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Communication

Highly regio- and stereoselective synthesis of allylsilanes via palladium-catalyzed reductive metallation of allylic phosphates with a SmI_2–HMPA system. Stereochemical aspect of the tandem electron transfer process in allylic systems[†]

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Summary — The new reduction system, Pd(0)–SmI_2-HMPA, was found to be highly effective for the facile generation of allylsamarium species from the corresponding allylic phosphates or acetates via a sequential oxidative addition-electron transfer reaction, which enables a convenient regio- and stereoselective synthesis of allylsilanes. The reaction can be conducted under either kinetically or thermodynamically controlled conditions.

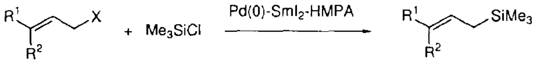
Pd(0)–SmI_2–HMPA system / allylic phosphate / stereoselective reductive silylation / allylsamarium / allylsilane

Résumé — Synthèses régio- et stéréosélectives d'allylsilanes via une métallation réductive de phosphates d'allyle catalysée par le palladium. Le nouveau système réducteur Pd(0)–SmI_2–HMPT s'est avéré efficace pour une génération facile d'espèces allylsamarium à partir des acétates ou phosphates allyliques, via une réaction séquentielle addition–transfert d'électrons qui conduit aisément à la synthèse régio- et stéréosélective d'allylsilanes. La réaction peut être conduite soit sous contrôle cinétique, soit sous contrôle thermodynamique.

Pd(0)–SmI_2–HMPT / phosphate allylique / silylation / réduction stéréosélective

Introduction

In recent years, low-valent lanthanide reagents have found a prominent role in organic synthesis [1]. Especially, samarium(II) iodide has been most widely used [2] since Kagan and co-workers first demonstrated its usefulness as an electron transfer agent [3]. Also in our laboratory an intensive study on the utilization of divalent samarium species in organic synthesis has been pursued. In 1986, we reported a unique polarity inversion of cationic π-allylpalladium complexes into allylic anion species by the use of SmI_2 [4, 5]. By using this method, direct reductive coupling reactions of allylic acetates with various electrophiles have been successfully performed. However, an attempt to prepare allylic silanes by the reductive silylation of allylic acetates under similar conditions failed. Meanwhile we found, for the first time, a remarkable effect of hexamethylphosphoric triamide (HMPA) on a variety of SmI_2-promoted electron transfer reactions [6], and quite recently, by the combined use of a palladium catalyst and HMPA, we succeeded in the above transformation in a highly regio- and stereoselective manner under extremely mild conditions [7] (eq 1).



(1)

X = OP(O)(OEt)$_2$, OAc

Allylsilanes are well-accepted important synthetic intermediates which serve as an allylic anion equivalent with a built-in stereochemical information since they can deliver allylic moieties in a highly stereospecific manner [8]. Therefore, a number of methods have so far been devised for the preparation of allylic silanes

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[†] Dedicated to Professor Henri B Kagan

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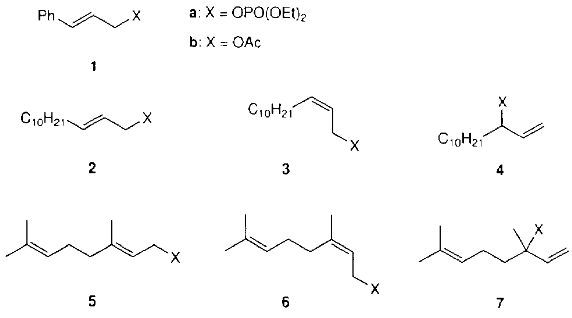
Table I. Regio- and stereoselective synthesis of allylsilanes[a].

Entry	*Substrate*	*Conditions*		*Method*[b]	*Product*		
		Temperature (°C)	*Time*		*Yield (%)*[c]	*Regioselectivity*[d]	*E/Z*[d]
1	**1a**	25[e]	1 h	A	90	>99:1	>99:1
2	**1b**	25[f]	30 min	A	84	–	–
3	**2a**	25	<1 min	A	89	>99:1	99:1
4	**2b**	25[f]	8 h	A	43	>99:1	>99:1
5	**2b**	25	50 min	A	80	>99:1	99:1
6	**3a**	25	<1 min	A	77	98:2	88:12
7	**3a**	−78	4 h	B	69	95:5	3:97
8	**4a**	25	<3 min	A	96	>99:1	88:12
9	**4a**	25[g]	8 min	A	92	>99:1	95:5
10	**4a**	−78	1 h	A	81	96:4	28:72
11	**5a**	25	1 min	A	75	99:1	98:2
12	**5a**[h]	25[f]	1 h	A	98	>99:1	>99:1
13	**5b**	25[f]	24 h	A	76	>99:1	>99:1
14	**6a**	25[f]	1 h	A	84	>99:1	<1:99
15	**6b**	25	1 h	A	59	>99:1	2:98
16	**6b**	25[f]	9.5 h	A	65	>99:1	<1:99
17	**7b**	25[f]	4 h	A	81	>99:1	74:26

[a] The reaction was carried out under argon by using substrate (0.2 mmol), TMSCl (2 mmol), $Pd(PPh_3)_4$ (5 mol%), SmI_2–THF (0.1 M, 5 mL, 0.5 mmol), and HMPA (2 mmol) unless stated otherwise. [b] Method A: the substrate was added lastly to a mixture of others. Method B: the palladium catalyst was added as the last. [c] Isolated yield of allylsilanes. [d] Determined by capillary GC-CIMS (isobutane) analysis. [e] Without $Pd(PPh_3)_4$ and HMPA. [f] Without $Pd(PPh_3)_4$. [g] Two equiv of TMSCl (0.4 mmol) was used. [h] The reaction was carried out in 2 mmol scale.



Compounds **1**–**7**

[8, 9]. Among them, the trapping of allylic organometallic compounds with silyl reagents seems to be the most straightforward way. However, regio- and stereocontrolled synthesis of allylic silanes by this method is not an easy task mainly because of the stereorandomization of allylic metals [10]. One good solution for this problem has been proposed by Yamamoto et al. They succeeded in the generation of allylic metals with high stereochemical purity by the direct insertion of alkali or alkaline–earth metals into allylic carbon–halogen bonds at very low temperature (−95 °C) [10a]. We were interested in the possibility of allylsamarium species [11, 12] for this purpose, since with our system allylsamarium can easily be generated under mild conditions from stable and easily obtainable allylic phosphates or acetates instead of allylic halides. Another advantage is that, based on the amount of palladium catalyst, a very low concentration of the reactive intermediates, allylic radical and anion species, can be maintained throughout the reaction in the presence of electrophiles, thus minimizing the unfavorable side reactions such as Wurtz-type reductive homo-coupling of substrates.

Thus, reductive silylation of various types of allylic phosphates and acetates (**1**–**7**) was carried out by using a Pd(0)–SmI_2–HMPA system in the presence of excess chlorotrimethylsilane. The results are summarized in table I.

The following features became clear from the above experiments. (1) The reaction proceeds rapidly especially when allylic phosphates are employed as substrates and the corresponding allylsilanes are synthesized in good to excellent yields. (2) Whereas reactive substrates such as cinnamyl phosphate or acetate do not always need palladium as a catalyst, HMPA is indispensable for the reaction of most substrates. (3) The addition of a small amount of $Pd(PPh_3)_4$ highly accelerates the reaction, which strongly suggests that the oxidative addition of palladium(0) takes place prior to the electron transfer reaction. (4) Silylation occurs regioselectively at the least sterically hindered terminus to give the one corresponding regioisomer almost exclusively.

Some other interesting features regarding the stereoselectivity of the double bond were also revealed. Allylic phosphates and acetates with disubstituted *E* olefins (**1** and **2**) exclusively afforded the allylsilanes with *E* configuration (entries 1–5), indicating that there is no isomerization of the double bonds during the reaction. A highly selective formation of *Z* allylsilane was also accomplished by conducting the reaction of *Z* allylic phosphate (**3a**) at −78 °C (entry 7). On the other hand, the reaction at room temperature gave rise to the formation of *E* allylsilane as the major product (entry 6). Surprisingly, however, the original stereochemistries of the double bonds of allylic phosphates with trisubstituted olefins (**5** and **6**) are completely retained even when the reaction was carried out at room temperature. No isomerization was observed especially when the reaction was performed without a palladium catalyst (entries 12–14 and 16). In the case of allylic esters bearing monosubstituted olefins (**4a** and **7b**), in which the terminal double bonds migrate during the reaction, high *E*-selectivity can be realized as far as the reactions are performed at room temperature (entries 8, 9, and 17). Interestingly, when the amount of chlorotrimethylsilane was reduced to two equivalents, *E*-selectivity increased (cf entries 8 vs 9) [13]. On the other hand, the reductive silylation of **4a** at −78 °C afforded the corresponding *Z* allylsilane as the major product (E/Z = 28:72) (entry 10). Although stereochemistry of the double bond of **3a** was almost retained in the product (E/Z = 3:97) in a low temperature reaction (entry 7), when the allylsamariun intermediate derived from **3a** was allowed to stand at −78 °C for 4.5 h and then quenched with chlorotrimethylsilane, the corresponding allylsilane was obtained in a low yield with decreased *Z*-selectivity (E/Z = 16:84). Since the palladium-catalyzed isomerization of **3a** turned out to be slow under the conditions [14], all these results indicate that the double-bond isomerization occurs mainly at the stage of allylic anion [15] and, different from allylic alkali or alkaline–earth metals, allylsamarium intermediate with *E*-configuration is thermodynamically highly favored [16].

Such an interesting stereochemical dependence of the double bond on the reaction temperature prompted us to examine the reaction of **2a**, **3a**, and **4a** in detail. Figure 1 shows the relationship between the E/Z ratio of the allylsilanes produced and the temperature at which the reaction was carried out.

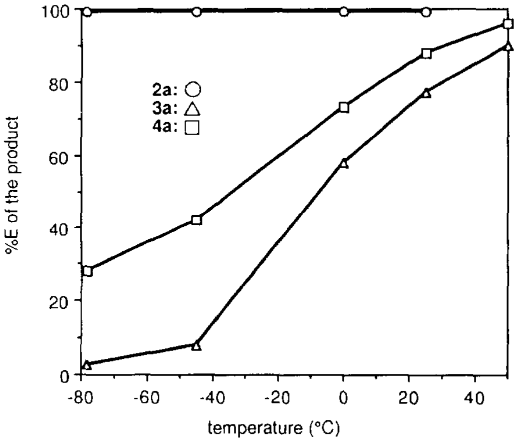
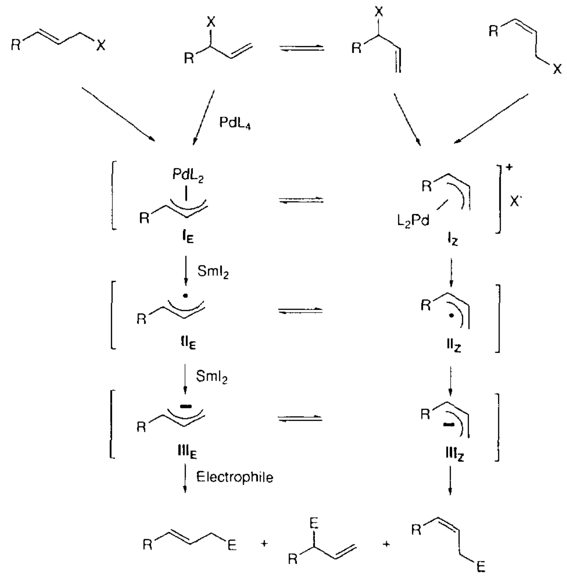


Fig 1. The E/Z ratio observed in the reductive silylation of **2a**, **3a**, **4a** at variable temperatures.

As expected, the reaction of **2a** proceeded with perfect retention of the double bond configuration regardless of the reaction temperature. On the other hand, as the reaction temperature was raised, the ratio of the thermodynamically more stable *E* allylsilane increased in the cases of **3a** and **4a**. Since the reaction of **3a** at −78 °C almost retained its double bond configuration in the product, one may expect that little isomerization occurs at this temperature throughout the reaction which would involve (1) oxidative addition of palladium(0) to allylic phosphate, (2) one-electron reduction of the corresponding π-allylpalladium (**I**) by SmI_2 to yield allylic radical (**II**), (3) second electron transfer giving allylsamarium species (**III**), and (4) silylation (scheme 1). Therefore, the predominant formation of *Z* allylsilane realized in the reaction of **4a** at −78 °C strongly suggests that the first oxidative addition of palladium(0) leading to *Z* π-allylpalladium ($\mathbf{I_Z}$) is kinetically more favored than the formation of the other isomer ($\mathbf{I_E}$).



Scheme 1

It is interesting to note that the competition reaction of **2a** and **3a**, which was carried out at −78 °C by using half-equivalent of SmI_2 to a 1:1 mixture of the substrates, yielded the corresponding *Z* allylsilane as the major product (E/Z = 24:76), indicating that the *Z* allylic phosphate (**3a**) is more reactive than the corresponding *E*-isomer (**2a**) under the same conditions. The role of HMPA is not clearly verified, but the fact that the addition of HMPA retards the oxidative addition of palladium(0) to allylic phosphates indicates that it comes into play in the following steps, namely, promotion of the samarium-mediated electron transfer process, stabilization of the resulting allylsamarium intermediate, and promotion of the C–Si bond-forming reaction.

In conclusion, we have developed a new and convenient method for securing *either cis or trans allylsilanes with high stereocontrol.*

Experimental section

Typical procedure: reductive silylation of (trans-2-tridecenyl) diethyl phosphate **2a**

To a mixture of SmI_2 (0.1 M solution in THF, 5 mL, 0.5 mmol), HMPA (0.35 mL, 2 mmol) and chlorotrimethylsilane (0.25 mL, 2 mmol) was added a solution of $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol, 5 mol%) in THF (0.45 mL) and **2a**

(66.8 mg, 67.6 μL, 0.2 mmol) successively. After stirring for 1 min at room temperature, silica gel (ca 1 g) and hexane (5 mL) was added. The whole mixture was passed through a short silica gel column and eluted with ether. The eluate was concentrated in vacuo and purified by column chromatography on silica gel (hexane) to give (*trans*-2-tridecenyl)trimethylsilane (45.3 mg, 89%, E/Z = 99:1).

Acknowledgments

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