Silicon-Stereogenic Aminomethoxysilanes

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Stereoselective Synthesis of Silicon-Stereogenic Aminomethoxysilanes: Easy Access to Highly Enantiomerically Enriched Siloxanes**

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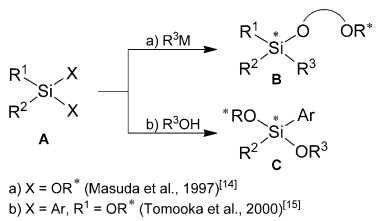
Abstract: *A route towards the synthesis of N,O-functionalized silicon-stereogenic organosilanes with excellent optical purities has been developed. Investigations into the stereoconvergence and configurational stability of an aminomethoxysilane suggest a kinetically controlled multistep substitution mechanism. Selective exchange of the Si-N bond by a second Si-O bond builds the basis for the controlled formation of chiral siloxane units with different oxygen-containing functional groups. Subsequent reactions of the chiral aminomethoxysilanes with hydroxy groups support a general inversion mechanism at the asymmetrically substituted silicon atom of N,O-functionalized organosilanes.*

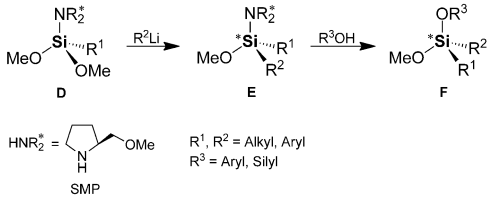


Scheme 1. Previously known substrate-controlled diastereoselective substitution reactions (a, b) for the construction of asymmetrically substituted silicon centers.

Over the past few years, some impressive preparative developments have revealed the high potential of organosilicon reagents for modern synthetic chemistry.[1,2] Despite the great importance of these substances, also shown on some recent examples in protecting group chemistry,[3,4] novel siloxane-based materials,[5] as well as in medicinal chemistry,[6] efficient synthetic access to silicon-stereogenic compounds is still very limited.[7] In contrast to carbon chemistry, where a large repertoire of asymmetric methods and prochiral double bond systems is available, access to silicon-stereogenic compounds generally depends on desymmetrization of tetracoordinate substrates.[7–20] However, owing to the different electronic structure of organosilicon compounds compared with their lighter homologues, nucleophilic substitution reactions can also be used for the construction of asymmetrically substituted silicon centers.[14–16a] To the best of our knowledge, only two asymmetric substitution reactions which proceed under substrate control[21] of the diastereoselectivity are hitherto known from the literature (Scheme 1).

The first of these kinds of reactions was established by Masuda and co-workers starting from C_2-symmetric cyclic alkoxysilanes,[14] which was further developed by Tomooka and co-workers into an enantioselective variant.[16] The second method is based on a diastereomeric desymmetrization of arylsilanes[15] and gives convenient access to functionalized silanols (Scheme 1). However, there is still a lack of synthetic routes leading to molecules with both a stereogenic silicon center and different reactive silicon-element bonds suitable for further transformations, and the known examples rarely proceed with high stereochemical control.[10,15,22]

We recently reported on a one-step conversion of Si-OMe groups in methoxysilanes to Si-NR_2 functions, which led us to mixed N,O-functionalized silanes.[23] Inspired by our achievements in the stereoselective α-deprotonation of organosilanes by means of the chiral coordinating auxiliary (*S*)-2-(methoxymethyl)pyrrolidine (SMP),[24] we wondered if this amine also served as a chiral directing group in the course of a substitution reaction at a silicon center. Herein, we present a substrate-controlled and highly diastereoselective access to silicon-stereogenic nitrogen-oxygen-functionalized organosilanes (**E**, Scheme 2) in only two steps starting from commercially available compounds. Using the different reactivity of Si-N and Si-O bonds, the precursors **E** are predestined for introducing chiral information into siloxane-based materials in a well-directed manner. A subsequent substitution of the chiral amine group[25] by hydroxy functions should then pave the way to highly enantiomerically enriched and diversely patterned silicon-stereogenic siloxane building blocks (**F**, Scheme 2).



Scheme 2. Silicon-stereogenic aminomethoxysilanes (**E**) as diverse building blocks for chiral siloxane-based compounds (**F**).

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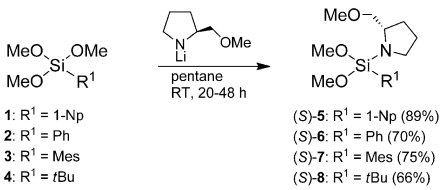


1: R^1 = 1-Np
2: R^1 = Ph
3: R^1 = Mes
4: R^1 = *t*Bu

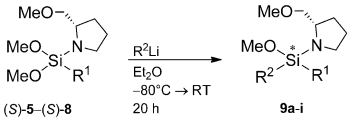
(*S*)-**5**: R^1 = 1-Np (89%)
(*S*)-**6**: R^1 = Ph (70%)
(*S*)-**7**: R^1 = Mes (75%)
(*S*)-**8**: R^1 = *t*Bu (66%)

Scheme 3. Synthesis of the chiral starting compounds (*S*)-**5**–(*S*)-**8**. Mes = mesityl, 1-Np = 1-naphthyl.

We chose the auxiliary-substituted dimethoxysilanes (*S*)-**5**–(*S*)-**8** as adequate starting compounds for the subsequent diastereoselective substitutions. Their synthesis was carried out in good yields by reacting the trimethoxysilanes **1**–**4** with the lithium amide of SMP (Scheme 3).

Afterwards, the aminodimethoxysilanes (*S*)-**5**–(*S*)-**8** were converted with alkyl- and aryllithium reagents at low temperatures under slow warming. This resulted in the highly chemoselective substitution of one methoxy group (Table 1). The chiral amine function was not only responsible for an effective stereochemical induction in the course of the diastereotopic differentiating nucleophilic attack. The silicon-bound auxiliary also turned out to be exceptionally inert towards a substitution by organolithium reagents.[26] The silicon-stereogenic silanes **9a**–**i** were obtained in very good to excellent optical purities without any additional step of optical enrichment. The best results (Table 1, entries 7 and 8) were achieved by reacting the mesitylsilane (*S*)-**7** with phenyllithium and 3,5-bis(trifluoromethyl)phenyllithium (**9f** and **9g**; d.r. ≥ 99:1).

Table 1: Diastereoselective synthesis of silicon-stereogenic N,O-functionalized organosilanes.



(*S*)-**5**–(*S*)-**8** **9a-i**

Entry	R^1	R^2	**9**	Yield [%][a]	d.r.[c]
1	1-Np	Ph	**9a**	93	88:12[d]
2	1-Np	3,5-$(CF_3)_2C_6H_3$	**9b**	75	92:8
3	1-Np	2-$(CH_2NMe_2)C_6H_4$	**9c**	77	91:9[e]
4	1-Np	*n*Bu	**9d**	86	91:9
5	1-Np	*i*Pr	**9e**	91	95:5
6	Ph	1-Np	**9a**	83	88:12
7	Mes	Ph	**9f**	81	≥99:1
8	Mes	3,5-$(CF_3)_2C_6H_3$	**9g**	84	99:1
9	Mes	*i*Pr	**9h**	94	91:9
10	*t*Bu	3,5-$(CF_3)_2C_6H_3$	**9i**	36[b]	96:4

[a] Yields of isolated products. [b] 50% conversion after 4 days. [c] The diastereomeric ratio was determined by means of ^{1}H NMR spectroscopy. [d] After recrystallization from pentane, **9a** was achieved in diastereomerically pure form (d.r. ≥ 99:1). [e] **9c** was obtained as the diastereomerically pure BH_3 adduct (d.r. ≥ 99:1).

The major diastereomer of the aminomethoxysilane **9a** (d.r. = 88:12) crystallized from pentane in the orthorhombic crystal system in the space group $P2_12_12_1$ and could thus be obtained in optically pure form (d.r. ≥ 99:1; Figure 1, top). The absolute configuration at the silicon center of **9a** was determined as (S_{Si}) by means of single-crystal X-ray diffractional analysis. Only by synthesizing the aminoborane **9c**·BH_3 we were also able to obtain optically pure single crystals of compound **9c** (d.r. = 91:9), which allowed the determination of the absolute configuration in the same way (Figure 1, bottom).[27]

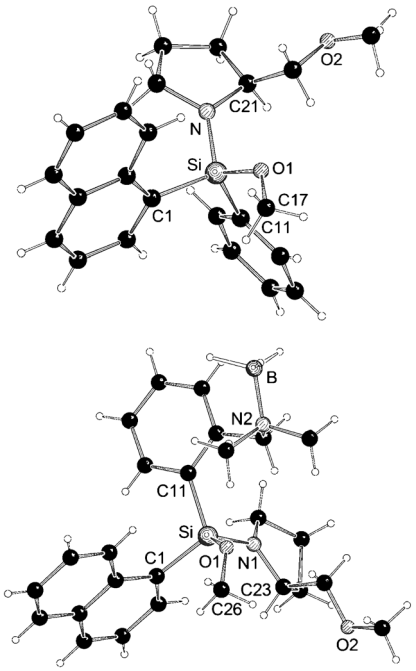
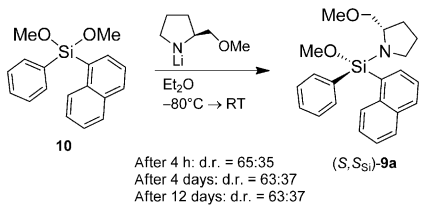


Figure 1. Molecular structures of compounds (S,S_{Si})-**9a** (top) and (S,S_{Si})-**9c**·BH_3 (bottom) in the crystal.[28]

Remarkably, (*S*)-**5** reacted with phenyllithium (Table 1, entry 1) and (*S*)-**6** with 1-naphthyllithium (Table 1, entry 6) in a stereoconvergent transformation to give the same (S,S_{Si})-configured major diastereomer of **9a** with exactly the same diastereomeric ratio of 88:12. It follows from this observation that both reactions cannot be ascribed to the same mechanism. The minor diastereomer (S,R_{Si})-**9a** is configuratively stable and could be isolated in optically enriched form after crystallization of (S,S_{Si})-**9a**. Thus, we can exclude an epimerization process, caused by the intramolecular methoxymethyl group, as an explanation for the occurrence of stereoconvergence.

In a final step we attempted to synthesize compound **9a** also by a reagent-controlled route to clarify the question whether lithium methoxide intervenes into the stereochemical course of the substitution reactions (Scheme 4). For this, the prochiral naphthylphenylsilane **10** was reacted with lithiated SMP at low temperatures. After warming, the mixture was stirred at room temperature for further 12 days. During this time we observed hardly any change of the diastereomeric ratio, which remained constant with a value of 63:37. This is a considerable decrease in selectivity in comparison with the ratio of 88:12 resulting from a substrate-induced diastereoselctivity (see Table 1). Hence, the stereochemical result of the substitutions cannot be attributed

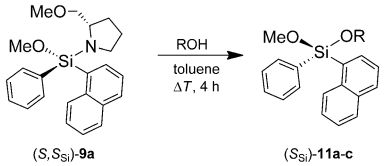


Scheme 4. Reagent control of the diastereoselectivity leading to a decrease in stereochemical induction.

to a thermodynamic epimerization process. Instead, all observations rather support a multistage substitution mechanism in which stable intermediates may play an important role. Therefore, the kinetics of an interconversion of higher coordinate species,[16a,29] for example long-lived pentacoordinate silicon intermediates, possibly has to be regarded in a detailed mechanistic consideration, too.

In order to use the novel silicon-stereogenic nitrogen-oxygen-functionalized silanes as building blocks for synthetic applications, such as modifications of surfaces,[30] transformations must comply with two preconditions: They must proceed chemoselectively and show a high degree of stereoselectivity. We therefore examined whether the chiral amine group can be removed without any loss of the stereochemical integrity at the silicon center to receive highly enantiomerically enriched functional alkoxysilanes. The conversion of (S,S_{Si})-**9a** (d.r. $\geq$ 99:1) with three hydroxy-substituted reagents in boiling toluene signified a complete substitution of the amine function after 4 h. Using HPLC on a chiral stationary phase, evidence was provided that these reactions on N,O-functionalized organosilanes were indeed highly stereoselective (Table 2).

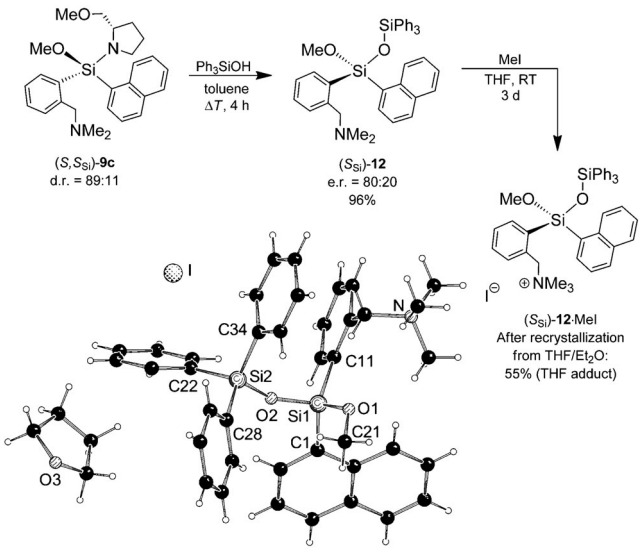
Table 2: Stereoselective synthesis of highly enantiomerically enriched alkoxy-functionalized siloxanes.



Entry	R	(S_{Si})-**11**	Yield [%][b]	e.r.[c]
1	$SiPh_3$	(S_{Si})-**11a**[a]	85	99:1[d]
2	1-Np	(S_{Si})-**11b**	92	95:5
3	Ph	(S_{Si})-**11c**	84	97:3

[a] The racemic compound (*rac*)-**11a** was obtained in the form of single crystals.[28] [b] Yields of isolated products. [c] The enantiomeric ratio was determined by means of HPLC on a chiral stationary phase. [d] After recrystallization from Et_2O/pentane (1:1); crude product: e.r. = 95:5.

To date, only little information is available concerning the stereochemistry of the Si-N function.[31] After conversion of the diastereomerically enriched silane (S,S_{Si})-**9c** (d.r = 89:11) with triphenylsilanol and subsequent N-methylation of **12** with iodomethane, we could determine the absolute configuration of the siloxane **12** with the help of single-crystal X-ray



Scheme 5. Elucidation of the stereochemical course of the N/O substitution (top) and molecular structure of compound (S_{Si})-**12**·MeI·THF in the crystal (bottom).[28]

crystallographic analysis of the quaternary ammonium salt (S_{Si})-**12**·MeI·THF. Thus, the stereochemical course of the N/O exchange on aminomethoxysilanes could be elucidated (Scheme 5). A substitution mechanism with inversion of the configuration at the stereogenic silicon center was recently also confirmed by Oestreich and Mewald on the basis of aminotriorganosilanes.[31d]

In summary, novel access is provided to N,O-functionalized silicon-stereogenic organosilanes with very good to excellent optical purities. Studies regarding the stereoconvergence and the configurational stability of the aminomethoxysilane **9a** supported a multistage substitution mechanism with kinetic control. The selective exchange of the Si-N bond for a second Si-O bond is the basis for the controlled synthesis of chiral siloxane units with different oxygen functionalities, which are also present in polymeric structures. Furthermore and as a result of the transformations of the chiral aminomethoxysilanes with hydroxy functions, an inversion mechanism at the asymmetrically substituted silicon atom could be supported in general.

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[25] For a review on removable directing groups in synthesis, see: G. Rousseau, B. Breit, *Angew. Chem.* **2011**, *123*, 2498 – 2543; *Angew. Chem. Int. Ed.* **2011**, *50*, 2450 – 2494.

[26] In this context, Wada and co-workers reported on a ring opening reaction on 1,3-oxazasilacyclopentanes with Grignard reagents that proceeds exclusively with a silicon-nitrogen bond cleavage (Ref. [22g]).

[27] The different relative configurations of (S,S_{Si})-**9a** and (S,S_{Si})-**9c**·BH_3 do not allow the assignment of absolute configurations at the silicon center of the silanes **9b** and **9d–i** by analogy.

[28] CCDC 957860 [(*rac*)-**11a**], CCDC 957861 [(S,S_{Si})-**9a**], CCDC 957862 [(S,S_{Si})-**9c**·BH_3], and CCDC 957863 [(S_{Si})-**12**·MeI·THF] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[29] For current work on rearrangement mechanisms of pentacoordinate intermediates, see: a) E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers, K. Lammertsma, *J. Am. Chem. Soc.* **2010**, *132*, 18127 – 18140; b) Highlight: C. Moberg, *Angew. Chem.* **2011**, *123*, 10473 – 10475; *Angew. Chem. Int. Ed.* **2011**, *50*, 10290 – 10292.

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Communications

Silicon-Stereogenic Aminomethoxysilanes

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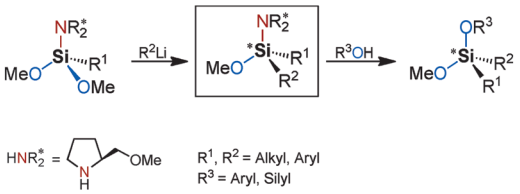
Stereoselective Synthesis of Silicon-Stereogenic Aminomethoxysilanes: Easy Access to Highly Enantiomerically Enriched Siloxanes



Broad access to silicon-stereogenic N,O-functionalized organosilanes in optically pure form is provided by a highly chemo- and diastereoselective substitution on aminodimethoxysilanes. The novel compounds could be further transformed stereoselectively with alcohols and a silanol and are predestined as building blocks for a controlled development of chiral siloxane units.

