Selective Formation of Both Enantiomerically Pure Disilanes from One Fluorosilane Antipode with Silyllithium

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Summary: *Stereochemistry crossover from retention to inversion of configuration at about −20 °C was observed in the nucleophilic substitution of optically active (R)-fluoromethyl(1-naphthyl)phenylsilane ((R)-**2**$_F$; >99% ee) with the achiral silyllithium species (dimethyl(4-methoxynaphth-1-yl)silyl)lithium (**1**) to give optically active 1,1,2-trimethyl-2-(4-methoxy-1-naphthyl)-1-(1-naphthyl)-disilane (**3**). It became possible to synthesize both enantiomerically pure stereoisomers of disilane with one chiral center from a single antipode of the fluorosilane enantiomer by using HMPA, $LiClO_4$, LiBr as additives, or by changing the temperature.*

Disilane derivatives are versatile precursors for polymers with a silicon−silicon moiety, such as oligo- and polysilanes[1] including polysilane dendrimers[2] and poly(disilanylene-π-conjugated systems),[3] to which considerable attention has been paid because of their unique electrical and optical properties. The nature of σ and $\sigma-\pi$ conjugation along the polymer backbone and the global conformational structures have been extensively investigated in relation to the electronic structure and photophysical properties of the polymers.[4] The conformation of a polymer, which is one of the most important structural parameters to control the physical properties of the polymer, is principally controlled by its stereoregularity. If stereoregularity is controlled, the resulting polymers are expected to exhibit novel unique properties different from those without controlled stereoregularity. To realize such systems, optically active bis-functionalized disilanes are typically needed.

Silyllithiums are useful reagents for the formation of silicon−silicon bonds[5] and for the study of the stereochemistry of the reaction. However, in contrast to intensively investigated reactions of optically active halosilanes with carbanions (alkyl- and aryllithium),[6] those of silyl anions have received only brief attention, probably because of the limitation of a synthetically versatile method to obtain optically active organosilylmetals.[7,8] The ability to functionalize an optically active disilane without cleavage of the silicon−silicon bond has been also limited.

Recently, we reported the successful preparation of a configurationally stable naphthyl-substituted optically active silyllithium.[7] The stereochemistry of the nucleophilic substitution reaction of halosilanes (mainly chlorosilane) with silyllithium to afford optically active disilanes having one or two chiral centers was established to be highly stereoselective.[9,10] Stereoselective functionalization of the resulting disilane by the cleavage of the silicon−naphthyl bonds with bromine without cleaving the silicon−silicon bond was also established.[10]

During the course of the study, we found a unique stereochemical feature of optically active fluorosilane in the reaction with silyllithium. In this communication, we report the stereochemistry crossover steered by temperature, solvent, and common salt in the nucleophilic substitution reaction of an optically active fluorosilane with an achiral silyllithium.

Although the yield of (dimethyl(4-methoxynaphth-1-yl)silyl)lithium (**1**), prepared by the cleavage reaction of the silicon−tin bond of dimethyl(4-methoxynaphth-1-yl)silylstannane by methyllithium in THF at −78 °C, varied in each experiment, the reaction of (*S*)-chloro-, (*S*)-bromo-, and (*R*)-fluoromethyl(1-naphthyl)phenylsilane (**2**$_X$; X = Cl, Br, F, >99%ee)[11] with **1** gave an almost

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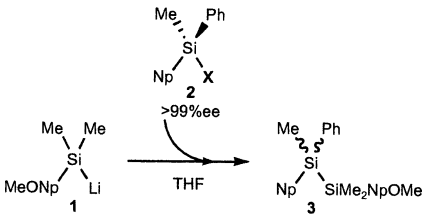
Table 1. Nucleophilic Substitution Reaction of Optically Active Halosilanes 2_X with the Achiral Silyllithium 1 under Various Conditions



entry	X	temp, °C	solvent[a]	yield, %[b]	stereoselectivity, %[c]
1	Cl	room temp	THF	52	racemization
2		room temp	Et_2O	46	77 (inversion)
3		room temp	pentane	40	79 (inversion)
4		−78	THF	44	89 (inversion)
5		−78	Et_2O	49	96 (inversion)
6		−78	pentane	45	99 (inversion)
7	Br	room temp	THF	40	racemization
8		room temp	Et_2O	48	racemization
9		room temp	pentane	35	72 (inversion)
10		−78	THF	38	racemization
11		−78	Et_2O	39	89 (inversion)
12		−78	pentane	37	90 (inversion)
13	F	room temp	THF	37	80 (inversion)
14		room temp	Et_2O	39	84 (inversion)
15		room temp	pentane	39	81 (inversion)
16		−78	THF	44	93 (inversion)
17		−78	Et_2O	40	93 (inversion)
18		−78	pentane	36	97 (inversion)

[a] Solution of **2** in each solvent (0.2 M, 2.5 mL) was added to **1** in THF (0.12 M, 5 mL). [b] Based on **1**. [c] The absolute configuration of **3** was determined by HPLC using a Daicel OD column.

quantitative yield of **3** based on actually produced **1**.[12] The stereochemistry in the reaction of optically active $\mathbf{2_X}$ with **1** is shown in Table 1. (*S*)-$\mathbf{2_{Cl}}$ in THF, Et_2O, and pentane gave racemic and 77 and 79% inverted (*R*)-**3**, respectively (entries 1−3), when added dropwise to **1** in THF at room temperature (inversion configuration of chiral silicon center was assumed[9,10,13]). At −78 °C, the stereoselectivity was higher than that at room temperature, probably because racemization of **2**[14,15] was suppressed by lowering the temperature and solvent polarity, and gave 89, 96, and 99% inversion products, respectively (entries 4−6).[15] (*S*)-$\mathbf{2_{Br}}$ showed tendencies similar to those of chlorosilane, although the selectivity was lower. The reaction in pentane proceeded with 72% inversion at room temperature (entry 9). The reaction in THF gave a racemized product even at −78 °C (entry 10). These tendencies are similar to the corresponding reactions of the halosilanes with carbanions.[6]

Interestingly enough, (*R*)-$\mathbf{2_F}$, with configuration opposite to (*S*)-$\mathbf{2_{Cl}}$, also gave the same antipode (*R*)-**3** as the major product at room temperature, not only in pentane and Et_2O but also even in THF, indicating retention of configuration at the chiral silicon center (entries 13−15). Surprisingly, in contrast to the reaction at room temperature, the opposite antipode (*S*)-**3** was produced as 97% inverted product at −78 °C in pentane. Changes of solvents from pentane to Et_2O and THF showed only a slight influence on the stereoselectivity (entries 16−18).

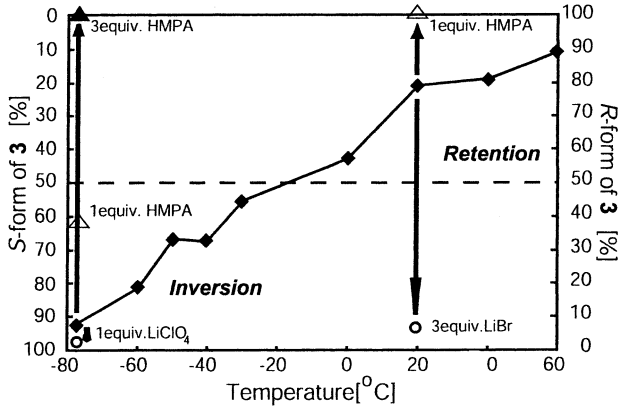


Figure 1. Stereochemistry crossover in the reaction of (*R*)-$\mathbf{2_F}$ (in THF) with **1** under various conditions.

Figure 1 shows the change of percentage of (*S*)-**3** depending on the temperature, with or without an additive such as HMPA, $LiClO_4$, or LiBr, in THF.[16] At −78 °C, (*S*)-**3** was obtained as 93% inverted product from (*R*)-$\mathbf{2_F}$. When the temperature was elevated from −78 to 60 °C, the percentage of (*S*)-**3** gradually decreased with the increase of (*R*)-**3**. At around −20 °C, the stereochemistry crossover point, where (*R*)-**3** = (*S*)-**3** (50/50), was observed. The reaction proceeded with 90% retention at 60 °C.

Very interestingly, the presence of 1 equiv of HMPA at −78 °C increased the fraction of retention product (62% inversion), and reaction with 3 equiv of HMPA selectively afforded (*R*)-**3** (100% ee) with completely opposite configuration compared with that without HMPA. At room temperature, the presence of 1 equiv of HMPA in **1** also afforded (*R*)-**3** with 100% ee. In the presence of 1 equiv of $LiClO_4$ at −78 °C and 3 equiv of LiBr at room temperature, the reaction proceeded with 97 and 93% of inversion, respectively.

Such stereochemical steering is considered to strongly reflect the state of ions in the solution. To obtain some insights about the state of ion pairs, variable-temperature ^{29}Si NMR and electronic spectra were measured. At room temperature, the ^{29}Si resonance of **1** appeared

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(12) The yield of **1** was determined by the amounts of dimethyl(4-methoxynaphth-1-yl)silane after quenching the system with H_2O.

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(14) Although the configuration of optically active chlorosilanes is reported to be stable in various solvents,[15] optically active $\mathbf{2_{Cl}}$ and $\mathbf{2_{Br}}$ seem to racemize in THF at room temperature.

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(16) A solution of (dimethyl(4-methoxynaphth-1-yl)silyl)trimethylstannane (0.76 g, 2.0 mmol) in THF (10 mL) added to a solution of methyllithium (2.0 mL, 1.14 M Et_2O solution, 2.28 mmol) in THF (5 mL) over 30 min at −78 °C afforded **1**. To the resulting solution of **1** was slowly added $\mathbf{2_{Cl}}$ (2 mmol, >99%ee) in pentane (10 mL) at −78 °C over 30 min, and the reaction system was stirred for 60 min. The resulting solution was poured into 1 N HCl solution, extracted with Et_2O, and dried over anhydrous $MgSO_4$. After the solvent was removed, crude product was purified by silica gel column chromatography with hexane/toluene = 10:1 to 10/2 as an eluent (R_f = 0.21) to afford 0.37 g of (*R*)-**3** as a highly viscous oil. Optical purity: 99% ee. (*R*)-(−): R_t = 92.8 min. (*S*)-(+): R_t = 116 min. $[\alpha]^{28}_D$ = +15.56° (*c* = 1.08, cyclohexane). ^1H NMR (500 MHz, $CDCl_3$): δ 0.51 (s, 3H, NpOMeSi*Me*), 0.59 (s, 3H, NpOMeSi*Me*), 0.74 (s, 3H, NpSi*Me*), 4.00 (s, 3H, NpO*Me*), 6.76−6.77 (d, *J* = 7.8 Hz, 1H), 6.99−7.02 (m, 1H), 7.13−7.16 (m, 1H), 7.27−7.45 (m, 8H), 7.56−7.57 (d, *J* = 7.8 Hz, 1H), 7.59−7.61 (m, 2H), 7.80−7.83 (t, *J* = 7.8 Hz, 3H), 8.22−8.24 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -14.21, −2.354, −0.995, 0.227, 14.14, 22.66, 31.58, 55.22, 103.3, 103.4, 122.3, 124.7, 125.3, 125.6, 127.7, 127.8, 128.4, 128.6, 128.7, 129.8, 134.4, 135.1, 135.3, 135.4, 137.2, 138.0, 156.7. ^{29}Si NMR (99.5 MHz): δ −20.85. MS: *m/e* 462 (M^+), 447 ([M − CH_3]$^+$), 247 ($NpPhMeSi^+$), 215 ($MeONpMe_2Si^+$). FT-MS (EI): *m/z* found 462.183, calcd 462.184; Anal. Calcd for $C_{30}H_{30}OSi_2$: C, 77.87; H, 6.53. Found: C, 77.23; H, 6.66.

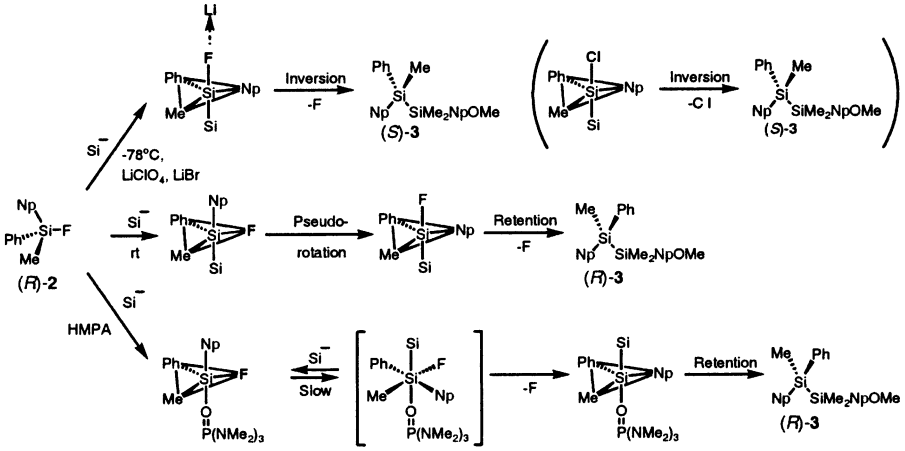

Figure 2. Plausible mechanism of the nucleophilic substitution reaction at the silicon atom.

at δ −21.97 as a singlet, which suggests rapid exchange of the counterion compared to the NMR time scale. The signal shifted slightly to upper field to δ −23.794 at −80 °C, but no coupling was observed, indicating still rapid exchange of counterions. Solvent-separated ion pairs seem to be the major ionic species in the system. The presence of HMPA and MTHF (2-methyltetrahydrofuran) did not have any significant effect on the ^{29}Si chemical shift and coupling state of **1**, supporting the solvent-separated nature of the methylphenylnaphthylsilyl anion nucleophile. The change of the coupling of silyllithium and lithium in phenyl-substituted silyllithium species was reported.[18] Electronic spectra also support such speculation by the fact that there is no change in λ_{max} of **1** in THF and THF−HMPA.[19] Thus, the origin of the dramatic stereochemical steering effect was caused by the subtle change of the ionic state by temperature, solvent, and common salt.

Such effects to steer the stereochemistry of reaction of (*R*)-$\mathbf{2_F}$ with **1** are reasonably understood as follows. At room temperature without a stereochemical steering agent, the nucleophilic substitution involving pseudorotation at the silicon atom occurs, resulting in retention of stereochemistry. When the temperature is lowered, direct apical attack of the silyl anion with more solvent-separated nature, supported by ^{29}Si NMR, becomes a major path. This mechanism seems to be intensified by the presence of the common salt lithium cation, which assists the polarization of the silicon−fluorine bond.[20] Corey et al. reported the slow scrambling of chiral silicon centers of 1,2-difluorodisilanes by chloride anion.[21] High stereosectivity assisted by the presence of lithium bromide or perchlorate may be an indirect support for our mechanism. HMPA, which is usually considered to increase the free ionic nature of the ion pairs, is considered in this case to coordinate to fluorosilane to form a pentacoordinate intermediate, as suggested by Corriu.[6] Nucleophilic attack by the silyl nucleophile forms a six-coordinate intermediate, which results in high retention of stereoselectivity through pseudorotation[22] with the departure of the fluorine anion from the apical position (Figure 2).

It became possible to synthesize both optically pure stereoisomers of chiral disilanes from a single antipode of fluorosilane enantiomer as the starting material and to open the way to control the stereoregularity of disilane-containing polymers.

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Supporting Information Available: Text, a table, and a figure giving a detailed description of experimental procedures, ^{29}Si NMR spectra, and electronic spectra of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) To the solution of **1** in the presence of additives such as HMPA, $LiClO_4$, and LiBr was added (*R*)-$\mathbf{2_F}$ in THF at the corresponding temperatures to give **3**.

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