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Regio- and Stereo-defined Synthesis of Organosilicon Compounds via Rearrangement of Silyl Group

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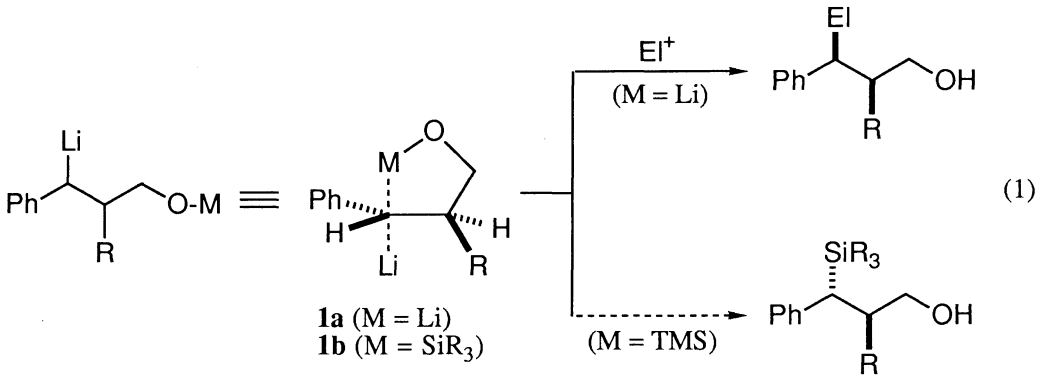
On treating with LDBB, 2-substituted 3-phenylthioalkyl silyl ethers were converted to the corresponding 3-silylated alkanols with high *anti* selectivity. Application to silyl ethers containing allylic sulfide moieties provided a useful methodology for the regio- and stereo-defined synthesis of allylsilanes.

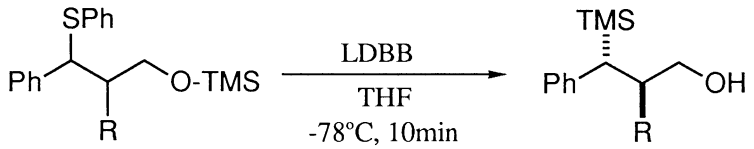
Stereochemistry of organosilicon compounds, e.g. allylsilanes, has often played important roles to control the strereochemical outcome of several useful organic transformation,[1] but there have been few reports on stereo-defined synthesis of carbon-silicon bond.[2] Such drawback is mainly due to the synthetic procedure of organosilicon compounds; the most general ones involve silylation of the corresponding carbanionic species which are expected to undergo a rapid epimerization under usual reaction conditions. In the previous paper, we described remarkable feature of dilithiated species to allow stereoselective carbon-carbon bond formation and proposed a fixed conformation[3] as (**1a**) for such species (Eq. 1).



(1)

This feature as well as a facile migratory aptitude[4] of silyl group suggested selective conversion of siloxyalkyllithiums to silylated alkanols via pentavalent silicon species (**1b**) shown in Eq 1. Indeed, such transformation has been cleanly realized. Expecting general applicability, we generated lithiated species from the corresponding sulfides by using lithium di-*t*-butylbiphenylide (LDBB).[5] Thus, treatment of 2-substituted 3-phenyl-3-phenylthioalkyl silyl ethers **2** with LDBB at -78 °C led to the formation of the corresponding 3-silylated alcohols **3**[6] with high *anti* selectivity (Eq. 2). The configuration was determined by using stereo-defined elimination of 2-silylalkanol obtained from **3b** as shown in Scheme 1.

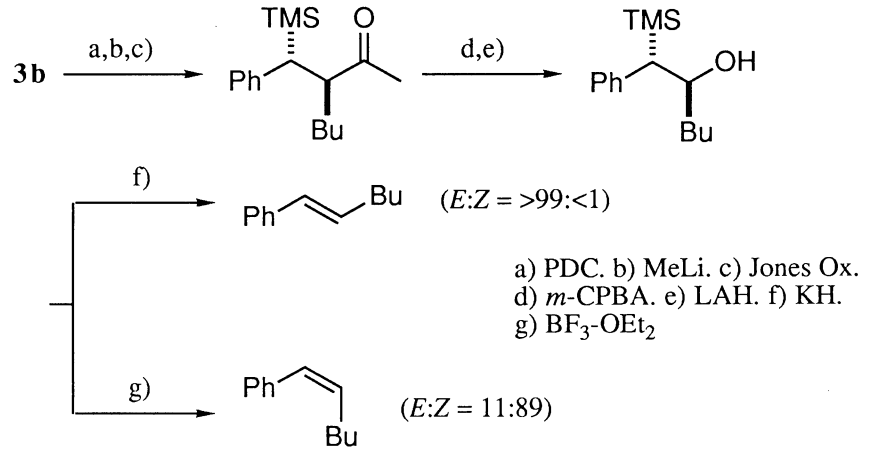
Interestingly, 1,5-migration could also be effected with high diastereoselectivity[7] (Eq. 3).



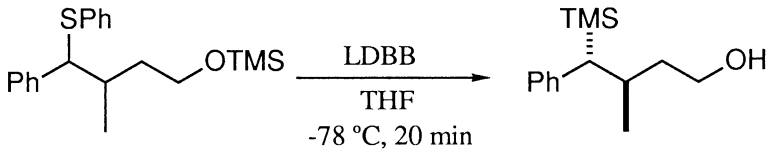
(2)

2a: R = Me (*syn*:*anti* = 64:36)
2b: R = Bu (*syn*:*anti* = 98:2)

3a: R = Me, 94% (*anti* :*syn* = 98:2)
3b: R = Bu, 95% (*anti* :*syn* = >99:<1)



Scheme 1.



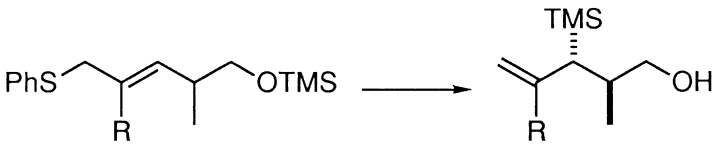
(3)

2c

3c 88% (>99% *anti*)

The present procedure has also provided an efficient method for synthetically useful allylsilanes: Acyclic as well as cyclic allylsilanes were prepared in highly regio- and stereo-controlled manner under essentially same reaction conditions as shown in Eqs. 4-6.

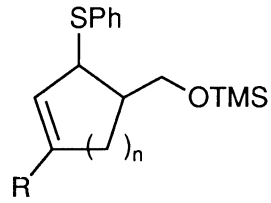
The following characteristic features seem to be very useful for synthetic purposes: (1) both types of allylic sulfides, 5-phenylthio-3-enes (**4a**, **4b**, and **4f**) and 3-phenylthio-4-enes (**4c**, **4d**, and **4e**) gave the corresponding 3-silylated 4-alkenols **5**[8] via 1,4-migration of silyl group with excellent regio- and stereoselectivities. (2) The *cis* substituted products **5c-f** were obtained exclusively in reactions of cyclic derivatives **4c-f**. (3) Use of optically active substrates allows us to prepare the corresponding optically active allylsilanes. Thus, **4b**-(2*S*)[9]

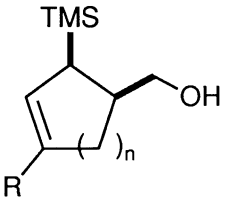


(4)

4a (R = H)
4b (R = Me)

5a (R = H), 80% (*anti*:*syn* = 96:4)
5b (R = Me) 97% (*anti*:*syn* = >99:<1)

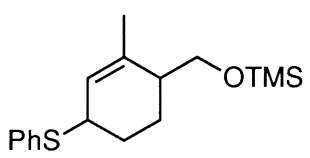


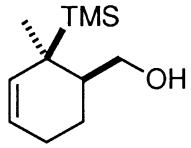


(5)

4c (n = 1, R = H)
4d (n = 2, R = H)
4e (n = 2, R = Me)

5c (n = 1, R = H) 70%
5d (n = 2, R = H) 93%
5e (n = 2, R = Me) 80%





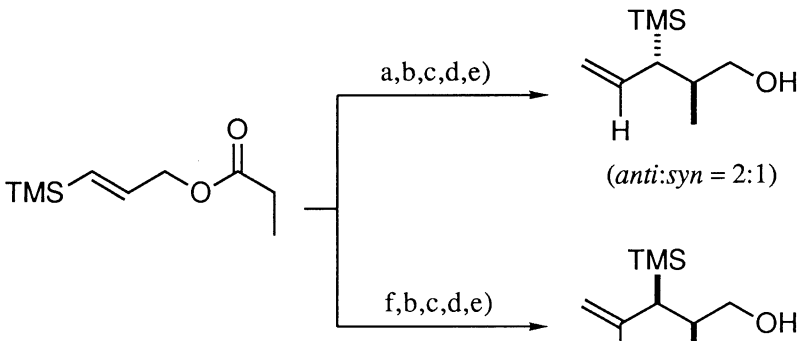
(6)

4f **5f** 80%

(92% ee) gave **5b** (2*R*,3*R*) in 88% yield without any decrease of ee.

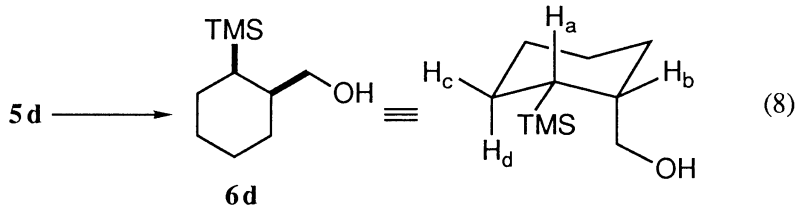
Stereochemical results were typically determined on **5a**, **5d**,and **5f:** Claisen-Ireland rearrangement[10] of 3-silylallyl propionate followed by DIBAL reduction gave the authentic sample of **5a** as a mixture of *syn* and *anti* isomers (Eq. 7). The product **5d** was confirmed by ^{1}H NMR coupling constants of its hydrogenated one which supports the conformation having axial hydroxymethyl and equatorial TMS group (Eq. 8).

The structure of **5f**[11] was identified by NOE between H_a and TMS, H_a and Me, and H_b and Me (Eq. 9).



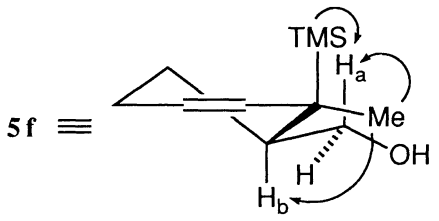
(7)

a) LDA. b) TMS-Cl. c) heat. d) CH_2N_2.
e) DIBAL. f) LHMDS/HMPA



(8)

$J_{a\text{-}b}$ and $J_{a\text{-}c}$ = 4.0, 4.2 Hz
$J_{a\text{-}d}$ = 10.6 Hz



(9)

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6) Spectral and analytical data of **3a:** ^{1}H NMR (270 MHz, $CDCl_3$) d -0.04 (s, 9 H), 0.90 (d, J = 6.2 Hz, 3 H), 2.07 (d, J = 8.0 Hz, 1 H), 2.1-2.3 (m, 1 H), 3.43 (dd, J = 10.2 Hz, 6.0 Hz, 1 H), 3.60 (dd, J = 10.2 Hz, 5.4 Hz, 1 H), 6.9-7.3 (m, 5 H); Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.49; H, 9.70.

7) Stereochemistry of **3c** was determined by comparison with the authentic sample prepared from **3a**.

8) Spectral and analytical data of **5b:** ^{1}H NMR (270 MHz, $CDCl_3$) d 0.11 (s, 9 H), 0.99 (d, J = 6.4 Hz, 3 H), 1.48 (d, J = 9.8 Hz, 1 H), 1.68 (s, 3 H), 1.8-2.1 (m, 1 H), 3.42 (dd, J = 10.2 Hz, 7.2 Hz, 1 H), 3.72 (dd, J = 10.2 Hz, 4.6 Hz, 1 H), 4.56 (s, 1 H), 4.73 (s, 1 H); Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.68; H, 12.18.

9) The optically active **4b**-(2*S*) was prepared from (*R*)-(-)methyl 3-hydroxy-2-methylpropionate.

10) R. E. Ireland, R. H. Mueller, and A. K. Wilard, *J. Am. Chem. Soc.*, **98**, 2868 (1976).

11) Spectral and analytical data of **5f**: ^{1}H NMR (270 MHz, $CDCl_3$) d 0.03 (s, 9 H), 1.09 (s, 3 H), 1.4-1.6 (m, 3 H), 1.8-1.9 (m, 1 H), 2.0-2.1 (m, 2 H), 3.45 (dd, J = 10.4 Hz, 9.0 Hz, 1 H), 3.89 (dd, J = 10.4 Hz, 3.2 Hz, 1 H), 5.34 (dt, J = 10.0 Hz, 2.2 Hz, 1 H), 5.61 (dt, J = 10.0 Hz, 3.2 Hz, 1 H); Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.90; H, 10.88.

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