1.
- 44 J. K. Crandall and M. Apparu, *Org. React. (N.Y.)*, 1983, **29**, 345.
- 45 R. L. Danheiser, D. M. Fink, K. Okano, Y.-M. Tsai and S. W. Szczepanski, *J. Org. Chem.*, 1985, **50**, 5393.
- 46 M. Kato, A. Mori, H. Oshino, J. Enda, K. Kobayashi and I. Kuwajima, *J. Am. Chem. Soc.*, 1984, **106**, 1773; I. Kuwajima, *J. Organomet. Chem.*, 1985, **285**, 137.
- 47 H. J. Reich, R. C. Holtan and C. Bolm, *J. Am. Chem. Soc.*, 1990, **112**, 5609.
- 48 J. Dunoguès, M. Bolourtchian, R. Calas, N. Duffaut and J.-P. Picard, *J. Organomet. Chem.*, 1972, **43**, 157.
- 49 E. A. Williams, *NMR Spectroscopy of Organosilicon Compounds*, in *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, pp. 511-554.
- 50 D. Seyferth, R. L. Lambert, Jr. and E. M. Hanson, *J. Organomet. Chem.*, 1970, **24**, 647.
- 51 S. E. Denmark, K. L. Habermas and G. A. Hite, *Helv. Chim. Acta*, 1988, **71**, 168.
- 52 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
- 53 G. M. Sheldrick, SHELXS-86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 54 G. M. Sheldrick, SHELXL-93, 1993, University of Göttingen, Germany, 1993.

Paper 7/02722B
 Received 21st April 1997
 Accepted 20th May 1997