

## The Stereochemistry of the Vinylogous Peterson Elimination

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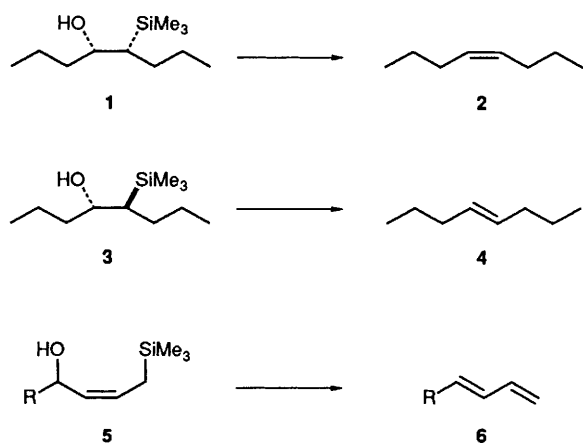
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The base-catalysed eliminations of the vinylogous  $\beta$ -hydroxysilanes **7**, **9**, **11** and **12** are stereospecifically *syn*, giving largely the *trans,trans*-diene **8** from **7** and **11**, the *cis,trans*-diene **10** from **9**, and the *trans,cis*-diene **13** from **12**; when a *cis* double bond is produced, it is selectively placed adjacent to the carbon atom that originally carried the hydroxy group.

The base-catalysed elimination of  $\beta$ -hydroxysilanes **1**  $\rightarrow$  **2** and **3**  $\rightarrow$  **4** has been shown by Hudrlík and his co-workers to be stereospecifically *syn*.<sup>1</sup> A vinylogous version of this elimination, **5**  $\rightarrow$  **6** has also been observed by Clive,<sup>2</sup> in which he noted the formation of only a *trans* double bond. We now report the full stereochemistry of this diene synthesis (Scheme 1), which is, as expected, *syn*. For example, the hydroxysilane **7** gives the *trans,trans*-diene **8**, but its diastereoisomer **9** gives the *cis,trans*-diene **10**. More interestingly, the reaction shows a remarkable regioselectivity in those cases where the stereo-

specificity demands that one of the double bonds be *cis*: the isomer **9**, having the hydroxy group adjacent to the cyclohexyl group gives largely the *cis,trans*-diene **10**, with the *cis* double bond adjacent to the cyclohexyl group, but the isomer **12**, with the hydroxy and silyl groups transposed, gives largely the *trans,cis*-diene **13**, with the *cis* double bond adjacent to the methyl group.

We prepared the hydroxysilanes by adding the appropriate acetylenes,<sup>3,4</sup> to the appropriate aldehydes, and reducing the triple bonds to the *cis* double bonds by hydrogenation. The



Conditions: KH, THF, room temp., 1 h (15 min for 5 → 6)

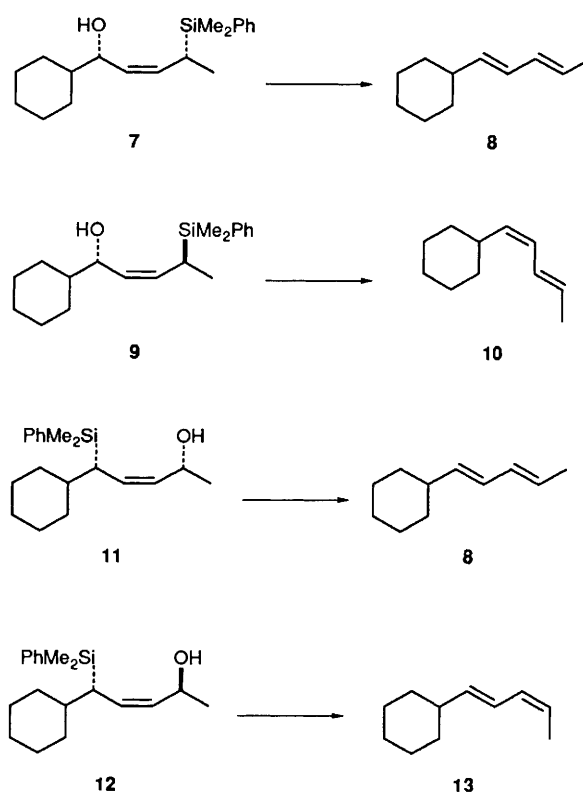
**Table 1** Stereoselectivity in the vinylogous Peterson reactions (Scheme 2)

Substrate	Yield (%)	<i>trans,trans</i> <b>8</b> (%) <sup>a</sup>	<i>cis,trans</i> <b>10</b> (%) <sup>a</sup>	<i>trans,cis</i> <b>13</b> (%) <sup>a</sup>	<i>cis,cis</i> (%) <sup>a</sup>
<b>7</b> <sup>b</sup>	37	100	0	0	0
<b>9</b> <sup>c</sup>	80	2.3	92.7	5	0
<b>11</b> <sup>d</sup>	79	99.6	0	0.4	0
<b>12</b> <sup>d</sup>	47	2.6	1.9	95.5	0

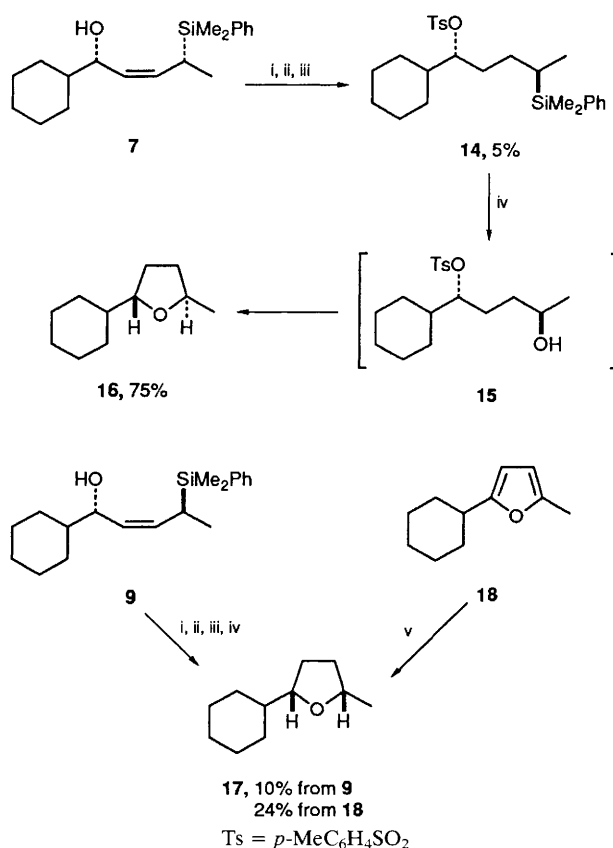
<sup>a</sup> Measured by GLC and probably accurate to  $\pm 0.1\%$ ; the diastereomeric purity of the starting materials is  $>95\%$ , as assessed by <sup>1</sup>H NMR spectroscopy. <sup>b</sup> The trimethylsilyl analogue gave a 57% yield of the pure *trans,trans*-diene. <sup>c</sup> The trimethylsilyl analogue gave a 16% yield of the same three dienes in ratios of: 1.7 : 1.1 : 97.2. <sup>d</sup> The trimethylsilyl analogues were inseparable, but the approximately 1 : 1 mixture of diastereoisomers gave a mixture of all four dienes in 87% yield in the ratios: 47.15 : 52.2 : 0.6 : 0.05.

diastereoisomers were then separated by column chromatography. The reactions were carried out by treating the individual hydroxysilanes with an excess of potassium hydride in tetrahydrofuran (THF) at room temperature for 20 min or more, and the product mixture was analysed by GLC, using a capillary column (BP5, 0.5  $\mu\text{m}$  film thickness; 5% phenylmethylsiloxane; H<sub>2</sub>, 2 ml/min; 90 °C) that separated the four stereoisomers, all of which are known.<sup>5</sup> The proportions of the dienes obtained are given in Table 1; the yields are not optimised nor should they be taken as representative of the efficiency of the reaction, which is generally very clean. The *trans,trans*-diene **8** and both *trans,cis*-dienes **10** and **13** were pure enough for structural assignment by <sup>1</sup>H NMR spectroscopy, and we prepared an authentic sample of the *cis,cis*-isomer by hydroboration-protodeboronation<sup>6</sup> of the diyne,<sup>7</sup> in order to identify it on the GLC trace.

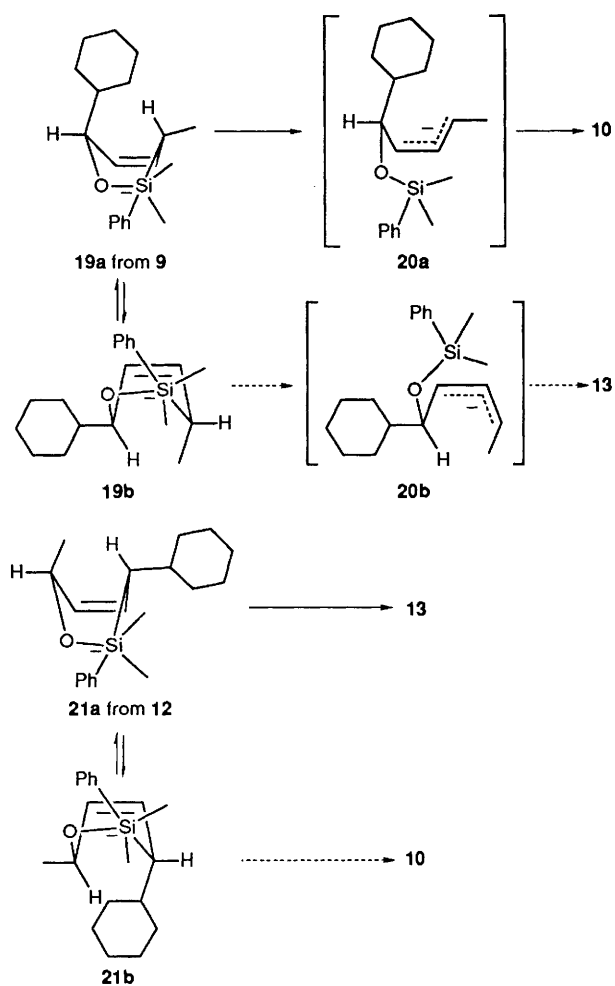
We proved the relative stereochemistry of the starting materials **7** and **9** by the sequence of reactions shown in Scheme 2. Hydrogenation of the alkene **7** gave the saturated  $\delta$ -hydroxysilane, although not in good or even reproducible yield, and with some loss of the silyl group, presumably by a retro-hydrosilylation process. Tosylation of the alcohol gave the tosylate **14**, and conversion of the phenyldimethylsilyl group into a hydroxy group, **14** → **15**,<sup>8</sup> directly gave the



Scheme 1 Conditions: KH, THF, room temp.



**Scheme 2** Reagents and conditions: i, H<sub>2</sub>, Pd/C, MeOH; ii, Bu<sup>n</sup>Li, iii, TsCl; iv, Hg(OAc)<sub>2</sub>, AcOOH, AcOH, room temp., 3 h; v, Ni, Pr<sup>n</sup>OH



corresponding tetrahydrofuran **16**, for which we can reasonably assume an inversion process at the carbon carrying the tosyloxy group. A similar sequence on the diastereoisomer **9** gave the tetrahydrofuran **17**. The known tetrahydrofurans were identified, using NMR spectroscopic and GLC comparisons with the reported data,<sup>9</sup> and by direct comparison with a sample of the *cis*-isomer **17**, prepared stereoselectively by hydrogenation<sup>10</sup> of the known furan **18**.<sup>11</sup> The hydrogenation of furans is well established to lead largely to *cis*-2,5-disubstituted tetrahydrofurans.<sup>12</sup>

That the elimination process is *syn* stereospecific is hardly surprising, but the selectivity for placing the *cis* double bond at the carbon atom that carried the hydroxy group was unexpected. The pentacoordinate silyl anions **19a** and **21a**, derived from the diastereoisomers **9** and **12**, respectively, are probably intermediates. These will break down by a process that resembles, in outline at least, a retro-Diels-Alder reaction. Insofar as the transition state is boat-like, resembling the structure of the intermediates, it is not obvious why reaction is favoured from the boats **19a** and **21a**, in which the carbon atoms at the prow adjacent to the oxygen atoms should be the ones to carry the axial substituent, rather than from the alternative boats **19b** and **21b**. However, the retro-cycloaddition is likely, by analogy with the probable mechanism of the Peterson elimination,<sup>13</sup> to involve in the transition state the development of a substantial negative charge on the

carbon atom from which the silyl group is departing, and it is better to consider the movements involved as the presumed intermediates **19** and **21** change to the products **10** and **13** than it is to look at the structures of the intermediates themselves. As the Si-C bond stretches, the carbon atom becomes trigonal, and rotation must take place about the axis of the developing C=C double bond. Starting from **19a**, rotation along the shorter path leads to a sickle-shaped configuration in the allyl anion-like species **20a**, and starting from **19b** it leads to a U-shaped configuration **20b**. The allyl anions **20a** and **20b** are probably not fully formed intermediates, but they are drawn here as such for clarity of argument. Although the *cis* arrangement is known to be lower in energy than the *trans* in 1-substituted allyl-metal systems,<sup>14</sup> we can be reasonably confident that the sickle-shaped configuration in 1,3-disubstituted allyl-metal systems is lower in energy than the U-shaped configuration. Hence Si-C bond stretching takes place more easily from **19a** than from **19b**, and a sickle-shaped allyl anion-like configuration **20a** is set up more rapidly than the U-shaped ion **20b**. Thus the regiochemistry of double bond formation is determined by which of the double bonds in the product is the more substantially set up in the transition state; since the Si-C bond is probably more stretched than the O-C bond, it is the double bond at this end of the system that comes out *trans*. The other double bond is then forced to adopt the configuration demanded by the stereospecificity of the overall process: *cis* from **9** and **12** and *trans* from **7** and **11**. This would seem to be a good candidate for a computational investigation.

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