Pergamon

Tetrahedron Letters 40 (1999) 9255–9257

TETRAHEDRON
LETTERS

Synthesis of alkenylsilanes via palladium(0)-catalyzed silylation of alkenyl iodides with hydrosilane

Miki Murata, Shinji Watanabe and Yuzuru Masuda *

Department of Materials Science, Kitami Institute of Technology, Kitami 090-8507, Japan

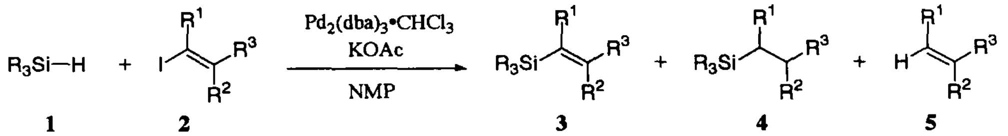
Received 24 August 1999; accepted 13 September 1999

Abstract

Various alkenyl iodides were silylated with hydrosilanes in the presence of KOAc and a catalytic amount of $Pd_2(dba)_3 \cdot CHCl_3$ to afford the corresponding regio- and stereodefined (*E*)-alkenylsilanes in high yields.

Keywords: hydrosilane; alkenylsilane; alkenyl halides; palladium catalyst; coupling reactions.

Alkenylsilanes have been shown to be versatile intermediates in organic synthesis.[1] Various methods are available for their preparation.[2] Most of these methods utilize alkynes, alkenes, or alkenyl halides as starting materials. Among other methods, the catalytic cross-coupling reaction of organic halides using disilanes as a silicon source has proven to be a versatile method for synthesizing regio- and stereodefined organosilanes.[3] Recently, we have developed the atom economical metalations of aryl halides utilizing trialkoxysilanes[4] or dialkoxyboranes[5] as metalating reagents in the presence of palladium(0) complexes. During the course of our studies, we found a new and available synthetic route to alkenylsilanes. We describe here a palladium(0)-catalyzed selective silylation of alkenyl iodides **2** with hydrosilanes **1** to provide the corresponding alkenylsilanes **3** (Eq. 1).



(1)

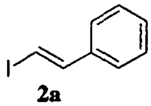
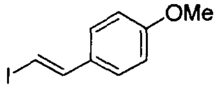
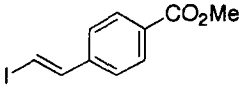
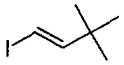
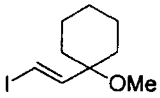
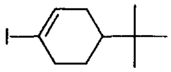
The representative results examined are listed in Table 1. At room temperature in *N*-methylpyrrolidinone (NMP), the reaction of (*E*)-β-iodostyrene **2a** with 1.5 equiv. of triethoxysilane $HSi(OEt)_3$ **1a** in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ (dba=dibenzylideneacetone) and potassium acetate gave the corresponding (*E*)-β-silylstyrene **3a** (79% GLC yield based on **2a**) together with a small amount of 2-phenylethylsilane **4a** (2%) and styrene **5a** (6%) (entry 1). The present silylation proceeded

---

* Corresponding author. E-mail: masuda-yuzuru/mtrl@king.cc.kitami-it.ac.jp

0040-4039/99/$ - see front matter
PII: S0040-4039(99)01793-1

Table 1
Silylation of representative **2** with **1** (Eq. 1)[a]

entry	hydrosilane 1	alkenyl halide 2	yield (%)[b]	ratio (%)[c]	
				3	4
1	(EtO)$_3$Si—H **1a**	 **2a**	81[d]	97	3
2	(MeO)$_2$MeSi—H **1b**	**2a**	65	93	7
3	Et$_3$Si—H **1c**	**2a**	70	87	13
4	Ph$_2$MeSi—H **1d**	**2a**	83	87	13
5	Ph$_3$Si—H **1f**	**2a**	77	90	10
6	**1a**	 **2b**	83	84	16
7	**1a**	 **2c**	72	>99	
8	**1a**	 **2d**	74	>99	
9	**1a**	 **2e**	69	>99	
10	**1a**	 **2f**	60	>99	

[a] All reactions were conducted in NMP (4 mL) at room temerature for 2 h using **1** (1.5 mmol) and **2** (1.0 mmol) in the presence of Pd$_2$(dba)$_3$•CHCl$_3$ (0.015 mmol) and KOAc (3 mmol). [b] Isolated yields of a mixture of **3** and **4** were based on **2**. [c] Determined by GLC and ^{1}H NMR analysis of isolated products. [d] GLC yield.

stereoselectively with retention of the carbon–carbon double bond in the alkenyl iodides, i.e. neither α- nor (Z)-isomer were produced. The use of amide solvents, such as NMP and DMF, were essential for this silylation. No reaction occurred in dioxane or toluene. The base also appeared to play an important role in swaying the yields and the selectivity. Although the complete control of selectivity was unsuccessful, KOAc was recognized to be a most effective base for the selective formation of alkenylsilanes **3**. In this connection, the use of tertiary amine, ^{i}Pr$_2$NEt, which was employed as a base for the silylation of aryl iodides with **1a**, resulted in the low yield (**3a**, 22%) accompanying the contamination with reduced by-products (**4a**, 30%; **5a**, 8%).[6]

It is well-known that the reactivity of hydrosilane is strongly dependent on substituents on the silicon atom.[7,8] However, the differences in yields and in selectivity from the nature of hydrosilanes were not very significant in the present reaction (entries 1–5). It is interesting to note that the silylation with trialkylsilanes (**1c**–**f**) proceeded selectively in preventing the formation of **5**, whereas commonly such hydrosilanes have been applied for the palladium-catalyzed reduction of organic halides (entries 3–5).[7,9]

Thus, a variety of (*E*)-alkenyl iodides **2** were silylated efficiently with $HSi(OEt)_3$ **1a** to afford the desired (*E*)-alkenylsilanes **3** in high isolated yields (entries 6–10) in which **2**, containing either electron-rich or electron-deficient substituents, participated effectively.[10] Also, the silylation of cyclic alkenyl halides can be used to achieve the synthesis of cycloalkenylsilanes (entry 10). In all runs shown in Table 1, the stereochemistry of **3** was consistent with that of (*E*)-**2**.

In conclusion, the silylation of alkenyl iodides with hydrosilanes provides useful access to (*E*)-alkenylsilanes; however, the mechanism for this silylation is unclear at the present stage. The investigation for silylations with other organic halides or pseudo-halides is currently in progress in our laboratory.

The following is a typical experimental procedure for the present silylation: To a suspension of KOAc (296 mg, 3.0 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (15 mg, 0.014 mmol) in NMP (4 mL) was added (*E*)-1-iodo-3,3-dimethylbut-1-ene (212 mg, 1.01 mmol) and triethoxysilane (249 mg, 1.5 mmol). After being stirred for 2 h at room temperature, the reaction mixture was taken up in benzene, washed three times with water to remove the NMP, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel (pentane:ether=10:1) to give 183 mg (74% yield) of analytically and spectroscopically pure (*E*)-3,3-dimethyl-1-(triethoxysilyl)but-1-ene.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 10750615) from the Ministry of Education, Science, Sports and Culture of Japan.

References

1. For a recent review, see: Colvin, E. W. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 11, p. 313.
2. For recent reviews, see: (a) Ojima, I. In *The Chemistry of Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; p. 1479. (b) Takeda, T. In *Synthesis of Organometallic Compounds*; Komiya, S., Ed.; Wiley: New York, 1997; p. 391.
3. (a) Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 4715. (b) Matsumoto, H.; Nagashima, S.; Kato, T.; Nagai, Y. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 279.
4. Murata, M.; Suzuki, K.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 8569.
5. Murata, M.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 6458.
6. It is known that the tertiary amine can act as a hydride source in the presence of palladium complex. See: (a) Murahashi, S.-I.; Watanabe, T. *J. Am. Chem. Soc.* **1979**, *101*, 7429. (b) Hagiwara, H.; Eda, Y.; Morohashi, K.; Suzuki, T.; Ando, M; Ito, N. *Tetrahedron Lett.* **1998**, *39*, 4055.
7. Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M.; Yamamoto, Y. *Organometallics* **1994**, *13*, 3233.
8. In the palladium-catalyzed silylation of aryl halides with hydrosilanes (Ref. 4), Et_3SiH **1c** was not suitable as a silylating reagent.
9. Boukherroub, R.; Chatgilialoglu, C.; Manuel, G. *Organometallics* **1996**, *15*, 1508.
10. Unfortunately, in the case where (Z)-β-iodostyrene was used, the inversion of starting geometry occurred to give (*E*)-**3a** (35%) along with **4a** (4%) and **5a** (51%).