

Synthesis of highly enantio-enriched allylsilanes via palladium-catalyzed intramolecular bis-silylation. Determination of the enantiomeric excesses through regio- and stereoselective hydroboration with 9-BBN

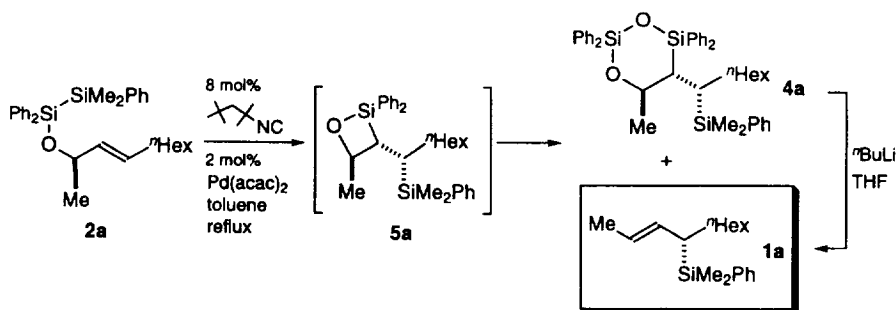
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Abstract: Highly enantio-enriched (*E*)-allylsilanes were synthesized by palladium-catalyzed intramolecular bis-silylation of chiral allyl alcohols and subsequent Peterson-type elimination with organolithium reagents. The enantiomeric excesses of the allylsilanes were determined after hydroboration with 9-BBN followed by oxidation, revealing remarkably high stereospecificity for the present synthesis. © 1997 Elsevier Science Ltd. All rights reserved.

Allylsilanes have been widely utilized as useful synthetic tools in organic synthesis.¹ The high stereo- and γ -regioselective allylations of electrophiles have found useful synthetic application.² Hence, efficient preparation of allylsilanes, particularly highly enantiomerically enriched allylsilanes, is desired from the viewpoint of stereoselective organic synthesis.³ We recently disclosed a new stereospecific access to enantio-enriched (*E*)-allylsilanes, which involved 1,3-chirality transfer from chiral allylic alcohols through palladium-catalyzed intramolecular bis-silylation and subsequent Peterson-type elimination.^{4,5} The new and simple synthetic methodology features the formation of the highly enantio-enriched allylsilanes with (*E*)-geometry. Herein, we describe the synthesis of highly enantio-enriched (*E*)-allylsilanes with various substituents on the silicon atoms. We also report a new e.e. determination via hydroboration, which revealed that the synthesis via the bis-silylation provided the enantio-enriched allylsilanes with almost complete stereospecificity.

The synthesis of allylsilane **1a** from disilanyl ether **2a** prepared from enantio-enriched (*R*)-(*E*)-3-decen-2-ol **3a** (99.7% ee) is depicted in Scheme 1.



Scheme 1.

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Table 1. Enantiomeric excesses of the alcohols derived from enantio-enriched allylsilane **1a**

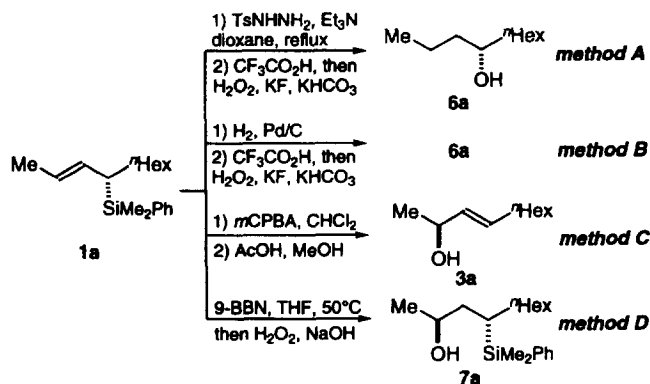
Entry	%E.e. of (<i>R</i>)-(<i>E</i>)-3-decen-2-ol ^a	Method	Alcohol	%Yield	%E.e.	%Specificity ^b
1	99.9	A	6a	49	97.3	97.4
2	99.7	B	6a	52	30.4	30.5
3	99.9	C	3a	50	96.8	96.9
4	99.7	D	7a	85	99.1	99.4
5	89.5	D	7a	83	89.1	99.6

^aEnantiomeric excesses of (*R*)-(*E*)-3-decen-2-ol used for the preparation of **1a**.

^bCalculated by (%ee of **3a**, **6a**, or **7a** obtained)/(%ee of (*R*)-(*E*)-3-decen-2-ol used).

The intramolecular bis-silylation promoted by a catalyst generated from Pd(acac)₂ and 1,1,3,3-tetramethylbutyl isocyanide gave a 1:1 mixture of the desired (*E*)-allylsilane **1a** and six-membered ring siloxane **4a** in high total yield, presumably through the highly stereoselective formation of four-membered ring **5a** followed by its thermal disproportionation. Subsequent treatment of the mixture with *n*-BuLi resulted in transformation to **1a** from **4a** via nucleophilic cleavage of the Si–O bonds of **4a** followed by Peterson-type *syn*-elimination.⁶ The sequence of the reactions exclusively provided (*E*)-allylsilane **1a** in high overall yield without contamination with the corresponding (*Z*)-isomers.

On the basis of the mechanism involving exclusive formation of the *trans* four-membered ring **5a**, the allylsilane **1a** was expected to have high enantiopurity via 1,3-chirality transfer. Because of difficulty in direct determination of the enantiomeric excess of **1a**, the enantioselectivity of **1a** has, however, been determined by a chiral HPLC analysis⁷ of alcohol **6a** (97.3% ee, Table 1, entry 1), which was obtained by method A, i.e. hydrogenation of the double bond by diimide⁸ followed by oxidation of the silicon–carbon bonds (Scheme 2).⁹

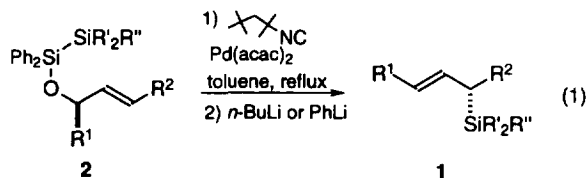


^aHPLC analyses with a chiral stationary phase column were carried out for *N*-(3,5-dinitrophenyl)carbamate derivatives of the alcohols.

Scheme 2. Transformations for the determination of the enantiomeric excess of allylsilane **1a**.^a

However, the slight but significant decrease in the enantiopurity, which might have occurred during transformation of **1a** to **6a**, prompted us to examine other transformations for e.e. determination (methods B–D). Surprisingly, low e.e. (30% ee) of the same alcohol **6a** was observed for method B (entry 2), in which hydrogenation was effected by a Pd/C catalyst under a hydrogen atmosphere. The decrease in e.e. may be attributed to the palladium-catalyzed isomerization of the carbon–carbon double bond, which results in the formation of racemic **6a** via achiral vinylsilane.^{10,11} A slight loss of the enantiopurity was also seen for method C, i.e. reaction of **1a** with *m*-chloroperbenzoic acid,

Table 2. Synthesis of enantio-enriched allylsilanes 1



Entry	2 (%e.e.)	R ¹	R ²	R ¹ RSi	1 (%yield) ^a	%E.e. ^b	%Specificity
1	(<i>R</i>)- 2a (99.7)	Me	ⁿ Hex	PhMe ₂ Si	(<i>S</i>)- 1a (90)	99.1 (97.3)	99.4
2	(<i>S</i>)- 2b (>99.0)	Ph	ⁿ Hex	PhMe ₂ Si	(<i>S</i>)- 1b (99)	98.7 (96.3)	99.7
3	(<i>S</i>)- 2c (99.8)	<i>c</i> -Hex	ⁿ Hex	PhMe ₂ Si	(<i>S</i>)- 1c (96)	99.0 (98.0)	99.3
4	(<i>R</i>)- 2d (98.2)	Me	Ph	PhMe ₂ Si	(<i>R</i>)- 1d (92)	98.1 (94.8)	99.9
5	(<i>R</i>)- 2e (99.6)	Me	ⁿ Hex	Me ₃ Si	(<i>S</i>)- 1e (81)	99.1 (95.0)	99.4
6	(<i>R</i>)- 2f (99.6)	Me	ⁿ Hex	<i>t</i> -BuMe ₂ Si	(<i>S</i>)- 1f (82)	99.4	99.8
7	(<i>R</i>)- 2g (99.6)	Me	ⁿ Hex	Et ₃ Si	(<i>S</i>)- 1g (94)	99.2 (96.2)	99.6
8	(<i>R</i>)- 2h (99.6)	Me	ⁿ Hex	<i>i</i> -Pr ₃ Si	(<i>S</i>)- 1h (62)	98.8	99.1

^aSatisfactory spectroscopic (¹H and ¹³C NMR) and elemental analyses were obtained on all compounds.

^bDetermined by method D. The values in parentheses are enantiomeric excesses determined by method A (for entries 1–4) or method C (for entries 5 and 7).

which provided (*E*)-3-decen-2-ol **3a** as the major product along with considerable formation of its (*Z*)-isomer (entry 3).¹² Finally, we found that alcohol **7a** prepared by method D presented the highest enantiomeric excess (entry 4). The reaction of **1a** with 9-BBN proceeded with excellent regio- and stereoselectivity to give **7a** with 99.1% ee.¹³ The observed stereospecificity as well as that of **1a** derived from **2a** with 89.5% ee (entry 5) apparently indicates the present synthesis provides allylsilane **1a** with >99% stereospecificity based on the e.e. of starting **2a**.

Method D was applied to determination of enantiomeric excesses of the allylsilanes **1b–d** prepared by the bis-silylation–elimination sequence (eq 1; Table 2, entries 2–4). In comparison with ee determined by method A,⁴ method D presented generally high enantiomeric excesses. Thus, the synthesis of allylsilanes is now found to proceed with nearly complete 1,3-transfer of the chirality of the starting allylic alcohols. Furthermore, enantiomerically enriched allylsilanes with various substituents on the silicon were successfully synthesized (entries 5–8). Trimethylsilyl, *t*-butyldimethylsilyl, and triethylsilyl-substituted allylsilanes **1e–g** were obtained in good yield, and triisopropylsilyl substituted **1h** in moderate yield with high stereoselectivity. In addition to the high stereospecificity during the transformations, method D has the advantage of generality over method A, which can not be applied to the allylsilanes without phenyl groups on the silicon atom, and method C, which fails to give the corresponding allyl alcohols for the allylsilanes with bulky substituents at the silicon.

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