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Asymmetric retro-[1,4]-Brook rearrangement of 3-silyl allyloxysilanes *via* chirality transfer from silicon to carbon†

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An asymmetric retro-[1,4]-Brook rearrangement of 3-silyl allyloxysilanes has been developed *via* Si-to-C chirality transfer. Mechanistic studies reveal that the silyl group migrates with retention of configuration. The stereochemical outcome of the newly formed stereogenic carbon center, which has remained a longstanding question, is also clarified, suggesting a diastereoselective Si to C chirality transfer without loss of enantiomeric excess.

Introduction

Intramolecular O-to-C silyl migration, now called retro-Brook (or West) rearrangement, was first reported by Speier and later systematically studied by West.[1] The retro-Brook rearrangement occurs only under special circumstances[2] and so has been less investigated than Brook rearrangement.[3] But, it comprises a powerful synthetic tool because diverse organosilanes could be constructed from more accessible silyl ethers by a rapid and regio- and stereoselective manner. A covalent Si–O bond is cleaved and a Si–C bond is formed *via* silyl migration. Thus, the stereochemical courses at the migrating silicon center and the stereochemical control at the forming carbon center comprise two important stereochemical issues. Tomooka and co-workers[4] reported the first example of practically useful level of retro-[1,4]-Brook rearrangement of allyloxysilane by use of HMPA as a co-solvent. In this work, they also showed, for the first time, that the silyl migration proceeded with retention of configuration at the silicon center (Scheme 1). In contrast, more efforts have been directed toward diastereoselective formation of the Si–C bond to generate synthetically useful chiral organosilanes. Nearly all previous studies have used stereogenic C1,[2b,d,e] C2 (ref. 2*h*) or C3 (ref. 2*a* and *j*) centers in substrate **I** to control diastereoselective formation of the Si–C bond in **III**. When the migrating silicon is stereogenic,[5] it might be used as a stereochemical controller by Si to C chirality transfer, which was redefined by Oestreich.[6] Achieving this in practice is quite challenging. There are only two examples we know come from a preliminary study by Tomooka and co-workers.[4] The 3-Me allyloxysilane with SiOMePh*t*-Bu as the migrating silyl group afforded a dr of 83 : 17, while the corresponding 3-$SiMe_3$ allyloxysilane only migrated with a dr of 66 : 34. In both cases, the stereochemistry of the formed stereogenic carbon center were not determined.

Oestreich rationalized the difficulties in achieving high diastereoselectivity during Si-to-C chirality transfer as follows.[6] The relatively long Si–C bond disfavors formation of a compact transition state **II**, which weakens diastereoselectivity. At the same time, all three substituents on the migrating silyl group can affect the stereochemical course, requiring the careful selection of three substituents that together allow efficient stereochemical control. Despite these difficulties, Oestreich described an intermolecular Pd- catalyzed asymmetric hydrosilylation using chiral silane (Scheme 2a),[7] and Leighton demonstrated an intramolecular Hosomi–Sakuraiallylation involving a chiral allylsilane intermediate (Scheme 2b).[8] In both

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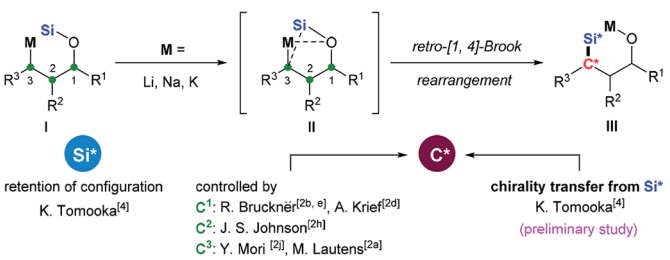
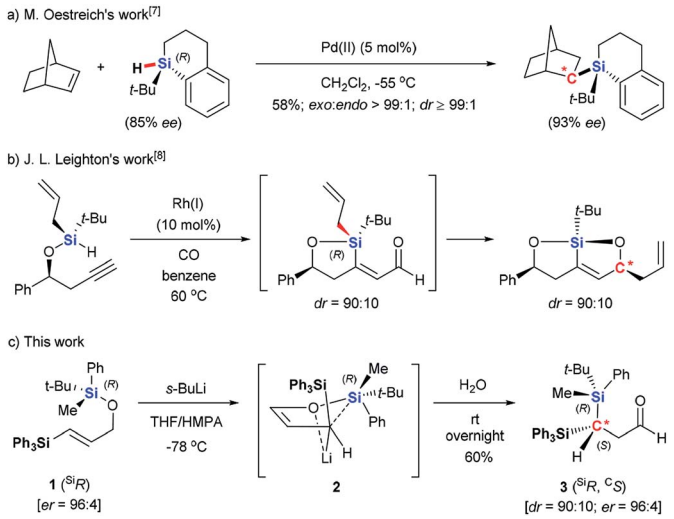


Scheme 1 Diastereoselective retro-Brook rearrangement.



Scheme 2 Chirality Transfer from Silicon to Carbon.

of these cases, either cyclic silanes or acyclic silane with three distinct, sterically demanding substituents were used to achieve the high stereochemical control.

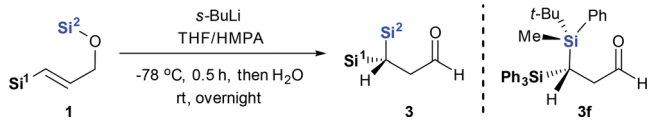
Here we report an asymmetric retro-[1,4]-Brook rearrangement of 3-silyl allyloxysilanes **1** *via* an efficient Si-to-C chirality transfer (Scheme 2c). The combination of SiMePh*t*-Bu as the migrating silyl group and $SiPh_3$ as the terminal silyl group proved most effective, giving geminal bis(silyl) aldehyde **3** and enol derivatives **4** in good yield with high diastereoselectivity. The overall stereochemical outcome of the migrating silicon center and the newly formed carbon center were clarified by detailed mechanistic studies.

Results and discussion

This project arose from our interest in developing chiral geminal bis(silanes) reagents and synthons.[9] These species contain two different silyl groups, making the carbon to which they are attached a stereogenic center. In previous work, we achieved asymmetric C–C or C–H bonds formation *via* 3,3-sigma tropic rearrangement of optically pure 3,3-bis(silyl) allylic alcohols, allowing asymmetric synthesis of crotyl geminal bis(-silanes).[10] We were curious whether asymmetric C–Si bond formation could be another efficient strategy to construct chiral geminal bis(silanes). Our *s*-BuLi-promoted retro-[1,4]-Brook rearrangement of 3-silyl allyloxysilanes[11] appeared to be a suitable model to test this possibility. The reaction tolerates a wide range of migrating and non-migrating silyl groups, making it practical for identifying the best pair of silyl groups.

We initially fixed *t*-BuPhMeSi as the migrating silyl group (Table 1). Entries 1–7 showed an obvious steric bias for the non-migrating silicons (Si^1) at the 3-position of **1**. When Si^1 was an $SiMe_3$ group, geminal bis(silyl) aldehydes **3a** were generated as a nearly 1 : 1 mixture of two diastereomers (entry 1). Even when one methyl was replaced with a phenyl group, dr did not improve for the corresponding products **3b** (entry 2). These results imply that the small methyl group does not permit good

Table 1 Screening of Silyl Groups[a]



Entry	Sub.	Si^1	Si^2	Prod.	Yield[b]	dr[c]
1	**1a**	Me_3Si	*t*-BuPhMeSi	**3a**	62%	56 : 44
2	**1b**	Me_2PhSi	*t*-BuPhMeSi	**3b**	65%	47 : 53
3	**1c**	Et_3Si	*t*-BuPhMeSi	**3c**	53%	67 : 33
4	**1d**	$(n\text{-Pr})_3Si$	*t*-BuPhMeSi	**3d**	50%	65 : 35
5	**1e**	$(i\text{-Pr})_3Si$	*t*-BuPhMeSi	**3e**	45%	83 : 17
6	**1f**	Ph_3Si	*t*-BuPhMeSi	**3f**	60%	90 : 10
7	**1g**	Ph_3Si	1-NpPhMeSi	**3g**	65%	65 : 35
8	**1h**	Et_3Si	1-NpPhMeSi	**3h**	73%	83 : 17
9	**1i**	Me_3Si	1-NpPhMeSi	**3i**	63%	86 : 14
10	**1j**	*t*-BuPhMeSi	Ph_3Si	**3f**	55%	74 : 26

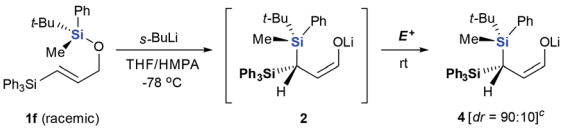
[a] Reaction conditions: **1** (0.15 mmol), *s*-BuLi (0.60 mmol), HMPA (0.6 mmol), 0.5 mL of THF, at −78 °C for 0.5 h, then H_2O at rt overnight. [b] Isolated yields. [c] Ratios were determined from ^1H NMR analysis of crude product.

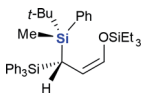
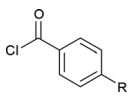
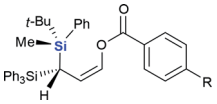
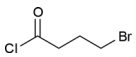
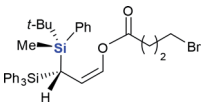
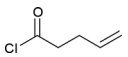
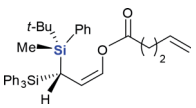
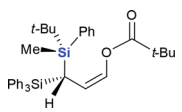
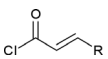
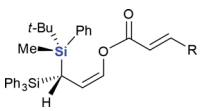
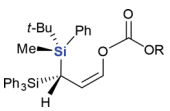
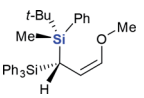
diastereochemical control. Diastereoselectivity improved progressively when steric demand at Si^1 increased from $SiMe_3$ to $SiEt_3$, $Si(n\text{-Pr})_3$, $Si(i\text{-Pr})_3$ and finally $SiPh_3$ (entries 3–6). The largest $SiPh_3$ group imposed the strongest stereochemical control, providing **3f** at the highest dr of 90 : 10 (entry 6). Interestingly, an inverse steric bias for Si^1 was observed when the migrating silicon was switched from *t*-BuPhMeSi to 1-NpPhMeSi. The largest $SiPh_3$ group afforded a dr of only 65 : 35, while the smallest $SiMe_3$ provided the best dr of 86 : 14 (entries 7–9). We also tested the silicon combination in which the *t*-BuPhMeSi functioned as a chiral auxiliary, while $SiPh_3$ migrated (entry 10). The reaction gave the aldehyde **3f** with a dr of 74 : 26 lower than that obtained in entry 5.

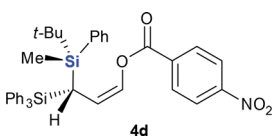
Next we examined the scope of electrophiles for quenching the lithium enolate intermediate generated from **1f**. The reaction tolerated triethylsilyl chloride (entry 1), various acyl chlorides (entries 2–9) and chlorocarbonates (entries 10 and 11) to provide 3,3-bis(silyl) enol derivatives **4** in good yields with high diastereoselectivity (Table 2). The enol double bond formed exclusively with *Z*-selectivity. The relative stereochemistry of the products was unambiguously established based on X-ray diffraction analysis of **4d** crystals.[12] Methyl iodide was also a suitable electrophile, but less reactive than acyl chloride, giving **4l** in 40% yield with *O*-alkylation selectivity (entry 12).

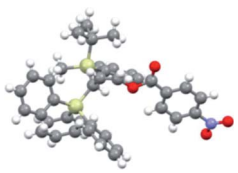
The silicon can migrate with either retention or inversion of configuration. Thus, the relative stereochemistry of **3f** may not reflect the stereochemical course of the migrating silicon, or how it controls the stereochemical outcome of the resulting stereogenic carbon center. In particular, if the enantiomerically defined silyl group racemizes during migration, the carbon center can be constructed diastereoselectively, but not enantioselectively. The observation by Tomooka and co-workers that silicon migrates with retention of configuration in their simple allyloxy system[4] does not necessarily apply to our case, since the

Table 2 Scope of Electrophiles[a]



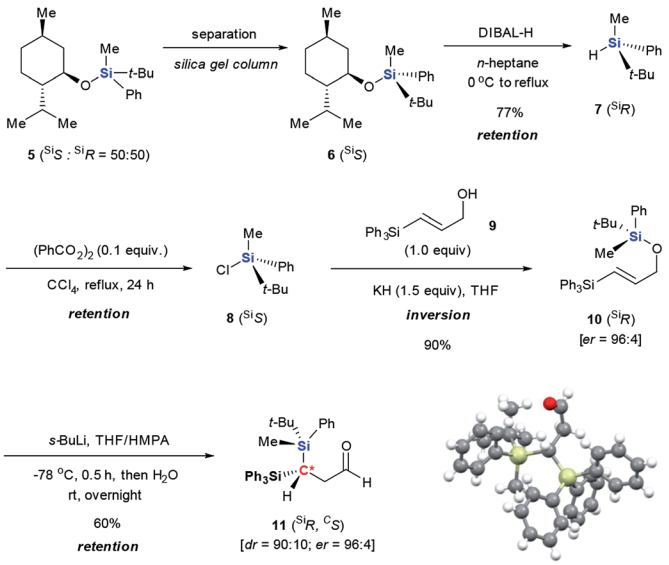
Entry	Electrophiles	Product	Yield[b]
1	Et_3SiCl		**4a** (60%)
2 3 4			**4b** (R = H, 65%) **4c** (R = Br, 65%) **4d** (R = NO_2, 60%)
5			**4e** (67%)
6			**4f** (50%)
7			**4g** (66%)
8 9			**4h** (R = Me, 50%) **4i** (R = Ph, 55%)
10 11			**4j** (R = Me, 70%) **4k** (R = Ph, 70%)
12	MeI[d]		**4l** (40%)





[a] Reaction conditions: **1f** (0.15 mmol), *s*-BuLi (0.60 mmol), HMPA (0.6 mmol), 0.5 mL of THF, at −78 °C for 0.5 h, then electrophile at rt for 2 h. [b] Isolated yields. [c] Ratios were determined from crude ^{1}H NMR analysis of product. [d] 10.0 equiv. of MeI.

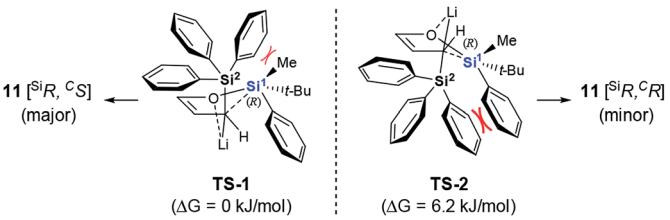
non-migrating silicon may affect the stereochemical course. To gain a definitive answer to this question, we used enantiomerically defined **10** as a stereochemical probe (Scheme 3).[13] Following the procedure developed by Oestreich,[14] a 1 : 1 mixture of **5** was separated by several cycles of silica gel chromatography, affording **6** in diastereomerically pure form. Reduction of **6** with DIBAL-H provided hydrosilane **7** in 77% yield. Subsequent chlorination of **7** with CCl_4 delivered



Scheme 3 Preparation of enantiomerically defined **10** and its retro-[1,4]-Brook rearrangement to form **11**.

chlorosilane **8**, which directly reacted with the potassium salt of **9**, giving **10** in 90% yield. The high *er* of **10** (96 : 4) suggests that transformation from **6** to **10** proceeds in a stereospecific manner at the silicon center, and should follow the known sequence of retention-retention-inversion.[15] Thus, the absolute configuration of the silicon in **10** was assigned as *R*. Under the optimal retro-[1,4]-Brook rearrangement conditions, **10** was converted into aldehyde **11**. The major isomer showed an *er* of 96 : 4, indicating that the silicon migrated stereospecifically. X-ray diffraction analysis of **11**[16] unambiguously confirmed the *R*-configuration of the silicon, indicating that migration proceeds with retention of configuration as in Tomooka's case. The X-ray diffraction analysis of **11** also established the *S*-configuration of the new stereogenic carbon center. The result revealed that the migration proceeded by a diastereoselective Si to C chirality transfer without loss of enantiomeric excess.

A plausible mechanism to explain our results is proposed in Scheme 4, based on the model we proposed for the racemic version of the reaction.[11] The α-deprotonation of **10** gives the corresponding allylic anion, which adopts the *endo*-orientation assisted by Li–O coordination.[17] The O-to-C silyl migration takes place irreversibly *via* two possible pentacoordinated silicate transition states or intermediates, **TS-1** and **TS-2**.[18] In this way, the configuration of the silicon center is retained without



Scheme 4 Plausible reaction mechanism.

racemization. While **TS-2** suffers a severely steric repulsion between the Ph group on Si^1 and one of the Ph groups on Si^2, the interaction between the Me group on Si^1 and the Ph group on Si^2 appears being tolerable in the case of **TS-1**. These considerations are supported by the preliminary results from density functional theory calculations, which showed **TS-1** to be more stable than **TS-2** by 6.2 kJ mol^{-1}. Our model also explains the observed steric bias for substituents on Si^1. Substituents smaller than the Ph group might not be large enough to create an appreciable difference between the non-bonded interaction with the Me group in **TS-1** and with the Ph group in **TS-2**. As a result, **3** forms with poor diastereoselectivity (Table 1, entries 1–4).

Conclusions

In summary, Si-to-C chirality transfer has been used as an efficient strategy to achieve asymmetric retro-[1,4]-Brook rearrangement of 3-silyl allyloxysilanes. The SiMePh*t*-Bu and $SiPh_3$ groups, in which SiMePh*t*-Bu migrates, function as the best combination to give geminal bis(silyl) aldehyde and enol derivatives with high diastereoselectivity. The silyl group migrates with retention of configuration. Enantioselective generation of the stereogenic carbon center suggests that Si-to-C chirality transfer is a promising method to construct optically pure chiral organosilanes. Further applications of this strategy are being explored in our group.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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