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[2,3]-Wittig Rearrangements of (Trimethylsilyl)methyl Allyl Ethers

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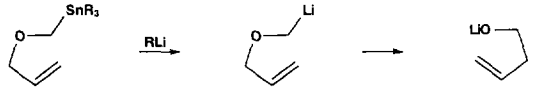
Abstract: A Wittig-Still type [2,3]-sigmatropic rearrangement of (trimethylsilyl)methyl allyl ethers has been developed. Copyright © 1996 Elsevier Science Ltd

The [2,3]-Wittig rearrangement[1] of allyloxy carbanions **1** to homoallylic alkoxides **2** is one of the most powerful stereoselective carbon-carbon bond forming reactions. In the Wittig-Still variation[2], the carbanion is generated *via* tin-lithium exchange of a (trialkylstannyl)methyl allyl ether **3** (Scheme 1).

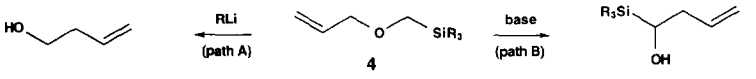
Scheme 1



3 **1** **2**

Although silicon-lithium exchange reactions are known,[3] and (trimethylsilyl)methyl ethers can be deprotonated with *s*-BuLi,[4] neither the exchange (path A) nor the deprotonation (path B) route to allyloxy carbanions has been performed with (trialkylsilyl)methyl ethers **4**. In this communication, first results regarding the [2,3]-Wittig rearrangement of ethers **4**, *via* silicon-lithium exchange (path A) are reported (Scheme 2).

Scheme 2



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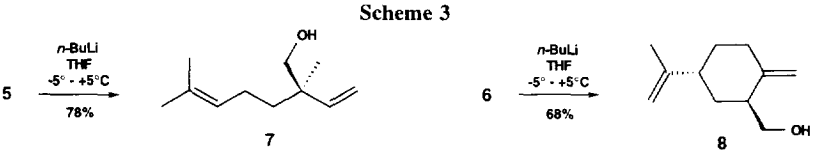
The synthesis of the required ethers[5] could best be achieved by deprotonation of the corresponding allylic alcohols with *n*-butyllithium, followed by addition of commercially available (trimethylsilyl)methyl triflate. (Trimethylsilyl)methyl ethers **5** and **6**[6] were thus obtained in 90% and 72% yield from geraniol and (R)-(+)-perilla alcohol, respectively.

5 **6**

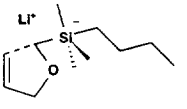
The envisaged silicon-lithium exchange and subsequent [2,3]-sigmatropic rearrangement to the homoallylic alcohol **7**[7] proceeded smoothly on treating the allyl ether **5** with five equivalents of *n*-butyllithium in THF at low temperature. When ether **6** was subjected to the same conditions, alcohol **8** was obtained as a single diastereoisomer. The axial position of the hydroxymethyl group was confirmed by 800 MHz NOESY experiments (Scheme 3). To optimise the process, a "one pot" procedure for the conversion of geraniol into alcohol **7** was developed[8].

Scheme 3



7 **8**

It is an interesting mechanistic question, whether this rearrangement proceeds *via* a pentavalent silicon intermediate **9** and/or the Wittig-Still intermediate **10**, which has previously been found by *ab initio* molecular orbital calculations[9].



9

10

In conclusion, we have developed a new variation of the [2,3]-Wittig rearrangement, and a new synthesis of (trimethylsilyl)methyl ethers. Compared to the classical Wittig-Still reaction, this new methodology offers two advantages: 1. (trimethylsilyl)methyl triflate is commercially available, whereas iodomethyl tributylstannane[10] has to be synthesised. 2. Organosilanes are much less toxic than organostannanes.

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6. **^{1}HNMR** (250MHz, $CDCl_3$) of **6**: δ = -0.03 (s, 9H); 1.33-1.51 (m, 1H); 1.70 (t, J = 1.0Hz, 3H); 1.71-2.23 (m, 6H); 2.96 (s, 2H); 3.74 (d, J = 12.9Hz, 1H); 3.79 (d, J = 12.9Hz, 1H); 4.665 (d, J = 1Hz, 1H); 4.669 (d, J = 1Hz, 1H); 5.61ppm (m, 1H). **^{13}CNMR** ($CDCl_3$) of **6**: δ = -3.2, 20.7, 26.0, 27.4, 30.4, 41.1, 63.0, 78.9, 108.4, 123.9, 134.9, 149.8ppm.
7. **^{1}HNMR** (250MHz, $CDCl_3$) of **7**: δ = 1.02 (s, 3H); 1.33 (m, 2H); 1.43 (bs, 1H); 1.58 (s, 3H); 1.67 (d, J = 1Hz, 3H); 1.90 (m, 2H); 3.37 (m, 2H); 5.05 (dd, J_1 = 1.4Hz, J_2 = 17.6Hz, 1H); 5.09 (m, 1H); 5.16 (dd, J_1 = 1.4Hz, J_2 = 10.9Hz, 1H); 5.74ppm (dd, J_1 = 10.9Hz, J_2 = 17.6Hz, 1H). **^{13}CNMR** ($CDCl_3$) of **7**: δ = 17.5, 19.4, 22.4, 25.5, 37.1, 42.2, 70.0, 114.5, 124.5, 131.3, 143.9ppm.
8. Geraniol (110mg, 125µl, 0.705mmol) in 4ml of dry THF at -20°C was treated with 485µl (0.776mmol, 1.1eq) of 1.6M *n*-BuLi in hexane, and after 20min with 183mg (155µl, 0.776mmol, 1.1eq) of $TMSCH_2OTf$. The mixture was warmed to +2°C during 2.5h. The solution was diluted with dry THF (4ml), cooled to -20°C, and 2.64ml (4.23mmol, 6eq) of 1.6M *n*-BuLi were added. The mixture was warmed to +20°C during 2.5h, and treated with 15ml of Et_2O and 0.5ml of sat. NH_4Cl. After drying with $MgSO_4$, filtration, evaporation and column chromatography (10% EtOAc/hexane) on silica gel, 104mg (0.620mmol, 88%; 95% according to consumed geraniol) of **9** along with 9mg (0.056mmol, 8%) of geraniol were isolated.
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