

# Palladium-catalysed isomerisation of vinyldisilanes to allyldisilanes

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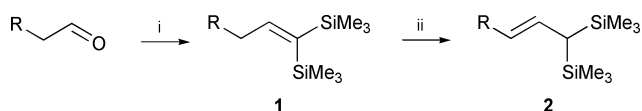
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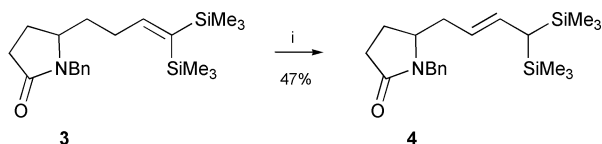
The isomerisation of vinyldisilanes **1** to allyldisilanes **2** catalysed by palladium-on-carbon in diethyl ether under hydrogen is described.

Three principle aspects of allylsilane chemistry have contributed to the tremendous utility of allylsilanes in organic synthesis.<sup>1</sup> Firstly, a variety of methods are available for preparing the allylsilane group with high regio- and stereo-control.<sup>2</sup> Secondly, the allylsilane group is stable to many commonly used reagents, thus allowing the group to be carried through many synthetic sequences unchanged. Thirdly, is the ability of allylsilanes to act as allyl anion equivalents with a range of electrophiles (intramolecular C–C bond formation is particularly useful), generally with high and predictable stereo- and regio-control in the product alkene. Allyldisilanes **2** might be anticipated to possess broadly similar attributes to allylsilanes for use in synthesis. In contrast to allylsilanes however, allyldisilanes **2** are a relatively unexplored class of materials. A deterrent to investigating their chemistry is the lack of concise, general methods available for their preparation, particularly under mild conditions. Lautens and co-workers have developed a six step sequence to allyldisilanes from propargylic alcohols,<sup>3</sup> and Pernet *et al.* have reported a specific synthesis of the simplest allyldisilane [3,3-bis(trimethylsilyl)prop-1-ene] in two steps from 3-(trimethylsilyl)prop-1-yne.<sup>4</sup> The synthetic potential of allyldisilanes is indicated by observations from both Lautens and Pernet that disilylpropenes react with electrophiles (aldehydes and iminium ions) to give *trans*-vinylsilanes.



**Scheme 1** Reagents and conditions: i, Br<sub>2</sub>C(SiMe<sub>3</sub>)<sub>2</sub>, CrCl<sub>2</sub>, DMF, 25 °C, 24 h; ii, see text.

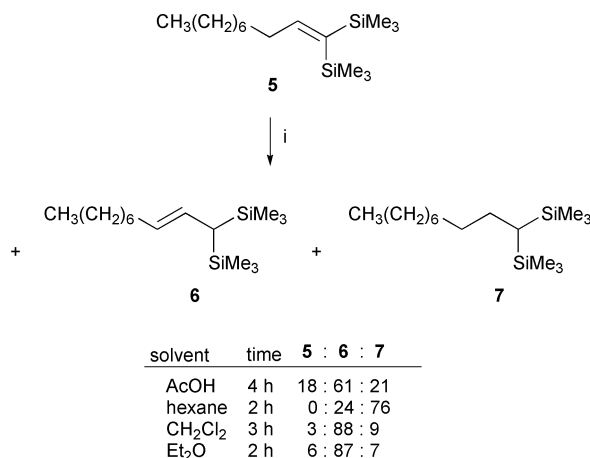
We recently reported a one step highly chemoselective method for the preparation of vinyldisilanes **1** from aldehydes (Scheme 1).<sup>5</sup> During our investigations into the synthetic applications of vinyldisilanes,<sup>5,6</sup> we attempted debenzoylation of lactam **3** using Pearlman's catalyst which, however, surprisingly generated the *trans*-allyldisilane **4** in an unoptimised 47% yield (Scheme 2). We communicate here our preliminary results concerning the development of this unusual isomerisation for the synthesis of allyldisilanes **2**.



**Scheme 2** Reagents and conditions: i, 20% Pd(OH)<sub>2</sub>/C, H<sub>2</sub> (1 atm.), AcOH, 25 °C, 12 h.

Double-bond migrations can occur during homogeneous or heterogeneous hydrogenation to an extent which is profoundly affected by the catalyst used (palladium catalysts being particularly active during heterogeneous hydrogenation),<sup>7</sup> but in many cases the process is not noticeable in the reduced

product. Isomerisation of isolated olefins to allylsilanes has been reported under homogeneous catalysis by Matsuda and co-workers using cationic rhodium or iridium catalysts pre-activated with H<sub>2</sub>.<sup>8</sup> Also, Mori *et al.* have recently reported the isomerisation of isolated olefins to allyl bis-metalated [(SnR<sub>3</sub>)<sub>2</sub> and SnR<sub>3</sub>/SiR'<sub>3</sub>] compounds (formed as 1:1, *cis*-*trans* mixtures) using RuClH(CO)(PPh<sub>3</sub>)<sub>3</sub>.<sup>9</sup> However, application of Matsuda's conditions {using [Rh(norbornadiene)(dppb)]BF<sub>4</sub>} or Mori's conditions to simple vinyldisilanes failed to generate any isomerisation and therefore our attention focused on the heterogeneous process. Initial experiments with Pearlman's catalyst under the original conditions using vinyldisilane **5** established that the presence of H<sub>2</sub> was essential for reaction to proceed, but that incomplete isomerisation was observed and reduction to the disilane **7** was a significant competing reaction (Scheme 3).

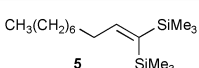
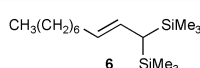
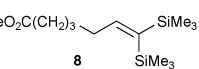
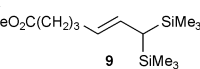
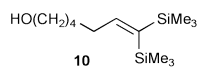
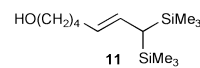


**Scheme 3** Reagents and conditions: i, 20% Pd(OH)<sub>2</sub>/C, H<sub>2</sub> (1 atm.), solvent, 25 °C.

Although a number of different reaction variables with Pearlman's catalyst in acetic acid (and also 10% Pd/C in EtOH) were investigated for the isomerisation of vinyldisilane **5** to allyldisilane **6** (temperature, time, catalyst pre-activation, stirring and not stirring), the most notable variations were obtained by varying the solvent (Scheme 3), which is known to have a large influence on the extent of double bond migration.<sup>7</sup> For Pearlman's catalyst, hexane produced mainly reduction, whereas moving to DCM or ether resulted in a very encouraging ratio of isomerised to reduced material after 2–3 h (the proportion of reduced material increased at longer reaction times). Within the scope of the present study, 10% Pd/C in ether was found to give the best results (Table 1): complete conversion of vinyldisilane **5** to *trans*-allyldisilane **6** and (chromatographically inseparable) disilane **7** (94:6 respectively, 94% yield of allyldisilane **6**). These conditions also successfully isomerised other vinyldisilanes to allyldisilanes: **8** to **9** (88%) and **10** to **11** (91%), for which hydrogenated disilane was also observed at similarly low levels (6 and 7% respectively).

Reaction of vinyldisilane **5** using 10% Pd/C in ether under D<sub>2</sub> instead of H<sub>2</sub> gave allyldisilane **6** for which the <sup>1</sup>H NMR

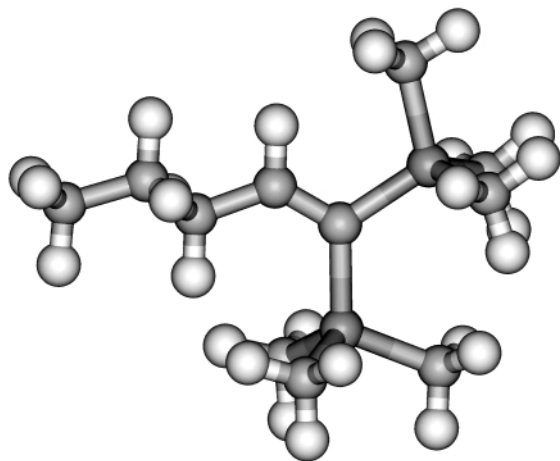
**Table 1** Synthesis of allyldisilanes using 10% Pd/C, H<sub>2</sub> (1 atm.), Et<sub>2</sub>O, 25 °C, 1.5 h

Vinylsilane <sup>5</sup>	Allyldisilane	Yield (%) <sup>a</sup>
 <p>5</p>	 <p>6</p>	94
 <p>8</p>	 <p>9</p>	88
 <p>10</p>	 <p>11</p>	91

<sup>a</sup> Hydrogenated disilane also observed (see text).

spectrum indicated that D had not been incorporated into either of the olefinic positions, but had been incorporated (51% by mass spectrometry) at the carbon atom bearing the two trimethylsilyl groups. One possible mechanistic sequence for the isomerisation consistent with this observation involves initial olefin coordination to palladium, followed by formation of a  $\pi$ -allylpalladium hydride which can undergo partial H/D exchange prior to hydride delivery selectively<sup>3</sup> to the more substituted end of the allylic system.

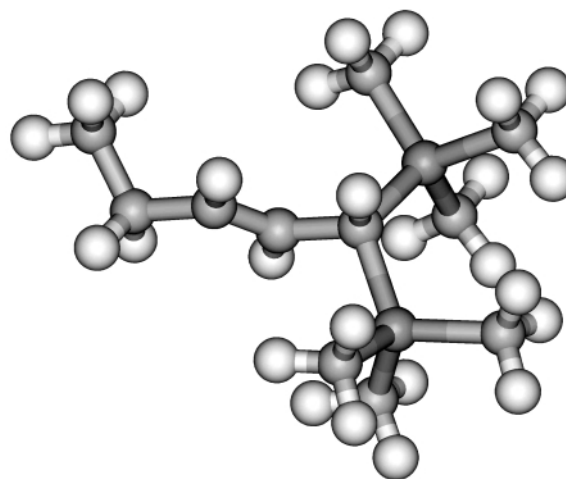
Density functional theory (DFT) calculations at the B3LYP/6-31+ G\* level indicate that the vinylsilane **1** (R = Et) is less stable than the allyldisilane **2** (R = Et) by 7.2 kJ mol<sup>-1</sup> (a predicted ratio of 5:95 at 25 °C). The energy minimised structure for the vinylsilane **1** (R = Et, Fig. 1) shows that the *cis* SiMe<sub>3</sub> group orients itself to minimize allylic strain (with the H of the allylic methylene that eclipses the double bond) at the expense of a 1,2-eclipsing interaction [Me–Si(*cis*)–C–Si(*trans*)]. In contrast, the *trans* SiMe<sub>3</sub> group has a relatively less demanding 1,3-allylic strain maximised (with the vinylic H) as this leads to the two SiMe<sub>3</sub> groups adopting a staggered arrangement of their Si–Me bonds with respect to each other. The 1,2-eclipsing interaction and allylic strain in vinylsilane **1** (R = Et) could be the origin of its instability compared with the allyldisilane **2** (R = Et).



**Fig. 1** The B3LYP/6-31+ G\* optimised structure of vinylsilane **1** (R = Et).

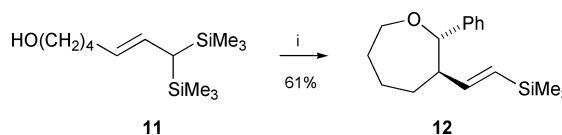
The energy minimised structure for the allyldisilane **2** (R = Et, Fig. 2) suggests that the presence of a SiMe<sub>3</sub> substituent both above and below the plane of the double bond might retard (re)association with the catalyst and hence reduction; moreover, since the allylic H substituent [of CH(SiMe<sub>3</sub>)<sub>2</sub>] eclipses the C=C double bond it is now in an unfavourable orientation to reform the  $\pi$ -allylpalladium hydride suggested above.

As discussed earlier, Lautens and Pomet have shown that disilylpropenes undergo reactions with electrophiles. However,



**Fig. 2** The B3LYP/6-31+ G\* optimised structure of allyldisilane **2** (R = Et).

Lautens and co-workers also observed that higher 1,1-disilylalk-2-enes failed to undergo reaction with aldehydes using a range of Lewis acids.<sup>3</sup> Nevertheless, we have preliminary evidence that such allyldisilanes can undergo synthetically useful reactions. For example, following the conditions of Ito *et al.* for acetalisation–intramolecular allylsilane cyclisation<sup>10</sup> gave, with allyldisilane **11** and benzaldehyde the *trans*-2,3-disubstituted oxepane **12** ( $J_{C(2)H-C(3)H}$  = 10 Hz)<sup>10</sup> possessing a *trans*-vinylsilane moiety ( $J_{CH=CHSi}$  = 19 Hz) for further synthetic elaboration (Scheme 4).



**Scheme 4** Reagents and conditions: i, PhCHO (1.4 equiv.), TMSOTf (2 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, –78 °C, 3.5 h.

In summary, we have developed an experimentally straightforward method for the synthesis of allyldisilanes from vinylsilanes; this allows access to allyldisilanes in two steps from aldehydes and should better allow the potential of allyldisilanes in organic synthesis to be realised.

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