

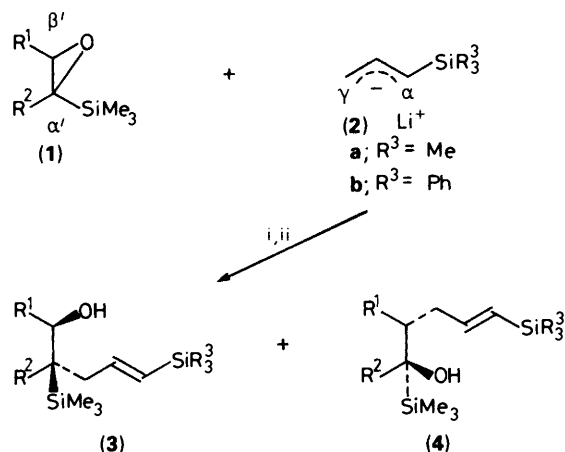
## Regiospecific Synthesis of 1-Silyl Substituted 1,4-Dienes

Ernst Schaumann\* and Andreas Kirschning

Institut für Organische Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Federal Republic of Germany

The reaction of epoxysilanes with lithiated allylsilanes gives predominantly  $\alpha$ -silyl-substituted alcohols (**3**) which are convenient precursors for the preparation of 1-silyl-substituted 1,4-dienes.

In the ring-opening of oxiranes by allyl anions, there is a delicate balance between  $\alpha$  and  $\gamma$  attack of the allyl component, whereas the oxirane always reacts at the less substituted carbon.<sup>1</sup> This situation may change for silyl-substituted oxiranes, which are known to undergo characteristic ring-opening at the  $\alpha$  carbon.<sup>2</sup> The resulting  $\alpha$ -silyl alcohols are useful precursors for olefins under the conditions of a Peterson olefination. However, very few examples of the reaction of epoxysilanes with organometallic nucleophiles have been reported.<sup>3</sup>



**Scheme 1.** Reagents and conditions: i, THF,  $-78^\circ\text{C}$ , (2) (1 equiv.), addition of (1) (1 equiv.), 10 h,  $-10^\circ\text{C}$  for (1c), 2–4 h,  $-20$  to  $-40^\circ\text{C}$  for (1a) and (1b); ii, 10% aqueous  $\text{NH}_4\text{Cl}$ .

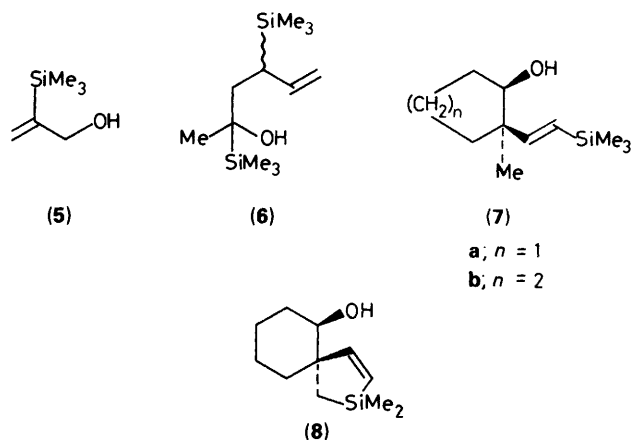
Here we report on the reaction of the silyl-substituted epoxides (1a–d)<sup>4a</sup> with lithiated allylsilanes (2a) and (2b)<sup>4b</sup> to give the unsaturated alcohols (3) and on the successful conversion of the latter into the 1,4-dienes (13) for which until now no selective synthesis was available.<sup>5</sup>

As expected, the alcohols (3) resulting from  $\gamma \rightarrow \alpha'$  attack are formed as main products in the reaction of the anions (2) with the oxiranes (1) (Table 1). Noteworthy exceptions are found using the epoxysilane (1b), where the environment of the silicon-substituted oxirane carbon is sterically very different from the

alternative carbon atom; this favours the  $\gamma \rightarrow \beta'$  route, and the epoxysilane (1d) (Table 1). In the resulting alcohols (3) and (4), the *E*-configuration is assigned to the vinylsilane moiety based on a comparison with our earlier  $^1\text{H}$  NMR data.<sup>1</sup>

Apart from alcohol (3b), (1b) gives the allyl alcohol (5) as the second major product (39%).<sup>6</sup> Its formation may be explained by assuming that the lithiated allylsilane (2a) deprotonates the methyl substituent to induce isomerization. Furthermore, (6) is also formed in 3% isolated yield resulting from  $\alpha \rightarrow \beta'$  attack of the allylsilane.

The interesting side-products (7a) (16%) and (7b) and (8) (22%; ratio 3:1) are formed in the reaction of the cyclic silyl substituted oxiranes (1c) and (1d). To account for their formation, we assume the usual ring-opening of the oxirane as the initial step to give the anion (9). After 1,3 C $\rightarrow$ O migration of the adjacent silyl group, transformation of the resulting secondary carbanion (10) into the more favourable primary anion (12) is possible *via* the spirocyclopropane species (11). Simple protonation then yields the rearranged product (7b), whereas intramolecular nucleophilic attack on the trimethylsilyl group leads to elimination of methyl-lithium to provide (8) (Scheme 2).



**Table 1.** Reactions of (1) with (2).<sup>a</sup>

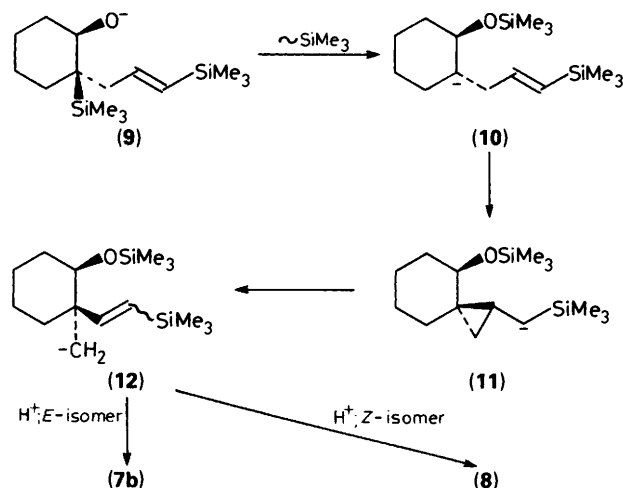
Allylsilane	R <sup>1</sup>	R <sup>2</sup>	Oxirane	Product ratio		Overall yield (%) <sup>c</sup>
				(3)	(4) <sup>b</sup>	
(2a)	H	H	(1a)	(3a), (4a)	>10 <1	75
(2a)	H	Me	(1b)	(3b), (4b)	4 1	40
(2a)	-(CH <sub>2</sub> ) <sub>3</sub>		(1c)	(3c), (4c)	>10 <1	63
(2a)	-(CH <sub>2</sub> ) <sub>4</sub>		(1d)	(3d), (4d)	2.5 1	56 <sup>d</sup>
(2b)	H	H	(1a)	(3e), (4e)	>10 <1	92
(2b)	-(CH <sub>2</sub> ) <sub>4</sub>		(1d)	(3f), (4f)	5 1	74

<sup>a</sup> According to Scheme 1. <sup>b</sup> Ratios determined by <sup>1</sup>H NMR spectroscopy of the crude product. <sup>c</sup> Isolated yields of chromatographically purified samples. <sup>d</sup> The ratio is 5:1 and the yield totals 78%, if the formation of (7b) and (8) is taken into account.

**Table 2.** Formation of Peterson products (13).

Alcohol <sup>a</sup>	Olefin	Yield (%) <sup>b</sup>	<sup>1</sup> H NMR data (δ)				
			1-H	2-H	3-H	4-H	J <sub>3,4</sub> /Hz
(3a)	(13a) <sup>c</sup>	76	5.84–5.51 (3 H)	3.16	6.20	5.90	18.2
(3c)	(13c)	89	5.35 (1 H)	2.87	6.04	5.67	19.0
(3d)	(13d)	69	5.42 (1 H)	2.73	6.0	5.66	18.2
(3f)	(13f)	79	5.42 (1 H)	2.86	6.2	6.2	18.4

<sup>a</sup> R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> refer to Table 1. <sup>b</sup> Isolated yields after chromatography or distillation. <sup>c</sup> B.p. 50 °C/7 Torr; the product is contaminated with a trace of hexamethyldisiloxane.

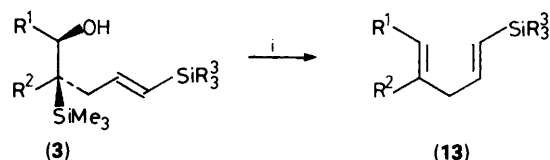
**Scheme 2.**

Products (7a), (7b), and (8) are isolated as single diastereomers. The indicated configuration is based on the assumption that the carbanion (10) does not invert.

Whether (7b) or (8) is formed, may well depend on the stereochemistry of the vinylsilane moiety, the *E*-isomer providing (7b), and the *Z*-isomer (8). The suggested mechanism is substantiated by the isolation of protonated and desilylated (10) after aqueous

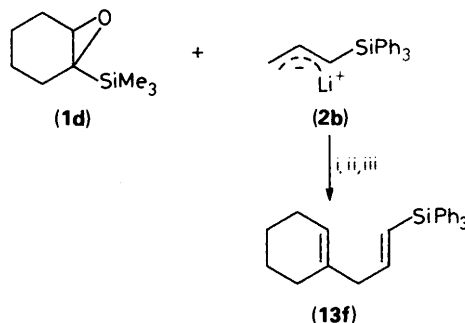
work-up in low yield. Moreover, an analogy to the step (12) → (8) has recently been reported.<sup>7</sup>

In a second set of experiments we looked at the utility of alcohols (3) as substrates in a Peterson-type olefination. After deprotonation of (3) with NaH and addition of a 5 mol % of 15-crown-5, 1,4-dienes (13) can be isolated after 2 to 7 h at 50 to 70 °C. The temperature and the reaction time depend on the alcohol. The sterically fixed six-membered representatives (3d) and (3f) give a slow conversion (5–7 h, 70 °C), whereas (3a) and (3c) are eliminated smoothly (2 h, 50 °C) (Table 2). Interestingly, (7) or (8) could not be detected under these conditions (Scheme 3).



**Scheme 3.** Reagents and conditions: i, THF, NaH (dispersion in mineral oil; 1 equiv.), 15-crown-5, 5–7 h, 70 °C for (3d) and (3f), 2 h, 50 °C (3a) and (3c), (cf. Table 2).

The sequence of oxirane-opening and elimination can be carried out as a one-pot sequence (Scheme 4). Thus, under the



**Scheme 4.** Reagents and conditions: i, THF, –78 °C, then 6 h, –20 °C; ii, 5 mol % 12-crown-4, reflux, 7 h; iii, 10% aqueous NH<sub>4</sub>Cl (61%).

conditions indicated, (1f) and (2a) give (13f) in 61% isolated yield. This sequence opens up the first straightforward access to silyl-substituted 1,4-dienes.<sup>5</sup> The extension using allyl anions is currently under investigation.

### Acknowledgements

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- (a) The epoxysilanes (1) were synthesized from the corresponding vinylsilanes by epoxidation with 3-chloroperoxybenzoic acid in CH<sub>2</sub>Cl<sub>2</sub>. (b) The lithiated species (2a) was generated by deprotonation of trimethylsilylpropene with Bu<sup>t</sup>Li in THF in the presence of 1 equiv. of tetramethylethylenediamine (TMEDA) at –50 °C for 2 h. Compound (2b) was obtained under the same conditions, but in the absence of TMEDA.

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