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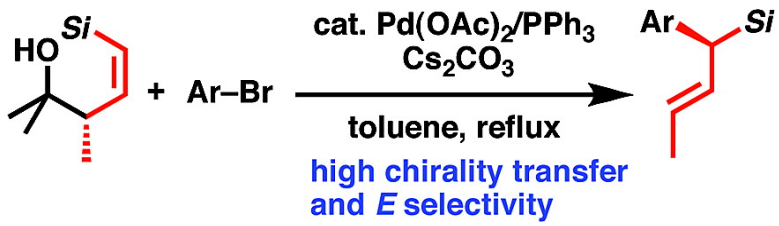
J. Am. Chem. Soc., **2007**, 129 (42), 12650-12651• DOI: 10.1021/ja0755111 • Publication Date (Web): 29 September 2007



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Synthesis of (Arylalkenyl)silanes by Palladium-Catalyzed Regiospecific and Stereoselective Allyl Transfer from Silyl-Substituted Homoallyl Alcohols to Aryl Halides

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We have reported palladium-catalyzed allyl transfer from homoallyl alcohols to aryl halides through carbon−carbon bond cleavage.[1,2] The allyl transfer proceeds in a regio- and stereospecific manner, reflecting the structure of homoallyl alcohols used. Here we report regiospecific and stereoselective allyl transfer reactions for the synthesis of aryl-substituted (*E*)-1- or 2-alkenylsilanes from silyl-substituted homoallyl alcohols. Alkenylsilanes are indispensable reagents in modern organic synthesis.[3] Developing new methods for highly selective synthesis of vinyl- and allylsilanes, including optically active ones, is thus still quite important.[4]

Treatment of 1-bromonaphthalene (**2a**) with **1a**, containing an allylic silane moiety, in the presence of K_2CO_3 under $Pd(OAc)_2$/$P(^cHex)_3$ catalysis provided vinylsilane **3a′** in good yield with moderate *E* selectivity (Scheme 1). The reaction with **1b** having a bulkier ^{t}BuMe$_2$Si group proceeded to yield **3a** with excellent selectivity of *E*/*Z* = 95:5. The improvement of the stereoselectivity would originate from the stronger preference of the ^{t}BuMe$_2$Si group being at the pseudoequatorial position in the transition state of the retroallylation. It is worth noting that only one silyl group at the allylic position can be a decisive factor in determining the stereoselectivity, whereas tedious preparation of diastereomerically pure and differently 1,1,2-trisubstituted homoallyl alcohols was essential to attain high *E* selectivity in the previous report.[1]

The scope of aryl halides is wide enough to afford a variety of (*E*)-3-aryl-1-propenylsilanes in excellent yields (Table 1).[5,6] Sterically demanding (entry 1), electron-deficient (entries 2−5), and electron-rich (entry 6) aryl bromides participated in the reaction. The use of $P(^cHex)_3$ as a ligand allowed us to use aryl chlorides as substrates (entries 7 and 8).

We then focused on homoallyl alcohol **4a**, containing a (*Z*)-1-alkenylsilane moiety. The reactions of **4a** with aryl bromides in the presence of Cs_2CO_3 under $Pd(OAc)_2$/PAr_3 catalysis provided 1-aryl-2-propenylsilanes in high yields (Table 2,[5] entries 1−6). $P(^c$Hex$)Ph_2$ was exceptionally essential to attain high yield when electron-rich aryl bromide **2g** was used (entry 7).

Interestingly, silylated homoallyl alcohols **4b**−**d** having one methyl group at the allylic position were converted to (*E*)-1-aryl-2-butenylsilanes stereoselectively (entries 8−16). Fortunately the allyl transfer reaction to 1-bromonaphthalene **2a** always provided the *E* isomers exclusively (entries 8, 10, and 15). The exclusive formation of the *E* isomers would result from the steric factor of the 1-naphthyl group on palladium in the transition state of the retroallylation. The Me_3Si, ^{t}BuMe$_2$Si, and Me_2PhSi groups were compatible under the reaction conditions. The bulkiness of the silyl groups had little influence on stereoselectivity (entries 9 vs 11 and 13 vs 16). On the other hand, when the larger substituent, ^{n}Bu, was introduced at the allylic position, the *E* selectivity of the reaction was excellent (entry 13 vs 17). The *E* selective formation

Scheme 1

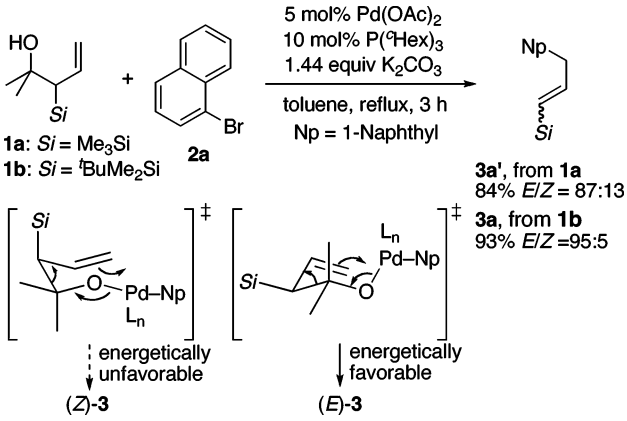
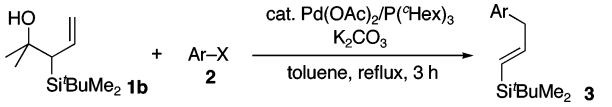


Table 1. Synthesis of (*E*)-3-Aryl-1-propenylsilanes **3**[a]



entry	Ar–X	2	3	yield (%)	*E*/*Z*
1	2,6-$Me_2C_6H_3$Br	**2b**	**3b**	92	93:7
2	4-$CF_3C_6H_4$Br	**2c**	**3c**	75	96:4
3	4-$CH_3COC_6H_4$Br	**2d**	**3d**	89	95:5
4	4-$HCOC_6H_4$Br	**2e**	**3e**	87	96:4
5	4-$EtOCOC_6H_4$Br	**2f**	**3f**	97	95:5
6	4-$CH_3OC_6H_4$Br	**2g**	**3g**	92	94:6
7	4-$EtOCOC_6H_4$Cl	**2f-Cl**	**3f**	89	97:3
8	4-$CH_3OC_6H_4$Cl	**2g-Cl**	**3g**	92	95:5

[a] The reaction conditions are the same as shown in Scheme 1.

can be explained in a fashion similar to that in Scheme 1 (Scheme 2).

The reactions of optically active (*S*)-**4d** (96% ee) with 2-substituted aryl bromides resulted in excellent chirality transfer to (*E*)-1-aryl-2-butenylsilanes **5** (Table 3[5]). The enantiomeric excesses of the products were indirectly determined after converting allylsilanes **5** to the corresponding 1-aryl-1-butanols **6**. The conversion consisted of hydrogenation with hydrazine, acid-mediated conversion of the phenyl group on silicon to a trifluoroacetoxy group, and Tamao−Fleming oxidation with retention of configuration of the chiral carbon.[7]

The excellent chirality transfer is rationalized as follows (Scheme 3). Comparing **7a** and **7b**, two possible chairlike transition states of the retroallylation step, **7a** would be the more preferable because the methyl group at the allylic position occupies the pseudoequatorial position. The palladium center would approach the *Re* face of the alkene moiety, which leads to the formation of **8a** having

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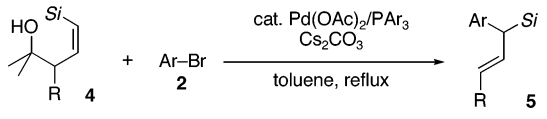
Table 2. Synthesis of 1-Aryl-2-alkenylsilanes



entry	2	Si	R	4	conditions[a]	5	yield (%)[b]
1	**2a**	^{t}BuMe$_2$Si	H	**4a**	A[c]	**5aa**	88
2	**2b**			**4a**	A	**5ba**	66
3	**2c**			**4a**	A	**5ca**	81
4	**2d**			**4a**	A[c,d]	**5da**	61
5	**2e**			**4a**	A	**5ea**	68
6	**2f**			**4a**	A[d]	**5fa**	88
7	**2g**			**4a**	A[e]	**5ga**	74
8	**2a**	^{t}BuMe$_2$Si	Me	**4b**	B	**5ab**	92 (100:0)
9	**2d**			**4b**	B	**5db**	83 (89:11)
10	**2a**	Me$_3$Si	Me	**4c**	B	**5ac**	92 (100:0)
11	**2d**			**4c**	B	**5dc**	68 (95:5)
12	**2e**			**4c**	B	**5ec**	46 (96:4)
13	**2f**			**4c**	B	**5fc**	91 (96:4)
14	**2g**			**4c**	B[f]	**5gc**	46 (100:0)
15	**2a**	Me$_2$PhSi	Me	**4d**	B	**5ad**	93 (100:0)
16	**2f**			**4d**	C	**5fd**	84 (94:6)
17	**2f**	Me$_3$Si	^{n}Bu	**4e**	C[g]	**5fe**	92 (100:0)

[a] Conditions A: 5 mol % Pd(OAc)$_2$, 20 mol % P(*p*-tol)$_3$, 1.44 equiv Cs$_2$CO$_3$, reflux, 4−15 h. Conditions B: 5 mol % Pd(OAc)$_2$, 20 mol % PPh$_3$, 1.20 equiv Cs$_2$CO$_3$, reflux, 4−7 h. Conditions C: 2.5 mol % Pd(OAc)$_2$, 10 mol % PPh$_3$, 1.20 equiv Cs$_2$CO$_3$, reflux, 45 min. [b] *E*/*Z* Ratios of **5** are in parentheses. [c] PPh$_3$ was used instead of P(*p*-tol)$_3$. [d] Reaction run using 2.5 mol % of Pd(OAc)$_2$ and 10 mol % of the ligand. [e] P(^{c}Hex)Ph$_2$ (10 mol %) was used. [f] P(^{t}Bu)$_3$ (5 mol %) was used instead. [g] The reaction time was 5 h.

Scheme 2

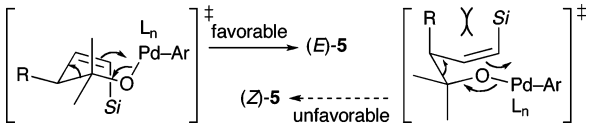
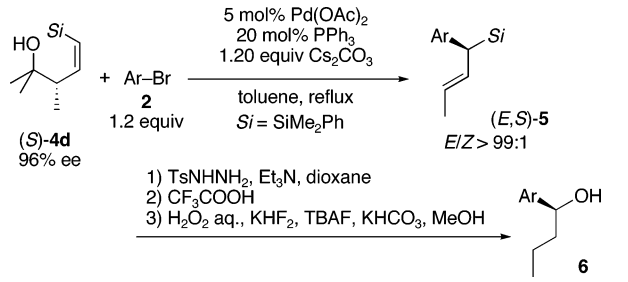
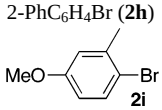
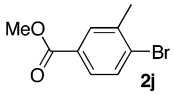


Table 3. Chirality Transfer from Optically Active (*S*)-**4d** to (*E*)-1-Aryl-2-butenylsilanes

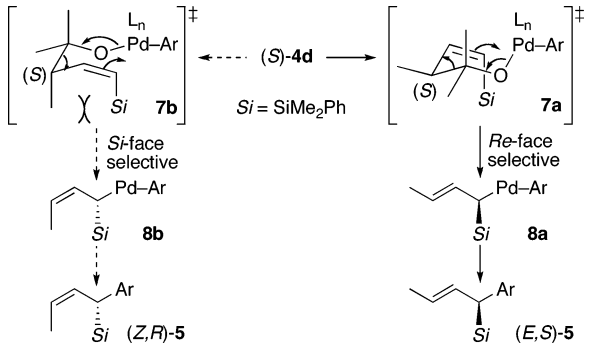


entry	2	yield of **5** (%)	ee of **6** (%)
1	**2a**	**5ad**, 92	**6ad**, 96
2	**2b**	**5bd**, 97	**6bd**, 96
3	2-PhC$_6$H$_4$Br (**2h**)	**5hd**, 94	**6hd**, 94
4	 **2i**	**5id**, 90	**6id**, 96
5	 **2j**	**5jd**, 87	**6jd**, 95

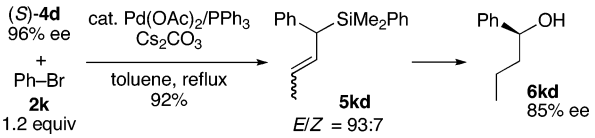
E,*R* configuration. Immediate reductive elimination from **8a** without loss of the chirality provides (*E*,*S*)-**5**.

The reaction of optically active (*S*)-**4d** (96% ee) with bromobenzene provided a mixture of (*E*)- and (*Z*)-**5kd** in a ratio of 93:7 (Scheme 4). Since we could not determine the enantiomeric excess

Scheme 3



Scheme 4



of each isomer, the mixture was converted to 1-phenylbutanol according to the procedure described in Table 3. The enantiomeric excess of **6kd** was 85% ee. The ee value of **6kd** strongly supports that complete chirality transfer to both (*E*)- and (*Z*)-**5kd** took place according to the mechanism shown in Scheme 3.

The present method provides a new access to (arylalkenyl)silanes, including optically pure allylic silanes, from silyl-substituted homoallyl alcohol and aryl halide.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research from MEXT and JSPS. S.H. and K.H. acknowledge JSPS for financial support. This paper is dedicated to the memory of the late Professor Yoshihiko Ito.

Supporting Information Available: Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) The regioselectivity of each reaction was greater than 99:1. One exception is the reaction in entry 6, Table 1, wherein the regioselectivity was 98:2. We assume that the bulky silyl groups would accelerate the reductive elimination steps and that the conceivable isomerization of the σ-allyl-(aryl)palladium intermediates scarcely took place.

(6) When allylsilane having an aryl or an isopropoxy group on the silicon was employed, decomposition of the allylsilane was observed and no coupling products were obtained.

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JA0755111